some Spectroscopic and Kinetic Studies of Nickel oxide and its Ion
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SOME KINETIC AND SPECTROSCOPIC
STUDIES OF NITROUS OXIDE
AND ITS ION

by

Michael G. Holliday

Thesis submitted to the Academic Board
of the University of Surrey for the
Degree of Doctor of Philosophy

Department of Chemistry, University of Surrey, October 1968.
ACKNOWLEDGEMENTS

The work presented in this thesis was carried out in the Physical Chemistry Department of the University of Surrey under the supervision of Dr. B.G. Reuben. I should like to say how grateful I am to Dr. Reuben for all his help and encouragement.

I should like to thank all those people who have helped with this thesis, the following in particular:

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Mrs. Angela Hamblyn for the hard work and trouble she took in the typing of the manuscript.

Mr. R. Williams for the loan of drawing equipment used in the preparation of the diagrams.

And finally to my wife, who although claiming to understand little of the contents of this work, understood me. It is to her that this thesis is dedicated.

Michael G. Holliday
October 1968
N.B. In general it is the practice to put diagrams and tables in the page immediately following the reference to them in the text.
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The work presented in this thesis deals with a number of aspects of the simple molecule, nitrous oxide. It is convenient to divide the work into four parts.

The first two and major parts, concern the oxidation reactions of nitrous oxide.

Many gas phase oxidation processes have been studied using molecular oxygen as the oxidant. The results have often been confused by the complexity of the systems involved. Branched reaction chains occur leading to explosions and results that are highly dependent on surface and the presence of trace impurities. Oxidation by nitrous oxide does not normally lead to chain branching since the reaction

\[ R + N_2O \rightarrow N_2 + OR \quad [R \text{ is any free radical}] \]

is not a chain branching process whereas the analogous reaction with molecular oxygen is.

It was therefore hoped that by studying oxidation in nitrous oxide the inherent difficulties of establishing reaction mechanisms would be less, and that data on the reactions of oxygen atoms (possibly energetically excited from the thermal decomposition of nitrous oxide) would be obtained.

Three important gas phase oxidation reactions involve no pressure change, namely, nitrous oxide/hydrogen, nitrous oxide/carbon monoxide and nitrous oxide/sulphur dioxide.

The oxidation of sulphur dioxide in nitrous oxide has been studied by Reuben and others \([6, 36]\). The reaction was followed spectroscopically by using the absorption of sulphur dioxide at 3100 Å.

A method is presented in this thesis by which it is possible to follow the concentration of nitrous oxide spectroscopically using the
Partly as a test of the method, the reaction with hydrogen was investigated first. The only comprehensive study of the N₂O/H₂ system that has been carried out was the careful and ingenious work of Melville in the 1930's [v. infra]. Modern techniques permit improvements to Melville's method. Also, now that the rate constants of all, or nearly all, the elementary processes that are likely to be involved in a mechanism are known, a more rigorous test of proposed mechanisms may be made.

The oxidation of carbon monoxide is an important final stage in the burning of hydrocarbons. Since H.B. Dixon's discovery in 1880 [37] that water had a marked influence on the combustion of carbon monoxide a great deal of work has been carried out on the reaction. Dixon's comment on his discovery (reported by W.A. Bone in the Liversidge Lecture of 1930 [77]) that "it loosed a hare which though since pursued by the hounds in full cry, is still uncaptured" is as true today. The role of water in combustion processes is still obscure. By studying the oxidation of carbon monoxide in nitrous oxide (a reaction which has scarcely been studied at all) it is hoped that, since chain branching is unlikely to occur, the effect of water will not be as dramatic as in the O₂/CO reaction. By studying both the "dry" and "wet" reactions further insight into the effect of water may be gained. The work described in this thesis is primarily concerned with the "dry" N₂O/CO reaction. Further work is in progress in the department to study the "wet" reaction more extensively [41].

The third part of this thesis deals with a phenomenon that made the first two parts possible.

It was found that although the absorption intensity of nitrous
oxide in the region of 2200 Å is very weak at room temperature; it increases with temperature. This provided a measurable absorption (at 2200 Å) at the temperatures at which the oxidation reactions were carried out (540° to 750°C) and enabled the concentration of nitrous oxide to be followed during the course of a reaction.

The effect of temperature on the electronic spectra of molecules has not been widely studied. An account of the variation of absorption intensity of nitrous oxide in the region 2800 to 1900 Å with temperature (0 to 700°C) and its relationship with some upper electronic states of N2O is presented in this thesis.

The fourth part involves ion-molecule reactions between hydrogen and its isotopes and nitrous oxide.

During the past 10 to 15 years there has been an upsurge in the interest in reactions of gas phase ions and molecules. A number of theories have been put forward to predict and explain these reactions. One of the earliest and also one of the more successful theories was developed by Gioumousis and Stevenson [91] in which they considered the path of the ion in the potential field set up between the ion and the ion-induced-dipole of the neutral molecule. They treated both the ion and molecule as hard spheres and predicted rate constants that depended solely on physical parameters such as charge, mass, velocity of the ion and mass and polarizibility of the neutral species, rather than on the chemical properties. Recently ion-molecule reactions have been observed which apparently cannot be treated using the simple Gioumousis-Stevenson theory (e.g. ion-molecule reactions in benzene studied by Reuben and Lifshitz [98]).

It was decided to compare two simple ion-molecule systems in which the physical parameters are identical (or nearly so). Ion-molecule
reactions between carbon dioxide and hydrogen have been studied by a number of workers, the data obtained have been shown to fit the Gioumousis Stevenson theory closely, the essentially similar N₂O/H₂ system has not been studied. Nitrous oxide is isoelectronic with, has the same molecular weight as, and has a polarizability similar to carbon dioxide. The Gioumousis-Stevenson theory predicts that similar rate constants would be obtained.

This thesis studies ion-molecule reactions in N₂O/H₂ mixtures and compares the results obtained with the CO₂/H₂ system. The aim is to see whether significant differences in rate constants are obtained and if so to try to provide an explanation.
Part I

Combustion of Hydrogen in Nitrous Oxide
INTRODUCTION

(i) Thermal Decomposition of Nitrous Oxide:

The initiation reaction in both the $N_2O/H_2$ and $N_2O/CO$ reactions involves the decomposition of nitrous oxide into nitrogen molecules and oxygen atoms. Although no specific investigation of the decomposition was made in this work a brief resume of the chief features of the decomposition will be given. The mechanism of the decomposition of $N_2O$ is now fairly well established. It is of importance not only as the initiation process in its oxidation reactions, but is also of theoretical interest as nitrous oxide is one of the simplest molecules capable of unimolecular reaction where the activation is ultimately supplied by collision.

Nitrous oxide decomposes at measurable rates above about 600°C. The products are almost entirely nitrogen and oxygen. Some nitric oxide is also formed varying from 0.28% at 700°C to 1.4% at 1200°C [1]. The reaction is found to be approximately 1.5 order over a surprisingly large pressure range (from about 10 mm Hg to a few atmospheres).

In an attempt to explain the experimental order of 1.5 obtained over such a large pressure region, Pease [3] suggested a chain mechanism that employed an initiation reaction that involves breaking the N-N bond:

$$N_2O \rightarrow N + NO + 113 \text{ kcal}$$

This reaction is energetically unfavourable and has been rigorously ruled out by Friedman and Bigeleisen who found that if $^{15}N^{14}NO$ is used no $^{14}N_2$ or $^{15}N_2$ is formed as products [4].

The formation of nitric oxide during the decomposition has been studied by Lindars and Hinshelwood [2] and by Kaufman, Gerri and Bowman [5]. In the initial stages up to 60% of the reacting $N_2O$ produces nitric oxide. At constant temperature the ratio (initial rate of NO formation)/(initial rate of $N_2O$ decomposition) increases with increasing pressure. The production of NO is self-inhibiting and it has been
shown by $^{15}$N tracer experiments [4] that most of the NO produced is formed by the reaction

$$0 + N_2O \rightarrow 2NO.$$  

The activation energy of the decomposition is about 58 kcal/mole[6], although Lewis and Hinshelwood found that it falls to about 50 kcal at low pressures [7]. Reuben and Linnett [8] have reinterpreted the results of Lindars and Hinshelwood and Kaufman et al, and give a more complete picture of the decomposition. Two processes are possible as initiation processes:

$$N_2O \left( ^1\Sigma \right) \rightarrow N_2 \left( ^1\Sigma \right) + 0 \left( ^3P \right) \quad \Delta H = + 39.4 \text{ kcal}$$

$$N_2O \left( ^1\Sigma \right) \rightarrow N_2 \left( ^1\Sigma \right) + 0 \left( ^1D \right) \quad \Delta H = + 84.8 \text{ kcal}$$

The first process involves a change in multiplicity but leads to products in their ground electronic states. The second is permitted but the dissociation energy is considerably greater than the observed activation energy. Herzberg [9] suggested that dissociation might occur via a triplet state of $N_2O$ which was about 58 kcal above the ground state.

Stearn and Eyring [10] develop a theory to calculate the absolute rate of the $N_2O$ decomposition. They obtained a potential energy diagram for $N_2O$ as a function of N-O distance, an extended form of which was published by Reuben and Linnett [8] and is shown in Fig. 1.1. In this diagram the potential energy curve for the first excited states ($^3\pi$ and $^3\Sigma$) cut the ground state potential energy curve at an energy between 55 and 60 kcal above the minimum of the latter.

It was proposed by Stearn and Eyring that decomposition of $N_2O$ to ground state nitrogen and oxygen occurs via this crossing point thereby explaining why the experimental activation energy is higher than the energy of dissociation to $^3P$ oxygen.

Reuben and Linnett have pointed out that this course of decomposition leads to the nitrogen molecule and oxygen atom separating with an
Fig: 1.1 Potential Energy Diagram for N$_2$O.
energy of 19 kcal/mole. Since \( \text{N}_2\text{O} \) is a linear molecule this will appear mainly as translational energy. The share of the oxygen atom will be about 12 kcal/mole, and hence oxygen atoms produced will be more reactive initially. Reuben and Limett also postulate that only "hot" oxygen atoms undergo collision with nitrous oxide to produce nitric oxide. They modified Kaufman's mechanism to take this into account:

\[
\begin{align*}
\text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O}^x \\
\text{O}^x + \text{M} & \rightarrow \text{O} + \text{M} \\
\text{O}^x + \text{wall} & \rightarrow \text{O} + \text{wall} \\
\text{O} + \text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O}_2 \\
\text{O}^x + \text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O}_2 \\
\text{O}^x + \text{N}_2\text{O} & \rightarrow 2\text{NO} \\
\text{O} + \text{NO} & \rightarrow \text{NO}_2 \rightarrow \text{NO}_2 + h\nu \\
\text{O}^x + \text{NO} & \rightarrow \text{NO}_2 \rightarrow \text{NO}_2 + h\nu \\
\text{O} + \text{wall} & \rightarrow \frac{1}{2}\text{O}_2 \\
\text{O}^x + \text{wall} & \rightarrow \frac{1}{2}\text{O}_2 \\
\text{NO}_2 + \text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O}_2 + \text{NO} \\
\end{align*}
\]

This mechanism seems to account reasonably well for most of the published work on the thermal decomposition of nitrous oxide, and amply confirms Hinshelwood's comment [2] that "The decomposition of nitrous oxide belies any expectation that the kinetic behaviour of molecules containing a few atoms should be simple".

More recently work has been carried out on the decomposition of nitrous oxide in shock tubes at high temperatures. This enables the reaction mechanism to be evaluated under extreme conditions, and by diluting \( \text{N}_2\text{O} \) with large excesses of carrier gas, bimolecular reactions can be avoided, changes in the number of particles during the reaction are negligible, and the reaction proceeds in a nearly ideal heat bath.
Bradley and Kistiakowsky [11] analysed reacting N₂O behind a reflected shock wave, using hydrogen as the carrier gas, with a Bendix time of flight mass spectrometer. They claim good agreement with rate constants and mechanism of the reaction obtained at much lower temperatures by earlier workers.

Olschewski, Træe, Wagner and others have published a number of papers dealing with the decomposition of N₂O in shock tubes [12][42] at pressures between 0.8 and 300 atm and temperatures between 1400 and 2500°K. They find that the velocity constant for the unimolecular step

\[ N₂O \rightarrow N₂ + O \]

changes with pressure, with changes occurring both in the activation energy (58 to 59.5 kcal from low to high pressure) and in the pre-exponential term (10^{14.7} to 10^{11.1} sec⁻¹).

(ii) Oxidation of Hydrogen in Nitrous Oxide:

The reaction of hydrogen with nitrous oxide to give nitrogen and water has been studied sporadically throughout the history of the study of gas phase combustion processes. Hinshelwood [13] investigated the reaction by following the change in thermal conductivity during the reaction, and found that the reaction proceeded slowly enough to be explained by initiation by N₂O decomposition followed by attack by oxygen atoms on the hydrogen. He seemed to be primarily interested in the catalytic reaction on platinum wire. Catalytic oxidation has been studied by a number of workers (for example, Melville [14], Kobes [15] and Tretiakov et al [16]).

The most extensive study of the N₂O/H₂ reaction was carried out by Melville [17]. He followed the reaction by absorbing the water vapour formed on phosphorous pentoxide contained in a side arm of the
reaction vessel which projected out of the furnace. He carried out elaborately experiments to show that water was absorbed as rapidly as it was formed, and that he was measuring a rate of reaction and not a rate of absorption of water. Despite the fact that the method must have introduced peculiar wall effects and large temperature gradients the results obtained seemed reasonably self consistent and agree in most instances with the work that is presented in this thesis.

Unlike Hinshelwood [13], Melville found that the rate of reaction in the region 500 to 800°C was many times greater than the rate of decomposition of \( \text{N}_2\text{O} \) alone. He showed that the rate was directly proportional to nitrous oxide concentration at high pressures (> 60 mm Hg) but at low pressures the rate depended on the square of nitrous oxide concentration. In both pressure regions the order with respect to hydrogen was low (≤ 0.5).

Melville obtained an activation energy of about 32 kcal/mole for the reaction in the "high" pressure region but this increased to 49 kcal/mole at low pressures. The addition of nitrogen and argon had no effect on the rate but packing the reaction vessel with silica tubes inhibited the reaction.

The effect of adding oxygen to the reaction was investigated and Melville makes the following observations:

In the high pressure region:

1) oxygen considerably increases the rate.
2) rate is proportional to pressure of oxygen added.
3) oxygen is consumed in the initial stages
4) activation energy is lowered

At low pressures:

1) rate of a given \( \text{H}_2/\text{N}_2\text{O}/\text{O}_2 \) reaction decreases with pressure. (Above 50 mm this is not observed).
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**Table 1.1**

Summary of Nagatake's work on \[^{2}H\]/\(^{16}O\) reaction.
ii) packing experiments show inhibition by walls.

iii) a critical point is observed in the reaction curves where the curves abruptly change slope. This is assigned to the pressure of the mixture falling below the critical value (due to withdrawal of water), and is said to bear a striking resemblance to the lower limit in the \( \text{H}_2/\text{O}_2 \) reaction.

A similar set of experiments were carried out using mercury photosensitization to initiate the reaction. A summary of Melville's work is shown in Table 1.1.

The effect of replacing hydrogen with deuterium (66%) in the catalytic [18] and Hg photosensitized reactions [19] was observed by Melville. He found that in the presence of a nickel catalyst hydrogen reacts about twice as fast as deuterium, but that no difference in reaction rate between hydrogen and deuterium is found in the Hg photosensitized reaction.

Later workers have confined themselves to studying explosion limits in the \( \text{N}_2\text{O}/\text{H}_2 \) system and to studying reactions in \( \text{N}_2\text{O}/\text{H}_2 \) flames.

Fenimore and Kelso [20] claimed to be able to obtain reproducible explosion limits in \( \text{N}_2\text{O}/\text{H}_2 \) mixtures (something Melville was unable to do) if great care was used in removing oxygen from the \( \text{N}_2\text{O} \) used. They did this by passing \( \text{N}_2\text{O} \) through alkaline pyrogallol and then drying the gas. They found that a minimum was obtained in the graph of ignition pressure vs temperature for mixtures of fixed composition, and suggested that at higher temperatures (beyond the minimum) inhibition was due to the formation of the metastable species \( \text{HO}_2 \). They confirmed this conclusion by adding small amounts of oxygen which raised the explosion limits showing that the reaction was inhibited. To explain this inhibition Fenimore and Kelso added the reaction
H + O₂ + M → HD₂ + M

to Melville's reaction scheme (v. infra).

Destriau et al [21] extended the composition range of Fenimore and Kelso and showed that minima in the ignition pressure vs. temperature curves did not occur in hydrogen rich mixtures or in mixtures where the ratio of nitrous oxide to hydrogen was greater than 20:1. Destriau et al [22] showed that when nitric oxide is added to the N₂O/H₂ system the explosion limits are substantially raised showing inhibition of the reaction chains by NO.

In an attempt to investigate wall effects in combustion of gases Destriau and Heleschewitz [23] studied the effect of adding powdered silica and nickel oxide to the reaction vessel on the explosion limits of nitrous oxide/hydrogen mixtures. Their results appear inconclusive, the ignition pressures were raised or lowered (i.e. reaction inhibited or catalysed) depending on the relative proportions of hydrogen and nitrous oxide.

A small amount of work has been carried out on nitrous oxide/hydrogen flames. Fenimore and Jones [24] using a probe technique with mass spectrometric analysis of products have obtained values for the rate constants of some of the elementary reactions involved in the combustion of hydrogen by nitrous oxide. Gray, Mackinven and Smith [25] claim that at the high temperatures that are involved in hydrogen, air, nitrous oxide flames, nitric oxide acts simultaneously as an inhibitor and as an oxidant and so resembles an inert diluent.

In both the explosion limit and flame work, little or no evidence is produced to support a mechanism for the oxidation of hydrogen by nitrous oxide. Where it has been necessary to use a mechanism to evaluate a particular result Melville's mechanism has been assumed.

The mechanism proposed by Melville is as follows:
The initiation reaction is more complex than represented and involves bimolecular activation of nitrous oxide molecule.

Finally, in this survey of work carried out on the oxidation of hydrogen by nitrous oxide, Check and Swinnerton [26] report a chain reaction between $N_2O$ and $H_2$ in aqueous solution when the system is irradiated with ultraviolet light.
APPARATUS

(i) **Introduction:**

The main reason why so little work has been carried out on nitrous oxide/hydrogen and nitrous oxide/carbon monoxide reactions is that an adequate method for following the reactions did not exist. No pressure change accompanies either of these reactions, Melville's method has inherent uncertainties about temperature gradient and wall effects, and the study of explosion limits (Fenimore and Kelso, Destriau et al) is not an easy way to obtain evidence for a reaction mechanism.

Mass spectrometric analysis of reaction mixtures would be difficult in the N₂O/CO reaction since reactants N₂O and CO have the same masses as the products CO₂ and N₂ respectively. Gas chromatographic methods suffer (as does mass spectroscopy) from the need to disturb the system by having to take individual samples.

Ultra-violet spectroscopy has the advantage of not disturbing the system and of flexibility. However virtually all the reactants and products expected in these reactions are transparent up to the air cut off limit of about 1900 Å. Nitrous oxide exhibits a very weak continuum stretching from about 3000 Å into the vacuum ultra-violet. At room temperature the absorption intensity is so weak that measurement would be extremely difficult. However in a paper by Jost and others [12] mention was made that at the high temperatures obtained in shock-tubes the absorption intensity of nitrous oxide appeared to increase with temperature. This fact, plus the improvements made in recent years in the lamps, quartz and detectors used in ultraviolet spectroscopy, provides a strong case for using a spectroscopic method.

A single beam optical system was chosen because although it is basically less stable than a good double beam arrangement, it is simpler to construct. The practical difficulties involved in making an adequate
double beam system with the 5 or 6 ft. light paths that were necessary and the more complex electronics that must be employed made it a less attractive proposition.

A general view of the apparatus is shown in Plate 1 and a block diagram of the apparatus is shown in Fig. 1.2. A conventional gas handling system enabled gases to be prepared, stored, mixed and delivered to the reaction vessel. The reaction vessel was housed in a tubular furnace and was maintained at a constant temperature.

Light from a deuterium lamp supplied by a stabilised power supply was collimated and passed through the reaction vessel and focused on the slit of a single prism monochromator. The light leaving the monochromator fell onto a photomultiplier, the output of which, across a resistor, was measured with a potentiometric recorder. The change in light intensity during the course of a reaction is recorded automatically and related to change in nitrous oxide pressure by previous calibration.

(ii) Gas Handling System:

The layout of the vacuum system is shown in Figure 1.3. The main line is pumped at two points using a Metrovac two stage oil diffusion pump (type 022A) using Apiezon B oil backed by a Metrovac rotary oil pump (type GS10). To protect the pumps from harmful gases and the line from pump oil, a liquid air trap was placed after the diffusion pump and before the main line. Discharge tubes (D) were mounted at each end of the main line to provide an indication of vacuum. Later a thermocouple vacuum gauge was obtained (Genevac T.C.5.). The ultimate pressure obtained on the line was about $10^{-4}$ torr, but to save time between runs pump out pressures in the order of $10^{-2}$ to $10^{-3}$ torr were accepted. All taps were greased with Apiezon N grease.
PLATE I. GENERAL VIEW OF APPARATUS
Fig. 12
Block Diagram
of Apparatus.
Fig: 1.3 Vacuum Line.
and all cones and sockets with Apiezon L.

The main line may be divided into three sections: gas preparation and storage, mixture preparation and reaction vessel.

The preparation lines enable gases to be prepared using standard 'Quickfit' apparatus and to be purified by drying and distillation. A "hot and cold wall" drying trap is included in the preparation line so that more efficient drying of gas may be achieved than is usually obtained using conventional cold traps. The trap is like a small Dewar flask with gases flowing between the inner and outer walls which are about 1 mm apart (see inset on Fig.13). The inner finger is filled with liquid air and the outer jacket surrounded by warm water. This trap is said to remove water vapour that may escape conventional cold traps as a "mist" of ice particles. A full account of its mode of action is presented in reference 6. A 'blow off' completes the preparation line, which enables addition of gas to the five 5-litre storage volumes to be carried out under control.

The mixing section has a 1-litre mixing vessel which contains a glass stirrer with a small bar of iron sealed in it. The stirrer is rotated by a magnet driven by a variable speed motor. A Töpler pump was used to get small amounts of gas at low pressure into the mixer or reaction vessel at a higher pressure. In extreme cases it was necessary to connect the pump to the laboratory nitrogen supply in order to achieve the required pressures.

The mixing section is equipped with two mercury manometers for pressure measurement. It also has two outlets to atmosphere to enable the attachment of extra mixing volumes, sample volumes, charcoal drying trap etc., to the line.

The reaction vessel was made of clear quartz (by Thermal Syndicate Ltd.) and was cylindrical, 10 cm long by 5 cm diameter. The ends were
of polished spectrosil quartz which permitted the transmission of ultra-violet light down to about 1600 Å. The reaction vessel was prepared by cleaning in chromic acid mixture over night, rinsing with distilled water, ammonia, distilled water, phosphoric acid and repeated washings of distilled water. The phosphoric acid was used to protonate the silica walls, and was used instead of the more normally used hydrofluoric acid which would have slightly etched the optical windows thereby reducing the transparency to ultra-violet light.

The reaction vessel was connected to the line via 3 mm capillary tubing and a black waxed B10 joint. A mercury manometer provided the means for pressure measurement. Gases were let into the reaction vessel by a diaphragm valve. The diaphragm was made of Viton 'A' rubber and gave better control of the addition of gases than glass stopcocks.

(iii) Thermal Section:

The reaction vessel is situated at the centre of a 2 ft. tubular furnace. The ends of the furnace are closed by two spectrosil discs to cut down temperature gradients. The furnace was controlled by an A.E.I. thermocouple temperature controller (type T.C.3) with a 2 kw voltage power regulator. The T.C.3 is a fully proportional temperature controller for use with thermocouples. The controller provides for adjustment over 0 to 40 millivolts (smallest division 20 μV).

A chromel/alumel thermocouple was used with the T.C.3 unit to control the temperature of the furnace. It was also used in conjunction with the millivolt setting on the input unit to measure the temperature of the reaction vessel. The thermocouple was contained in a stainless steel sheath (2 mm diameter) and was supplied calibrated by M.E.L. Equipment Limited (Type Thermocoax 2AB At.20). It was
situated touching the reaction vessel wall as shown in Fig.14. The cold junction was maintained at a constant temperature (app. 42°C) in an A.E.I. Cold Junction Thermostat (Type C.J.1.). A calibration graph of e.m.f. of the thermocouple versus temperature was constructed, after making necessary corrections for the thermocouple's individual calibration and for the temperature of the cold junction, from standard tables [38]. With the use of this graph the furnace could be set to any desired temperature by setting the millivolt adjustment on the T.C.3. unit to the thermo e.m.f. given by the thermocouple at that temperature. It is estimated that the absolute temperature of the reaction vessel is within 5°C of that calculated from the controller settings and that temperature differences (between two different settings) are well within 1°C of those calculated.

The furnace winding is tapped in two places making three sections. Each section is shunted with a rheostat, [Fig.14]. Three chromel/alumel thermocouples (Thermocoax 2AB At 20) are arranged along the length of the reaction vessel. By connecting a galvanometer (Fye Scalamp 7901/S) across 1 and 3 and 2 and 4 in turn, the temperature gradient between the ends and centre of the reaction vessel could be measured. By altering the shunts across the furnace winding so that more current is supplied to the outside sections than to the centre, the temperature gradient across the reaction vessel can be reduced to a minimum. In practice the temperature gradient along the whole length of the reaction vessel was never more than 1°C compared with 7° to 10°C before any adjustment of the shunt resistors was made.

Stainless steel sheathed thermocouples were used since it was felt that the junction would suffer less deterioration by being kept continuously at high temperatures than would more normal unsheathed types. This would result in much greater long term stability.
Fig. 14 Furnace Control.
Optical System:

The light path through the apparatus is shown in Fig.1.5a. Light from a deuterium discharge lamp is supplied by a stabilised power supply. Both the lamp and power supply unit were obtained from Unicam who use them in their S.P. 500 spectrophotometers. The power supply is claimed to have a current stability of 0.01%. The light is collimated by a 5 cm diameter, 15 cm focal length convex mirror and passes through the reaction vessel. It is reflected by a plane mirror onto a 20 cm focal length convex mirror (5 cm diameter) which focused the light onto the slit of a single prism monochromator of low resolution. The light emerging from the monochromator falls on a photomultiplier whose output across a resistor is measured by a potentiometric recorder.

The monochromator was constructed in the workshops of the Chemistry Department of this University. The layout of the monochromator is shown in Fig.1.5b. The slit is constructed so that it defines both the light entering the monochromator and the light falling on the photomultiplier. The width of the slit is variable and the edges are made from two stainless steel razor blades (Wilkinson). After entering the monochromator the light falls on a 30 cm focal length mirror which collimates the light and directs it onto a 30° prism. The prism is made of spectroisil quartz and the back face is silvered which allows the light to be refracted through 60°, and also enables the collimating mirror to be used to focus the analysed light back onto the portion of the slit that covers the photomultiplier. A small mirror directs the light onto the cathode of the photomultiplier.

The prism is mounted on a turntable that may be rotated by a lever system operated by a micrometer screw control. The monochromator was calibrated in the region 2700 to 1850 Å using substances with known absorption spectra and in the blue end of the visible region using the
Fig. 1.5 Optical System.
emission bands from the deuterium lamp. The calibration procedure is described in a later section. When the light path and monochromator was first set up it was found that at short wavelengths ($<2200 \text{ Å}$) the majority of the signal from the photomultiplier was found to arise from "stray light" rather than light at the set wavelength. Eventually it was found that incoming light was being reflected down the ground edges of the razor blade slits to the photomultiplier. By placing a small mask of cardboard across the slit to mask the incoming light from the photomultiplier compartment, a substantial reduction in stray light was obtained. It was found necessary to cover the whole light path to prevent variations in photomultiplier current arising from the varying intensity of laboratory illumination.

a) Measurement of Light Intensity:

The measuring circuit is shown in Fig.16. The photomultiplier used is an E.M.I. 6256B. This is a high gain, 13 stage photomultiplier tube with a quartz window and has a response range from 1650 to 6500 Å. Photons hitting the cathode (K) liberates electrons which are accelerated by the electric field between the cathode and the first dynode (1). These in turn liberate many more electrons which are further accelerated down the dynode chain (1-13). By the time the electrons are collected at the anode (A) an amplification of many orders of magnitude of the original electron current is obtained. The gain of the photomultiplier is dependent to the fifth power of the voltage applied across the resistor chain, and it is necessary to use a highly stabilised high tension supply. The voltage drop across the resistor chain (normally between 1000 and 1800 kV) is provided by an Isotope Developments Limited E.H.T. Unit type 532 for which the manufacturers claim output regulation of 0.02% of setting change for $\pm$ 10% mains change and a stability of 0.02% of setting per 24 hours.
Fig: 1.6 Light Intensity Measuring Circuit.

Fig: 1.7 Typical Calibration.

- O 24 May '66
- + 13 June '66

Intensity %

N₂O Pressure mm. Hg

20 40 60 80 100 120 140 160
The final electron current at the anode (A) is led to a variable decade resistor (0 to 99.9 kΩ) and the voltage thus developed is measured by a Honeywell potentiometric recorder which enables the change in light intensity (as nitrous oxide is consumed) with time to be followed. The recorder is fitted with a continuously variable span control with which one can alter the sensitivity of the recorder from 1 mV to 21 mV full scale. In practice it was found that the recorder could not cope with the decade resistor set greater than 20 kΩ as its response became too sluggish. A resistance of lower than about 1 kΩ meant that the photomultiplier was called upon to deliver too great a current. The system therefore had a sensitivity range of about 200 at a given E.H.T. setting. The recorder was also fitted with a control that could suppress the zero by up to 20 mV. This enabled the stray light component (about 10 to 15% at 2200 Å) of the photomultiplier signal to be "backed off" so that the instrument zero represented the zero in usable light. It could also be used to expand the measurement scale when low pressures of nitrous oxide were being measured.

Noise levels were between ½% to 1% of the total signal and were due to electronic pickup from other components and to vibrations in the laboratory which were magnified by the long light path. Stability was at times not as good as desired; usually a gradual decrease in signal occurred during a day's experiments. This was probably due to the slow decrease in deuterium lamp intensity as the time that it had been switched on increased, and also to a small decrease in photomultiplier gain that occurred as the period of illumination increased. Invariably a partial recovery of signal intensity was observed when the apparatus was switched on the next day. The drift in maximum signal was never more than about 5%, and usually much less, during the time of an indivi-
dual run and correction could be made for this by measuring the light intensity obtained with the reaction vessel evacuated immediately before and after a run and assuming a linear decline.

The instrument was calibrated at least daily by putting known pressures of nitrous oxide into the reaction vessel, measuring the signals and expressing them as a percentage of the signal obtained when the reaction vessel was evacuated. Reproducibility between successive calibrations was good but a slow change was noticed over the weeks due to the ageing of the deuterium lamp and photomultiplier, and to slow corrosion of mirror surfaces. The replacement of mirrors once every six months or so was found to be necessary. A typical calibration is shown in Fig. 1. The points from two calibrations are shown and it may be seen that reproducibility is good over the period of a month or so.

The accuracy of measurement was about 2 mm Hg nitrous oxide in a "normal" calibration (i.e. where instrument zero was zero usable light intensity) which was used in the range 0 to 250 mm Hg nitrous oxide. An "expanded" calibration, which was used for nitrous oxide pressures between 0 and 100 mm Hg, was based on an arbitrary instrument zero such that 100 mm Hg N₂O gave about 10% scale reading, provided an accuracy of about 1 mm Hg nitrous oxide. The limit of the system for meaningful measurements was about 15 mm Hg of nitrous oxide at the start of a run.

In order to measure the weak chemiluminescence (10³ to 10⁶ times weaker than the deuterium light intensity) that occurred during nitrous oxide/carbon monoxide reactions, it was necessary to run the measuring system at the limit of its sensitivity. This inevitably increased instrumental noise and instability. An accuracy of no better than 10% was achieved in the measurement of glow intensity.
b) Calibration of Monochromator:

The problem involved in calibrating the monochromator was that in the ultra-violet region below about 2700 Å the intensity of the light signal dropped sharply with decreasing wavelength (due to lamp drop off and increased scattering of light from mirrors, silica windows etc). It was therefore necessary to find substances that had very sharp absorption bands in the region of interest (2700 to 1900 Å).

The following were chosen:

- 2700 to 2300 Å: 5 x 10⁻³ M Benzene in hexane
- 2300 to 2050 Å: 100 mm of nitric oxide in the reaction vessel
- 2000 to 1850 Å: Schumann-Runge bands of atmospheric oxygen.

The benzene solution was contained in a 1 cm silica cell placed in the light path just in front of the monochromator slit. Benzene in hexane exhibits a very sharp banded spectrum between 2700 and 2300 Å.

A spectrum run on a Unicam S.P.800 was used to locate the peaks.

Nitric oxide has an extensive spectrum progressing from 2300 Å into the vacuum ultra-violet. It consists of a number of very sharp bands of varying intensity and a spectrum published by Thompson, Harteck and Reeves [39] was used to locate the peaks.

Oxygen shows a weak banded structure from about 2000 Å which rapidly gains intensity as wavelength shortens. A spectrum published by Johnson [40] was used to locate the peaks and exact values of the band heads were obtained from Pearce and Gaydon [78].

The deuterium discharge lamp exhibits a series of emission peaks in the visible region of the spectrum. Such a spectrum was plotted by hand using the deuterium lamp of a Unicam S.P.500 and this was used to calibrate the monochromator in the blue region of visible spectrum.

The calibration procedure adopted consisted in setting up the
light measuring system so as to provide a maximum signal near the start of the band system being used as a calibrant, switching on the recorder and scanning manually towards the shorter wavelengths. In this way a rough spectrum was obtained that could be compared with the published spectrum, and the peaks identified. The peaks were then located exactly by rotating the prism until a minimum light intensity was obtained and the micrometer reading recorded. Each calibration peak was scanned three times and the average micrometer reading taken. There was never a difference of more than ±0.05 of a micrometer division between different readings in any one peak. This represents less than ±5 Å at 2800 Å to less than ±3 Å at 2000 Å. These must be regarded as maximum limits of error in the wavelength calibration. The calibration curve obtained is shown in Fig. 1.8.

(v) Gases Used:

Nitrous oxide was obtained from the British Oxygen Company and was stated to comply with British Pharmacopoeia standards. It was used direct from the cylinder in the nitrous oxide/hydrogen work. No detectable impurities (except perhaps a small amount of water and possibly oxygen) could be observed by mass spectroscopic analysis. For the nitrous oxide/carbon monoxide reaction, where very dry gases were required, the nitrous oxide was condensed in liquid air and then distilled from solid carbon dioxide with the first and last portions being discarded. Very careful mass spectroscopic analysis of the nitrous oxide showed that less than 0.01% water was present (the limit of detection).

Carbon monoxide was prepared by dropping 'Analar' sulphuric acid onto sodium formate (B.D.H. Laboratory reagent). Great care was taken to remove water. The sodium formate was dried at 110°C over
night and was then placed in a 500 ml flask on the preparation line. It was pumped on for a number of hours before the preparation of carbon monoxide was begun. The carbon monoxide was passed through a drying chain that consisted of a soda lime column (which also removed CO$_2$ and acid spray), a liquid air trap, the interior of which contained copper foil to aid condensation of water vapour, and finally through the hot/cold wall trap that has been described in an earlier part of this thesis. Again mass spectroscopic analysis showed less than 0.01% water.

Carbon dioxide was prepared by cooling solid carbon dioxide in liquid air, pumping off uncondensed gases, and then allowing the carbon dioxide to sublime slowly.

Hydrogen and oxygen were obtained from B.O.C. cylinders and used without further purification.

Carbon tetrafluoride, nitric oxide and deuterium were obtained from Cambrian Chemicals Ltd. and produced by the Matheson Company. The deuterium was 98% pure.
NITROUS OXIDE/HYDROGEN REACTION

EXPERIMENTAL

The majority of runs were carried out using pre-mixed gases. However a violent and damaging explosion occurred the first time a run was attempted (the reaction vessel was at too high a temperature) and the early runs were carried out by adding the reactants separately as a precaution.

Adding reactants separately introduces uncertainty as to their initial concentrations since the second gas to be added sweeps some of the first gas present in the dead space into the reaction vessel. The pressure of the first gas would be slightly higher and of the second slightly lower than measured on the manometer. To estimate this discrepancy nitrous oxide was placed in the reaction vessel and the absorption intensity was measured. Nitrogen was then added and the increase in absorption intensity measured. This increase showed the amount of nitrous oxide swept out of the dead space and into the reaction vessel and was between 1% and 3% of the initial pressure.

The majority of runs were carried out at 560°C. The activation energy was obtained from a series of runs carried out between 540 and 593°C.

A run was carried out by setting the recorder zero (as described previously) and recording the light intensity at 2200 Å with the reaction vessel evacuated (taken as 100% intensity). With the recorder still running the (usually) pre-mixed mixture of nitrous oxide, hydrogen and any additional gases was added as quickly as possible to the reaction vessel (about 10 secs). At the end of a run the reaction vessel was evacuated and the recorder reading for "100% intensity" and for the zero was noted. Recorder readings at fixed time intervals (measured
on the recorder time base) were expressed as percent of total light intensity, making, if necessary, corrections for zero and "100% intensity" drift during the course of a run, and converted to nitrous oxide pressures by the calibration curve. Fig. 1.10 shows the recorder trace from a typical run.

RESULTS

(i) Order of Reaction:

The rate of reaction for mixtures of nitrous oxide/hydrogen is about 500 to 1000 times greater than the decomposition of nitrous oxide alone. Fig. 1.11 shows typical reaction curves that were obtained and also for comparison the thermal decomposition of nitrous oxide. The nitrous oxide decomposition curve is calculated from data obtained at 700°C during the investigation of the N₂O/CO reaction (Runs 93 to 98 in Appendix 1.2), assuming an activation energy for N₂O decomposition of 58 kcal. These curves show that reaction rate is only slightly dependent on hydrogen. In the case where nitrous oxide is in excess it will be seen that the reaction proceeds at a moderate rate until almost all the hydrogen has reacted when the reaction abruptly stops. In all cases where excess nitrous oxide was present it was found that, within the limits of experimental error, the reaction stopped when the stoichiometric amount of nitrous oxide had reacted.

The reaction order with respect to nitrous oxide and hydrogen was obtained from series of runs in which the initial pressure of one reactant (say H₂) was held constant whilst the pressure of the other (say N₂O) was varied. Graphs of the logarithms of the initial rate against the logarithm of reactant pressure (N₂O) gave straight lines.
Gases admitted to reaction vessel.

Figure 1.10 Recorder Trace.
whose slope is equal to the reaction order (e.g. Fig. 1.12).

Tables 1.2 show the orders of reaction obtained at 600°C and 560°C. The error limits give an indication of the uncertainty in drawing straight lines from plots of log initial rate versus log reactant pressure due to the scatter of the experimental points. (In these tables and throughout the rest of this thesis the symbol \([ \cdot ]\) represents pressure, \([ \cdot ]_o\) initial pressure, \([ \cdot ]_t\) pressure at time \(t\) and so on). It can be seen that the reaction is approximately first order in nitrous oxide. There is a tendency, at low pressures, for the order in nitrous oxide to increase. The initial reaction rate is not very dependent on hydrogen pressure and the order of reaction with respect to hydrogen is between 0.2 and 0.3. There may be a slight trend for the order in hydrogen to decrease as the temperature is raised but the results are not accurate enough to establish this.

The apparent increase in nitrous oxide order at low pressures suggested a more thorough investigation of the order of reaction at low pressures. Accordingly a series of runs, in which the total pressure did not exceed 60 mm Hg, were carried out to determine the order of reaction at low pressures (Melville [17] differentiated between a high and low pressure reaction). Experimental errors inherent in determining initial rates coupled with the low dependence of rate upon hydrogen prevented any accurate estimate of order with respect to hydrogen in this region. Within experimental scatter the initial reaction rate at constant \([\text{N}_2\text{O}]_o\) remained constant with changing hydrogen pressure (Runs 174 to 191, Appendix 1.1) and it must be concluded that the reaction at low pressures is approximately zero order in hydrogen.

The results obtained from investigating the reaction order with respect to nitrous oxide at low pressures are shown graphically in Fig. 1.12 which is a plot of log initial rate against log initial
Fig: 1.11 Typical Reaction Curves.

Fig: 1.12 Order of "Low Pressure" Reaction.
Table 1.2  Order of reaction from initial rate data

a) at 600°C. Runs 34 to 67**

<table>
<thead>
<tr>
<th>Constant $\left[ H_2 \right]_0$</th>
<th>Order w.r.t. $N_2O$</th>
<th>Constant $\left[ N_2O \right]_0$</th>
<th>Order w.r.t. $H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>204 mm Hg</td>
<td>1.1 ± 0.1</td>
<td>120 mm Hg</td>
<td>0.20 ± 0.1</td>
</tr>
<tr>
<td>153</td>
<td>1.0 ± 0.1</td>
<td>92</td>
<td>0.20 ± 0.05</td>
</tr>
<tr>
<td>102</td>
<td>1.0 ± 0.1</td>
<td>80</td>
<td>0.15 ± 0.1</td>
</tr>
<tr>
<td>51</td>
<td>1.3 ± 0.2</td>
<td>41</td>
<td>0.21 ± 0.05</td>
</tr>
<tr>
<td>26</td>
<td>1.3 ± 0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b) at 560°C. Runs 68 to 100**

<table>
<thead>
<tr>
<th>Constant $\left[ H_2 \right]_0$</th>
<th>Order w.r.t. $N_2O$</th>
<th>Constant $\left[ N_2O \right]_0$</th>
<th>Order w.r.t. $H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>205 mm Hg</td>
<td>0.9 ± 0.1</td>
<td>205 mm Hg</td>
<td>0.25 ± 0.05</td>
</tr>
<tr>
<td>154</td>
<td>0.9 ± 0.1</td>
<td>120</td>
<td>0.30 ± 0.1</td>
</tr>
<tr>
<td>102</td>
<td>1.0 ± 0.1</td>
<td>102</td>
<td>0.23 ± 0.05</td>
</tr>
<tr>
<td>51</td>
<td>1.3 ± 0.3</td>
<td>80</td>
<td>0.33 ± 0.1</td>
</tr>
<tr>
<td>26</td>
<td>1.6 ± 0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* These values were obtained from the runs investigating the order of reaction with respect to $N_2O$, by taking two arbitrary nitrous oxide pressures (120 and 80) and determining the initial rate from the graphs of log initial rate versus $\left[ N_2O \right]_0$.

** See Appendix 1.1 for summary of runs carried out.
nitrous oxide pressure. The solid line represents second order behavior (i.e. has a slope of 2). There is no real trend in the rates of reaction at different hydrogen pressures which confirms the approximate zero order in hydrogen. The scatter of results in an individual series of runs at constant \([H_2]_0\) arises from the experimental inaccuracies of measuring small nitrous oxide pressures. Wall termination of the reaction chains is more likely at low pressures and slightly changing wall conditions could be partly responsible for the erratic nature of the results.

a) Experimental rate equation:

It is convenient on the evidence just presented to consider the nitrous oxide/hydrogen reaction in two parts:

A "high pressure" reaction at total pressures above about 100 mm Hg which is, at least in the early stages of reaction, first order in \(N_2O\) and about 0.25 order in hydrogen. This may be represented by

\[
\left\{ \frac{-d[N_2O]}{dt} \right\}_0 = k_A [N_2O][H_2]^{0.25} \tag{A}
\]

A "low pressure" reaction at total pressures below about 60 mm Hg which is second order in nitrous oxide and of negligible order in hydrogen

\[
\left\{ \frac{-d[N_2O]}{dt} \right\}_0 = k_B [N_2O]^2 \tag{B}
\]

Figures 1.13a and b show the results from all runs carried out at 560°C, in which the reaction mixture contained solely nitrous oxide and hydrogen, fitted to expressions A (runs with a total pressure > 100 mm Hg) and B (runs with a total pressure < 60 mm Hg). The straight line in each case is the least squares fit. There is good agreement in the "high pressure" reaction and shows that the reproducibility over the 18 month period in which experiments were carried out was good. The fit
a. "High Pressure" Reaction.

b. "Low Pressure" Reaction.

Fig. 1.13 Experimental Rate Equations.
for the low pressure runs is not so good. The initial rate data in this region is not as reliable as in the high pressure reaction since the nitrous oxide pressures measured were much smaller. It must be accepted that there must be a small contribution to the reaction order from hydrogen. It is also likely that the condition of the reaction vessel walls changed during the course of experiments, and there appears a slight trend for the initial reaction rate to have increased in later runs.

The "rate constants" $k_A$ and $k_B$ obtained from Figures 1.1 a and b are

$$ k_A \text{ at } 560^\circ \text{C} = 5.48 \pm 0.21 \times 10^{-2} $$

$$ k_B \text{ at } 560^\circ \text{C} = 2.61 \pm 0.11 \times 10^{-3} $$

expressed in mm Hg min$^{-1}$ units. The error limits are the standard deviation of the experimental points about the least squares line.

If the activation energy of 62.5 kcal for both the "high" and "low" pressure reactions is considered the experimental rate equations become:

$$ \left\{ \frac{-d[N_2O]}{dt} \right\}_{t=0} = 1.37 \pm 0.05 \times 10^{15} \exp(-62.5 \pm 2.1/RT)[N_2O][H_2]^{0.25} $$

for pressures $> 100$ mm Hg, and

$$ \left\{ \frac{-d[N_2O]}{dt} \right\}_{t=0} = 8.26 \pm 0.30 \times 10^{13} \exp(-62.5 \pm 2.1/RT)[N_2O]^2 $$

for pressures $< 60$ mm Hg.

(ii) Tentative Reaction Mechanism:

The $N_2O/H_2$ reaction is clearly a chain reaction with a chain length of about 500. Any proposed mechanism must explain the change in reaction order with decreasing pressure.

The most likely initial process would be the formation of oxygen
atoms from the thermal decomposition of nitrous oxide. This is a complex process but may be represented by:

$$N_2O \rightarrow N_2 + O$$  \hspace{1cm} (1)

At 560°C the reaction of oxygen atoms with $N_2O$ to give either nitric oxide or oxygen and nitrogen would be very slow (Kaufman [5], Reuben [6], Hinshelwood [2]) and reaction (1) will almost certainly be followed by:

$$O + H_2 \rightarrow OH + H$$  \hspace{1cm} (2)

and the chain propagating steps

$$H + N_2O \rightarrow N_2 + OH$$  \hspace{1cm} (3)

$$OH + H_2 \rightarrow H_2O + H$$  \hspace{1cm} (4)

At this stage, for simplicity, only chain terminations involving hydrogen atoms will be considered, since hydrogen atoms have a much higher molecular velocity than any of the other free radicals.

$$H+H+M \rightarrow H_2 + M$$  \hspace{1cm} (5)

$$H \rightarrow \text{Wall}$$  \hspace{1cm} (8)

Applying Bodenstein's steady state approximation the rate of reaction is given by:

$$-\frac{d[N_2O]}{dt} = k_1[N_2O] + k_2[N_2O][H]$$

and the expression for hydrogen atoms

$$\frac{d[H]}{dt} = 2k_1[N_2O] - (k_0 + k_5[M][H])[H] = 0$$

(The rate constant for a reaction, numbered $n$, is represented by $k^*_n$).

At high pressures the gas phase termination process, $5$, would be expected to predominate. If the wall termination process is neglected (i.e. $k_0 \ll k_5[M][H]$) the rate is given by

$$-\frac{d[N_2O]}{dt} = k_1[N_2O] + k_2[N_2O] \sqrt{\frac{2k_1[N_2O]}{k_5[M]}}$$  \hspace{1cm} (6)

The third body term $[M]$ can be regarded, as an approximation, as
proportional to the nitrous oxide pressure. Expression C is therefore 1st order in nitrous oxide and zero order in hydrogen. This approximates to the behaviour of the high pressure reaction. The fact that the overall rate is about 500 times faster than the $N_2O$ decomposition shows that the first term is negligible in comparison with the second, and it may be ignored.

At low pressures the probability that hydrogen atoms will be destroyed by termolecular step 5 before they reach the reaction vessel walls is small ($k_8 \gg k_5 [H][N_2]$). The rate equation, neglecting quadratic termination, becomes second order in nitrous oxide if the first term is neglected.

$$\frac{d[N_2O]}{dt} = k_1[N_2O] + \frac{k_2 k_1[N_2O]^2}{k_8}$$

This is what is found in the "low pressure" reaction.

Hydrogen contributes as a third body in both the initial step 1 and gas phase termination 5, and so expressions C and D would be expected to show some hydrogen dependence. Other termination processes undoubtedly occur which lead to more complicated rate equations. The expressions above appear to account well for the change in the order of reaction with pressure and provide a basis for further elucidation of the mechanism, which in its present form is very similar to that of Melville.

(iii) Inert Gas Effects:

The addition of inert gas provides a method of testing the hypothesis that the change in reaction order with pressure represents a change from chain termination occurring predominantly in the gas phase to termination at the reaction vessel walls.

The initiation step (1) is a complex reaction which may be represented:
\[
\begin{align*}
N_2O + M & \stackrel{\text{(0)}}{\longrightarrow} N_2O^* + M \\
N_2O^* & \stackrel{\text{(1')} }{\longrightarrow} N_2 + O
\end{align*}
\]

where \(N_2O^*\) represents a nitrous oxide molecule with sufficient energy to undergo the decomposition step \(1'\), and \(M\) any other molecule in the system.

**Addition of an inert gas would**

i) increase the rate of initiation

ii) increase quadratic termination, and

iii) decrease wall terminations.

In the region where gas-phase termination is important i) and ii) would compete and the reaction rate should not alter much. In the region where wall termination predominates, i) and iii) would be complementary resulting in an increase in reaction rate. The region of second to first order change should therefore occur at lower pressures of reactants.

The effect of adding carbon dioxide and carbon tetrafluoride to reaction mixtures was investigated. Carbon dioxide is isoelectronic with, and the same mass as \(N_2O\) and would be expected to have very similar "third body" properties to nitrous oxide. The water gas reaction at these temperatures is too slow to interfere with the reaction. In a recent investigation Tingey [58] obtained an overall rate equation for the \(CO_2/H_2\) reaction of

\[
d[CO]/dt = 7.6\times10^4 \exp(-39,200/RT)[H_2]^{3/2}[CO_2]
\]

(mole\,l\,-1\,sec\,-1\,units). This predicts a rate \(10^2\) to \(10^3\) slower than the \(N_2O/H_2\) reaction at 560°C.

The half-life data plotted in Fig 1.14 for 1:1 mixtures of \(N_2O\) and \(H_2\) clearly show the change from first to second order at around 100 mm total pressure. A graph of log half-life \(t_f^{1/2}\) against log pressure of reactant at half reaction \([N_2O]_t^{1/2}\) has a slope equal to \((1 - \text{Order of reaction})\). The addition of 50\% carbon dioxide to
the reaction mixture indicates that a small extension of the first order region occurs but the experimental points are too scattered for a firm assessment to be made. The addition of 50% CF₄ extends the first order region markedly and even at the lowest pressures second order kinetics are not attained. There appears to be a slight increase in the rate of the first order reaction with the addition of inert gases and a greater increase in the rate of the second order reaction.

(iv) Isotope Effects:

The rate equations (C and D) derived from the tentative reaction scheme contain the propagation step

\[ H + N₂O \rightarrow N₂ + OH \]  \hspace{1cm} (3)

in competition with the termination steps

\[ H+H+M \rightarrow H₂ + M \] \hspace{1cm} (5)
\[ H \rightarrow \text{Wall} \] \hspace{1cm} (6)

If hydrogen is replaced by deuterium reaction 3 would be slower as D atoms have a lower velocity than H atoms and would result in the overall reaction being slower. The termination reactions would also be slower with deuterium, this would make the reaction proceed faster. The two effects would tend to cancel out and little or no isotope effect would be expected.

A series of runs were carried out in which a reaction with hydrogen was followed by a reaction with deuterium with the same conditions of mixture composition and pressure (Runs 296 to 335). In this way it was hoped that reaction vessel conditions would be as near as possible the same for each pair of reactions. The ratio of the overall rate constants for the hydrogen and deuterium reactions \( (k_{H₂}/k_{D₂}) \) were calculated using the method described in Appendix 1.2. This method employs the whole reaction curve (not just initial rate) and serves as
a test to determine if the two reactions obey the same form of rate equation. The isotope effects obtained are shown in table 1.3.

In all cases (except one) the deuterium reaction is slower than the comparable hydrogen reaction. A small positive isotope effect is observed which is smaller than the normal primary isotope effect usually observed in reactions involving the breaking of an X-H bond. It must be observed that in runs with stoichiometric concentrations of nitrous oxide and hydrogen and those with excess hydrogen the isotope effect remains essentially constant over the entire pressure range (about 1.59 and 1.32 respectively), but when nitrous oxide is in excess the isotope effect is constant at high pressures (1.54) and decreases to unity at low pressures.

The initial rates of the deuterium reactions fit the experimental rate equations for the "high and low" pressure reactions moderately well (Fig. 1.15). The slopes (from least squares approximation) give (units of mm Hg \( A \) \( \text{min}^{-1} \))

\[
k_A \text{ (high pressure)} = 2.31 \pm 0.23 \times 10^{-2} \\
k_B \text{ (low pressure)} = 2.28 \pm 0.11 \times 10^{-3}
\]

This provides an alternative means of estimating the isotope effect and gives values of

\[
k_H/k_D \text{ (high pressure)} = 2.36 \\
and \quad k_H/k_D \text{ (low pressure)} = 1.14
\]

These differ slightly from the picture obtained from the ratios of individual rate constants but serve to accentuate the result that at low pressures the isotope effect approaches unity.

(v) **Effect of Oxygen**

Fenimore and Kelso [20], using alkaline pyrogallol washed gases, observed inhibition of the nitrous oxide/hydrogen explosive reaction at
<table>
<thead>
<tr>
<th>Ratio $\text{N}_2\text{O}:\text{H}_2$</th>
<th>Total pressure</th>
<th>$k_{\text{H}<em>2}/k</em>{\text{D}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>200 mm Hg</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.00</td>
</tr>
<tr>
<td>1:1</td>
<td>300</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.59</td>
</tr>
<tr>
<td>1:3</td>
<td>440</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.33</td>
</tr>
</tbody>
</table>
Fig: 1.15 D₂ Reaction Fitted to Experimental Rate Equation.
high temperatures (> 800°C) which they claimed was due to the formation of molecular oxygen. They also found that inhibition occurred if small amounts of oxygen were added. This result was in apparent contradiction to Melville's observation that the addition of oxygen markedly catalysed the slow reaction [17].

In an attempt to resolve this contradiction and to gather, if possible, evidence for the chain termination reaction suggested Fenimore and Kelso of

\[ H + O_2 + M \rightarrow HO_2 + M \]

a series of runs were carried out in which varying amounts of oxygen were present. Pre-mixed gas mixtures were used and at oxygen concentrations greater than about 2% the initial reaction was so fast that appreciable amounts of nitrous oxide were consumed in the short time taken for the reaction mixture to be admitted to the reaction vessel. When oxygen comprised 4% or more of the reaction mixture a "kick" was observed on the manometer as the gases were admitted to the reaction vessel showing an explosion had occurred.

Fig. 1.16a illustrates the main features obtained when oxygen is added to N₂O/H₂ mixtures. The results shown are for a 1:1 mixture of N₂O/H₂ to which increasing amounts of oxygen were added. In each run the initial pressure of nitrous oxide was 50 mm Hg. Two features are apparent:

i) the initial rate of reaction is markedly increased as increasing amounts of oxygen are added.

ii) after the initial increase in rate (after 1 to 2 mins) the reaction is inhibited. This is especially marked in the runs with > 1.7% oxygen and the reactions in which noticeable explosions occurred (e.g. Run 245) on admitting gases to the reaction vessel take place at a very slow rate.
Fig: 1 16 O₂ Catalysis.
In this system oxygen acts both as a catalyst and an inhibitor. The inhibition observed could be explained by the chain termination step (as suggested by Fenimore and Kelso),

\[ H + O_2 + M \rightarrow HO_2 + M \]

since water, which is a product of reaction, is about an order of magnitude more efficient as a third body than the other molecules in the system (vide Schofield's tabulation of rate constants [59]). The addition of water to reaction mixtures containing \( O_2 \) in concentrations up to about 20% of total pressure produced neither a noticeable reduction in the initial rate of reaction nor an increased inhibition in the later stages (Fig. 1.16b). This tends to be evidence against the \( HO_2 \) forming termination since inhibition starts to occur after about 10 mm H\( _2 \)O has been formed (i.e., app. 10% water). The results shown must be treated with some caution. The point at which inhibition is observed depends to some extent on how much reaction occurs as the gases are admitted to the reaction vessel, even using identical mixtures it was difficult to obtain reproducible results. The runs containing water (294 and 295) follow the behaviour of the reaction without water (293) fairly well in the first few minutes of reaction. In the latter stages however Run 294 appears to become faster and joins the reaction curve for the uncatalysed reaction (291/2). This was probably due to an instrumental fault but this was not noticeable when the recorder trace was analysed.

The abrupt change in rate after about 1 minute of reaction suggested that the added oxygen was quickly used up possibly producing an inhibitor. An attempt was made to follow the "fate" of molecular oxygen during the reaction by taking samples of the reaction mixture at different reaction times and analysing them mass spectrometrically. The procedure adopted was as follows:
(vi) Effect of Nitric Oxide:

In studying the explosive reaction of \( \text{N}_2\text{O}/\text{H}_2 \) mixtures both Fenimore
Table 1.4 Mass Spectrometric analysis of oxygen catalysed reaction

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample Time</th>
<th>[N₂O] at Sample Time</th>
<th>Peak Heights (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O₂</td>
</tr>
<tr>
<td>259</td>
<td>1 min</td>
<td>Not measured</td>
<td>35</td>
</tr>
<tr>
<td>260</td>
<td>8</td>
<td>&quot;</td>
<td>28</td>
</tr>
<tr>
<td>261</td>
<td>20</td>
<td>&quot;</td>
<td>12</td>
</tr>
<tr>
<td>262</td>
<td>1</td>
<td>41.5 mm Hg</td>
<td>0.6</td>
</tr>
<tr>
<td>263</td>
<td>8</td>
<td>22.3</td>
<td>0.4</td>
</tr>
<tr>
<td>264</td>
<td>20</td>
<td>9.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Please note

i) 259 to 261 Runs with app. 3% O₂
ii) peak heights can only be regarded as being approximately related to the concentrations of molecules in the reaction vessels.
iii) the two series of runs were carried out on two different days, and uncertainty about the behaviour of the mass spectrometer on the two days preclude direct quantitative comparison of peak heights between the two sets of results.
and Kelso [20] and Destriau and Navailles [21] obtained minima in their explosion limit versus pressure curves. Typically the minimum occurred in the region of 800°C and was more pronounced in nitrous oxide rich mixtures. Fenimore and Kelso, as was mentioned in the previous section, attributed the raising of the explosion limit above 800°C to the chain termination involving hydrogen and molecular oxygen. It must be borne in mind however that at these temperatures appreciable amounts of nitric oxide would be formed by the thermal decomposition of N₂O.

At the temperatures at which this present work was carried out little or no nitric oxide would be expected to be formed and the reaction proceeds at a moderate rate. An explanation is needed to account for the inhibition observed after the initial stages in the oxygen catalysed reaction. The addition of nitric oxide to the N₂O/H₂ reaction would be expected to inhibit the chain reaction as the propagating radicals could react with the NO. A sequence of reactions such as studied by Clyne [112] would be expected to occur.

\[ H + NO + M \rightarrow HNO \]
\[ H + HNO \rightarrow NO + H₂ \]

plus two minor reactions

\[ HNO + HNO \rightarrow H₂O + N₂O \]
\[ HNO + NO \rightarrow OH + N₂O \]

A similar set of reactions probably occur with the OH radical. In each case chain termination takes place followed by regeneration of the nitric oxide.

By observing the effect of adding small amounts of NO to mixtures of N₂O/H₂ the role of nitric oxide as an inhibitor could be studied. The runs were carried out in duplicate and average reaction curves were drawn. By comparing these curves with the comparable ones from the uninhibited reactions the ratio of the overall rate constants for
the uninhibited and inhibited reactions were determined (see Appendix 1.2 for details of the method). The results obtained are summarised in Fig. 1.17a in which the ratio of rate constant for the inhibited reaction to that of the uninhibited (k_{NO}/k_{normal}) is plotted against the percentage of nitric oxide in the mixture. The inhibitory effect of nitric oxide is about the same for N_{2}O/H_{2} ratios of 3:1 and 1:1 but is greater in mixtures with excess hydrogen (1:3).

It is worth noting that the plots from which the rate constant ratios were obtained were linear over the reaction period. This indicates that the reaction curves for the inhibited and uninhibited reactions were congruent over the experimental range (up to about 20% total reaction). The inference that may be drawn is that the nitric oxide concentration remains approximately constant during the course of reaction, which is what was predicted by the postulated inhibition mechanism. It may be seen from Fig. 1.17b that the inhibited reaction is approximately proportional to [NO]^{-2} (the actual values from graph 1.17b are, [NO]^{-0.4} for 3:1 and 1:1 mixtures and [NO]^{-0.5} for 1:3 mixtures). The postulated inhibition mechanism may be considered as an overall process of:

\[
2H + NO + M \xrightarrow{k_i} H_2 + NO + M
\]

If this is added to the tentative reaction mechanism the rate of reaction is given by

\[
\frac{-d[N_2O]}{dt} = k_1[N_2O] + k_2[N_2O] \sqrt{\frac{2k_1[N_2O]}{(k_5 + k_4[NO])[M]}} \quad (E)
\]

compared with

\[
\frac{-d[N_2O]}{dt} = k_1[N_2O] + k_2[N_2O] \sqrt{\frac{2k_1[N_2O]}{k_5[M]}} \quad (D)
\]

for the uninhibited reaction. The inhibited mechanism is \(-\frac{1}{2}\) order in
a). Nitric Oxide Inhibition.

![Graph showing Nitric Oxide Inhibition](image)

\[ \frac{N_2O}{H_2} \]

3:1 ×
1:1 ○
1:3 △

% NO.

1 2 3 4 5 6

b). Order of Inhibition Reaction.

![Graph showing Order of Inhibition Reaction](image)

Log\(_2\) (K/NO/normal)

Log\(_{10}\) (% NO).

1.0 0.0 0.2 0.4 0.6 0.8

Fig: 1.17 Effect of Nitric Oxide.
nitric oxide. As the NO inhibition experiments progressed slight "tailing" of the mercury in the reaction vessel manometer was observed. This was due to attack by NO₂, small amounts of which must be formed by oxygen atom reaction with nitric oxide.

(vii) Activation Energy:

According to Melville the high and low pressure reactions possess different activation energies (32 kcal and 49 kcal respectively). Both values are lower than the generally accepted value of 58 kcal for the thermal decomposition of N₂O. If these values are correct two completely different mechanisms must be expected for the high and low pressure regions, and an initiation mechanism other than the production of oxygen atoms by unimolecular N₂O decomposition must be considered.

A study of both the high and low pressure reactions over a temperature range 540 to 593°C and mixture compositions 1:3, 1:1 and 3:1 N₂O/H₂ was made. Arrhenius plots using both initial rate and half reaction time data were drawn. The experimental points were badly scattered but the activation energy obtained was the same, within the limits of experimental scatter, in both the high and low pressure reaction regions. A more satisfactory method of determining the activation energy was to plot the logarithm of the ratio of the overall rate constant at different temperatures and the rate constant at the "standard" temperature of 560°C (k₅/k₅60) for the different mixtures against reciprocal temperature. This had the advantage that the whole reaction curve was taken into account (not just one point as with initial rate and half-life data) and that the results from all mixtures were normalised permitting them to be plotted on a single graph. The Arrhenius plot obtained is shown in Fig. 1.18. There is still considerable scatter but it can be seen that there is no
Fig: 1.18 Arrhenius Plot.
difference in activation energy between different mixtures or the high and low pressure reactions. The activation energy obtained from the least squares fit is 62.5 kcal mole$^{-1}$ with a standard deviation of ±2.1 kcal. This value is slightly higher than that for the nitrous oxide decomposition.
DISCUSSION

In the preceding section tentative proposals were put forward to explain some of the experimental results. These proposals enabled further experiments to be constructed to yield more information of the reactions involved in the combustion of hydrogen in nitrous oxide. This discussion collects the experimental evidence and explains the experimental results more fully.

(1) Reaction Mechanism:

Any mechanism must explain the experimental result that the order of reaction changes from first to second order in nitrous oxide as the pressure is lowered and that the order with respect to hydrogen is low throughout. The inert gas effects support the hypothesis that the change in order is due to a change from quadratic chain termination in the gas phase to chain termination on the walls of the reaction vessel. The tentative reaction mechanism proposed in the results section embodies these features. To recapitulate:

\[
\begin{align*}
    N_2O & \rightarrow N_2 + O \\
    O + H_2 & \rightarrow OH + H \\
    H + N_2O & \rightarrow N_2 + OH \\
    OH + H_2 & \rightarrow H_2O + H \\
    H + H + M & \leftrightarrow H_2 + M \\
    H & \rightarrow \text{Wall}
\end{align*}
\]

The overall reaction rate is given by:

\[
-\frac{d[N_2O]}{dt} = k_1[N_2O] + k_3[N_2O][H] \tag{F}
\]

Steady state treatment gives

\[
-\frac{d[N_2O]}{dt} = k_1[N_2O] + k_3[N_2O] \sqrt{\frac{2k_4[N_2O]}{k_5[M]}} \tag{C}
\]

if wall termination is neglected, and
The test of any reaction mechanism is whether it provides sensible agreement with the experimental results when the rate constants for the individual steps are substituted into the final rate equation. Over the last ten years a large amount of data has been collected on the rate constants of individual reactions. Table 1.5 gives the published rate constants of the main reactions considered in this discussion. The majority of these were obtained from a recent article by Schofield [59] in which a large number of rate constants for reactions involving atmospheric neutral species have been collected and evaluated.

The value of the rate constant for the initiation reaction was estimated approximately from runs carried out during the investigation of carbon monoxide oxidation. At 700°C an initial rate for the decomposition of nitrous oxide (100 mm Hg) was found to be 7.7 mm Hg min⁻¹ (Runs 96, 171, 176, appendix 2.1). In the initial stages of decomposition every nitrous oxide molecule decomposing results in another molecule reacting (Reuben and Linnett [8]).

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \quad (1) \]

Thus the measured rate is approximately twice that of the decomposition step (1). An approximate value for the pseudo first order rate constant in min⁻¹ is therefore obtained by dividing the observed rate by (2 x initial pressure x 60). If this value is coupled with the experimentally observed activation energy of 57.8 kcal (vide section dealing with N₂O/CO reaction) the rate constant for reaction (1) is given by:

\[ k_1 = 6.30 \times 10^9 \exp \left( -\frac{57.8}{RT} \right). \]
### Table 1.5 Rate Constants for \textsubscript{N\textsubscript{2}O/H\textsubscript{2}} Reaction

(all units in cm\textsuperscript{3} molecule\textsuperscript{-1} sec\textsuperscript{-1} unless otherwise stated)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant</th>
<th>(k_{550^\circ C})</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O})</td>
<td>(6.3 \times 10^3 \exp(-57.8/RT))</td>
<td>(4.3 \times 10^{-6})</td>
<td>This work</td>
</tr>
<tr>
<td>2. (\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H})</td>
<td>(2.1 \times 10^4 \exp(-9.40/RT))</td>
<td>(7.2 \times 10^{-14})</td>
<td>[59]</td>
</tr>
<tr>
<td>3. (\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH})</td>
<td>(4.9 \times 10^4 \exp(-10.77/RT))</td>
<td>(7.3 \times 10^{-14})</td>
<td>[59]</td>
</tr>
<tr>
<td>4. (\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H})</td>
<td>(6.3 \times 10^4 \exp(-5.49/RT))</td>
<td>(2.3 \times 10^{-12})</td>
<td>[59]</td>
</tr>
<tr>
<td>5. (\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M})</td>
<td>(2 \times 10^{-32})</td>
<td>(2.1 \times 10^{-32})</td>
<td>[59]</td>
</tr>
<tr>
<td>6. (\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M})</td>
<td>(2 \times 10^{-30})</td>
<td>(2 \times 10^{-30})</td>
<td>[59]</td>
</tr>
<tr>
<td>7. (\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M})</td>
<td>(3 \times 10^3 \times 10^{-30})</td>
<td>(5 \times 10^{-30})</td>
<td>[59]</td>
</tr>
<tr>
<td>8. (\text{H} \rightarrow ) wall</td>
<td>(\gamma = 7 \times 10^{-3})</td>
<td>(3.5 \times 10^{-3})</td>
<td>[85, 86]</td>
</tr>
<tr>
<td>9.(\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M})</td>
<td>(4 \times 10^{-33})</td>
<td>(4 \times 10^{-33})</td>
<td>[59]</td>
</tr>
<tr>
<td>10. (\text{N}_2\text{O} \rightarrow 2\text{NO})</td>
<td>(7.16 \times 10^{-11} \exp(-24.1/RT))</td>
<td>(3.6 \times 10^{-17})</td>
<td>[59]</td>
</tr>
<tr>
<td>11. (\text{OH} + \text{H})</td>
<td>(4.19 \times 10^{-10} \exp(-16.79/RT))</td>
<td>(1.7 \times 10^{-14})</td>
<td>[59]</td>
</tr>
<tr>
<td>12. (\text{O} + \text{N}_2\text{O} \rightarrow 2\text{NO})</td>
<td>(4 \times 10^{-33} \exp(1.93/RT))</td>
<td>(1.3 \times 10^{-32})</td>
<td>[59, 79]</td>
</tr>
<tr>
<td>13. (\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M})</td>
<td>(4.2 \times 10^{-32} \exp(-47/RT))</td>
<td>(4.9 \times 10^{-32})</td>
<td>[112]</td>
</tr>
<tr>
<td>15. (\text{H} + \text{N}_2\text{O} \rightarrow \text{NO} + \text{H}_2)</td>
<td>(\geq 5 \times 10^{-14})</td>
<td>[112]</td>
<td></td>
</tr>
</tbody>
</table>
The value of the pre-exponential term is a surprising $10^5$ times smaller than that quoted by Olschewski, Tröe and Wagner \[42\] (they obtain $k_1 = 10^{14.7} \exp(-58/RT) \text{sec}^{-1}$ for shock tube decomposition in the region of 2000$^\circ$K.). Kaufman, Gerri and Bowman studied the thermal decomposition of N$_2$O under conditions similar to those used in this thesis \[5\]. They obtained an initial rate of N$_2$O decomposition of 0.71 mm/min at 927$^\circ$K and 100 mm Hg pressure. This compares fairly well with a value of 1.85 mm/min predicted by $k_1$ in Table 1.5.

The rate constants for the third body termination reactions are only approximate. For reactions 5 and 6 the rate constant for the reaction when H$_2$ is the third body are given since hydrogen appears to be between 5 and 10 times more efficient a third body than nitrogen or water, and therefore in the early stages of reaction the termination step with hydrogen as third body would be expected to predominate. Water is shown as an efficient third body for the recombination of hydroxyl radicals (reaction 6 $\text{H}_2\text{O} \approx \text{H}_2 + \text{O}_2 \approx \text{CO}_2 \approx \text{N}_2$), there is no value reported for hydrogen. The figure quoted gives the range of values for H$_2$O, O$_2$, CO$_2$ and N$_2$ as third bodies.

One is now in a position to test the tentative reaction mechanism. In this test and all subsequent tests a 1:1 mixture of N$_2$O/H$_2$ at a total pressure of 200 mm Hg is considered. The predicted result will be compared with the experimental initial rate of reaction, obtained from Fig. 1.13, of 20 mm/min. Equation C shows that the initial rate is equal to

$$\text{Rate} = k_2 [N_2O] \sqrt{\frac{2k_1 [N_2O]}{k_2 [M]}}$$

(the initiation step term is negligible and has been omitted). If [M] is taken to be the hydrogen pressure, the equation reduces to the simple expression.
Rate = \( k_3 \sqrt{\frac{2k_1}{k_5}} [N_2O] \)

The expression is dimensionally correct and yields a rate of \( 9.1 \times 10^3 \) mm Hg./min. on substitution of the rate constants. This is \( 4.5 \times 10^2 \) too high (c.f. the experimental value of \( \approx 20 \) mm/min) and indicates that this very simple mechanism is not adequate.

One now considers the effect of introducing a second termination process involving OH radicals as well as H atoms.

\[
H + OH + M \rightarrow H_2O + M
\]  (6)

Rates of radical formation are given by

\[
\frac{d[O]}{dt} = k_1[N_2O] - k_2[H_2][O]  \]  (G)

\[
\frac{d[H]}{dt} = k_2[H_2][O] - k_3[N_2O][H] + k_4[H_2][OH] - k_5[H]^2[M] - k_6[H][OH][M]  \]  (H)

\[
\frac{d[OH]}{dt} = k_2[H_2][O] + k_3[N_2O][H] - k_4[H_2][OH] - k_6[H][OH][M]  \]  (I)

Applying the steady state approximation:

\[
[O] = \frac{k_1[N_2O]}{k_2[H_2]}
\]

The subtraction of equations H and I give

\[
0 = 2k_3[N_2O][H] - 2k_4[H_2][OH] + k_5[H]^2[M]
\]

which yields

\[
[OH] = \frac{(2k_3[N_2O] + k_5[M][H])[H]}{2k_4[H_2]}
\]

But \( k_3[N_2O] \gg k_5[M][H] \)

\[
\therefore \quad [OH] = \frac{k_3[N_2O]}{k_4[H_2]} \cdot [H]
\]
Adding equations H and I

\[ 2k_2[H_2][O] = k_3[M][H]^2 + 2k_6[M][OH] \]

and substituting for [OH] and [O]

\[ [H]^2 = \frac{2k_1[N_2O] \cdot k_5[H_2]}{[M](k_5 \cdot k_4[H_2] + 2k_6 \cdot k_2[N_2O])} \]

This gives a rate of

\[ -\frac{d[N_2O]}{dt} = k_3[N_2O] \sqrt{\frac{2k_1k_4[N_2O][H_2]}{[M](k_5\cdot k_4[H_2] + 2k_6\cdot k_2[N_2O])}} \]

This expression is again approximately first order in \( N_2O \) and a small order in hydrogen is also predicted. Assuming that \( [N_2O] = [H_2] = [M] \) the rate becomes

\[ \text{Rate} = k_3 \sqrt{\frac{2k_1k_4}{(k_5k_4 + 2k_6k_2)}} [N_2O] \]

again the equation is dimensionally acceptable and predicts a rate of \( 3.37 \times 10^3 \text{ mm Hg/min.} \) This is slightly better than the previous approximation but is still 170 times too large.

It is obvious that a more efficient chain termination process must be introduced into the mechanism. The recombination of hydroxyl radicals is between \( 10^2 \) and \( 10^3 \) times as efficient as hydrogen atom recombination but it introduces an added complication that the hydrogen peroxide formed might decompose yielding molecular oxygen that would then be able to start further reaction chains. As a compromise it will be assumed that this reaction's effect is to terminate the chain and to produce an oxygen atom which will be capable of further reaction. If the H+H+M reaction is neglected then the chain termination processes are:

\[ \text{H + OH} \rightarrow \text{H}_2\text{O} + \text{M} \quad (6) \]

and \( \text{OH + OH} \rightarrow \text{H}_2\text{O}_2 + \text{M} \rightarrow \text{H}_2\text{O} + \text{O} + \text{M} \quad (7) \)

Steady state approximation yields:
\[
[O] = \frac{k_1[N_2O] + k_7'[H_2O_2]}{k_2[H_2]}
\]

The \(k_7'[H_2O_2]\) term will only be equal to \(k_1[N_2O]\) term if all chains are terminated by step 7 and if all \(H_2O_2\) eventually leads to \(O\) atoms which react with hydrogen to start reaction chains. Since the rates of step 6 and step 7 are approximately equal, \(k_7'[N_2O]\) will at best be only 50% of \(k_1[N_2O]\), it is convenient to consider the steady state oxygen atom concentration as

\[
[O] = \frac{k_1[N_2O]}{k_2[H_2]}
\]

\[\frac{-d[H]}{dt} \text{ becomes } k_2[H_2][O] + k_3[N_2O][H] + k_4[H_2][OH] - k_6[H][OH][M] \quad (J)\]

and

\[\frac{-d[OH]}{dt} = k_2[H_2][O] + k_3[N_2O][H] - k_4[H_2][OH] - k_6[H][OH][M] - k_7[OH]^2[M] \quad (K)\]

If (J) is subtracted from (K)

\[0 = 2k_3[N_2O][H] - (k_4[H_2] - k_7[M][OH])[OH]\]

as \(k_4[H_2] \gg k_7[M][OH]\)

then

\[[OH] = \frac{k_2[N_2O][H]}{k_4[H_2]}\]

which is the same expression as was obtained in the previous case.

Adding (J) and (K) one obtains

\[0 = 2k_2[H_2][O] - 2k_6[M][H][OH] - k_7[M][OH]^2\]

which on substitution for \([O]\) and \([OH]\) gives:

\[\frac{[H]^2}{(2k_6k_3k_4[N_2O][H_2] + k_7k_3^2[N_2O]^2)[M]}\]

The rate is given by:

\[\text{Rate} = k_3 \sqrt{\frac{2k_6k_4^2}{(2k_6k_3k_4 + k_7k_3^2)}} \cdot [N_2O]\]

if it is assumed that \([M] = [H_2] = [N_2O]\). The overall rate equation is again first order in \(N_2O\) with some slight dependence on \(H_2\).
Substitution for the rate constants predicts a rate of $3.5 \times 10^3$ mm Hg/min. This result is nearly the same as the previous case. This reflects the efficiency of the chain propagating step (4) which is introduced into the rate equation when termination by OH radicals is considered. The effect on reaction rate from considering the different termination steps is summarised in Table 1.6.

It is not possible to consider all three termination steps together and obtain, from steady state considerations, an expression for the rate of reaction by algebraic manipulation. Accordingly a computer programme was devised to solve for $[H]$, $[O]$ and $[OH]$ the three steady state expressions for $d[H]/dt$, $d[O]/dt$, $d[OH]/dt$. These equations

\[
\begin{align*}
\frac{d[H]}{dt} &= k_2[H_2][OH] + k_3[N_2O][H] - k_4[H_2][OH] - k_5[M][H][OH] \\
\frac{d[O]}{dt} &= k_1[N_2O] + k_4[OH]^2[M] - k_2[H_2][O] \\
\frac{d[OH]}{dt} &= k_2[H_2][OH] + k_3[N_2O][H] - k_4[H_2][OH] - k_5[M][H][OH] - k_7[M][OH]^2
\end{align*}
\]

are set equal to zero and solved for the steady state radical concentrations with the rate constant values shown in Table 1.5 and the pressures of $H_2$ and $N_2O$ inserted. For 1:3, 1:1 and 3:1 $N_2O/H_2$ mixtures at a fixed concentration of $N_2O$ the radical concentrations obtained are shown in Table 1.7. The rate of reaction can be calculated from the hydrogen atom concentration ($-d[N_2O]/dt = k_3[N_2O][H]$). For the 1:1 mixture an initial rate of reaction of $2.39 \times 10^3$ mm/min is predicted. This is still $1.19 \times 10^2$ larger than the observed rate.

The programme was also designed to vary each of the 7 rate constants in turn over a range $10^{-1}$ to $10^1$ of the published value and obtain values of $[H]$, $[O]$ and $[OH]$ for each variation of rate constant. This was done in order to see which reaction (or reactions) in the mechanism is (are) the most susceptible to inaccuracies in the published rate constants. The effect of varying the rate constants on the reaction
### Table 1.6 Approximations to Reaction Mechanisms

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>Chain termination</th>
<th>Predicted Rate / Exptl. rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H+H+M \rightarrow H_2+M$</td>
<td>$4.5 \times 10^2$</td>
</tr>
<tr>
<td>2</td>
<td>$H+H+M \rightarrow H_2+M$</td>
<td>$1.7 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>$H+OH+M \rightarrow H_2O+M$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$H+OH+M \rightarrow H_2O+M$</td>
<td>$1.8 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>$OH+OH+M \rightarrow H_2O_2+M$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow H_2O+O$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$H+H+M \rightarrow H_2+M$</td>
<td>from computed value for $[H]$</td>
</tr>
<tr>
<td></td>
<td>$OH+H+M \rightarrow H_2O+M$</td>
<td>value for $[H]$</td>
</tr>
<tr>
<td></td>
<td>$OH+OH+M \rightarrow H_2O_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow H_2O+O$</td>
<td></td>
</tr>
</tbody>
</table>

### Table 1.7 Computed Values of $O$, $H$ and $OH$ Radical Concentrations

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$30 \text{ mm N}_2\text{O}$</th>
<th>$100 \text{ mm N}_2\text{O}$</th>
<th>$300 \text{ mm N}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mm $H_2$</td>
<td>100 mm $H_2$</td>
<td>100 mm $H_2$</td>
<td>100 mm $H_2$</td>
</tr>
<tr>
<td>$[H]$</td>
<td>$5.1 \times 10^{-4}$ mm Hg</td>
<td>$4.7 \times 10^{-4}$ mm Hg</td>
<td>$3.6 \times 10^{-4}$ mm Hg</td>
</tr>
<tr>
<td>$[OH]$</td>
<td>$5.5 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$3.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$[O]$</td>
<td>$1.8 \times 10^{-9}$</td>
<td>$5.5 \times 10^{-9}$</td>
<td>$1.9 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate</th>
<th>Predicted</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{mm/min}$</td>
<td>$7.7 \times 10^2$</td>
<td>$4 \text{ mm/min}$</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^3$</td>
<td>$20 \text{ mm/min}$</td>
</tr>
<tr>
<td></td>
<td>$5.5 \times 10^3$</td>
<td>$48 \text{ mm/min}$</td>
</tr>
</tbody>
</table>
is shown graphically in Fig. 1.19. In this figure the predicted initial rate is plotted (on a log_{10} scale) against the variation of rate constant (also on a log_{10} scale). It can be seen that the reaction rate is independent of $k_2(O+H_2 = OH+H)$ and depends to only a small extent on the termination reactions $k_5(H+H+M)$ and $k_7(OH+OH+M)$. The rate is proportional to the square root of $k_1(N_2O=N_2+O)$, slightly greater than the $3/2$ power of $k_3(H+H_2=H_2O+H)$ and slightly smaller than the $3/2$ power of $k_4(OH+H_2=H_2O+H)$. The rate is inversely proportional to the square root of the termination step $k_6(H+OH+M)$. The rate equation must therefore be of the form:

$$-\frac{d[N_2O]}{dt} \propto (k_1 k_3 k_4)^{3/2} k_6^{-1/2}.$$

If one applies the steady state treatment to the reaction scheme

1. $N_2O \rightarrow N_2+O$
2. $O+H_2 \rightarrow OH+H$
3. $H+N_2O \rightarrow N_2+OH$
4. $OH+H_2 \rightarrow H_2O+H$
5. $H+OH+M \rightarrow H_2O+M$

the rate equation

$$-\frac{d[N_2O]}{dt} = k_3[N_2O] \sqrt{\frac{k_1 k_4[N_2O][H_2]}{k_6 k_3[N_2O][M]}}$$

is obtained. It can be seen that this possesses the required dependence on rate constants and furthermore predicts an order of reaction of 1 in $N_2O$ and negligible order in $H_2$ which agrees with experiment.

The discrepancy between the observed reaction rate and the one calculated from published rate constants raises a dilemma. One must postulate that:

1) the published rate constants are in error by factors much larger than ten (c.f. Fig. 1.19)
Fig: 1.19 Dependence of Rate on Rate Constants.
or ii) there must be an efficient chain termination step not already considered,

or iii) the steady state approximation does not apply.

The first approach is not intellectually satisfying and the third heresy, particularly in a reaction as slow as this. Therefore the second possibility must be considered.

A chain termination step is required that will not alter the overall reaction dependence on $N_2O$ and $H_2$. All possible quadratic terminations of the chain propagating $H$ and $OH$ radicals have been considered and therefore attention must be turned to possible reactions that can compete with the chain initiation reaction.

$$0 + H_2 \rightarrow H + OH \quad (2)$$

The reaction

$$0 + N_2O \rightarrow 2NO \quad (11)$$

is at first sight attractive since it produces nitric oxide that would be able to inhibit the overall reaction both by reacting with further $O$ atoms ($O+NO+M \rightarrow NO_2+M$) and by inhibiting the chain mechanism by reaction with $H$ and $OH$. However, as Table 1.5 indicates, reaction (11) has a higher activation energy than (2). At 560°C its rate constant is about 2000 times smaller than that of reaction (2) and its inclusion in the mechanism will not cause any change in rate. The only other molecule that is available for oxygen to react with is hydrogen. The bimolecular chain initiating step 2 has a moderate activation energy (16.8 kcal) and therefore only a small fraction of collisions will be reactive. A termolecular process resulting in the formation of water would be expected to have a low or even negative activation energy.

viz. $$O + H_2 + M \rightarrow H_2O + M \quad \Delta H = -116 \text{ kcal} \quad (9)$$

It is postulated therefore that reaction 9 competes with reaction 2 for the available oxygen atoms. An idea of the rate of reaction 9 may
be obtained from the observed discrepancy between the "computer predicted" rate and the observed reaction rate. For a 1:1 N₂O/H₂ mixture at a pressure of 200 mm Hg the difference is 1.2 x 10⁻². The rate constant for reaction 2 is 7.3 x 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹ at 560°C, and therefore the pseudo bimolecular rate constant for reaction 9 (k₉[M]) will be of the order 8.7 x 10⁻¹². If [M] = 200 mm Hg (2.32 x 10¹⁸ molecules cm⁻³) then k₉ = 3.75 x 10⁻³⁰ cm⁶ molecule⁻² sec⁻¹, which compares favourably with the values of other termolecular reactions (e.g. Q₂+H⁺+H₂O → H₂O₂ of 3 x 10⁻³¹, H⁺OH+M of 2 x 10⁻³⁰ and OH+OH+M of between 3 and 18 x 10⁻³⁰ cm⁶ molecule⁻² sec⁻¹ [59]).

A rough estimate of the activation energy of reaction 9 may be obtained from the observed difference in the overall activation energy of the N₂O/H₂ reaction compared with that for N₂O decomposition. In the reaction the overall activation energy may be regarded as the activation energy of the initiation process minus the activation energy of the O+H₂+M termination reaction, since this will be the main termination step.

i.e. [E(activation) - E(O+H₂+M)] = E(overall)

E(activation) is the activation energy of N₂O decomposition, namely 58 kcal. The overall activation energy was found experimentally to be 62.5 ± 2.0 kcal, thus reaction 9 has a negative activation energy of 4.5 ± 2.0 kcal. Negative activation energies for termolecular processes are not unknown and Amadur and Hemsley list activation energies for processes such as X + X + M → X₂ + M where X is an halogen atom ranging from 0 to -8 kcal [84]. If an activation energy of -4.5±2.0 kcal is assumed the rate constant for k₉ becomes

k₉ = 3.9 x 10⁻³¹ exp(-4.5 ± 2.0/kT) cm⁶ molecule⁻² sec⁻¹.

To quote Schofield "Our knowledge of termolecular rate constants is still quite poor. Data is either lacking altogether, e.g.
of the fifteen (termolecular) reactions listed it was possible to quote temperature dependent expressions for only five. The value for \( k_9 \) fulfils two of Schofield's wishes though the limits of error are too large for satisfaction.

To check the feasibility of \( k_9 \), the reaction \( O+H_2+M \rightarrow H_2O+M \) may be added to the reaction scheme postulated for the low pressure reaction. In this case the only chain termination step considered is destruction of hydrogen atoms at the reaction vessel walls. Steady state treatment now gives

\[
\frac{\text{d}[N_2O]}{\text{dt}} = k_1[N_2O] + \frac{2k_5k_3}{k_8k_9}[N_2O]^2 [1]
\]

It is necessary to obtain a value for the rate of recombination of hydrogen atoms at the reaction vessel walls before one can predict the rate of the low pressure reaction. There is some doubt as to the order of the H atom recombination on quartz surfaces. Wood and Wise [85] in some comparatively recent work claim that the recombination is first order at room temperature but rises to second order at temperatures greater than 500°K. Green, Jennings, Linnett and Schofield [86] on the other hand found that the process was first order up to 600°C.

There is remarkably good agreement, however, between the two papers for the value of the recombination coefficient \( \gamma \) (WW found \( \gamma = 3.3 \times 10^{-2} \) at 550°C, and GJLS found \( \gamma = 4 \times 10^{-2} \) at 600°C). Green and co-workers found that acid washing of the silica surface reduced the value of \( \gamma \) to about 0.2 of the original value. If second order recombination
occurred in this work the rate equation for the low pressure reaction would not be second order in \( N_2O \), in fact it would vary from about 1 to a maximum of 1.5. It will be assumed therefore that a first order process is taking place.

The rate constant for wall termination \( (k_9) \) may be obtained by equating the rate of wall termination reaction to the number of collisions that \( H \) atoms undergo with the reaction vessel walls which result in recombination.

\[
e.g. \quad k_9[H] = Z \cdot \gamma
\]

where \( Z \) is the number of collisions of \( H \) atoms with reaction vessel walls per second. The value of \( \gamma \) will be taken to be \( 7 \times 10^{-3} \) (this is obtained from an average value of the \( \gamma \)'s obtained by GJLS and WW, and the observation of GJLS that acid washing of the quartz recombination surface results in a reduction of \( \gamma \) to about one fifth of the value for an untreated quartz surface).

Kinetic theory of gases predicts that the total mass of gas striking one square centimetre of containing vessel wall per second \( (\mu) \) is given by [87]:

\[
\mu = P \left( \frac{M}{2\pi nRT} \right)^{\frac{3}{2}}
\]

where \( P \) is the gas pressure and \( M \) the molecular weight of the gas. For the expression to be dimensionally correct the units must be as follows:

\[
\mu = g \cdot cm^{-2} \cdot sec^{-1}
\]

\[
P = \text{ergs} \cdot cm^{-2}
\]

\[
M = \text{gram molecular weight}
\]

\[
R = \text{ergs} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}
\]

\[
T = \text{K}
\]

It is convenient to express \( \mu \) in terms of number of moles striking a square centimetre per second in which case expression \( (M) \) becomes
\[ \mu^i = \frac{P}{M} \left( \frac{M}{2n\mu M} \right)^{\frac{1}{2}} \]  

If one considers \( P \) as representing the partial pressure of hydrogen atoms and multiplies expression \( N \) by the surface area of the reaction vessel the collision number \( Z \) in equation (1) is obtained.

Therefore,

\[ k_8[H] = [H] \cdot \text{area} \cdot \left( \frac{1}{2n\mu M} \right)^{\frac{1}{2}} \gamma \]  

provided \([H]\) is expressed in moles \( \text{cm}^{-3} \) and area in \( \text{cm}^2 \).

\[ k_8 = \text{area} \cdot \left( \frac{1}{2n\mu M} \right)^{\frac{1}{2}} \gamma \]

The surface area of the reaction vessel is 334 sq cm, \( R = 8.315 \times 10^7 \) erg \( \text{mole}^{-1} \text{K}^{-1} \), \( T = 833^\circ \text{K} \), \( M = 1 \) and \( \gamma = 7 \times 10^{-3} \) which gives

\[ k_8 = 3.53 \times 10^{-6} \text{ sec}^{-1} \]

This value of \( k_8 \) may now be used to calculate a rate for the low pressure reaction which may then be compared with the experimental value.

For the low pressure reaction (including the step 0+H\(_2\)+M \( \rightarrow \) H\(_2\)O+M)

\[ \frac{-d[N_2O]}{dt} = \frac{2k_1k_2k_3}{k_8k_9k_3} [N_2O]^2 \]

The rate constants \( k_1, k_2 \) and \( k_3 \) are given in Table 1.5; \( k_9 \), the value being tested, is \( 3.75 \times 10^{-3} \text{ molecule}^{-1} \text{sec}^{-1} \) and \( k_8 = 3.53 \times 10^{-6} \text{ sec}^{-1} \). A typical low pressure reaction will be taken as a 1:1 mixture of N\(_2\)O/H\(_2\) at a total pressure of 50 mm Hg, therefore

\[ 2[N_2O] = [M] \]  

and the rate becomes

\[ \frac{-d[N_2O]}{dt} = \frac{k_1k_2k_3}{k_8k_9} [N_2O] \]  

The rate constant term in expression (P) has units of \( \text{sec}^{-1} \) and gives:

\[ \text{Rate} = 4.28 \times 10^{-2} \text{ mm N}_2\text{O/sec} \]
\[ = 2.57 \text{ mm N}_2\text{O/min} \]

This predicted rate of 2.57 mm N\(_2\)O/min compares very favourably with
the experimentally obtained rate of about 2 mm N₂O/min.

The agreement between the experimental and calculated rates provides striking corroboration of the need to include the oxygen atom termination step O+H₂+M → H₂O+M (9) and of the value of the rate constant (k₉ = 3.75 x 10⁻³⁰ cm⁶ molecule⁻¹ sec⁻¹) derived earlier. It also supports the hypothesis that at low pressures termination of hydrogen atoms at the reaction vessel walls is the major chain breaking step.

Since this section of the discussion is somewhat long, a summary of the main conclusions reached is presented below.

i) the change of first order to second order in the N₂O/H₂ reaction represents a change from chain breaking due to gas phase radical recombination to chain termination due to the destruction of H atoms at the reaction vessel surfaces.

ii) to explain the fact that rates computed from steady state treatment of the postulated reaction mechanism using published rate constants were at least 100 times larger than the observed reaction rate, a termination step involving oxygen atom combination with H₂ in the presence of a third body to form water is proposed, i.e.

\[ O+H₂+M \rightarrow H₂O+M \quad (9) \]

iii) an approximate rate constant for reaction 9 was derived from the discrepancy between observed and calculated rates and the activation energy data giving

\[ k₉ = 3.9 \times 10⁻³¹ \exp\left(+4.5 \pm 2.0/RT\right) \text{ cm}⁶ \text{ molecule}⁻² \text{ sec}⁻¹ \]

iv) the mechanism proposed is

\[ N₂O \rightarrow N₂+O \quad (1) \]

\[ O+H₂ \rightarrow OH+H \quad (2) \]

\[ O+H₂+M \rightarrow H₂O+M \quad (9) \]

\[ H+N₂O \rightarrow N₂+OH \quad (3) \]
\[
\begin{align*}
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H} \quad (4) \\
\text{H} + \text{H} + \text{M} & \rightarrow \text{H}_2 + \text{M} \quad (5) \\
\text{H} + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M} \quad (6) \\
\text{OH} + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O}_2 + \text{M} \quad (7)
\end{align*}
\]
\[\text{or } \frac{1}{2}(2\text{H}_2\text{O} + \text{O}_2)\]

for reactions above a total pressure of 100 mm Hg. The predominant chain breaking step appears to be 6, \((\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M})\) with steps 5 and 7 having only a marginal effect.

For reactions below a total pressure of 60 mm Hg the destruction of \(\text{H}\) atoms at reaction vessel walls replaces the gas phase termination steps 5, 6 and 7.

\(\text{e.g. } \text{H} \rightarrow \text{Wall} \quad (8)\)

(ii) Isotope Effect:

The isotope effect observed when hydrogen is replaced by deuterium results in a relatively small reduction in reaction rate \((k_H/k_D\) varies from about 2 to about 1\) compared with those commonly observed when an \(X-H\) bond is broken. It is also much smaller than the maximum isotope effect predicted by the Bigeleisen theory of isotope effects when deuterium is substituted for hydrogen (Laidler gives \(k_H/k_D\) maximum as 18 at 25°C \([64]\)).

The mechanism proposed shows a dependence of overall rate on rate constants as follows

\[-d[N_2\text{O}]/dt \propto (k_1k_3k_4/k_9k_6)^{1/2}\]

and the effect of replacing hydrogen by deuterium will now be considered.

\(k_1(\text{N}_2\text{O}=\text{N}_2+\text{O})\) is not affected by the replacement of hydrogen by deuterium. \(k_9(\text{O}+\text{H}_2+\text{M})\) and \(k_6(\text{H}+\text{OH}+\text{M})\) have virtually zero activation energy, but the dependence of collision number on molecular weight
suggests $k_H/k_D = \sqrt{2}$ in both cases.

Reaction 3 ($H+N_2O = N_2+OH$) would be expected on zero-point energy considerations to go faster with deuterium, but the collision number effect favours hydrogen. In the analogous reaction

$$H + O_2 \rightarrow OH + O$$

Kurzus [109] found that $k_H/k_D = 1.91 \exp(-1.3/RT)$ which gives a value of 0.87 at 560°C. This value will be assumed for reaction 3.

In reaction 4 ($H+OH = H_2O+H$) the isotope effect will be due both to changes in collision number, which favours hydrogen ($k_H/k_D \approx 1.414$), and on zero-point energy considerations. Ung and Baek [110] obtained a difference in activation energy of $E_{D_2} - E_{H_2} = 2.4$ kcal. This gives

$$k_H/k_D = 1.414 \exp(\frac{+2.4}{RT})$$

$$= 5.82$$

at 560°C.

The overall isotope effect is given by substituting the isotope effects for the individual steps into the rate equation.

$$\text{Rate} (H_2) = \frac{(1 \times 0.87 \times 5.82/2)^{\frac{1}{2}}}{\text{Rate} (D_2)} = 1.6$$

Considering the nature of the assumptions made, this represents excellent agreement with experiment. This comparatively small isotope effect is confirmed by Melville [19] who was unable to observe any increase in rate when he replaced hydrogen by 66% deuterium in the Hg photosensitized $N_2O/H_2$ reaction.

(iii) **Nitric Oxide Inhibition:**

Experimentally it was found that the ratio of the rate of the NO inhibited reaction to that of the normal uninhibited reaction was inversely proportional to the square root of the nitric oxide pressure. It has been demonstrated in the experimental section that if inhibition
is considered to occur via removal of hydrogen atom (and/or OH) chain carriers by the following mechanism:

\[ \text{H + NO + M} \rightarrow \text{HNO + M} \]  
(15a)

followed by

\[ \text{H + HNO} \rightarrow \text{NO + H}_2 \]  
(15b)

and the overall process (15a and b) considered to be

\[ \text{H + H + NO} \rightarrow \text{H}_2 + \text{NO} \]

then 

\[
\frac{\text{rate of inhibited reaction}}{\text{rate of normal reaction}} \propto \frac{1}{[\text{NO}]^{0.5}}.
\]

Alternatively, the inhibition may arise from NO competing with hydrogen for the available oxygen atoms.

viz.

\[ \text{O + NO + M} \rightarrow \text{NO}_2 + \text{M} \]  
(14)

This also predicts that the ratio of rates will be inversely proportional to the square root of the nitric oxide pressure. The two possibilities will now be examined in the light of the published rate constants.

a) Competition for Oxygen Atoms:

For inhibition to be apparent, the reaction O+NO+M (14) must occur at a rate comparable to the chain initiating step of \( \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \) (2).

The rate constants at 700°C are \( k_{14} = 1.3 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1} \) and \( k_2 = 7.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \). The reaction vessel pressures for all the runs investigating NO inhibition was 200 mm Hg \( (2.32 \times 10^{18} \text{ molecule/cc}) \) and for 1% nitric oxide

\[
\frac{\text{Rate } 14}{\text{Rate } 2} \approx \frac{3 \times 10^{-16}}{7 \times 10^{-14}} \approx 4.3 \times 10^{-3}
\]

The chain propagation step is very much faster than the reaction of O atoms with NO and therefore the observed inhibition cannot be due to reaction 14.

b) Inhibition of Chain Process:

The introduction of nitric oxide produces chain termination reactions that will compete with the quadratic chain termination processes.
i.e. \[ H + NO + M \rightarrow HNO + M \] (15a)
\[ H + HNO \rightarrow H_2 + NO \] (5b)

competing with
\[ H + H + M \rightarrow H_2 + M \] (5)
\[ H + OH + M \rightarrow H_2O + M \] (6)

(For simplicity only termination of H atoms will be considered. An analogous series of reactions with OH radicals is also likely to occur). Reaction (6) has a rate constant approximately 200 times larger than reaction (5). Only Reaction (6) will be considered as competing with the H atom NO reactions.

The rate constant for 15a is \( k_{15a} = 4.9 \times 10^{-32} \) cm\(^6\) molecule\(^{-2}\) sec\(^{-1}\) compared with that for reaction 6 of \( 2 \times 10^{-30} \) cm\(^6\) molecule\(^{-2}\) sec\(^{-1}\). The relative rates of the termination processes are therefore given by

\[ \frac{k_{15a}[NO][M][H]}{k_6[OH][M][H]} = \frac{5 \times 10^{-32}[NO]}{2 \times 10^{-30}[OH]} \]

The steady state concentration of [OH] will be much less than the [NO] concentrations and so reaction 15a would be expected to predominate.

The regeneration of nitric oxide by
\[ H + HNO \rightarrow NO + H_2 \] (15b)
has a rate constant of \( k_{15b} \gg 5 \times 10^{-14} \) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\) at 300\(^\circ\)K [112]. Reaction 15b will therefore occur at a comparable rate to 15a and so the termination may be considered to be a process that is second order in H atoms.

i.e. \[ H + H + NO \rightarrow H_2 + NO \]

Destrieu and Bonnefois [22] have investigated the role of nitric oxide as an inhibitor of the explosion of N\(_2\)O rich N\(_2\)O/H\(_2\)/NO mixtures. While it is difficult to make direct comparisons between exploding
systems (with their non-isothermal behaviour) and the work carried out in this thesis (isothermal), it is of interest to note that Destriau and Bonnefois postulate that the reaction

$$O + NO + M \rightarrow NO_2 + M$$

is responsible for inhibition. In their work they used mixtures with the stoichiometry $H_2 + 15(xN_2O + yNO)$ where $x + y = 1$ and NO concentrations varied between 1 and 95% $[N_2O]$ which meant that their NO/$H_2$ ratios were higher than in this work. However, even when $[NO] = [H_2]$ the $O + H_2$ reaction is 2 to 3 times faster than $O + NO + M$, and at these concentrations Destriau obtained explosion limits $100^\circ C$ higher than in nitric oxide free mixtures showing marked inhibition.

It is probable that at the lower percentages of nitric oxide the raising of the explosion limits is due mainly to $H$ atom (and probably $OH$ radical) reaction with nitric oxide.

(iv) **Effect of Oxygen**

When oxygen was added to the $N_2O/H_2$ system it was observed that after a marked increase in initial rate, inhibition occurred. The two effects will now be discussed.

a) **Initial Catalysis.**

Oxygen molecules will compete with $N_2O$ for the available hydrogen atoms. This can be thought of as a conventional $H_2/O_2$ branched chain mechanism

$$H + O_2 \rightarrow OH + O$$

$$OH + H_2 \rightarrow H_2O + H$$

$$O + H_2 \rightarrow OH + H$$

modified by the reaction

$$H + N_2O \rightarrow N_2 + OH \quad (3)$$

which does not affect the number of free radicals in the system.
Data on the explosion limits of $\text{H}_2/\text{O}_2$ mixtures in the presence of such a large excess of hydrogen (typically $\text{O}_2$ is present in concentrations that are about 4% those of hydrogen) is sparse, but in stoichiometric mixtures at 560°C the first limit is about 1 mm and the second about 160 mm, and the latter is markedly reduced by the presence of nitrous oxide [111]. This may readily be understood in terms of the non-branching reaction 3, above, delaying chain branching as well as the role which it is usually assigned as the third body in the reaction

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$$

It is to be expected therefore that the branched chain mechanism will increase the rate of the $\text{N}_2\text{O}/\text{H}_2$ reaction and lead to an increase in the steady state concentration of oxygen atoms.

b) Inhibition in the later stages of $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ Reaction:

It was observed that after about 20% reaction, the reaction curve from the $\text{O}_2$ catalysed reaction abruptly changed slope and thereafter the reaction proceeded at a slower rate than the normal oxygen free $\text{N}_2\text{O}/\text{H}_2$ reaction (Fig. 1.16a). Typically for 1.7% $\text{O}_2$ present in the reacting mixture the rate of the $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ reaction was about 0.3 to 0.4 that of the normal reaction.

The arguments presented in section a) suggest that initially the concentration of $\text{O}$ atoms is increased. It is likely therefore that small amounts of nitric oxide will be formed by the reaction

$$\text{O} + \text{N}_2\text{O} \rightarrow 2\text{NO} \quad (12)$$

(In the normal $\text{N}_2\text{O}/\text{H}_2$ reaction it was argued that the amounts of NO would be negligible). It has been shown that the presence of nitric oxide inhibits the $\text{N}_2\text{O}/\text{H}_2$ reaction. Concentrations of nitric oxide of the order of 0.25% would be sufficient to reduce the rate of reaction to 0.3 to 0.4 times that of the normal $\text{N}_2\text{O}/\text{H}_2$ reaction. It is suggested therefore that the inhibition observed after initial catalysis by oxygen
is due to the presence of 0.2 to 0.3% NO. Mass spectrometric analysis of reaction products has shown that molecular oxygen can be detected (albeit decreasing in amount as the reaction proceeds) throughout the course of reaction. This is to be expected as the nitric oxide formed would also inhibit the branched chain reaction responsible for the initial catalysis and for the removal of O₂.

One is now in a position to compare these predictions with the results of other workers. Melville [17] also observed a marked increase in reaction rate when oxygen was added. He postulated that oxygen was consumed in the initial stages, though the arguments given above suggest that this need not be the case. Melville found that in the "low pressure" reaction region the reaction curves abruptly changed slope after some reaction had occurred (i.e. inhibition), but that no change in slope was observed in the "high pressure" region. It is certainly the same effect as was observed in both the "high and low pressure" regions in this work. The probable reason why Melville did not observe the inhibition in the high pressure region is that the P₂O₅ was not able to absorb the large quantities of water produced in the initial stages of reaction fast enough to be able to follow the reaction closely.

Fenimore and Keiso [20] and Destriau and Navailles [21] investigated the explosion limits of the N₂O/H₂ system. They both obtained minima in their pressure at explosion limit vs. temperature curves. In other words the rate of the N₂O/H₂ explosion reaction increased with temperature until a certain temperature was reached (usually between 750 and 800°C), thereafter the reaction became slower with increasing temperature. The minimum was more pronounced in N₂O rich mixtures. The investigation of the "explosion limits" of non-chain branching systems is of questionable value since the position of the explosion limit is
more likely to depend on the ability of the system to dissipate the heat of reaction rather than on the chemical nature of the reactions taking place. The non-isothermal conditions accompanying such measurements make meaningful comparison with the present work difficult.

Fenimore and Kelso, who used pyrogallic washed gases, postulated the reaction

\[
H + O_2 + M \rightarrow HO_2 + M
\]

to account for the inhibition observed at higher temperatures (the oxygen being formed by N\textsubscript{2}O decomposition). They support this claim by the observation that the addition of small quantities of oxygen to the N\textsubscript{2}O/H\textsubscript{2} mixtures raised the explosion limits (i.e. inhibition occurred).

Fenimore and Kelso's experimental results are disputed by Destriau and Navailles who found that the same results were obtained whether or not the reacting gases had been washed with pyrogallic (to remove O\textsubscript{2}). They also found that the addition of oxygen lowered the explosion limits (i.e. catalysed the reaction). This serves to underline the difficulties involved in making meaningful comparisons on data obtained from the "limits" of thermal explosions.

The formation of HO\textsubscript{2} as an explanation of the inhibition of the O\textsubscript{2} catalysis observed in the present work was ruled out by the addition of 20\% H\textsubscript{2}O to the reaction vessel before the N\textsubscript{2}O/H\textsubscript{2}/O\textsubscript{2} mixtures were added. No change in the inhibition was noted. Water is a very efficient third body for the H+O\textsubscript{2}+M \rightarrow HO\textsubscript{2}+M reaction [59] and therefore if the reaction were responsible for the inhibition it would be expected to occur earlier in the reaction.

The most likely explanation of the appearance of minima in the explosion limit/temperature curves obtained by Fenimore and by Destriau is that as the temperature increases, so the proportion of nitric oxide formed is increases (this occurs because the reaction 12, O+N\textsubscript{2} \rightarrow 2NO,

It deals with the phenomenon of the minima observed in the explosion limit/temperature curves. They attempt to explain it in terms of thermal explosion theory and pay little attention to a mechanistic explanation. They also claim to have measured the activation energy of the slow reaction (by analysing reaction mixtures using gas chromatography) between 650 and 810°C. They obtain values which vary with temperature and pass through a maximum at about 700°C (the values vary from 46 kcal at 650°C to 53 kcal at 700°C to 23 kcal at 800°C).
has a higher activation energy than 2, \( O + H_2 \rightarrow OH + H \). At 800°C (the approximate position of the minimum) the rate constants for the two reactions (2 and 12) predict that for 1:1 mixtures the formation of NO will occur only about 7 times slower than the chain propagation reaction, and therefore significant quantities of nitric oxide will be formed and chain termination will occur. This also rules out the \( H + O_2 + M \rightarrow H_2 + O_2 + M \) reaction since the formation of NO is at least twice as fast as the formation of molecular oxygen [5], and therefore under conditions where sufficient oxygen would be formed for \( H_2 \) production to be important, there would be even more nitric oxide present which would have a greater inhibiting effect.

---

(v) Comparison with Melville's Work and Summary:

Melville [17] is the only worker who has studied the \( N_2O/H_2 \) reaction under similar conditions to the present work. He followed the reaction by absorbing the water formed on phosphorous pentoxide and measuring the resultant pressure change. This method was virtually the only one available at the time. It is vulnerable, however, to a number of criticisms. The necessity to have a side arm containing the \( P_2O_5 \) desiccant outside the furnace meant that a large temperature gradient existed across the reaction vessel. It is probable that in fast reactions a delay occurred in the removal of water. Changes in reaction behaviour, especially near the beginning of the reaction, might therefore be obscured. The removal of water from the reaction mixture eliminates the isobaric nature of the system and makes interpretation of the behaviour in the later stages of reaction more complex. In the present case these objections are removed and the reaction could be followed under almost ideal conditions. Nonetheless, the general features and mechanism of the reaction obtained in this work are very similar to
those discovered by Melville.

The following mechanism accounts for the experimental results:

**Initiation**
\[
\begin{align*}
\text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O} \\
\text{O} + \text{H}_2 & \rightarrow \text{OH} + \text{H}
\end{align*}
\]

**Propagation**
\[
\begin{align*}
\text{H} + \text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{OH} \\
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H}
\end{align*}
\]

**Termination**
\[
\begin{align*}
\text{H} + \text{H} + \text{M} & \rightarrow \text{H}_2 + \text{M} \\
\text{H} + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M} \\
\text{OH}^\cdot + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O}_2 + \text{M} \\
\text{H} & \rightarrow \text{Wall} \\
\text{O} + \text{H}_2 + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M}
\end{align*}
\]

Computer analysis of the mechanism showed that termination steps 5 and 7 have only a small effect. The reaction is first order at high pressures and becomes second order at low pressures. The transition pressure is in the region 60 to 80 mm Hg which is the same region as was observed by Melville. The change from first to second order is a result of the decreasing importance of quadratic gas phase termination of chain carrying radicals and the increasing predominance of hydrogen atom recombination on the reaction vessel walls. In agreement with Melville it is found that both the high and low pressure reactions show very small dependence on hydrogen pressure. In the high pressure reaction the initial rate of reaction may be expressed by

\[
(-\frac{d[N_2\text{O}]}{dt})_0 = 1.37 \pm 0.06 \times 10^{15} \exp(-62.5 \pm 2.1/RT)[N_2\text{O}][\text{H}_2]^{0.25}
\]

and for the low pressure reaction

\[
(-\frac{d[N_2\text{O}]}{dt})_0 = 8.26 \pm 0.30 \times 10^{13} \exp(-62.5 \pm 2.1/RT)[N_2\text{O}]^2
\]

with the pressures in mm Hg, the rate in mm Hg min\(^{-1}\), and the activation energy in kcal.

The reaction is initially catalysed by oxygen but is inhibited in
the later stages. This may be explained by assuming that the initial increase in rate arises from a branched chain mechanism introduced by the reaction $H + O_2 \rightarrow OH + O$.

Small quantities of nitric oxide are formed (0.2 to 0.3%) which inhibits the reaction in the later stages by removing hydrogen atoms (and OH) from the chain propagation cycle.

A small isotope effect is observed when hydrogen is replaced by deuterium ($k_{H_2}/k_{D_2} \approx 2$) which diminishes as the total pressure is lowered.

An addition to the reaction mechanism proposed by Melville is removal of oxygen atoms by combination with hydrogen in the presence of a third body to form water. This step is necessary to explain the difference between the computed reaction rate (using published rate constants for the individual reactions and omitting reaction 9) and the observed rate of reaction. The rate constant for the reaction

$$O + H_2 + M \rightarrow H_2O + M \quad (9)$$

is deduced to be $k_9 = 3.9 \times 10^{-31} \exp(-4.5 \pm 2.0/RT) \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$, for a third body term [M] being made up of 1:1 mixture of N$_2$O and H$_2$.

Melville was unable to observe an inert gas effect when nitrogen or argon was added to the system. This should extend the first order reaction region if the change to second order is caused by wall termination replacing quadratic termination. The first order reaction region is slightly extended when 50% carbon dioxide is added to the system. It is markedly extended when 50% carbon tetrafluoride is added. Both nitrogen and argon would be likely to have lower third body efficiencies than CO$_2$ and therefore their effect would be negligible.

The greatest discrepancy between this work and that of Melville is in the activation energy. Melville found that the high and low pressure reactions had different activation energies (32 kcal and 49 kcal respectively).
The present work shows that the activation energy for both the high and low pressure reactions is 62.5 ± 2.1 kcal. Melville's low values are certainly a result of the large temperature gradient across his reaction vessel. The difference in the activation energies of the high and low pressure reactions is probably due to the inability of the P₂O₅ to absorb water at a sufficiently rapid rate. This effect would be most marked in the faster reactions (i.e. those at high temperatures and pressures).

It is humbling to find that with the benefit of modern techniques the chemistry of the N₂O/H₂ reaction has changed so little over the space of 35 years. That this is so is a tribute to Melville's scientific skill and experimental prowess.
Part II

Oxidation of Carbon Monoxide by Nitrous Oxide
INTRODUCTION

Unlike the hydrogen/oxygen reaction, in which the mechanism is well established, the mechanism of the carbon monoxide/oxygen reaction is far from being understood.

The CO/O_2 reaction exhibits similar features to the H_2/O_2 reaction in that it has three explosion limits. The third, however, is ill defined and is attributed to a thermal rather than to a branched chain explosion.

For a long time it has been known that water catalyses the reaction but it was thought that a "dry" reaction also occurred[27]. Doubt was cast on the existence of a "dry" (thermal) reaction when Dickens, Dove and Linnett [28] obtained 2nd explosion limits at temperatures at least 100°C higher than had been previously obtained, by using rigorously dried gases. The results were irreproducible and the paper contained a hint that the reaction might not occur at all if the gases were completely dry. Semenov [29] in a recent review of his life's work states categorically, citing a number of Russian authors, that under normal thermal conditions oxygen will not oxidise carbon monoxide if the system is completely dry.

A growing amount of work is being published on the oxygen/carbon monoxide system in shock tubes. The shock tube work has involved both the shock heating of carbon dioxide in order to study the recombination reaction of oxygen atoms with carbon monoxide [30], and by shock heating mixtures of oxygen and carbon monoxide [31] [32][33]. The main point of agreement in these papers is that water, hydrogen and hydrocarbons in p.p.m. quantities leads to catalysis and to marked changes in reaction mechanism of the reaction of oxygen (both atomic and molecular) with carbon monoxide.

Sulzmann et al [31] claimed to have studied the reaction of oxygen with carbon dioxide with less than 1 p.p.m. of water present.
They suggest a chain mechanism in which atomic oxygen is the chain carrier.

\[ CO + O \rightarrow CO_2 + O \text{ (slow)} \]
\[ CO + O (\ddagger M) \rightarrow CO_2 (\ddagger M) \]
\[ CO_2^\ddagger + O \rightarrow CO_2 + 2O \]

[\(CO_2^\ddagger\) is electronically excited]

For the wet reaction they produce a lengthy scheme in which H, OH and O are chain carriers, HO_2 is an intermediate and H_2O_2 a product. Their dry mechanism is basically supported by Brabbes and Belles [30], but is challenged by Brokaw [32] who suggests the mechanism leads to unreasonably high rate constants and points out that the results would be better explained if it were assumed that hydrogen impurities still played a part.

In extending their work with Sulzmann, his co-workers, Myers and Bartle, studied the reaction of oxygen atoms with carbon monoxide where the chains were initiated by the decomposition of small amounts of ozone in the O_2/CO mixtures. They claim to have definite evidence for deactivation of CO_2^\ddagger by oxygen which in turn leads to electronically excited oxygen, but does not involve decomposition of the oxygen to atoms [33].

In comparison with kinetic data published on oxygen/carbon monoxide reactions work carried out on the oxidation of carbon monoxide by nitrous oxide is so scant as to be almost non-existent.

Bass [34] reported a reaction between carbon monoxide and nitrous oxide at temperatures (400 to 550°C) well below those at which nitrous oxide decomposes at an appreciable rate. The reaction was followed by conventional analysis. He found that reaction took place (in part at any rate) on the surface, the rate being proportional to \([N_2O]/[CO]\)

i.e. carbon monoxide was strongly absorbed. The reaction was
not influenced by inert gases, retarded slightly by nitric oxide and markedly catalysed by carbon dioxide. Between certain limits of temperature and pressure the slow reaction passed into explosion. This was markedly inhibited by nitric oxide and the effect of inert gases indicated a thermal explosion.

Bawn found an activation energy of 22 kcal/mole which supports the evidence that this was a mainly heterogeneous reaction.

Pickering [35] investigated both "wet" and "dry" reactions. In the wet reaction he found that the reaction rate occurred at a reasonable rate above 570° C. The rate of reaction increased with the amount of water added, up to about 4 mm Hg of water, above which no increase occurred. The kinetics appeared to be approximately first order. The rate decreased slightly with increasing surface area and no heterogeneous reaction of the type observed by Bawn appeared to be taking place. The activation energy appeared to be slightly high at 70 kcal/mole.

By drying his gases and storing over P₂O₅ for a number of weeks, Pickering was able to observe a "dry" reaction. This reaction, under all conditions, was slower than the wet reaction. Again, first order kinetics were observed and an activation energy of 55 kcal/mole (identical to the value Pickering obtained for the decomposition of N₂O) was found. Pickering ventured the following mechanism for the dry reaction:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \]
\[ \text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M} \]

but had very few results to support it. For the wet reaction he suggested:
This fitted his results closely but the last three reactions must be regarded as a little unusual and have not been postulated before.

Recently Deckers reported, in a review article, that bimolecular reaction between \( \text{N}_2\text{O} \) and \( \text{CO} \) with \( \text{CO}_2 \) as a product had been observed in a molecular beam system [60]. No experimental details or results have since been published. It appears that Decker's original interpretation was incorrect and that the only product obtained was polymeric nitrous oxide [61].

**EXPERIMENTAL**

The procedure for following the disappearance of nitrous oxide was the same as used for the \( \text{N}_2\text{O/H}_2 \) work. Two additional parameters were also followed:

A) **Chemiluminescence:**

It proved possible to measure the intensity of the blue chemiluminescence observed during the reaction. The chemiluminescence appeared quite intense when viewed by the naked eye, but the light being non-directional (as opposed to the collimated light beam from the deuterium lamp) the intensity falling on the monochromator slit and eventually being detected by the photomultiplier was very small (10^3 to 10^4 times smaller than the intensity of light at 2200 Å from the deuterium lamp). The light intensity measuring circuit had to be used at its maximum sensitivity, and because of the instability...
and noise the actual readings had only about a 10% to 15% accuracy. It was not possible to calibrate the glow intensity in terms of excited species or in quanta emitted, and the intensity was usually measured in terms of the current produced by the photomultiplier (in $10^{-8}$ A units) at a fixed E.H.T. voltage. It was assumed that over a series of runs the sensitivity of the light measuring circuit did not change. The procedure for measuring glow intensity during a run was as follows:

a) The deuterium lamp was switched off and the monochromator was set at 4000 Å.

b) The E.H.T. voltage was set at a sufficiently high voltage to provide the necessary sensitivity (usually 1.2 kV).

c) The recorder was set at its most sensitive range (i.e. 0 to 1 mV f.s.d.) and the decade resistor set so that the glow intensity that would be obtained at the start of a particular run would produce about a 60% to 80% reading on the recorder. After a few runs it was possible to set the resistor without having to carry out a trial run.

d) The dark current from the photomultiplier (which included any stray light from the furnace glow) was "backed off" so that zero reading was obtained on the recorder.

e) The gases were let into the reaction vessel. The photomultiplier output was measured by the recorder in millivolts and converted to units of $10^{-8}$ amps using the value of the decade resistor and Ohm's Law.

B) Pressure change:

A small pressure change occurred during the reaction and was measured using a mercury manometer. It was necessary to apply a "dead space" correction to the measured pressure change to relate it to the actual pressure change in the reaction vessel.
it was possible to measure nitrous oxide pressure in the reaction vessel by its U-V absorption it is possible to allow for the dead space by the following technique:

(i) **Dead space correction:**

At the temperatures at which the $N_2O/CO$ reaction was carried out (650° to 750°) nitrous oxide decomposes at a moderate rate. It is possible to follow this decomposition manometrically since the reaction $2N_2O \rightarrow 2N_2 + O_2$ results in a pressure increase corresponding to $\frac{1}{2}$ the partial pressure of $N_2O$ that decomposed (the production of nitric oxide would also produce the same pressure change). It is possible to calculate the amount of $N_2O$ that had decomposed from the pressure increase and the stoichiometric equation. The value thus calculated would be too low since the gases expelled from the hot reaction vessel contract in the colder space between the reaction vessel and the manometer. By following the decomposition of nitrous oxide spectroscopically the true pressure of nitrous oxide in the reaction vessel may be followed. A plot of the true $N_2O$ pressure against the $N_2O$ pressure calculated manometrically assuming no dead space correction gives a straight line. The slope of this line is the factor by which the manometrically calculated $N_2O$ pressure has to be multiplied to bring it up to the true pressure. The dead space correction was determined in this manner over the temperature range 650 to 750°. Second order effects such as the loss of a portion of the reacting $N_2O$ into the dead space as the reaction proceeds, the possible reduction of pressure due to some of the nitric oxide produced reacting with oxygen to give nitrogen dioxide, and the very small change in dead space volume as the pressure increases and the mercury in the manometer is pushed out have been neglected in the above analysis. The graphical result is shown in Fig. 2.1.
True N\textsubscript{2}O Pressure (mm. Hg).

Fig:2.1 Dead Space Correction.
It will be seen that within experimental scatter the points obtained at all temperatures lie on the same straight line. If the secondary effects had a serious influence a straight line would not have been obtained. The dead space correction is 1.28.

(ii) Dryness of apparatus:

Special attention was paid to the drying of both carbon monoxide and nitrous oxide (vide the section of this thesis describing gas preparation). To prevent the build-up of any traces of water in the vacuum line a "charcoal pump" was left open to the line and reactions vessel at the end of each day's experiments. The "charcoal pump" consisted of a tube filled with granular activated charcoal that had been thoroughly degassed by heating to about 400°C under vacuum for a number of hours. This was immersed in a Dewar flask of liquid air and efficiently removed gases absorbed on the walls of the vacuum system. The trap maintained the line at a pressure of less than $10^{-4}$ torr with the main pumping system switched off.

Runs were carried out at 700°C except for a series carried out between 650 and 750°C to determine the activation energy. The majority of runs were made using pre-mixed gas mixtures.

RESULTS

(i) General features of the reaction:

The "dry" N₂O/CO reaction differs markedly from the nitrous oxide oxidation of hydrogen in that it only takes place at temperatures at which N₂O itself decomposes at an appreciable rate. The general features of the reaction are shown graphically in Fig. 2.2. Initially, the reaction is about three times as fast as the decomposition of N₂O. This drops to about twice as fast in the later stages of reaction.
Fig. 2.2a Typical Reaction Curves.

Fig. 2.2b Relative Rates
$N_2O/CO:N_2O$ decompos.
Fig. 2.2b demonstrates this drop in relative rates. In the figure the time taken for the $N_2O$ reaction to reach a given $N_2O$ pressure ($t_{N2O}$) is plotted against the time taken for the $N_2O/CO$ reaction to reach the same pressure of $N_2O$ ($t_{N2O/CO}$). Unexpectedly the reaction is also accompanied by a small pressure increase. The stoichiometric equation

$$N_2O + CO \rightarrow N_2 + CO_2$$

involves no change in pressure. The size of the pressure increase depends both on the initial pressure of nitrous oxide and on the percentage of carbon monoxide in the reaction mixture. The greatest increases are obtained in $N_2O$ rich mixtures at high pressures. The extra product is predominantly oxygen (v. infra) and presumably arises from the thermal decomposition of nitrous oxide.

The reaction is accompanied by a deep blue chemiluminescence which is due to the radiative deactivation of electronically excited $CO_2$ formed by the reaction of oxygen atoms with carbon monoxide. The intensity of the chemiluminescence is dependent on both the initial pressures of carbon monoxide and nitrous oxide.

The carbon monoxide/oxygen reaction is very dependent on traces of water or other hydrogen donating molecules, and it was expected that the $N_2O/CO$ reaction would also be catalysed by water. Small amounts of water were added to the reaction vessel by equilibrating a 62.5% w/w sulphuric acid/water solution at 0°C with the reaction vessel for 15 minutes. This solution has a vapour pressure of 0.5 mm at 0°C [72]. Premixed 1:1 $N_2O/CO$ mixtures were then added to the reaction vessel. The addition of the reacting gases swept the water vapour in the dead space into the reaction vessel so that the final water pressure in the reaction vessel was nearer 0.6 mm Hg. It was found that even small traces of water markedly catalysed the reaction,
and in concentrations greater than about 1% explosions occurred as the reaction mixture entered the reaction vessel. The effect of added water is summarised in table 2.1. Even the smallest percentage of water (Run 11) caused the pressure change to disappear.

(ii) Thermal decomposition of N₂O:

Since the rate of the dry N₂O/CO reaction is only 2 to 3 times faster than the thermal decomposition of nitrous oxide, it was thought advisable to obtain some data on the decomposition. A series of runs were carried out at nitrous oxide pressures ranging from 30 to 200 mm Hg. The initial rates of the decomposition are given in table 2.2. The reaction curve for decomposition of 100 mm Hg of N₂O is shown in Fig. 2.3a. This is the average curve of three separate runs with a three month period separating the first and last runs. The initial rate data suggest that the reaction is 1.5 order since a plot of log₁₀ initial rate against [N₂O]₀ gives a straight line of slope 1.5 (Fig. 2.3b). This is in complete agreement with the results of earlier work [1,2,6].

(iii) Order of N₂O/CO reaction:

The overall order of reaction is about 1.6, this value was obtained from a plot of log₁₀ (half life) against log₁₀ (half pressure) for all runs in which the N₂O/CO ratio was 1:1. This data had been obtained over a seven month period and is shown in Fig. 2.4. The half life refers to the time taken for half the initial nitrous oxide pressure to react. This time is not the same as the time taken for half the carbon monoxide to react since N₂O is removed by two consecutive processes. The points in Fig. 2.4 are badly scattered showing that the reproducibility of the
### Table 2.1 Effect of Water on N₂O/CO reaction

<table>
<thead>
<tr>
<th>Run</th>
<th>Total Pressure</th>
<th>Initial rate(R₀)</th>
<th>RₙH₂O/R₀ dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>404 mm Hg</td>
<td>0</td>
<td>57 mm/min</td>
</tr>
<tr>
<td>11</td>
<td>412</td>
<td>0.15</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>264</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>264</td>
<td>0.23</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>160</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>162</td>
<td>0.37</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.9</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0</td>
<td>4.8</td>
</tr>
<tr>
<td>16</td>
<td>102</td>
<td>0.59</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15.6</td>
</tr>
<tr>
<td>5</td>
<td>62</td>
<td>0</td>
<td>2.8</td>
</tr>
<tr>
<td>17</td>
<td>60</td>
<td>1.00</td>
<td>Explodes</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>18</td>
<td>40</td>
<td>1.50</td>
<td>Explodes</td>
</tr>
</tbody>
</table>

### Table 2.2 Thermal Decomposition of N₂O

<table>
<thead>
<tr>
<th>Run</th>
<th>[N₂O]₀</th>
<th>Initial Rate(R₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>31 mm Hg</td>
<td>1.0 mm Hg/min</td>
</tr>
<tr>
<td>94</td>
<td>50</td>
<td>2.4</td>
</tr>
<tr>
<td>95</td>
<td>76</td>
<td>4.6</td>
</tr>
<tr>
<td>96, 171, 176</td>
<td>102</td>
<td>7.7</td>
</tr>
<tr>
<td>97</td>
<td>153</td>
<td>13.7</td>
</tr>
<tr>
<td>98</td>
<td>201</td>
<td>19.7</td>
</tr>
</tbody>
</table>

* Results obtained from the average rate curve of 3 runs
a). Decomposition Curve.

Time (minutes).

b). Order of Decomposition.

Fig: 2.3  N₂O Decomposition.
N\textsubscript{2}O/CO reaction is poor compared with N\textsubscript{2}O decomposition. The solid line drawn through the points is the least squares fit which has a slope of 0.63 with a standard deviation of \(\pm 0.05\) (i.e. an order of 1.6 \(\pm 0.05\)). It was difficult to perceive a trend in rate of reaction with the different batches of gases prepared for reaction, and often quite large discrepancies occurred between runs carried out under the same conditions with the same batches of gases.

The lack of reproducibility was also observed in the initial rates of reactions which hampered investigations into the individual orders of reaction with respect to N\textsubscript{2}O and CO. By plotting the \(\log_{10}\) (initial rate) for all runs carried out over the entire experimental period at a constant initial CO pressure (or N\textsubscript{2}O pressure) against the \(\log\) of initial N\textsubscript{2}O pressure (or CO pressure), sufficient points were obtained to enable a reasonably reliable value for the order of reaction with respect to N\textsubscript{2}O (or CO) to be obtained. The least squares slopes together with their standard deviations are shown in table 2.3. It was noticed that the greatest scatter of results occurred at low pressures of N\textsubscript{2}O and CO. It is apparent that the reaction is slightly greater than first order in nitrous oxide. The order in carbon monoxide varies from about 0.2 to 0.5 with large error limits in the individual determinations. A full discussion of the irreproducibility appears at the end of this "Results" section.

(iv) \textit{Pressure change and Identity of Extra Product:}

The pressure increase that accompanies the reaction is small, between 0 and 30 mm Hg (0 to 6\% total pressure) depending on the conditions. The only method of following the change was to use the
Table 2.3 Individual Orders of Reaction

<table>
<thead>
<tr>
<th>[CO]₀ (mm Hg)</th>
<th>Order</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.02 ± 0.16</td>
<td>± 0.16</td>
</tr>
<tr>
<td>50</td>
<td>1.17 ± 0.12</td>
<td>± 0.12</td>
</tr>
<tr>
<td>100</td>
<td>1.21 ± 0.14</td>
<td>± 0.14</td>
</tr>
<tr>
<td>150</td>
<td>1.15 ± 0.08</td>
<td>± 0.08</td>
</tr>
<tr>
<td>200</td>
<td>1.02 ± 0.03</td>
<td>± 0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[N₂O]₀ (mm Hg)</th>
<th>Order</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.22 ± 0.16</td>
<td>± 0.16</td>
</tr>
<tr>
<td>50</td>
<td>0.37 ± 0.13</td>
<td>± 0.13</td>
</tr>
<tr>
<td>100</td>
<td>0.30 ± 0.07</td>
<td>± 0.07</td>
</tr>
<tr>
<td>150</td>
<td>0.32 ± 0.06</td>
<td>± 0.06</td>
</tr>
<tr>
<td>200</td>
<td>0.47 ± 0.09</td>
<td>± 0.09</td>
</tr>
</tbody>
</table>

The values for the order of reaction were obtained from the slopes of graphs of log (initial rate) v.s log (initial pressure) of one of the reactants at constant initial pressures of the other reactant (see Appendix 2.3). The error limits are the standard deviation of the slope about the least squares line.
Fig: 2.4 Half Life Data.

\[
\log_{10} \left( \frac{1}{2} \right) = \log_{10} [N_2O]_{t/2}
\]

Fig: 2.5 Oxygen Formation.

\[
\frac{N_2O:CO}{[N_2O]_0} = 150 \text{mm.}
\]

\[
\begin{array}{c}
2:1 \\
1:1 \\
1:2
\end{array}
\]

Time (minutes)
mercury manometer attached to the reaction vessel inlet tube. Any change was corrected for the "dead space" between the reaction vessel and manometer using the correction factor described earlier. The accuracy of the results obtained is low and at initial nitrous oxide pressures below about 100 mm Hg, the change is too small to permit any reliable measurements to be made. All that could be said about the pressure change in this region is that it occurred and there was a tendency for the increase to be larger the greater the percentage of \( \text{N}_2\text{O} \) present in the reaction mixture. At the higher pressures the trend is well defined. Typical pressure change curves are shown in Fig. 2.5. In this Figure the results are shown for 1:2, 1:1 and 2:1 \( \text{N}_2\text{O}/\text{CO} \) mixtures all with an initial nitrous oxide pressure of 150 mm Hg. It can be seen that in the case of the 2:1 mixture a pronounced increase in the rate of change occurs after about 6 minutes reaction. At about this point all the carbon monoxide has reacted and the rest of the curve represents the decomposition of the excess \( \text{N}_2\text{O} \).

In order to determine the identity of the extra reaction product mass spectrometric analyses were made of the reaction vessel contents after the reaction mixture had been allowed to react for different times. The sampling procedure adopted has already been described in the section dealing with the effect of oxygen on the \( \text{N}_2\text{O}/\text{H}_2 \) reaction. Samples were taken at \( \frac{1}{2}, 2, 5, 10, 15 \) and 20 minutes of reaction and the pressure change and \( \text{N}_2\text{O} \) concentration followed during the course of each reaction.

The mass spectrum of \( \text{N}_2\text{O} \) has a peak due to \( \text{NO}^+ \) which is about 15% that of the parent \( \text{N}_2\text{O}^+ \) peak. This might obscure any nitric oxide present in the reaction mixture. In order to resolve this problem the mass spectrometric analyses of reaction mixtures were
carried out at high resolution so that the doublets at m/e = 44 due to $N_2O$ and $CO_2$, and at m/e = 28 due to $N_2$ and CO were resolved. It was therefore possible to see whether the $NO^+$ peak arose predominantly from nitrous oxide or whether as the reaction proceeds the ratio of $NO^+/N_2O^+$ increases. The results of the mass spectrometric analyses are tabulated in appendix 2.2. The following points emerge:

1) $N_2O^+$ peak decreases linearly with $N_2O$ pressure (i.e. as the reaction proceeds), a plot of $N_2O^+$ peak height against $N_2O$ pressure has a positive intercept on the $N_2O^+$ axis due to the $N_2O$ present in the dead space between the sampling volume and reaction vessel.

2) $CO_2^+$ peak increases as the reaction proceeds.

3) The ratio $NO^+/N_2O^+$ remains constant within experimental error ($\pm 10\%$) over the whole reaction period.

4) The $O_2^+$ peak increases with reaction time up to about 10 minutes reaction and then decreased.

5) There was no $NO_2$ detected.

The pressure increase during the course of the reaction is shown in Fig. 2.6a. It will be seen that in the later stages of the reaction there is a slight decrease in the size of the pressure change. A plot of $O_2^+$ peak height against pressure increase is a very good straight line for the first 4 samples ($\frac{1}{2}$, 2, 5 and 10 minutes of reaction), the line passes through the origin. At 15 and 20 minute sample times the $O_2^+$ peak height decreases (Fig. 2.6b). The evidence therefore confirms that the pressure increase observed during the course of reaction is due to the production of oxygen. It appears that oxygen is slowly used up in the later stages of reaction, presumably because of reaction with carbon monoxide.
a. Pressure Change, $\Delta p$.

b. $\Delta p$ vs. $O_2$ Peak Height.

Fig 2.6 Identification of By-Product.
(v) Order of Oxygen Producing Reaction:

Because a mercury manometer is relatively insensitive to small pressure changes, reliable data on the initial rates of oxygen production were difficult to obtain. In mixtures containing initial N₂O pressures below about 100 mm Hg and/or containing a large excess of carbon monoxide the pressure increase was too small for even moderately reliable measurement. A plot of the log (initial rate of oxygen production) against the log of nitrous oxide pressure for all reaction mixtures with an initial CO pressure of 100 mm Hg gives a straight line of slope 2. The points are scattered but there is a sufficient number of them to see that the oxygen producing reaction is second order in nitrous oxide (Fig. 2.7). Plots of log₁₀ (initial rate of O₂ production) against log₁₀ carbon monoxide pressure have a negative slope of about 0.6. As Fig. 2.7 shows, the points are badly scattered, but the negative order of reaction in carbon monoxide is clearly in evidence. The scatter in experimental points is as much a result of the difficulty in measuring accurately the small pressure changes involved as of irreproducibility of the overall kinetics. The points shown on the graphs are taken from runs carried out over the whole 7 month experimental period.

(vi) Chemiluminescence:

The overall combination reaction of ground state oxygen atoms with carbon monoxide to yield ground state carbon dioxide is spin forbidden and highly exothermic:

\[ \text{O}(^3P) + \text{CO}(^1Σ^+) \rightarrow \text{CO}_2(^3Σ^+) \quad Δ H_{298} = -127.2 \text{kcal/mol} \]

The reaction initially results in the formation of electronically excited carbon dioxide. The excited CO₂ may lose energy in two ways;
Order w.r.t. $N_2O$, $[CO]_o = 100$ mm Hg.

Order w.r.t. CO, $[N_2O]_o = 200$ mm Hg.

$ \times $ Order w.r.t. CO, $[N_2O]_o = 100$ mm Hg.

Fig: 2.7 Order of $O_2$ Production.
by a radiative transition to ground state CO$_2$ or by a non radiative transfer of energy in a bimolecular collision with another molecule.

\[ \text{Radiative deactivation } \quad \text{CO}_2^* \xrightarrow{h\nu} \text{CO}_2 + h\nu \quad (3) \]

\[ \text{Collisional deactivation } \quad \text{CO}_2^* + M \rightarrow \text{CO}_2 + M \quad (4) \]

\((\text{CO}_2^* = \text{electronically excited CO}_2)\)

It is reaction 3 that accounts for the observed chemiluminescence.

Dixon [57] has shown that the chemiluminescence observed in the oxidation of carbon monoxide is due to transitions from an electronically excited $^1\Sigma_u^+$ state of CO$_2$ to the $^1\Sigma_g^+$ ground state. This is contrary to the earlier suggestion of Gaydon (in an extensive review of evidence up to 1957 relating to CO flame emission), that the chemiluminescence was due to a radiative transition from a bent triplet state derived from $^3\Pi_1$ CO$_2$ to higher vibrational levels of the ground state [73]. Dixon's spectroscopic analysis and interpretation of the CO flame bands confirmed Clyne and Thrush's suggestion that spin reversal of the excited CO$_2$ occurred before radiation took place [74].

In the N$_2$O/CO reaction the intensity of the "glow" arising from the CO$_2^*$ chemiluminescence decreases sharply in the initial stages of reaction. The initial intensity of the glow depends on both the initial pressures of CO and N$_2$O. Figures 2.8a and b show the general features of the decay of glow intensity. It will be noticed that the rate of decrease of glow intensity in the initial stages of reaction increases with increasing percentage of N$_2$O present in the reacting mixture. Thus curve 128 is steeper than curve 120 in Fig. 2.8a, and curve 132 is steeper than curve 125 in Fig. 2.8b for the early part of reaction.

(vii) Production of Carbon Dioxide:

The amount of carbon dioxide produced during the N$_2$O/CO reaction
a). Constant \([\text{CO}]_0 = 100\) mm. Hg.

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{N}_2\text{O}])) mm. Hg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>200</td>
</tr>
<tr>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>50</td>
</tr>
</tbody>
</table>

Glow Intensity (10^6 amps)

Time (minutes).

b). Constant \([\text{N}_2\text{O}]_0 = 100\) mm. Hg.

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{CO}])) mm. Hg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>200</td>
</tr>
<tr>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>132</td>
<td>50</td>
</tr>
</tbody>
</table>

Glow Intensity (10^6 amps)

Time (minutes).

Fig: 2.8 Glow Intensity Curves.
is not equal to the amount of \( N_2O \) consumed because a small amount of \( N_2O \) decomposes giving oxygen by the overall reaction:

\[
2N_2O \rightarrow 2N_2 + O_2
\]

Two molecules of nitrous oxide yield one molecule of oxygen. At any given time, \( t \), during the reaction, the amount of \( \text{CO}_2 \) produced is given by the total pressure of \( N_2O \) consumed minus twice the pressure of oxygen produced.

\[
\text{[CO}_2\text{]}_t = [N_2O]_0 - ([N_2O]_t + 2[O_2]_t)
\]

It is therefore possible to construct reaction curves showing the increase in carbon dioxide pressure during the course of a reaction. Typical curves are shown in Fig. 2.9. It can be seen that at constant initial \( \text{CO} \) pressure (Fig. 2.9a) there is a smooth increase in rate of reaction as the percentage of \( N_2O \) is increased. Where the initial pressure of \( N_2O \) is held constant, however, the increase in rate with \( [\text{CO}]_0 \) in mixtures with an excess of carbon monoxide is smaller than expected.

The "glow" intensity observed at a particular time during a reaction is proportional to the rate of production of \( \text{CO}_2 \) by the radiative process 3.

\[
\text{CO}_2^+(1^2S_g) \rightarrow \text{CO}_2^{(1)^2S_g} + h\nu
\]  

The total amount of \( \text{CO}_2 \) produced by the reaction up to that time is therefore proportional to the area under the glow intensity vs. time curve. Integration of these "glow curves" provides a measure of the carbon dioxide produced. In practice, the integration was carried out manually by dividing the curve into small trapezium shaped segments and summing the areas of the segments at different time intervals.

The integral glow v.s. time curves corresponding to the glow curves in Fig. 2.8 and to the \( \text{CO}_2 \) production curves in Fig. 2.9 are shown in Fig. 2.10. The integral glow curves have the same general shape as the \( \text{CO}_2 \) production curves which suggested that the production of
a). Constant \([\text{CO}]_0 = 100 \text{ mm. Hg}\).

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{N}_2\text{O}]) mm. Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>127</td>
<td>200</td>
</tr>
<tr>
<td>109</td>
<td>100</td>
</tr>
<tr>
<td>119</td>
<td>50</td>
</tr>
</tbody>
</table>

![Graph](image)

b). Constant \([\text{N}_2\text{O}]_0 = 100 \text{ mm. Hg}\).

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{CO}]) mm. Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>200</td>
</tr>
<tr>
<td>109</td>
<td>100</td>
</tr>
<tr>
<td>131</td>
<td>50</td>
</tr>
</tbody>
</table>

![Graph](image)

Fig: 2.9 Production of \(\text{CO}_2\).
Fig. 2.10 Integral Glow Curves.
CO₂ by the radiative process was "congruent" with the total production of CO₂ during the reaction. A series of runs was carried out using 2:1, 1:1 and 1:2 N₂O/CO mixtures to test this congruency. A run observing the consumption of N₂O at a given reaction mixture pressure was immediately followed by a run in which the decrease in glow intensity with time was measured. In this way it was hoped that each pair of runs would be carried out under as nearly identical conditions as possible, and so the irreproducibility was minimised. The production of oxygen during both runs in the pair was observed and the average pressure of O₂ was used to construct the CO₂ production curve.

Plots of integral glow against calculated CO₂ pressure at fixed times for each pair of runs were straight lines showing that carbon dioxide production by the radiative process is proportional to the total CO₂ production in the reaction. The slope of an integral glow/[CO₂] line is proportional to the relative rate of the radiative process against the total rate of CO₂ production. Fig. 2.11 shows the integral glow/[CO₂] plots for the reactions considered in Figs. 2.8, 9 and 10, and table 2.4 gives the slopes obtained from all the runs in this series. It may be seen that the rate of the radiative process relative to the total rate of CO₂ production tends to increase as the total pressure decreases. This suggests that, as expected, carbon dioxide is also produced by a non-radiative, pressure dependent process.

(viii) Activation Energy:

There are three primary processes being measured in the N₂O/CO reaction, namely, the overall disappearance of nitrous oxide (U.V. absorption measurement), the production of oxygen (pressure change)
a). \([\text{CO}_2]_0 = 100 \text{ mm.Hg.}\)

- Runs \([\text{N}_2\text{O}]_0\) mm.Hg.
  - 127/8 200
  - 109/10 100
  - 119/20 50

b). \([\text{N}_2\text{O}]_0 = 100 \text{ mm.Hg.}\)

- Runs \([\text{CO}]_0\) mm.Hg.
  - 125/6 200
  - 109/10 100
  - 131/2 50

Fig:2.11 Integral Glow/Rate of CO\(_2\) Formation.
Table 2.4 Rate of Radiative Process/Rate of CO₂ Production

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{N}_2\text{O}]_o/\text{[CO]}_o)</th>
<th>Total pressure</th>
<th>Integral glow/([\text{CO}_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>105/6</td>
<td>1:1</td>
<td>402 mm Hg</td>
<td>0.117 ± 0.006</td>
</tr>
<tr>
<td>107/8</td>
<td></td>
<td>302</td>
<td>0.145 ± 0.003</td>
</tr>
<tr>
<td>109/10</td>
<td></td>
<td>203</td>
<td>0.188 ± 0.002</td>
</tr>
<tr>
<td>111/2</td>
<td></td>
<td>151</td>
<td>0.240 ± 0.004</td>
</tr>
<tr>
<td>113/4</td>
<td></td>
<td>99</td>
<td>0.293 ± 0.009</td>
</tr>
<tr>
<td>115/6</td>
<td></td>
<td>60</td>
<td>0.278 ± 0.012</td>
</tr>
<tr>
<td>123/4</td>
<td>1:2</td>
<td>450</td>
<td>0.129 ± 0.004</td>
</tr>
<tr>
<td>125/6</td>
<td></td>
<td>303</td>
<td>0.186 ± 0.003</td>
</tr>
<tr>
<td>117/8</td>
<td></td>
<td>226</td>
<td>0.236 ± 0.009</td>
</tr>
<tr>
<td>119/20</td>
<td></td>
<td>150</td>
<td>0.299 ± 0.014</td>
</tr>
<tr>
<td>121/2</td>
<td></td>
<td>90</td>
<td>0.400 ± 0.013</td>
</tr>
<tr>
<td>127/8</td>
<td>2:1</td>
<td>303</td>
<td>0.170 ± 0.004</td>
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<td>129/30</td>
<td></td>
<td>228</td>
<td>0.208 ± 0.007</td>
</tr>
<tr>
<td>131/2</td>
<td></td>
<td>151</td>
<td>0.265 ± 0.003</td>
</tr>
<tr>
<td>133/4</td>
<td></td>
<td>113</td>
<td>0.295 ± 0.006</td>
</tr>
<tr>
<td>135/6</td>
<td></td>
<td>75</td>
<td>0.346 ± 0.016</td>
</tr>
<tr>
<td>137/8</td>
<td></td>
<td>44</td>
<td>0.246 ± 0.007</td>
</tr>
</tbody>
</table>

Table 2.5 Activation Energies for N₂O/CO reaction

<table>
<thead>
<tr>
<th>Process</th>
<th>(E_n) kcal</th>
<th>(\sigma) kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2\text{O}) decomp.</td>
<td>57.8</td>
<td>± 1.5</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}/\text{CO}) reaction</td>
<td>59.7</td>
<td>± 1.5</td>
</tr>
<tr>
<td>(\text{O}_2) production</td>
<td>59.9</td>
<td>± 4.4</td>
</tr>
<tr>
<td>Total (\text{CO}_2) production</td>
<td>57.7</td>
<td>± 2.0</td>
</tr>
<tr>
<td>Integral glow</td>
<td>46.4</td>
<td>± 1.5</td>
</tr>
<tr>
<td>(\text{Integral glow} \quad \text{CO}_2) production</td>
<td>-7.3</td>
<td>± 1.4</td>
</tr>
</tbody>
</table>
and the production of carbon dioxide by the radiative process (glow intensity measurement). The effect of temperature on these processes and on the decomposition of N₂O alone was investigated over a temperature range 650 to 750°C. At each temperature runs were carried out in the following sequence using a 1:1 mixture of N₂O/CO at a total pressure of 200 mm Hg.

1. Thermal decomposition of N₂O (100 mm Hg)
2. N₂O/CO reaction, N₂O disappearance.
5. N₂O/CO reaction, N₂O disappearance.
6. Thermal decomposition of N₂O (100 mm Hg)

Each effect was therefore studied in duplicate and average reaction curves were drawn for N₂O consumption (both in N₂O/CO reaction and N₂O decomposition) and for integral glow. The pressure change during the N₂O/CO reaction was measured in all runs (2 to 5 inclusive), and an average curve showing the production of oxygen was constructed from the results of four runs, which minimized the errors involved in following the small pressure changes.

The reaction curves for N₂O consumption, integral glow and O₂ production in the N₂O/CO reaction and for N₂O decomposition at the different temperatures were compared with those for the "standard" reaction at 700°C. The ratios of the overall rate constants for a particular process at 700°C (kₜ/k₇₀₀) were calculated using the method described in appendix 1.2. The Arrhenius plots (log₁₀ kₜ/k₇₀₀ vs. reciprocal temperature) are shown in Fig. 2.12. Table 2.5 gives the activation energies (Eₐ) together with their standard deviations (σ) for the processes obtained from the least squares slopes. The activation energy of 57.8 ± 1.5 kcal for N₂O decomposition is in good agreement with the 58.5 kcal obtained by other workers. The overall N₂O/CO...
Fig.2.12 Arrhenius Plots.
reaction appears to have an activation energy slightly higher than
\( \text{N}_2\text{O} \) decomposition, though the discrepancy lies almost within the
error limits. The production of oxygen during the reaction has the
same activation energy as the overall reaction. The larger error
limits are due to pressure measurement uncertainties. The radiative
reaction

\[
\text{CO}_2^* \rightarrow \text{CO}_2 + h_v
\]

has, however, a significantly smaller activation energy than the overall
\( \text{N}_2\text{O}/\text{CO} \) reaction. The discrepancy is of the order of 12 kcal and shows
that as the temperature rises the reactions not involving radiation
from the excited \( \text{N}_2 \) state of \( \text{CO}_2 \) become more favoured than \( \text{O} + \text{CO} \)
\[
\rightarrow \text{CO}_2 + h_v
\]
This is borne out by the ratio of \( \text{CO}_2 \) production by
reaction 3 to total carbon dioxide production (integral glow/\( \text{CO}_2 \) pressure)
which has an apparent activation energy of \(-7.3 \pm 1.4\) kcal. Fig. 2.12
also shows the \( \log_{10} \) of integral glow/\( \text{CO}_2 \) pressure ratios plotted against
reciprocal temperature.

(ix) Reproducibility

It has been shown that the \( \text{N}_2\text{O}/\text{CO} \) reaction is markedly catalysed
by water and that although great care was taken to remove water both
from the prepared gases and from the vacuum system, very small traces
of water may be the cause of the observed irreproducibility. From
time to time during the course of the investigation of the \( \text{N}_2\text{O}/\text{CO} \)
reaction fresh samples of \( \text{CO} \) and \( \text{N}_2\text{O} \) were prepared to replenish the
storage volumes. An analysis of 100 or so runs used to determine the
order of reaction was carried out to see if a definite correlation could
be made between the initial rate data (i.e. whether a particular reaction
appeared faster or slower than the "normal" rate), and the preparation
of fresh batches of gases. The "normal" rate was taken as that given
by the least squares line in the individual order of reaction plots shown in appendix 2.3. The majority of runs provided points for both the order with respect to \( \text{N}_2 \text{O} \) and order with respect to CO plots. In most cases a run which appeared faster (or slower) than normal in one order plot also appeared faster in the other order plot. Appendix 2.3 lists the runs indicating whether they are faster or slower than normal, and also indicates where fresh gases were prepared. It can be seen that there is a tendency for long series of runs to be faster or slower than normal, but the correlation between them and the preparation of gases is not very marked. In some cases the series of runs carried out with the same batch of gases are in the main slower (Runs 39 to 67) or faster (Runs 105 to 138) than normal, but in others the rates may start off slower, become faster, and then become slower again (Runs 69 to 104). A definite effect was observed in the early stages of the investigation when water was deliberately added to the reaction mixtures. The next day the line was used the "dry" reactions appeared faster than normal even though the vacuum system had been thoroughly pumped down to \( 10^{-4} \) torr and left open to the charcoal/liquid air trap overnight. On another occasion the vacuum system leaked overnight and rose to atmospheric pressure. After pumping the line for a day and leaving it open to the charcoal/liquid air trap overnight the next run was slower than normal, even though the preceding runs using the same gases were faster.

It is possible that traces of water are a factor in causing irreproducibility. The amounts of water involved must be smaller than the 0.01% concentration which is the minimum level detectable with any degree of certainty using mass spectrometric analysis (no sample of gas prepared showed any evidence of water in the analyses). It is uncertain whether the cause is water initially present in the gases or absorbed on the walls.
It is possible, though less likely, that a heterogeneous process is occurring alongside the homogeneous gas phase reaction (c.f. Brown [34]). Such a process might be expected to be dependent on the condition of reaction vessel walls which in turn would depend on the history of the reaction vessel.

DISCUSSION

(i) Is there a dry reaction?

It is perhaps unconventional to head a thesis discussion with a question, but combustion reactions in which oxygen appears as a product are not common. An attempt at answering this question must be made as the role of water in the oxidation of carbon monoxide has not been completely elucidated. The main problem confronting investigations of the dry molecular oxygen/carbon monoxide system is the difficulty of developing chain branching processes bearing in mind the low rate of the initiation processes. There is no such problem in the case of nitrous oxide. At the temperatures of these experiments nitrous oxide decomposes at an appreciable rate and there is an abundant supply of oxygen atoms with which to initiate reaction chains. On the other hand N₂O does not provide a means for chain branching. Experimentally, it has been shown that the addition of small amounts of water increases the rate of the N₂O/CO reaction and what must be decided is whether water is indispensable to the mechanism of N₂O oxidation of CO.

Unfortunately the experimental results do not provide an unequivocal answer and as a basis for this discussion the evidence for and against a dry reaction is presented below:

Evidence for a dry reaction:

a) Oxygen is produced in small quantities during the reaction. If
water were present in significant amounts it would be expected that the oxygen formed would react with carbon monoxide and that no pressure change during the reaction would be observed.

b) The addition of very small amounts of water causes the pressure change to disappear. This is the corollary of point a). A 1:1 mixture of N₂O/CO at a pressure of 400 mm/Hg shows a pressure change of about 15 to 20 mm/Hg. The addition of about 0.1% water increases the reaction rate by only about threefold, whereas the pressure change disappears.

c) Coleman and Reuben, using the same apparatus as this work, have shown that the glow intensity is much reduced when water is added to the N₂O/CO reaction [41]. This suggests that either a different mechanism is involved in the "wet" N₂O/CO reaction or that H₂O is a much more efficient third body in deactivating electronically excited CO₂ than N₂O or CO (probably in the order of 100 times more efficient).

d) The activation energy of the dry N₂O/CO reaction is close to that of N₂O decomposition (59.5 and 57.8 kcal respectively). Coleman obtained an activation energy of 67 kcal for a "wet" N₂O/CO reaction. Pickering also observed an activation energy difference between the "dry" and "wet" reactions (55 and 70 kcal respectively). This again suggests that the "wet" reaction proceeds by a different reaction path.

Evidence against a "dry" reaction:

e) The last part of the results section examines in detail the poor reproducibility of some of the experimental results. The worst scatter occurred at low nitrous oxide pressures and to a lesser degree at low carbon monoxide pressures. If water takes part in the reaction free radicals could be formed by

\[ \text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]  

and/or possibly by excited carbon dioxide releasing sufficient energy
to dissociate H₂O on being deactivated. [63]

\[ \text{CO}_2^* + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H} + \text{OH} \]

If it is assumed that the CO prepared from sodium formate and sulphuric acid has very small traces of water as an impurity then it would account for the irreproducibility.

f) The introduction of OH or H radicals into the N₂O/CO system would result in a reaction cycle of the form:

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]  \hspace{1cm} (9)
\[ \text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH} \]  \hspace{1cm} (10)

These chain propagating steps are analogous to the chain propagating steps in the N₂O/H₂ reaction.

i.e. \[ \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \]  \hspace{1cm} (9')
\[ \text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH} \]  \hspace{1cm} (10')

The rate constants for reactions 9' and 9 at 700°C are of a similar size. Schofield's value for \( k_9' = 6.3 \times 10^{-11} \text{ exp} \left( -5490/RT \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) [59] gives a value at 700°C of \( 3.68 \times 10^{-12} \). Baulch, Drysdale and Lloyd recommend a value for \( k_9' = 7 \times 10^{-13} \text{ exp} \left( -1080/RT \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) [75] which gives \( 4.0 \times 10^{-12} \) at 700°C. It is to be expected, therefore, that a chain propagation involving 9 and 10 would be of a similar efficiency to the chain reaction of N₂O/H₂ system and a chain length of about 1000 would be expected. This would lead to a rapid consumption of N₂O and CO once a chain had been started.

g) The N₂O/CO reaction is 2 to 3 times faster than the N₂O decomposition. It is difficult to write a chain mechanism to account for this result involving only known reactions of N₂O and CO. The oxygen atoms produced in the initiation step can only recombine in some way (at walls or in the gas phase, or react with N₂O to give oxygen or nitric oxide), or react with carbon monoxide.
In this case the $N_2O/CO$ reaction would be expected to proceed at a similar rate to the $N_2O$ decomposition. If, however, $H$ and $OH$ radical propagation of the reaction chain occurred every 300 or so reactive oxygen atom collisions, then the $N_2O/CO$ reaction would be expected to be about 3 times faster than $N_2O$ decomposition.

h) Finally it must be pointed out that the modern consensus of opinion does not favour a mechanism for CO oxidation that does not involve the participation of hydrogen and hydroxyl radicals; except perhaps when hydrogen containing impurities are in less than p.p.m. quantities [29 to 33, 76]. These concentrations are well below the limits of detection employed in this work.

An explanation as to why the $N_2O/CO$ reaction is faster than $N_2O$ decomposition which does not invoke the $H$ and $OH$ radical chain mechanism discussed in points f) and g) could be provided if it were assumed that $CO_2^\equiv$ was capable of causing the decomposition of $N_2O$ on collision.

i.e. $CO_2^\equiv + N_2O \rightarrow CO_2 + N_2 + O$

In this way a cycle of the type:

$$0 + CO_2 \rightarrow CO_2^\equiv$$  \hspace{1cm} (2)

$$CO_2^\equiv + N_2O \rightarrow CO_2 + N_2 + O$$ \hspace{1cm} (4')

could be imagined. This hypothesis is an attractive one and would only require a chain length of about 10 to account for the observed increase in initial rates. It would also explain to some extent the tendency for the $N_2O/CO$ reaction rate to approach that of the $N_2O$ decomposition in the latter stages of reaction. If the excited $CO_2^\equiv$ was in the $^1B_2$ state proposed by Dixon [57] there would be sufficient energy released to cause $N_2O$ to dissociate. The peak intensity of the $^1B_2 CO_2$ emission occurs in the region 4000 to 4500 A and is almost certainly due to transitions to excited vibrational levels of ground state $CO_2$. 
state CO₂. Even if the maximum intensity corresponded to a transition to the ground vibrational level of the ground electronic state the energy released would be of the order of 70 kcal which is greater than the 58 kcal required to activate N₂O. The ability of electronically excited carbon dioxide to cause dissociation of molecules with which it has collided has been postulated for O₂ by Sulzmann, Myers and Bartle [31] who suggested that in shock heated mixtures of O₂/CO chain propagation occurred by the process

\[
\text{CO}²⁺ + \text{O}₂ \rightarrow \text{CO}_₂ + 20
\]

This was later disputed by Brokaw [32] who suggested that Sulzmann et al's results would be explained on the basis of an H and OH radical promoted chain if the hydrocarbon impurities in Sulzmann's gases were in 10 to 20 p.p.m. concentrations instead of the claimed 1 p.p.m.

For a "dry" reaction a possible mechanism could be of the form:

initiation \[ \text{N}_₂\text{O} \rightarrow \text{N}_₂ + \text{O} \] (1)

followed by the reaction of oxygen atoms with carbon monoxide to give excited CO₂

\[ \text{O} + \text{CO} \rightarrow \text{CO}²⁺ \] (2)

It is a debatable point whether the initial formation of excited CO₂ requires the presence of a third body or whether the CO₂⁺ is formed by a bimolecular process followed by stabilisation of the CO₂⁺ by collision with another molecule before it has redissociated. A fuller discussion concerning the formation and deactivation of CO₂⁺ is given in a later section.

Since the ratio of CO₂ produced by a radiative process to total CO₂ produced in the reaction increases as the total pressure decreases CO₂⁺ must be deactivated by both radiative and collision induced processes

\[ \text{CO}_²⁺ \rightarrow \text{CO}_₂ + h \nu \] (3)

\[ \text{CO}_²⁺ + \text{M} \rightarrow \text{CO}_₂ + \text{M} \] (4)
There must also be secondary reactions to account for the production of oxygen and these will be dealt with in the next section. As an explanation for the increased rate of reaction compared with $N_2O$ decomposition the reaction

$$CO_2^* + N_2O \rightarrow CO_2 + N_2 + O$$

must be tentatively included.

Because recent work has shown that water in p.p.m. quantities can affect results in oxygen/carbon monoxide systems the effect of introducing water into the reaction mechanism will now be considered.

If water is present a chain initiating step

$$O + H_2O \rightarrow 20H$$

(or much less likely $CO_2^* + H_2O \rightarrow CO_2 + H + OH$)

followed by propagation

$$OH + CO \rightarrow CO_2 + H$$

$$H + N_2O \rightarrow N_2 + OH$$

and various termination steps involving $H$ and $OH$ must be added to the reaction scheme. The reaction therefore may be considered as a competition between carbon monoxide and water for the oxygen atoms produced by $N_2O$ decomposition (neglecting the small amount of oxygen produced).

```
<table>
<thead>
<tr>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2CO + (M) \rightarrow CO_2^* \rightarrow CO_2$</td>
</tr>
</tbody>
</table>
```

The relative efficiencies of reactions 2 and 8 would be given by the ratio of their respective rates. Schofield suggests a value of $k_8 = 1.4 \times 10^{-10} \exp (-18,000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ \cite{[59]}, this gives a value of $k_8 = 1.27 \times 10^{-14}$ at 700°C. There are no reliable values for $k_2$ since the majority of experimental work on oxygen atom reaction with CO has been bedevilled by uncertainties over the extent to which hydrogen containing impurities play a part in the reaction. Baulch,
Drysdale and Lloyd [75], in attempting to correlate the widely scattered experimental data, predict a value of about
\[ 2 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} \] (9.5 \times 10^{-33} \text{ cm}^3 \text{ molecule}^{-2} \text{ sec}^{-1} )
for the overall reaction
\[ 0 + \text{CO} + \text{M} \rightarrow \text{CO}_2 \]
at 700°C and suggest an activation energy of about 2.5 kcal. Wong, Potter and Belles obtained an upper limit of
\[ 1.04 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1} \] at 500°C in a stirred flow reactor, and point out that in earlier work (on which Baulch et al's estimation is based) minute traces of hydronereous impurity would lead to higher values.

The efficiency of reaction 2 to reaction 8 is:
\[
\frac{\text{Rate}(2)}{\text{Rate}(8)} = \frac{k_2[\text{CO}][0][\text{M}]}{k_8[\text{H}_2\text{O}][0]} = \frac{k_2[\text{M}][\text{CO}]}{k_8[\text{H}_2\text{O}]} 
\]

If Wong et al's estimate for \( k_8 \) is taken and Baulch's activation energy of 2.5 kcal is assumed, \( k_2 = 1.54 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1} \). A usual pressure in the reaction studied here was 200 mm Hg which gives a value for \([\text{M}]\) of \( 2 \times 10^{18} \text{ molecule cm}^{-3} \) at 700°C,
\[
\therefore \quad \frac{k_2[\text{M}]}{k_8} = 2.43 \times 10^{-2}
\]
Assuming that the difference in relative rates of the \( \text{N}_2\text{O}/\text{CO} \) reaction and \( \text{N}_2\text{O} \) decomposition (3:1) is due entirely to \( \text{H} \) and \( \text{OH} \) propagated chains, then \( \text{Rate}(2) \) to \( \text{Rate}(8) \) would be about 300:1 (point g) then:
\[
\frac{k_2[\text{M}][\text{CO}]}{k_8[\text{H}_2\text{O}]} = 300 
\]

This provides an estimate of the relative concentrations of carbon monoxide and water
\[
\frac{[\text{CO}]}{[\text{H}_2\text{O}]} = \frac{3 \times 10^2}{2.43 \times 10^{-2}} = 1.24 \times 10^4
\]
The concentration of water in the system would therefore be of the order of 80 p.p.m. This is below the limits of detection by mass spectroscopic analysis. Variations in water concentrations of 10's p.p.m. would therefore account for the observed irreproducibility.

A further point must be added. Since oxygen is produced during the reaction there would be a likelihood that the water initiated chain reaction would become more predominant due to the addition of the chain branching reaction

\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]

and it would be expected that as the reaction proceeds its rate relative to \( \text{N}_2\text{O} \) decomposition would increase. In fact the opposite is true. However small amounts of nitric oxide must be formed alongside the oxygen formation [5]. It was shown in the first part of this thesis that the \( \text{N}_2\text{O}/\text{H}_2 \) reaction was inhibited by nitric oxide and therefore NO would have a modifying effect on the extent of the chain reaction and hence on the branching effect of molecular oxygen, and it is possible that the small amounts of NO formed cause the observed decline in the rate of the \( \text{N}_2\text{O}/\text{CO} \) reaction relative to \( \text{N}_2\text{O} \) decomposition.

There is a suggestion that the effect of water is not as great as the preceding discussion supposes. This is provided by the fact that the addition of water in quantities of the order of 0.1 to 0.4% in 1:1 mixtures of \( \text{N}_2\text{O}/\text{CO} \) (at pressures between 400 and 100 mm Hg) produce an increase in rate over the dry reaction of only 3 to 6 times (Table 2.1). These results were not repeated and can only be considered tentative. Noticeable reaction occurred as the gases were admitted to the reaction vessel so that the initial rates obtained are probably not reliable. The results of Coleman and Reuben [41] on the wet reaction will probably clarify the situation.
It is not possible to rule out the presence of 80 p.p.m. water in the prepared gases. On the other hand there is some evidence that the full effect of water is inhibited by small amounts of nitric oxide. It is impossible to accurately estimate the extent of the wet reaction, but it is possible to ascribe to it the irreproducibility of the "dry" reaction. The fact that molecular oxygen is produced and that appreciable chemiluminescence was observed suggests that a "dry" reaction (i.e. one in which CO₂ is produced by the reaction of O atoms with carbon monoxide) occurs at a comparable rate to any possible H and OH propagated system.

(ii) Oxygen Production

The production of oxygen during a combustion process is unusual though Reuben et al observed a slow pressure change during the reaction of N₂O with SO₂ and suggested that it might be due to the formation of oxygen [6,36]. There are four processes by which oxygen may be formed:

1) A termolecular recombination of oxygen atoms

\[ O + O + M \rightarrow O₂ + M \]  \hspace{1cm} (5)

2) Reaction of oxygen atoms with nitrous oxide to give nitrogen and molecular oxygen

\[ O + N₂O \rightarrow N₂ + O₂ \] \hspace{1cm} (6a)

or

3) With N₂O to give nitric oxide

\[ O + N₂O \rightarrow 2NO \] \hspace{1cm} (6b)

followed by oxidation of nitric oxide to give NO₂ which in turn reacts with further N₂O to yield molecular oxygen with the regeneration of NO [5,8]

\[ O + NO + M \rightarrow NO₂ + M \] \hspace{1cm} (6c)

\[ NO₂ + N₂O \rightarrow NO + O₂ + N₂ \] \hspace{1cm} (6d)

and finally,

4) The destruction of O atoms at the reaction vessel walls

\[ O \rightarrow \frac{1}{2}O₂ \text{ at wall} \] \hspace{1cm} (7)
Experimental evidence has shown that the production of oxygen is second order in nitrous oxide and has a small negative dependence on the CO pressure (order app. -0.6). The reaction mechanism for $N_2O$ oxidation of CO is of the form

$$ N_2O \rightarrow N_2 + O \quad (1) $$

$$ O + CO \rightarrow CO_2 + M \quad (2') $$

$O$ termination to give $O_2$

The inclusion of a water propagated reaction and the various possible fates for electronically excited $CO_2$ will not affect the overall kinetics and would complicate analysis.

Oxygen atom termination at reaction vessel walls as a major step can be ruled out since if

$$ O \rightarrow \frac{1}{2}O_2 \text{ at wall} \quad (7) $$

is added to the reaction scheme, steady state treatment suggests that the rate of oxygen production should be first order in nitrous oxide.

$$ \text{vis. } \frac{d[O_2]}{dt} = k_7 [N_2O] \quad \frac{\text{at}}{2 (k_2,[CO](M) - k_7)} $$

Destruction of $O$ atoms at the reaction vessel walls is unlikely to be important for the further reason that its rate is very much smaller than the competing reactions of $O + CO$, and $O + H_2O$. Kaufmann et al estimate that $k_7 = 17 \text{ sec}^{-1}$ [5] at $700^\circ\text{C}$ for their cylindrical silica reaction vessel at pressures of the order of $100 \text{ mm Hg}$. In order to compare this first order rate process with the bimolecular (or trimolecular) processes of $O + CO$, the rate constant $k_7$ must be converted to a pseudo 2nd order constant by dividing $k_7$ by the pressure. The value is about $8 \times 10^{-18}$ which is much smaller than the $k_2 (O + CO)$ of $3.08 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

(See Table 2.6 for a tabulation and comparison of rate constants).

Gas phase oxygen atom recombination

$$ O + O + M \rightarrow O_2 + M \quad (5) $$
yields a complicated steady state expression for the rate of $O_2$
production

$$\frac{2d[O_2]}{dt} = k_2'[CO] \pm \sqrt{(k_2'[CO])^2 + 4k_1k_5[N_2O][M]}$$

which at best is only first order in $[N_2O]$ and approximately first
order in $[CO]$. The rate of reaction (5) relative to oxygen atom
reaction with CO is of the order of $10^{-3}$:1 (assuming $[O]$ is 0.1% $[CO]$ 
and using $k_5$ given in Table 2.6), and so reaction 5 will be negligible
in oxygen formation.

The remaining two reactions postulated to account for oxygen
formation both involve oxygen attack on nitrous oxide. The overall
stoichiometry of both processes may be considered to be

$$O + N_2O \rightarrow N_2 + O_2$$  \hspace{1cm} (6')

Unlike the other processes reaction 6' occurs at a similar rate to
the $O + CO$ reaction ($k_6' = 2.94 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for NO production or $1.47 \times 10^{-16}$ for $N_2 + O_2$ compared with a value of $k_2$, of $3.08 \times 10^{-16}$). Steady state treatment gives the rate of
oxygen formation:

$$\frac{d[O_2]}{dt} = \frac{k_6'[N_2O]^2}{k_2'[CO] + k_6'[N_2O]}$$

The $k_2'[CO]$ term should include the reaction of $[CO]$ by the H and OH
chain cycle and/or by a cycle initiated by the dissociation of $N_2O$
by electronically excited $CO_2$. In which case it is probable that
the $k_2'[CO]$ term is greater than $k_6'[N_2O]$ and the $d[O_2]/dt$ becomes
second order in nitrous oxide, and approximately -1 order in carbon
monoxide which is close to the experimental result. The order with
respect to carbon monoxide must be modified to take into account that
portion of the CO that is oxidised in the H and OH chain process and
does not therefore compete for O atoms. The order with respect to
CO is probably closer to the experimental value of -0.6 than is
indicated by the steady state derivation of $d[O_2]/dt$. 
The formation of oxygen as a result of the reaction of oxygen atoms with nitrous oxide implies that nitric oxide must also be formed. Indeed since the rate constant for
\[ O + N_2O \rightarrow 2NO \] (6b)
has been estimated by Kaufmann et al [5] to be about twice that for the reaction
\[ O + N_2O \rightarrow N_2 + O_2 \] (6a)
the majority of oxygen formed must come from subsequent reactions of nitric oxide. Kaufmann suggested that the following reactions played a major part in the decomposition of \( N_2O \).
\[ O + NO + M \rightarrow NO_2 + M \] (6c)
and \[ NO_2 + N_2O \rightarrow N_2 + O_2 + NO \] (6d)
Kaufmann et al included 6d because they required a process that regenerated NO and produced \( O_2 \) whilst at the same time leading to the destruction of a further \( N_2O \) molecule. Nitric oxide inhibits its own formation during the course of reaction by NO removing oxygen atoms more efficiently than \( N_2O \). The reaction
\[ 0 + NO_2 \rightarrow N_2 + O_2 \] (6e)
was rejected by Kaufmann et al as it did not involve the removal of a further \( N_2O \) molecule. The \( 0 + NO_2 \) reaction as a competition for \( 0 \) atoms and as a source of molecular oxygen cannot be ignored as it is a much more efficient reaction than \( 0 + NO \). At 700°C \( k_6 = 1.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \), and therefore with \( NO_2 \) concentrations \( 10^{-5} \) times smaller than that of \( N_2O \) the reaction, \( 0 + NO_2 \rightarrow N_2 + O_2 \) would be competitive with the other \( 0 \) atom reactions. It is possible that NO formation in the \( N_2O/CO \) reaction is self inhibiting because reaction 6 (\( 0 + NO_2 \)) competes preferentially with the nitric oxide producing reaction 6b (\( 0 + N_2O \)) rather than reaction 6d (\( 0 + NO + M \)). If this were the case NO and \( NO_2 \) concentrations would be small and certainly less than the 0.5 to 1% that is detectable by mass spectrometric analysis.

It is concluded that the reaction \( 0 + N_2O \rightarrow 2NO \) and subsequent oxygen atom reactions on nitric oxide and nitrogen dioxide contribute a major part of the oxygen produced during the \( N_2O/CO \) reaction.
(iii) Chemiluminescence and Allied Topics:

The spin forbidden reaction

\( \text{O}(^3\Pi) + \text{CO}(^2\Sigma_g^+) \leftrightarrow \text{CO}_2(1\Sigma_g^+) \)

and its accompanying chemiluminescence have been studied by many workers.

Clyne and Thrush [74] examined the reaction of O atoms, generated by dissociation of \( \text{O}_2 \) in an electrodeless discharge, with carbon monoxide in a flow tube at pressures in the region of 1 mm Hg. They found that glow intensity was proportional to O atom and CO concentrations and was independent of total pressure. They found, however, that the total intensity for a given set of conditions varied with the nature of the diluent gas \( (\text{O}_2 \gg \text{N}_2 \gg \text{A} \gg \text{Ne} = \text{He}) \). Clyne and Thrush proposed the mechanism

Stabilization and dissociation

\[ \text{O} + \text{CO} + \text{M} \leftrightarrow \text{CO}_2 + \text{M} \] (1a)

Vibrational energy transfer between triplet and singlet excited states

\[ \text{CO}_2 + \text{M} \leftrightarrow \text{CO}_2 + \text{M} \]

Radiation

\[ \text{CO}_2 \rightarrow \text{CO}_2 + \hbar\nu \] (2a)

Collisional electronic quenching

\[ \text{CO}_2 + \text{M} \rightarrow \text{CO}_2 + \text{M} \] (3a)

(The numbers for the processes are given the letter c to distinguish them from the numbering of equations in the \( \text{N}_2\text{O/CO} \) reaction).

Mahan and Solo [80] claim that, at pressures similar to those of C and T, the production of \( \text{CO}_2 \) was independent of, and light intensity dependent on, total pressure. This contradicted the results of C and T. They also found that small amounts of molecular oxygen considerably quenched the light emission and increased the amounts of \( \text{CO}_2 \) formed.

Jonathan and Warneck [82] obtained results similar to C and T at
pressures in the 1 to 10 micron region (i.e., $10^3$ to $10^2$ less than those of C and T). The mechanism they proposed was more complex than that of C and T. They felt that a more complex mechanism was necessary because C and T's mechanism, if applied to the 10 micron region, suggests that the light intensity should become dependent on the pressure. Jonathan and Warneck's mechanism is, however, essentially similar to that of C and T. They also point out that Mahan and Solo's data can be reinterpreted to show that the light emission is directly proportional to the amount of CO$_2$ produced and in that case would not be pressure dependent. Using their own mechanism Jonathan and Warneck predict that in the pressure region 1 micron to 10 mm Hg the light intensity is independent of pressure, and that it should vary inversely as the pressure above this.

For the purposes of this discussion Clyne and Thrush's mechanism will be assumed, namely

$$\text{CO}_2^\pm + \text{M} \leftrightarrow \text{CO}_2$$

(2)

$$\text{CO}_2^\pm \rightarrow \text{CO}_2 + \text{h} \nu$$

(3)

$$\text{CO}_2^\pm + \text{M} \rightarrow \text{CO}_2 + \text{M}$$

(4)

The fate of CO$_2^\pm$ in the N$_2$/CO system will now be considered.

$$k_3 \rightarrow \text{CO}_2 + \text{h} \nu \quad \text{radiative (3)}$$

$$k_4[M] \rightarrow \text{CO}_2 + \text{M} \quad \text{non-radiative (4)}$$

The probability of CO$_2^\pm$ decomposing by the radiative path (3) is $k_3$ and that of the non-radiative path (4) is $k_4[M]$. The total rate of CO$_2$ production by both (3) and (4) divided by the rate of CO$_2$ production by path (3) alone is

$$\frac{\text{Rate (3 and 4)}}{\text{Rate (3)}} = \frac{(k_4[M] + k_3)[\text{CO}_2^\pm]}{k_3[\text{CO}_2^\pm]} = \frac{(k_3 + k_4[M])}{k_3}$$

i.e.,

$$= 1 + \frac{k_4[M]}{k_3}$$

(4)
The experimentally measured quantity, however, is not rate \((3 + 4)/\) rate \((3)\), but total rate of \(\text{CO}_2\) production by all paths/rate \((3)\). (The actual quantity measured and quoted in Table 2.4 is rate \((3)/\) total rate; i.e. integral glow/rate of \(\text{CO}_2\) production). In the \(\text{N}_2\text{O}/\text{CO}\) reaction a portion of the \(\text{CO}_2\) produced arises from a water initiated chain reaction which does not involve excited \(\text{CO}_2\). If the ratio of the rate of \(\text{CO}_2\) production via excited \(\text{CO}_2\) (processes 3 and 4) to the total rate of \(\text{CO}_2\) productions (3 and 4 and water initiated chain) is \(x\), then

\[
\frac{\text{Total } \text{CO}_2 \text{ production}}{\text{Rate } (3)} \times = \frac{\text{Rate } (3 + 4)}{\text{Rate } (3)}
\]

i.e.

\[
\frac{\text{Total } \text{CO}_2 \text{ production}}{\text{Rate } (3)} = x (1 + k_4[M]/k_3)
\]

Assuming that the percentage of water in the gases remains constant, \(x\) will be a constant independent of pressure and mixture composition.

Using the experimentally obtained values of total \(\text{CO}_2\) production/rate \((3)\) (i.e. the reciprocal of integral glow/\(\text{CO}_2\) production, which is in mm Hg, \(10^8\) amp. min\(^{-2}\) units) expression B becomes:

\[
\frac{\text{CO}_2 \text{ production}}{\text{Integral glow}} = x' (1 + k_4[M]/k_3)
\]

Where \(x'\) now takes into account the (unknown) factor to convert \(10^{-8}\) amp units to mm Hg min\(^{-1}\). A plot of the L.H.S. of equation C against total pressure \([M]\) has an intercept of \(x'\) and a slope of \(k_4 x'/k_3\). The ratio of \(k_4/k_3\) may therefore be obtained simply dividing the slope by the intercept. The value of \(k_4/k_3\) so obtained is independent of the contribution of the "wet" reaction (with the proviso that for a given mixture composition the % of "wet" reaction to "dry" reaction is constant), and also does not require assumptions to be made as to the ratio of integral glow units to mm Hg min\(^{-1}\).
Fig: 2.13 \( \text{CO}_2 \) Production/Integral Glow vs. Total Pressure.
Table 2.6  Slopes, Intercepts and Calculated Values for $k_4/k_3$ from Fig. 2.13.

<table>
<thead>
<tr>
<th>$\text{N}_2\text{O}:\text{CO}$</th>
<th>Slope</th>
<th>Intercept</th>
<th>$k_4/k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>$1.45 \pm 0.05 \times 10^{-2}$</td>
<td>$1.10 \pm 0.13$</td>
<td>$12.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>1:1</td>
<td>$1.56 \pm 0.12 \times 10^{-2}$</td>
<td>$2.15 \pm 0.27$</td>
<td>$7.37 \times 10^{-3}$</td>
</tr>
<tr>
<td>2:1</td>
<td>$1.23 \pm 0.23 \times 10^{-2}$</td>
<td>$1.85 \pm 0.47$</td>
<td>$6.64 \times 10^{-3}$</td>
</tr>
<tr>
<td>All points</td>
<td>$1.41 \pm 0.15 \times 10^{-2}$</td>
<td>$1.79 \pm 0.37$</td>
<td>$7.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Fig. 2.13 demonstrates the applicability of the above analysis to the experimental N₂O/CO system. The figure is a plot of CO₂ production/integral glow against total pressure for 2:1, 1:1 and 1:2 N₂O/CO mixtures. It will be seen that straight lines are indeed obtained and their slopes and intercepts are shown in Table 2.6. The ratio \( k_4 / k_3 \) decreases by about 50% in passing from reactions in which N₂O/CO = 1:2 to reactions in which N₂O/CO = 2:1. The rate constant for collisional deactivation of CO₂\(^{=}\) (\( k_4 \)) must therefore be dependent on the nature of the third body. Since the largest value of \( k_4 / k_3 \) is obtained in CO rich mixtures and the smallest in N₂O rich mixtures it is concluded that carbon monoxide is a more efficient third body than N₂O.

The ratio of \( k_4 / k_3 \) (which is in mm Hg. units) obtained from the least squares plot of all the points in Fig. 2.13 is \( 7.9 \times 10^{-3} \) (this may be regarded as an "average" value). At a pressure of, say, 100 mm Hg. the ratio of the rate of collisional deactivation to the rate of the radiative reaction is

\[
\frac{k_4[M]}{k_3} = 0.79
\]

The recommended rate constants published by Bauloh et al [75] for the overall reactions

\[
O + CO + M \rightarrow CO_2 + M \quad \text{non-radiative (4')} \\
O + CO \rightarrow CO_2 + h\nu \quad \text{radiative (3')}
\]

are

\[
k_4' = 1.1 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1} \\
k_3' = 3.6 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}
\]

These rate constants are in fair agreement with those obtained by Clyne and Thrush and lead to a ratio of non-radiative process to radiative process of
\[
\frac{\text{Rate } 4'}{\text{Rate } 3'} = 3.1 \times 10^6
\]

at 100 mm Hg. total pressure.

There is an obvious discrepancy between the result obtained in this work and those of other workers. The value of \( k_4/k_3 \) obtained in this work is independent of the "calibration factor" required to convert Integral glow units to a reaction rate in mm Hg/min. It is also independent of any \( \text{CO}_2 \) producing reaction that does not involve excited \( \text{CO}_2 \) (e.g. the water initiated chain reaction), provided the assumption that the fraction of such a reaction remains constant for a given mixture of \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) is correct. The \( \text{H}_2\text{O} \) catalyzed reaction only contributes app. 3/4 of the total \( \text{CO}_2 \) formed. If one assumes that the fraction of \( \text{H}_2\text{O} \) catalyzed reaction varies with pressure, the ratio of \( k_4/k_3 \) obtained is unlikely to be changed by more than an order of magnitude. It should be pointed out that the overall characteristics of the chemiluminescence agree with other workers:

i.e. i) that the glow intensity varies inversely with pressure (postulated by Jonathan and Warneck for \( \text{O} + \text{CO} \) reactions at pressures above 10 mm Hg. [82]).

and ii) that the value of \( k_4 \) depends on the nature of the third body present (Clyne and Thrush [74] and Jonathan and Warneck). One is therefore left with an anomaly; the characteristics of the chemiluminescence reaction agree with other workers but the rate constant ratio derived differs by a factor of \( 10^6 \).
(iv) **Mechanism:**

The mechanism of the \( \text{N}_2\text{O}/\text{CO} \) reaction under the "dry" conditions employed in this work must clearly be a process in which a number of reactions compete for the oxygen atoms made available by the thermal decomposition of \( \text{N}_2\text{O} \). The possible reactions with their rate constants are shown in Table 2.6. In order to make the comparison clearer, Fig. 2.14 shows the various reaction paths open to oxygen atoms. The ratios of the individual paths relative to the rate of the \( \text{O} + \text{CO} + \text{M} \) reaction are shown. A number of assumptions have been made in order to obtain the relative rates and these will be referred to as they arise.

If no "wet" reaction occurred then it would be expected that the \( \text{N}_2\text{O}/\text{CO} \) reaction would proceed at about the same rate as \( \text{N}_2\text{O} \) decomposition. Experimentally it has been found that the \( \text{N}_2\text{O}/\text{CO} \) reaction is about 3 times as fast as \( \text{N}_2\text{O} \) decomposition and it is suggested that this is due to water in 10's of p.p.m. quantities initiating an \( \text{H} \) and \( \text{OH} \) radical propagated chain.

If it is assumed that the percentage of water in the reaction mixture is 0.01% (the minimum limit of detection) then the reaction

\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]

takes place at a relative rate of \( 4 \times 10^{-3} \). However the production of \( \text{OH} \) radicals results in a chain reaction involving \( \text{CO} \) and \( \text{N}_2\text{O} \) which has a chain length of about 1000 (obtained by comparing with the \( \text{N}_2\text{O}/\text{H}_2 \) chain process). Hence the reaction of \( \text{O} \) atoms with water results in the removal of \( \text{N}_2\text{O} \) (and \( \text{CO} \)) about four times as fast as reaction 2.

The participation of the \( \text{H} \) and \( \text{OH} \) propagated chain reaction is confirmed by the activation energy data. It was shown that the production of \( \text{CO}_2 \) by the radiative process

\[
\text{O} + \text{CO} (+ \text{M}) \rightarrow \text{CO}_2^x \rightarrow \text{CO}_2 + h\nu
\]

had an activation energy about 13 kcal less than that for the overall
Table 2.6 Possible Reactions of $O$ atoms

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>$k_{700}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O \rightarrow N_2 + O$</td>
<td>$6.3 \times 10^{-5} \exp(-57.8/RT)$</td>
<td>$6.4 \times 10^{-4}$</td>
<td>This work</td>
</tr>
<tr>
<td>$O + CO + M \rightarrow CO_2 + M$</td>
<td>$5.62 \times 10^{-34} \exp(-2.5/RT)$</td>
<td>$1.54 \times 10^{-34}$</td>
<td>[75, 76]</td>
</tr>
<tr>
<td>$O + O + M \rightarrow 4x10^{-33}$ for $N_2O$ as 3rd body, $cm^6$ molecule$^{-2}$ sec$^{-1}$</td>
<td>$4x10^{-33}$</td>
<td>[59]</td>
<td></td>
</tr>
<tr>
<td>$O + N_2O \rightarrow N_2 + O_2$</td>
<td>$\frac{1}{2}(7.5 \times 10^{-11} \exp(-24.1/RT))$</td>
<td>$1.47 \times 10^{-16}$</td>
<td>[59, 5]</td>
</tr>
<tr>
<td>$O + H_2O \rightarrow 2NO$</td>
<td>$7.5 \times 10^{-11} \exp(-2.1/RT)$</td>
<td>$2.94 \times 10^{-16}$</td>
<td>[59]</td>
</tr>
<tr>
<td>$O + NO + M \rightarrow NO_2 + M$</td>
<td>$4x10^{-33} \exp(+1.93/RT)$</td>
<td>$1.09 \times 10^{-32}$</td>
<td>[59, 79]</td>
</tr>
<tr>
<td>$O \rightarrow Wall$</td>
<td>$17$ sec$^{-1}$ at 700°C</td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td>$O + H_2O \rightarrow 2OH$</td>
<td>$1.4 \times 10^{-10} \exp(-18.0/RT)$</td>
<td>$1.27 \times 10^{-14}$</td>
<td>[59]</td>
</tr>
<tr>
<td>$O + NO_2 \rightarrow NO + O_2$</td>
<td>$3.2 \times 10^{-11} \exp(-1.06/RT)$</td>
<td>$1.85 \times 10^{-11}$</td>
<td>[59]</td>
</tr>
</tbody>
</table>

The units are those for bimolecular reactions of $cm^3$ molecule$^{-1}$ sec$^{-1}$ unless otherwise stated.
<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + M</td>
<td>CO$_2$</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>CO$_2$ + hv</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>H$_2$O + chain (assumption 0.01% H$_2$O and chainlength $10^3$)</td>
<td>N$_2$ + CO$_2$</td>
<td>4</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>2NO</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>N$_2$ + O$_2$</td>
<td>0.5</td>
</tr>
<tr>
<td>NO + M</td>
<td>NO$_2$</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>varies with [NO]</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>N$_2$ + O$_2$</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>varies with [NO]</td>
</tr>
<tr>
<td>O +</td>
<td>O$_2$</td>
<td>3 x $10^{-2}$</td>
</tr>
</tbody>
</table>
N₂O/CO reaction. The activation energy of reaction 3 is low (2.5 kcal [75]) whereas the competing reaction 0 + H₂O → 2OH has a relatively high activation energy of 18 kcal [59]. Therefore, as the temperature is raised the rate of reaction 8 will increase faster than that of reaction 3. The difference in activation energies of reactions 3 and 8 is about 15 to 16 kcal which is close, allowing for the experimental error, to the activation energy difference observed between reaction 3 and the overall N₂O/CO reaction.

The production of oxygen must involve the appearance of nitric oxide in the reaction mixture as a result of 0 + N₂O → 2NO. This introduces further reactions that can compete for the available oxygen atoms

\[
\text{via. } \quad 0 + \text{NO} + M \rightarrow \text{NO}_2 + M \quad (6c)
\]

and

\[
0 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \quad (6d)
\]

or

\[
\text{NO}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 + \text{NO} \quad (6e)
\]

These reactions regenerate nitric oxide as oxygen is formed. Their rates will increase as the reaction proceeds whereas the NO producing reaction 0 + N₂O → 2NO (6b) will decrease. The further formation of NO will be inhibited as the rates of reactions 6c and d approach that of 6b. The rate of reaction 6c (0 + NO + M) will become equal to the 0 + N₂O reaction when the concentration of NO is about 2% that of N₂O. It is observed that initially the N₂O/CO reaction is about 3 times faster than N₂O decomposition, but that after about 30% reaction the difference decreases to twice as fast. The N₂O/CO reaction continues to be 2 times as fast as the N₂O decomposition until well over 70% reaction has occurred (Fig. 2.2b). It is possible that the change in relative rates represents the point where reactions 6c and/or 6d and e have reached a semi-equilibrium and compete with the other O atom reactions. The major reaction that contributes to
155.

The faster rate of the \( \text{N}_2\text{O}/\text{CO} \) reaction compared with \( \text{N}_2\text{O} \) decomposition is reaction 8, the water initiated chain reaction. It would require about 6\% \( \text{NO} \) to cause the rate of reaction 8 to drop to \( 2/3 \) its initial value. If nitric oxide were present in such quantities it would have been detected in the mass spectrometric analysis. Furthermore, such quantities would have been expected to have resulted in greater quantities of oxygen than the change in reaction vessel pressure indicated. However, a concentration of only 0.01\% \( \text{NO} \) would have the same effect since the \( \text{O} + \text{NO}_2 \) reaction is very much more efficient than \( \text{O} + \text{NO} + \text{M} \). As no rate constant is available for the \( \text{NO}_2 + \text{N}_2\text{O} \) reaction (6e) it is not possible to state definitely which reaction of \( \text{NO}_2 \) causes the inhibiting effect, and hence is responsible for the observed oxygen formation. However, reaction 6e (\( \text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{O}_2 + \text{NO} \)) is likely to have an appreciable activation energy (c.f. the 31 kcal for \( \text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO} \) [83]). If the rate determining step for \( \text{O}_2 \) production has an appreciable activation energy (say \( \approx 25 \text{ kcal} \)) then it would be expected that the overall activation energy for \( \text{O}_2 \) formation would be higher than that for the \( \text{N}_2\text{O}/\text{CO} \) reaction since there are other competitive reactions consuming oxygen atoms. The activation energy of the oxygen formation is, however, the same as that for the overall \( \text{N}_2\text{O}/\text{CO} \) reaction and it must be concluded that the rate determining reaction for \( \text{O}_2 \) formation has a small activation energy. The reactions 6a (\( \text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \)), 6b (\( \text{O} + \text{N}_2\text{O} \rightarrow 2\text{NO} \)) have activation energies of the order of 25 kcal, and it is probable that \( \text{NO}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 + \text{NO} \) has a similar activation energy. Therefore these reactions are not rate determining. On the other hand 6c (\( \text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 \)) and 6d (\( \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \)) have small activation energies (\(-1.93 \text{ kcal} \) and \(-1.06 \text{ kcal} \) respectively) [59, 79] and therefore will be rate determining. These arguments rule out reaction 6a as a
major source of molecular oxygen, and it has already been shown that
atom recombination at reaction vessel walls in the gas phase
make a negligible contribution to the $O_2$ produced. The possible
reaction $H + O_2 \rightarrow OH + O$ has a rate constant at 700°C of $1.63 \times 10^{-13}$
$\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and its participation in the overall $N_2O/CO$ reaction
is likely to be small as the competitive reaction

$$H + N_2O \rightarrow N_2 + OH \quad (10)$$

$k_{10}$ at 700°C = $1.87 \times 10^{-13}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

will occur about 100 times faster. The $H + O_2$ reaction may contribute
marginally in the later stages of reaction when the majority of $N_2O$
has reacted and when the majority of oxygen has been formed. It is
probably this reaction that accounts for the small observed pressure
decrease and the reduction of $O_2$ concentration in the latter stages
of reaction.

It has been shown that the bulk of $CO_2^\ddagger$ produced by $O$ atom reaction
with CO undergoes radiationless deactivation "before" the excited $CO_2$
($^3B_2$) has entered the $^1B_2$ state from which the chemiluminescence is
observed.

The following reaction mechanism accounts for the major aspects
of the $N_2O/CO$ reaction studied in this thesis:

$$N_2O \rightarrow N_2 + O \quad (1)$$
$$O + CO \rightarrow CO_2^\ddagger (^3B_2, ^1B_2) \quad (2)$$
$$CO_2^\ddagger (^1B_2) \rightarrow CO_2 (^1\Sigma^+) + h\nu \quad (3)$$
$$CO_2^\ddagger (^3B_2, ^1B_2) + M \rightarrow CO_2 (^1\Sigma^+) + M \quad (4)$$
$$O + N_2O \rightarrow 2NO \quad (6a)$$
$$O + NO + M \rightarrow NO_2 + M \quad (6a)$$
$$O + NO_2 \rightarrow NO + O_2 \quad (6a)$$
$$O + H_2O \rightarrow 2OH \quad (8)$$
$$OH + CO \rightarrow CO_2 + H \quad (9)$$
$$H + N_2O \rightarrow N_2 + OH \quad (10)$$
$$H + OH \rightarrow H_2O \quad (11)$$
The following reactions are of marginal importance:

\begin{align}
0 & \rightarrow \text{Wall} \quad (7) \\
0 + N_2O & \rightarrow N_2 + O \quad (6a) \\
H + O_2 & \rightarrow OH + O \quad (12) \\
& \text{(in the later stages)}
\end{align}

There is no substantial evidence to support a completely dry reaction based on a cycle initiated by the dissociation of $N_2O$ on collision with excited $CO_2$.

\textbf{(v) Summary}

The $N_2O/CO$ reaction at 700°C occurs at about three times the rate of $N_2O$ decomposition. It is accompanied by a blue chemiluminescence and the formation of small amounts of oxygen. The reaction is first order in nitrous oxide and about 0.3 order in carbon monoxide and has an activation energy of $59.7 \pm 1.5$ kcal. It is suggested that the increase in rate relative to $N_2O$ decomposition is a result of water in 10's of p.p.m. quantities initiating H and OH radical propagated reaction chains.

The reaction is explained on the basis of CO, $N_2O$ and $H_2O$ competing for the oxygen atoms made available by the decomposition of $N_2O$. The nitric oxide formed from the reaction of O atoms with $N_2O$ introduces further reactions that compete for the oxygen atoms. These reactions, $O + NO + M \rightarrow NO_2 + M$ and $O + NO_2 \rightarrow NO + O_2$ are rate determining for $O_2$ production.

The chemiluminescence observed is inversely proportional to pressure and arises from radiation from electronically excited $CO_2$ in the $^1B_2$ state (formed in the termolecular process $O + CO + M \rightarrow CO_2$ ($^3B_2, ^1B_2$) to the $^1B_2$ ground state. The variation of the ratio of $CO_2$ produced by the radiative process to the total rate of $CO_2$ production has been used to calculate the relative rate constants.
for the processes

\[
\text{CO}_2 (^{1}B_2) \xrightarrow{k_3} \text{CO}_2 + h \sqrt{v} \\
\text{CO}_2 (^{1}B_2) \xleftarrow{k_4 [M]} \text{CO}_2 + M
\]

It has been shown that \( k_4 [M]/k_3 \ll 1 \) at the pressures of the reaction (in the region of 100 mm Hg).
Part III

The Temperature Dependence of the Absorption Intensity of Nitrous Oxide in the Region 2600 to 1900 Å
INTRODUCTION

(1) U.V. continuum of N₂O

The spectrum of nitrous oxide in the region from 3000 Å to about 1900 Å has been studied by a number of workers [39, 81, 43 to 47] though not as extensively as its spectrum in the vacuum ultra-violet. There is general agreement that nitrous oxide exhibits a weak continuum in this region which rises to a maximum, variously reported at 1840 Å [46] and 1820 Å [47], just inside the vacuum ultra-violet.

There is a margin of doubt as to the assignation of the transitions that make up this continuum. Suggestions have been made that it consists of two, possibly three, overlapping continua. Sponer and Bonner [44] used a 33 metre light path with nitrous oxide at between 1.5 and 5 atmospheres pressure. They observed the spectrum shown in Fig. 3.1a and considered that it was made up of two weak continua, the weaker showing a slight maximum at about 2900 Å with a long wavelength limit up to 3065 Å. They ascribe these continua to transitions from the ground state to the lowest repulsive triplet states described by (see Fig 1.1)

\[ \text{N}_2\text{O} \left( ^3\pi \text{ or } ^3\Sigma^- \right) \rightarrow \text{N}_2 \left( ^1\Sigma \right) + \text{O} \left( ^3\Pi \right) \]  

(1)

Thermo-chemical data suggest that the dissociation energy is 13,750 cm⁻¹ (∼39 kcal), which means that absorption would be theoretically possible up to 7200 Å.

The other continuum observed by Sponer and Bonner, which was claimed to have a long wavelength limit at 2820 Å, was ascribed by comparison with Dutta's results [81] to a transition from the ground state to

\[ \text{N}_2\text{O} \left( ^3\pi \right) \rightarrow \text{NO} \left( ^2\Pi \right) + \text{N} \left( ^4S \right) \]  

(2)

No mention is made by Sponer and Bonner of possible transitions from ground state to

\[ \text{N}_2\text{O} \left( ^1\Sigma, ^1\Pi, ^1\Delta \right) \rightarrow \text{N}_2 \left( ^1\Sigma \right) + \text{O} \left( ^1\Pi \right) \]  

(3)
Fig. 1. Microphotometer tracings of absorption of N₂O taken through 33 m path at pressures of (A) vacuum; (B) 1 atm.; (C) 5 atm.


Fig. 4. Absorption coefficients of N₂O from 1605–2100 A.


Fig:3.1 N₂O Continuua.
Zelikoff [47] et al. in attempting to explain their work (the spectrum they obtained is shown in Fig. 3.1b) correlate it with the results of previous workers suggesting the following explanation. The transition to the lowest excited levels (Eqn. 1) would produce a continuous absorption which would be too weak to be observed even with the long path length used by Sponer and Bonner because it involves a forbidden singlet-triplet transition. They ascribe the continuum to transitions to a repulsive state or states which yield ground state nitrogen and 1D oxygen (Eqn. 3). They suggest that the second continuum between 2100 and 3300 Å could be explained by transitions to a repulsive state which yielded nitric oxide (2π) and nitrogen atoms (4s) (Eqn. 2). They state, using Sponer and Bonner's thermo-chemical calculations, that the long wavelength limit would be about 3300 Å. If more modern thermo-chemical data are used, especially the value for the dissociation energy of nitrogen [48], the dissociation energy for process (2) corresponds to 24,96 Å. Therefore any transition to (2) could not possibly occur at wavelengths longer than 2500 Å.

Zelikoff et al. ascribe the continuum that they observed above 2100 Å to transitions to a repulsive 1Σ state which leads to ground state nitrogen and oxygen (18) viz:

\[
\text{N}_2\text{O} \ (1\Sigma^+) \rightarrow \text{N}_2 \ (1\Sigma^+) + \text{O} \ (1\Sigma) \quad (4)
\]

This process has a dissociation energy of 47,600 cm\(^{-1}\) which corresponds, quite conveniently, to 2100 Å. They point out, however, that the oscillator strength calculated from the continuum is much weaker than they would have expected for this type of 1Σ → 1Σ transition.
Figure 3.1 shows the results of Sponer and Bonner and Watanabe et al on which the above arguments are based. It is difficult to distinguish the two continua claimed by Sponer and Bonner from their microphotometer traces. Watanabe et al's assumption that their continuum below 2100 Å was due to the transition described by Equation 2.4 is contradicted by later work of Thompson, Haycock and Reeves [39], who extended Zelikoff's result to 2400 Å without any sign of discontinuity in the continuum (see Fig. 3.2).

(ii) Temperature dependence of U.V. Spectra

Changes in the intensity of continuous absorption spectra with temperature have been recorded for chlorine by Gibson, Rice and Bayliss [49]. They found that as the temperature was raised the absorption curve in the region 4100 to 2700 Å (with a maximum at 3280 Å) broadened, the intensity of the maximum decreased but the area under the curve remained constant. They explained this on the basis of transitions from the ground state vibrational levels to an excited repulsive upper state. At room temperature the majority of molecules would be in the ground vibrational level, but at high temperatures higher vibrational levels would become appreciably populated leading to peak broadening. The fact that the area under the absorption curve remains constant with temperature suggests that the transition probability remains the same no matter how many vibrational quanta the molecule possesses.

Cohen and Reid have observed a temperature dependent transition in the $\alpha$ band of formaldehyde in the near ultra-violet [50]. They found that a plot of log absorption coefficient versus reciprocal temperature was linear. The slope corresponded to a temperature coefficient close to the energy difference between the first out-of-plane
bending vibration level and the ground vibrational level. They therefore ascribed the band to transitions to a pyramidal upper electronic state from ground state molecules possessing an out-of-plane vibrational quantum.

The transition is forbidden by classical selection rules owing to the different symmetry of the ground and excited electronic states. Cohen and Reid suggest that the "hot" transition has a higher transition probability than transitions from ground vibrational states. They feel that the out-of-plane vibration is "closer" to the symmetry of the pyramidal upper state than the planar vibrations. Thus the transition would be less strongly forbidden.

The change in absorption intensity of nitrous oxide in the region 2100 Å to 2600 Å has been noted at high temperatures by Jost et al. [12] (1000°K to 1800°K), and by Nicolle and Vodar [45] (at 20°C and -90°C). Jost found that at 2300 Å a graph of the logarithm of the extinction coefficient against reciprocal temperature gave a straight line with a slope corresponding to 2400 cm⁻¹. Nicolle and Vodar merely report that over the wavelength range 2250 to 2350 Å the ratio of the extinction coefficients at 20°C and -90°C was 2.95:1.

EXPERIMENTAL AND RESULTS

The apparatus described in Section I of this thesis was used without modification. The nitrous oxide was B.O.C. anaesthetic grade. By measuring the signal obtained at a number of different pressures of nitrous oxide, and comparing them with the signal obtained when the absorption cell (reaction vessel) was evacuated, the absorption coefficient (k) at a particular temperature and wavelength could be obtained using the Beer's Law relationship

\[ \frac{I}{I_0} = \exp (-kpd) \]

where I is the signal intensity obtained at a nitrous oxide pressure of
\( P \) (att.\) and \( I_0 \) the signal intensity with the absorption cell, of path length \( d \) cm, evacuated. As was mentioned in the section of this thesis describing light intensity measurement, the zero on the recorder could be suppressed. By setting the wavelength control on the monochromator to a position corresponding with a wavelength shorter than the "cut-off" due to atmospheric oxygen (\( \text{wavelength} < 1800 \ \text{\AA} \)), the remaining signal due to stray light could be "backed-off" so that the instrument zero approximately represented zero usable light.

Nitrous oxide was found to obey Beer's Law at the pressures (1 to 60 cmHg) and wavelengths (1900 to 2800 \( \text{\AA} \)) studied and the absorption coefficient was obtained in the majority of cases from linear plots of \( \log I/I_0 \) versus nitrous oxide pressure. At the short wavelengths (\( < 2200 \ \text{\AA} \)) scattered light made up a substantial portion of the signal and was not entirely eliminated by the "back off" procedure just described. In some instances the Beer's Law plots showed curvature at high pressures. In these cases the absorption coefficients were obtained by a different method which is described in Appendix 3.1.

In this investigation a temperature range from 20° to 680°C at wavelengths between 1900 and 2800 \( \text{\AA} \) was studied and all absorption coefficients (\( k, \text{cm}^{-1} \)) were reduced to S.T.P.; table 3.1 gives the absorption coefficients obtained. It must be pointed out that the accuracy of the absorption coefficients decreases both with shortening wavelength (as available light intensity decreases), and with the actual intensity of the absorption encountered. The most reliable values lie between 2100 and 2600 \( \text{\AA} \). At 680°C (the highest temperature used) nitrous oxide decomposes quite rapidly, but it was possible to measure the light intensity and pressure within about 20 seconds of admitting a sample of nitrous oxide into the absorption cell, during
Table 2.1  Absorption Coefficients of N₂

<table>
<thead>
<tr>
<th>Å</th>
<th>1898</th>
<th>2000</th>
<th>2100</th>
<th>2200</th>
<th>2300</th>
<th>2400</th>
<th>2500</th>
<th>2600</th>
<th>2700</th>
<th>2800</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>338</td>
<td>128</td>
<td>16.7</td>
<td>1.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>285</td>
<td>142</td>
<td>23.9</td>
<td>3.35</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>338</td>
<td>190</td>
<td>70.4</td>
<td>9.50</td>
<td>2.02</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>300</td>
<td>278</td>
<td>248</td>
<td>112</td>
<td>27.4</td>
<td>6.89</td>
<td>1.53</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>239</td>
<td>198</td>
<td>55.5</td>
<td>12.0</td>
<td>6.08</td>
<td>1.76</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>320</td>
<td>406</td>
<td>84.3</td>
<td>35.6</td>
<td>13.2</td>
<td>4.42</td>
<td>1.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>453</td>
<td>339</td>
<td>125</td>
<td>61.1</td>
<td>25.5</td>
<td>9.77</td>
<td>3.12</td>
<td>1.54</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>-</td>
<td>494</td>
<td>315</td>
<td>199</td>
<td>81.9</td>
<td>40.6</td>
<td>17.1</td>
<td>7.59</td>
<td>3.35</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Please note: Units are in cm⁻¹ x 10². All values have been reduced to S.T.P.

Table 2.2  Increase in Area of Absorption curve

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Relative Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>1.05</td>
</tr>
<tr>
<td>200</td>
<td>1.20</td>
</tr>
<tr>
<td>300</td>
<td>1.42</td>
</tr>
<tr>
<td>400</td>
<td>1.81</td>
</tr>
<tr>
<td>500</td>
<td>2.07</td>
</tr>
<tr>
<td>600</td>
<td>2.51</td>
</tr>
<tr>
<td>680</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Table 2.3  Parameters of "Activation Energy" Plots

<table>
<thead>
<tr>
<th>k</th>
<th>Slope (E cm⁻¹)</th>
<th>(E⁻) (cm⁻¹)</th>
<th>Intercept (log₁₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>591 ± 53</td>
<td></td>
<td>1.097</td>
</tr>
<tr>
<td>2100</td>
<td>1055 ± 46</td>
<td></td>
<td>1.233</td>
</tr>
<tr>
<td>2200</td>
<td>1722 ± 77</td>
<td></td>
<td>1.358</td>
</tr>
<tr>
<td>2300</td>
<td>2150 ± 46</td>
<td></td>
<td>1.317</td>
</tr>
<tr>
<td>2400</td>
<td>2950 ± 300</td>
<td></td>
<td>1.533</td>
</tr>
<tr>
<td>2500</td>
<td>3310 ± 770</td>
<td></td>
<td>1.243</td>
</tr>
<tr>
<td>2600</td>
<td>4100 ± 180</td>
<td></td>
<td>1.557</td>
</tr>
</tbody>
</table>
which time only about 2% decomposition had occurred. At all the other temperatures no measurable decomposition occurs and Beer's Law plots at a given wavelength could be made on the same sample of N₂O.

Fig. 3.2(a) shows the overall picture of the temperature dependence of the nitrous oxide absorption. To check that the method and apparatus used in this work was adequate the vacuum temperature results were compared with the absorption curves obtained by Zelikoff [47] and Harteck [39]. Fig. 3.2(b) shows that fair agreement is achieved. It may be seen that there is a substantial increase in absorption intensity at the longer wavelengths, and that this decreases as the continuum maximum is approached.

Though it was not possible using a non-evacuable optical system to locate the centre of the absorption band experimentally, it was possible to construct absorption curves at the different temperatures by plotting the absorption coefficients against wavelength and extrapolating back to the band centre at 1820 Å [47], assuming, as an approximation, that the intensity at 1820 Å remains constant with temperature. As may be seen from table 3.2 the area under the long wavelength half of the curve approximately doubles for a 500°C rise in temperature.

The absorption coefficient at any given wavelength rises exponentially with temperature. Fig. 3.3 shows the logarithms of the absorption coefficient plotted against reciprocal temperature. The results of Jost et al [12] obtained in a shock tube at much higher temperatures are also shown. There is good correlation with Jost's results and the plots are linear over a very large temperature range. The absorption coefficient at any wavelength can be thought of as being associated with an "activation energy"
Fig: 3.2a Temperature Dependence of $N_2O$ Absorption.

Fig: 3.2b Results at Room Temperature c.f. those of other workers.

--- Ref. 47
--- Ref. 39
This work.
Fig: 3.3 "Activation Energy" Plots.

N.B. Lines have been staggered on both axes for clarity.
E cm\(^{-1}\) molecule \(^{-1}\) such that
\[ k = A \exp \left( -\frac{E}{RT} \right) \]
from room temperature up to \(1800^\circ K\). The least squares slopes of these lines together with their standard deviation \((\sigma^*)\) and intercept are shown in Table 3.3. It can be seen that the activation energy increases with wavelength.

A plot of the "activation energy" against absorption frequency yields a straight line, the slope of which \((0.30 \pm .02)\) is a dimensionless constant (Fig. 3.4).

DISCUSSION

(i) Temperature dependence

There are two striking features about the effect of temperature on the U.V absorption of nitrous oxide: the very large increase in absorption intensity with temperature, and the linearity of the "activation energy" plots (Fig. 3.3) over such a large temperature range.

An analogy with the work of Gibson, Rice and Bayliss, and of Cohen and Reid, suggests that the change in the N\(_2\)O spectrum is due to "hot" transitions from excited vibrational levels of the ground state.

Nitrous oxide has three vibrational modes, an anti-symmetric stretch \((\nu_3 = 2224 \text{ cm}^{-1})\), a symmetric stretch \((\nu_1 = 1285 \text{ cm}^{-1})\) and a doubly degenerate bending vibration \((\nu_2 = 589 \text{ cm}^{-1})\) [51]. Three considerations suggest that it is the bending vibration that is involved:

(i) The smooth change of activation energy with frequency suggests closely spaced energy levels.
(ii) The increase in the area under the absorption curve with temperature is too large to be due to errors in extrapolation and indicates that the transition moment increases with vibrational amplitude in the ground state. This could occur in a symmetry forbidden transition of a linear molecule which is distorted by stretching or bending. If the upper state is bent in accordance with Walsh's result [52], transitions to it from bent molecules in the ground electronic state would be favoured both by the Franck-Condon principle and by the destruction of the $C_{\infty v}$ symmetry of the linear ground state. (The nature of the transition involved and of the excited state is discussed in greater detail in the next section). By analogy with formaldehyde, transitions from bending vibrational states provide the most obvious way of accounting for the increase in transition probability with temperature.

(iii) Carbonyl sulphide at room temperature shows a continuum in the region 2100 to 2600 Å which appears strictly analogous to the continuum of CO$_2$ in the region 1700 to 1400 Å [54] and to the N$_2$O continuum considered here. Ferro and Reuben [53] studied the temperature dependence of the whole COS continuum. Similar results to nitrous oxide were obtained (i.e. linear "activation energy" plots and an increase in the area of the continuum). It was found that only the continuum to the long wavelength side of the maximum is temperature dependent. It suggests that it is the bending vibration that is involved in the "hot" transition.

This may be explained crudely with the help of Fig. 3.5 which shows a typical potential energy diagram for a bending vibration of a triatomic molecule with a linear ground state and a bent excited electronic state. If, as a simplification, only vertical Franck-Condon transitions from classical turning points are
Fig: 3.5 Potential Energy Diagram for a Bending Vibration.
considered it may easily be seen that the transition with the greatest energy (i.e. shortest wavelength) will be that from the ground vibrational state (a). As the temperature is raised, higher vibration states become populated and the intensity of lower energy transitions (b) increases.

The similarity of the absorption spectra and of the temperature effects of the COS and N$_2$O continua suggest that the same "hot" transition is involved in both cases and provides further evidence that it is the bending vibrations that are involved in nitrous oxide.

To simplify the theoretical treatment of results and to enable a clear picture of what is occurring to be drawn, it is assumed that only the classical "vertical" transition is allowed. The bending vibration of nitrous oxide is doubly degenerate and the degeneracy of the $v$th level is $v + 1$. It is a reasonable assumption that the absorption at any particular wavelength is proportional to the number of molecules ($N_v$) possessing $v$ quanta in the bending vibrations. Normally if one ignores anharmonicity effects; the proportion of such molecules would be written as

$$\frac{N_v}{N} = \frac{[1 - \exp(-\frac{\varepsilon}{kT})]^2}{(v + 1) \exp(-\frac{\varepsilon}{kT})}$$

(5)

where $N$ is the total number of molecules and $\varepsilon$ is the spacing of vibrational levels. This partition function has the required exponential temperature dependence but plots of the logarithm of $N_v/N$ against reciprocal temperature show substantial curvature at higher temperatures due to depletion of the population of the ground vibrational level (Fig. 3.6). The expression $[1 - \exp(-\frac{\varepsilon}{kT})]$ representing the ground vibrational level population is always less than unity and is a squared term in the partition function expression.

This partition function gives the number of molecules that possess vibrational quanta spread between the degenerate vibrational modes.
(e.g., if \( v = 3 \) then one may have 2 quanta in one mode and 1 in the other, or 3 and 0, and vice versa at any given moment of time).

In this case, however, one is concerned with the number of quanta possessed separately by a molecule in one or other of the vibrational modes, since it is the number of quanta possessed by a molecule in one of the vibrational modes that determines whether or not it would undergo a transition if perturbed by light of a certain wavelength. The proportion of molecules possessing \( v \) quanta in one or other of the vibrational modes is

\[
N_v / N = 2[1 - \exp(-\frac{\varepsilon}{kT})] \exp(-\frac{\varepsilon}{kT})
\]

(6)

In this partition function depletion in the population of the ground vibrational level will not modify the expression (6) to as great an extent as in expression (5). Graphs of \( \log N_v / N \) against \( 1/T \) in this case remain linear over a wider temperature range (Fig. 3.7) and permit the results in Fig. 3.3 to be attributed to transitions from excited bent vibrational levels of \( \text{N}_2\text{O} \).

The arguments above and the results of the temperature variation experiments justify the assumption that by far the largest part of the absorption at any particular wavelength arises from a certain bending vibration level of the ground state.

(ii) **Nature of Upper Excited State**

In the following discussion the bent states of \( \text{N}_2\text{O} \) are treated as if they had \( C_{2v} \) rather than \( C_s \) symmetry. This is done in order to make easier the comparison with bent states of \( \text{CO}_2 \) and \( \text{NO}_2 \).

It has been suggested by Walsh [52] that the absorption of \( \text{N}_2\text{O} \) from 1800 Å upwards is due to transitions to three upper states which correspond to \( ^1\!B_2 \), \( ^1\!A_2 \) (correlating with \( ^1\!\Delta_u \) in the linear molecule), and \( ^1\!\Sigma_u^- \) (correlating with \( ^1\!\Gamma_u^- \)) states of carbon dioxide. The first two of these states would be expected to be strongly bent and the third slightly bent or linear. These states
would give $N_2 \left( ^1\Sigma \right)$ and $O \left( ^1D \right)$ on dissociation. Walsh considers that the continuous nature of the absorptions of $N_2O$ (and $CO_2$) is explained by the fact that at the wavelengths of maximum absorption intensity the energy absorbed is sufficient to cause dissociation. He suggests that the upper states may be stable in the equilibrium form and that at sufficiently high temperatures, where transitions from high vibrational levels of the ground state are possible at sufficiently long wavelengths, a banded spectrum would be observed. That the upper state may exist in an equilibrium form has been confirmed for $CO_2$ by Dixon (v. infra) [57] who assigned bands observed in the light emission from oxygen/carbon monoxide flames to transitions from an excited $^1B_2$ state of carbon dioxide.

The data in this work suggest that the whole absorption band from 1900 to 2800 Å is due to a single temperature dependent transition, otherwise it is necessary to postulate several transitions with identical temperature dependences. (Two overlapping processes with "activation energies" of, say 300 and 1700 cm$^{-1}$ molecule$^{-1}$, would not lead to an apparent activation energy of 1000 cm$^{-1}$ molecule$^{-1}$ but to an apparent activation energy of 300 at low temperatures, and 1700 at high temperatures with a brief transitional period). The various possible excited states of nitrous oxide which could be involved in this transition are shown in Table 3.4 which is an extension of an earlier table given by Sponer and Bonner [44].

The configurations given in the last columns are deduced from the Walsh diagram for triatomic $AB_2$ type molecules (the diagram for $N_2O$ will be similar).

The molecular orbitals making up $AB_2$ are shown in Fig. 3.8. To make the figure simpler only the atomic orbitals making up the molecular orbitals in the linear molecule are shown. The molecular
Table 3.4 Possible Low-lying States of Nitrous Oxide

<table>
<thead>
<tr>
<th>Linear molecule electronic state</th>
<th>Bent molecule electronic state, (The corresponding ( C_{2v} ) symbols are given in brackets.)</th>
<th>Dissociating energy (cm(^{-1})) and equivalent wavelength (( \AA ))</th>
<th>Dissociation products</th>
<th>Configuration (from Walsh diagram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ground state ( \sum^+ )</td>
<td>( ^1A''_u ) ( \rightarrow ^1A_1 ) ( 29,600 ) (3368)</td>
<td>( N_2 \left( ^1\Sigma^+_g \right) + O \left( ^1D \right) ) linear</td>
<td>bent</td>
<td>bent</td>
</tr>
<tr>
<td>2a ( \Delta )</td>
<td>( ^3A''_u ) ( \rightarrow ^3A_2 ) ( 13,750 ) (7249)</td>
<td>( N_2 \left( ^1\Sigma^+_g \right) + O \left( ^3P \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>2b ( \Sigma^+ )</td>
<td>( ^3\Sigma^+ ) ( \rightarrow ^3B_2 )</td>
<td>( N_2 \left( ^1\Sigma^+_g \right) + O \left( ^1D \right) ) linear</td>
<td>bent</td>
<td>bent</td>
</tr>
<tr>
<td>3 ( \Sigma^- )</td>
<td>( ^1A''_u ) ( \rightarrow ^1A_2 ) ( 29,600 ) (3368)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>4 ( \Sigma^- )</td>
<td>( ^3\Sigma^- ) ( \rightarrow ^3B_2 )</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>5a ( \Delta )</td>
<td>( ^1A''_u ) ( \rightarrow ^1A_2 ) ( 29,600 ) (3368)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>5b ( \Sigma^+ )</td>
<td>( ^1\Sigma^+ ) ( \rightarrow ^1B_2 )</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>6 ( \Sigma^- )</td>
<td>( ^1A''_u ) ( \rightarrow ^1A_2 ) ( 29,600 ) (3368)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>7 ( \Sigma^+ )</td>
<td>( ^1\Sigma^+ ) ( \rightarrow ^1B_2 )</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>8a ( \Pi )</td>
<td>( ^3\Sigma^- ) ( \rightarrow ^3A_2 ) ( 13,750 ) (7249)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>bent</td>
<td>bent</td>
</tr>
<tr>
<td>8b ( \Pi )</td>
<td>( ^3\Pi )</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>9a ( \Pi )</td>
<td>( ^1\Pi ) ( \rightarrow ^1A_2 ) ( 29,600 ) (3368)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>9b ( \Pi )</td>
<td>( ^1\Pi ) ( \rightarrow ^1B_2 )</td>
<td>( N_2 \left( ^1\Sigma^+ \right) ) linear</td>
<td>almost linear</td>
<td>almost linear</td>
</tr>
<tr>
<td>10a ( \Pi )</td>
<td>( ^3\Pi ) ( \rightarrow ^3A_1 ) ( 41,000 ) (2496)</td>
<td>( NO \left( ^2\Pi \right) + N \left( ^4S \right) )</td>
<td>linear</td>
<td>linear</td>
</tr>
<tr>
<td>10b ( \Pi )</td>
<td>( ^3\Pi ) ( \rightarrow ^3B_1 )</td>
<td>( NO \left( ^2\Pi \right) + N \left( ^4S \right) )</td>
<td>linear</td>
<td>linear</td>
</tr>
<tr>
<td>11 ( \sum^- )</td>
<td>( ^1\Sigma^- ) ( \rightarrow ^1A_1 ) ( 47,600 ) (2101)</td>
<td>( N_2 \left( ^1\Sigma^+ \right) + O \left( ^1S \right) ) linear</td>
<td>linear</td>
<td>linear</td>
</tr>
</tbody>
</table>

* Various other assignations for 11 are possible and these could be bent or linear.
<table>
<thead>
<tr>
<th>Linear AO's</th>
<th>Linear MO's</th>
<th>Bent MO's</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>i)</td>
<td></td>
<td>s₁ and s₂ orbitals</td>
<td>l₂</td>
</tr>
<tr>
<td>ii)</td>
<td></td>
<td>σ⁻ g, σ⁺ u</td>
<td>a₁, b₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sp × p</td>
<td></td>
</tr>
</tbody>
</table>

NB. the bent MO's are taken as being made up from p orbitals.

iii)       |             | σ⁻ g, σ⁺ u | a₁, b₁   |
| p × p × p  |             |           |           |

iv)        |             | σ⁻ g, σ⁺ u | a₁, b₂   |
| p × p      |             |           |           |

v)         |             | σ⁻ g, σ⁺ u | a₁, b₁   |
| p × p × p  |             |           |           |

vi)        |             | σ⁻ g, σ⁺ u | a₁       |
| p × s × p  |             |           |           |

**Fig: 3.8 Molecular Orbitals.**
orbitals for a bent molecule are correlated with the linear MO's they would tend to form as the molecule was straightened. The orbitals are arranged in approximately increasing energy. A full discussion on how these orbitals are built up and on their bonding characteristics appears in Walsh's paper. Fig. 3.9 shows how the energy of the individual MO's would vary with bond angle and is reproduced from Walsh's paper.

The highest "activation energy" observed in this work was 4200 cm\(^{-1}\) molecule \(^{-1}\). For the N\(_2\)O bending mode the force constant 
\[ k = 0.69 \times 10^{-11} \text{ dynes cm. radian}^{-2} \] 
This "activation energy" corresponds to the molecule having a bond angle of 152° at the maximum amplitude of vibration. Fig. 3.4 shows no sign of reaching a maximum at long wavelengths this must be considered a maximum value for the bond angle of the excited state. Table 3.4 shows that the only states of N\(_2\)O which would be expected to be bent to this extent are 2a and 2b, 5a and 5b, and possibly 11.

State 11 is prevented on energy grounds from being responsible for any of the continuum above 2100 Å. Walsh suggests levels 2a and 2b would be lower in energy than 3 and 4, and similarly 5a and 5b would be lower than 6 and 7. Transitions from the ground state to any of the bent triplet states would be forbidden by the change in multiplicity and would therefore be very weak. Transitions to these states are theoretically possible up to 7249 Å, but no absorption has been observed above 3065 Å which is below the dissociation limit for states 5a, 5b, 6 and 7. (Very weak absorption up to wavelengths \(>3500\) Å has been observed by Tröe in shock heated nitrous oxide at high pressures, but no account has been published [62]. This is above the wavelength limit for transitions from molecules in the ground vibrational level to states 5a, 5b, 6 and 7, but in this case
Fig: 3.9 Walsh Diagram for AB₂ Molecules.
the N₂O molecules would be highly vibrationally excited. By analogy with CO₂, transitions to 5a and 6 would be expected to be very weak, to 5b would be weak and to 7 would be fairly strong. However, these considerations would be weakened since here one is considering transitions from N₂O molecules which are in excited bending vibration levels. Only the transition to a ^1B₂ state is allowed by C₂v selection rules. At any rate only the states correlating with 1A are likely to have an apex angle less than 152°. The most likely upper electronic state is therefore 5b, the ^1B₂ state correlating with 1A in the linear molecule and dissociating to give N₂ (^1Σ⁺) and O(^1D).

The potential energy curve for the ground state bending vibration of N₂O is shown as curve I in Fig. 3.10. An approximation to parK of the potential energy curve of the upper state may be made by taking any given vibrational state and finding from Fig. 3.4 the energy of radiation which has an activation energy corresponding to this vibration. One can then construct, from the classical turning point on curve I, a line corresponding in length to this energy. This gives curve II in Fig. 3.10.

The feasibility of this upper potential energy curve may be tested by comparing it with the ground ^2A₁ state of NO₂. Nitrogen dioxide has 17 valency electrons and an electronic structure

\[ \ldots (1a₂)² (4b₂)² (6a₁) \]

The structure of the excited ^1B₂ state of nitrous oxide only differs from the NO₂ ground state in that it has only one electron in the penultimate b₂ orbital. Nitrogen dioxide has a bond angle of 134° and a bending force constant of \( 1.52 \times 10^{-11} \text{ dynes cm. radian}^{-1} \) [55]. The energy required to straighten it has been shown by Ritchie and Walsh to be ca. 10,000 cm⁻¹ [56]. Curve III on Fig. 3.10 is a
Fig: 3.10 Potential Energy Curves.
semiquantitative assessment of the potential energy curve of $^2A_2$ NO$_2$. It has been located for comparison purposes so that minimum energy (at a bond angle of $134^\circ$) lies 10,000 cm$^{-1}$ below the maximum energy suggested for the $^1B_2$ N$_2$O.

The 4$b_2$ orbital of NO$_2$ is made up of p orbitals on the end atoms perpendicular to the axis of the molecule and overlapping out of phase. It is anti-bonding between the end atoms and has zero amplitude at the central atom (case iv in Fig. 3.8). Removal of one electron, as in $^1B_2$ N$_2$O, would lessen the degree of anti-bonding. The molecule would be expected to have a bond angle smaller than $134^\circ$ since the outer electron is in the orbital described as $a_1S_A$ in the Walsh diagram (case v Fig. 3.8) which strongly favours the bent state. It is clear therefore that $^1B_2$ N$_2$O would require more energy to straighten than NO$_2$. The excited N$_2$O curve is apparently steeper than the NO$_2$ curve suggesting a larger force constant, but the experimental data do not extend to small enough angles to permit a quantitative assessment of it.

Dixon's work on the $^1B_2$ state of CO$_2$ (directly analogous to the $^1B_2$ state of N$_2$O being considered above) strengthens these considerations [57]. He has shown that $^1B_2$ CO$_2$ has a bond angle of 122 $\pm$ 2$^\circ$ and requires about 22,000 cm$^{-1}$ to straighten it. Nitrogen dioxide and carbon dioxide both belong to the C$_2v$ symmetry group. As nitrous oxide has only C$_8$ symmetry it is to be expected that the anti-bonding nature of the penultimate b$_2$ orbital would be less than that in CO$_2$, and therefore a bond angle greater than that of CO$_2$ would be expected. It is difficult to assess the energy required to straighten $^1B_2$ N$_2$O. However, Welsh [52] suggests that the unfilled $\pi_u$ state in N$_2$O (see Walsh diagram) is closer than in CO$_2$ to the filled $\pi_g$ levels. This is because the absorption involves a transition from an orbital largely
localised on the end atoms to one localised on the central atom, and the orbital on the end atoms would be less tightly bound in NNO than COO since the electronegativity of N is less than in O. Also the orbital localised on the central atom will be more tightly bound in N₂O than in CO₂ since the electronegativity of N is greater than that of C.

It is suggested therefore that the bond angle of \(^1\text{B}_2\) (or in \(C_S\) symmetry \(^1\text{A}'\)) nitrous oxide lies between 122° and 134°, and that the energy required to straighten it is between 22,000 and 10,000 cm\(^{-1}\).
Part IV

Ion-Molecule Reactions in \( \text{N}_2\text{O/H}_2 \) Mixtures
(i) **Ion-molecule reactions:**

The knowledge that secondary processes involving reactions between primary ions and unionized gas molecules take place in a mass spectrometer is as old as the art of mass spectroscopy. The first ion-molecule reaction was observed by J.J. Thompson [65] when he suggested that a line observed at mass 3 was due to the formation of the $\text{H}_2^+$ ion. It was later suggested [66] the most probable mode of formation of this ionic allotrope of hydrogen is by the reaction

$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$$

In the early development of mass spectrometry the main interest was in the study of primary ionization processes and its concomitant induced dissociations, and thus efforts were bent towards avoiding conditions that would lead to the occurrence of secondary processes. It was not until the early 1950's that investigations were started on the various reactions that can and do take place in a mass spectrometer ion source, in which knowledge of the nature of the reactions was the primary, rather than an incidental, object of the study. This first generation of work notably in the laboratories of Talrose [67]; Field, Franklin and Lampe [68]; Stevenson [69] culminated in a series of review articles. A more recent review appears in the Annual Reports of the Chemical Society [70] and a more detailed account of the current state of the art appears in a collection of papers in the Advances in Chemistry Series [71].

(ii) **Experimental Techniques:**

A large amount of work has been carried out using conventional mass spectrometers employing gas pressures in the ion source of at least a factor of 10 higher than is normally used for conventional
analysis (i.e. $\geq 10^{-5}$ torr). This has been aided by the availability of commercial instruments which employ differential pumping between the source and analyser sections of the mass spectrometer. Traditionally the method employed is to measure the variation of phenomenological reaction cross section, $Q$, with the repeller field (v. infra). The technique suffers from many limitations, e.g.

a) variation of the electron energy allows only limited control over the selection of the primary ions.

b) control of the translational energy of the primary ion (by varying the repeller field) is indirect since reactive events occur throughout an energy range (fixed by the repeller field and the ion-path length) and the cross-sections obtained relate to an average of these translational energies, whereas the ultimate desire is the variation of the microscopic cross-section $\sigma(v)$ with ion velocity $v$.

c) Information about the behaviour of thermal energy ions is difficult to obtain since at very low repeller fields significant distortion of the repeller field may be caused by penetration of the ion accelerating potential (of the order of kilovolts) into the region where the ion-molecule reactions occur.

Nevertheless, the technique has led to a successful theory for the prediction of cross-sections of ion-molecule reactions involving simple species (v. infra). It is this technique that is used in the present investigation.

In order to observe the reactions of ions at near thermal energies pulsed source techniques have been developed. Basically, in this technique a pulse of electrons ($\sim 0.5 \mu s$) is fired into the ionization chamber with the repeller switched off. A pulse is then applied to the repeller plate after a variable time delay (of the order of microseconds), and the resulting ions entering the analyser section of the mass spectrom-
meter are collected. In this way the rate constants for ions at thermal energies are obtained. The method also suffers from the effect of penetration of the ion accelerating field into the ionization region and a number of instrumental techniques have been developed to overcome this. Descriptions of different types of pulsed source may be found in articles by Harrison et al. [71] and Henschel et al. [88].

In order to be able to select the identity and energy of the primary ion tandem mass spectrometers have been built. They consist, as their name suggests, of two mass spectrometers coupled together. One mass spectrometer shoots a beam of selected ions with controlled energy into a collision chamber of reactant gas and in which another mass spectrometer extracts and analyses the product ions. They have the drawback of being very costly to make. Lindholm gives the details of their construction and supplies a number of references to different machines [71].

A problem in obtaining absolute rate constants for ion-molecule reactions in mass spectrometers is the measurement of pressure in the ion source. An indirect method commonly employed is to measure the total ion current obtained for a particular gas at a fixed ionizing electron energy by collecting all the ions formed at a negatively biased repeller. From a knowledge of the path length traversed by the electrons and the ionization cross-section of the gas the number of molecules per cc may be calculated (v. infra). This method is used in the present work. Recently various workers have measured the pressure in the source directly with a McLeod gauge.

(iii) Theories of Ion-Molecule Reactions:

The basic measurement with a mass spectrometer is the current produced by an ion of particular mass/charge ratio at the collector.
It is not possible to measure directly the total current due to a particular ion and it is usual to express the extent of an ion-molecule reaction as the ratio of the intensity of the signal, obtained at the collector, for the secondary ion to that of the primary ion. Where the masses of the secondary ion and primary ion are similar (as is the case with ion/hydrogen or hydrogen ion/molecule reactions) it is assumed that the collection efficiency (about 0.3% of total ions in the instrument used in this work) for the two ions is the same. Therefore the ratio of signal obtained for the secondary ion to that for the primary ion is equal to the ratio of the number of secondary ions to primary ions.

Fig. 4.1 shows a schematic diagram of the mass spectrometer source used in this work. Electrons produced by the filament are accelerated (plate 4) and enter the ion source where they are collimated by a weak magnetic field. Primary ions are formed in the ion source in the more or less well defined plane of the ionizing electron beam (a) located a distance 1 from the exit slit (l). The primary ions are swept continuously toward the exit slit by the repeller field E, produced by an adjustable potential difference between the ion repeller (R) and the exit slit. In traversing the distance 1 primary ions may undergo collision and reaction with unionized gas molecules forming secondary ions. An extremely small fraction of the gas flowing continuously through the ion source is ionized and the concentration of the gas in the source may be taken to be constant and equal to n molecules/cc. The phenomenological reaction cross-section, \( Q \), for an ion-molecule reaction

\[
p^+ + R \rightarrow S^+ + T
\]

(where \( p^+ \) = primary ion, \( R \) = neutral molecule, \( S^+ \) = secondary ion) is given by
Fig. 4.1 Diagram of MS 12 Ion Source.

F = filament
T = electron trap
e = electron beam
R = repeller plate

1. source slit
2. focusing plate
3. variable exit slit
4. electron accelerating plate
5. electron trap slit
Expression (A) is analogous to the Beer's Law expression for the absorption of photons (Q corresponding to the absorption coefficient).

The study of the variation of Q with repeller voltage and source temperature for a number of reactions showed that Q was proportional to \( (B)^{-\frac{1}{2}} \) and independent of temperature (Guthier [89] and Stevenson and Schissler [90]). This indicated that equation A could be written

\[
\frac{i_s}{i_p} = n \frac{Q_R}{\frac{1}{\sqrt{2}}}
\]

Where \( Q_R = Q \cdot E^{-\frac{1}{2}} \) and can be thought of as the reaction cross-section.

The terminal kinetic energy with which the primary ions \( \frac{nq}{m} \) reach the exit slit from the ion source is \( \frac{nqE}{m} \) (where \( q \) = charge on ion and \( m \) = mass of ion), since the thermal kinetic energy with which the ion is formed will, in general, be negligibly small compared with that which it acquires from the electric field. For a uniformly accelerated ion, starting from rest, the terminal kinetic energy will equal \( 2m \cdot \bar{v}^2 \) where \( \bar{v} \) is the (time) average speed with which the ion traversed its path to the exit slit. Equation B may be rewritten

\[
i_s = i_p \left( \frac{1}{\bar{v}} \right) n Q_R \left( \frac{1q}{2m} \right)^{\frac{1}{2}}
\]

\( \frac{1}{\bar{v}} \) is the mean residence time of the primary ions in the ion source and \( i_p \left( \frac{1}{\bar{v}} \right) \) is the average concentration of the primary ions in the ion source. \( i_s \) is the rate of formation of secondary ions. Thus \( Q_R \left( 1q/2m \right)^{\frac{1}{2}} \) can be thought of as the second order rate constant (k) for the ion-molecule reaction.

viz. \( k = Q_R \left( 1q/2m \right)^{\frac{1}{2}} \)  

The first, and very successful, theory to predict the phenomenological cross-section Q for ion-molecule reactions was developed by
Gioumousis and Stevenson [91] from Langevin's derivation of the cross-section of a charged particle (e.g. ion) with a neutral particle (molecule) [92]. Langevin treated the problem using classical mechanics. He considered the effect of bringing up a charged particle (unit charge = e) to a neutral particle of polarizability $\alpha$. The charged particle induced a dipole in the neutral molecule which leads to a mutual attraction between the two particles. On classical electrostatic theory this varies inversely with the fourth power of distance separating them. The potential energy function describing this attraction is given by

$$\varphi(r) = -\frac{e^2 \alpha}{2r^4}$$  \hspace{1cm} (B)

where $r$ = the distance separating the particles. Langevin showed that for a given velocity of the charged particle there was a critical distance of approach to the neutral particle below which the charged particle would spiral towards the neutral and a collision would take place. At distances above the critical value the charged particle would merely be deflected and no collision would occur. The critical distance depended on the velocity of the charged particle.

Gioumousis and Stevenson applied Langevin’s relationship to the collision between ions and molecules treating both as hard inelastic spheres. They assumed that when the perpendicular distance between ion and molecule was less than the critical distance predicted by Langevin collision occurred and a reaction took place. The velocity distribution of the molecule was Maxwellian whilst that of the ion had two components, Maxwellian plus that acquired from the repeller field. If the ion energy is large compared with the thermal energy the Maxwellian contribution may be neglected and the phenomenological reaction cross-section would be given by
\[ Q = 2 \pi a \sqrt{\frac{\alpha}{\mu}} \sqrt{\frac{2m}{eEL}} \]  

Where \( a \) = charge on the ion

\( m \) = mass of ion

\( \mu \) = the reduced mass of the reacting system

\( \alpha \) = the polarizability of the molecule

\( E \) = the electric field in the mass spectrometer source (V/cm)

and the rate constant, \( k \), (vide Eqn. D) is given by

\[ k = \frac{2me}{2 \mu (\alpha / \mu)^{\frac{1}{2}}} \]  

This theory leads to the result that the cross-section is independent of the specific chemical nature of the reactants, but rather is a function only of such classical parameters as mass, charge and electric polarizability.

The theory is in good agreement with experiment for a large number of simple ion-molecule reactions (e.g. \( H_2 \) - rare gas, \( H_2 \) - diatomic and a number of diatomic-diatomic systems). It is encouraging to note that it has been recently shown by Fehsenfeld, Schmeltekopf and Ferguson [93] that a number of ion-molecule reactions in pulsed-discharge flow systems (a regime dramatically different from the traditional mass spectrometer source) are in good agreement with the G-S theory.

As with the simple collision theory for neutral-neutral reactions the appearance of anomalous (or apparently anomalous) results, notably the failure to observe the predicted dependence of cross-section on \( E^{\frac{1}{2}} \), led to the formulation of a number of new theories. Hamill and co-workers [94] attempted to account for deviations from the G-S model in reactions of ions having kinetic energy in excess of a few electron volts by including a term in the cross-section expression for hard sphere ion-neutral impacts. Friedman suggests that a number of the apparently anomalous results considered by Hamill could be explained
on the basis of G-S theory if all possible reaction channels (including the back reaction) were considered [95].

Giese [96] considers the importance of quantum-mechanical resonance forces in the reaction and modifies the classical $r^{-4}$ potential energy function by an expression for the resonance potential. The theory predicts enhanced rates (c.f. G-S theory) when the ionization potential of the neutral species approaches the recombination energy of the primary ion.

Light [97] introduced the concept of phase-space in a new approach to ion-molecule reaction theory. He considered each particle in the reaction system to exist in $6N$ dimensional space with $6N$ co-ordinates which characterized the momentum and position of every particle in the system. Certain parts of the phase space are assigned to reactants and products. For a given amount of total energy in the system only certain parts of the phase space are accessible to the ions or molecules. Light assumes that transition complexes are formed at a rate given by the G-S theory and that these states decompose along the available reaction channels (including paths for back reactions) at rates which depend on the amount of phase space available to the reactants and products. The theory is equivalent to statistical Rate Theory of neutral-neutral reactions, but it can be applied to systems that do not have a Maxwell-Boltzmann energy distribution. The major drawback of the theory is that, at the moment, it can only be applied to simple systems (of the type $X^+ + H_2$, $H_2^+ + X$) because of the complexity of the mathematics involved, and these systems are adequately described anyway by the G-S theory.

(iv.) **Aim of Present Work:**

The G-S theory breaks down in complex systems. For example the
ion-molecule reactions that take place when benzene is ionized in a mass spectrometer source. Reuben and Lifshitz were unable to apply the G-S theory to their data on the reaction of \( \text{C}_6\text{H}_5^+ \) ions with benzene molecules to give a large number of association products of the type \( \text{C}_{12}^+\text{H}_{11}^- \), \( \text{C}_{12}^+\text{H}_9^- \) etc. \[98\]. Such systems are impossible to treat theoretically with any degree of confidence. Accordingly this work is concerned with a simple system in which the G-S parameters of mass, polarizability and charge are known.

The \( \text{N}_2\text{O}/\text{H}_2 \) ion molecule system has only been briefly studied by other workers. Hall \[99\] reported that in \( \text{N}_2\text{O}/\text{H}_2 \) mixtures with a 40-fold excess of hydrogen a peak at mass 45 is observed with a 1.5/4. peak height ratio of 2.6% is found. Hall suggests that as this ratio is greater than the isotopic contribution due to \( ^{15}\text{N}^{14}\text{N} \) and \( ^{14}\text{N}^{15}\text{N} \) the peak represents the formation of the \( \text{N}_2\text{OH}^+ \) ion. Fehsenfeld et al \[93\] have recently published a bimolecular rate constant for

\[
\text{N}_2\text{O}^+ + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H}
\]

obtained in a pulsed-discharge flow system that is 3.5 times smaller than that predicted by G-S theory. In this present work it is hoped to compare the ion molecule reactions in the \( \text{N}_2\text{O}/\text{H}_2 \) (and isotopes \( \text{D}_2 \) and HD) with the well characterized \( \text{CO}_2/\text{H}_2 \) system (e.g. Friedman and Moran \[100\]). Carbon dioxide has the same mass as, and isoelectronic with, \( \text{N}_2\text{O} \). The dipole moments (zero for \( \text{CO}_2 \)) and polarizabilities are similar (\( \alpha \) for \( \text{CO}_2 = 2.65 \, \text{Å}^3 \), \( \alpha \) for \( \text{N}_2\text{O} = 3.0 \, \text{Å}^3 \) \[101\]). The rate constants for the bimolecular reactions

\[
\text{N}_2\text{O}^+ + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H}
\]

and

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}
\]

predicted by G-S theory are also similar and the experimental values obtained \[93, 100\] for the \( \text{CO}_2 \) reaction are in good agreement with theory. The only difference between the two systems is a chemical
one, yet the experimental rate constant for the $N_2O/H_2$ reaction is lower by a factor of 3 than that predicted by the G-S theory and that experimentally found for $CO_2/H_2$. The aim therefore is to investigate the $N_2O/H_2$ system and attempt to explain the reason for the difference.

Unfortunately, a long series of instrumental faults prevented a complete investigation from being carried out within the time available. The results are therefore incomplete but demonstrate that the rates of ion-molecule reactions of this type are not governed by purely electrostatic factors.

DESCRIPTION OF APPARATUS

The instrument used in this work was an A.E.I. MS12 mass spectrometer. This is a single focussing instrument with a 12" radius 90° magnetic analyser and a conventional Nier source. The only modification to the normal source supplied by A.E.I. was that the source slit was 0.001" wide instead of the normal 0.005". The narrow slit reduced penetration of the ion accelerating voltage into the ion chamber. Fig. 4.1 is a schematic diagram of the ion source. The dimensions are as follows:

- Length of repeller (a) = 1.84 cm
- Distance of repeller from source slit = 0.32 cm
- Distance of electron beam from source slit = 0.16 cm
- Diameter of electron beam = 0.04 cm
- Distance of source slit to exit slit = 1.13 cm

Ions are accelerated on leaving the ion source, pass through the magnetic analyser and are focussed onto the cathode of an electron multiplier. The current delivered by the electron multiplier is
measured and is proportional to the ion current.

(i) Source Conditions:

The source conditions employed for the investigation of the ion-molecule reactions were as follows:

- Electron energy = 70 eV
- Electron current = 10μA
- Ion accelerating voltage = 2000V
- Repeller volts = 0 to 6.5 volts
  i.e. Repeller field = 0 to 21 volts cm$^{-1}$
- Source temperature = 250°C
- Source slit = 0.004"
- Collector slit = 0.030"

(ii) Field Penetration:

It is of importance in the measurement of the reaction cross-section ($Q_R$) to know the size of the repeller field in the ion source. The repeller field may be distorted by penetration of the ion accelerating field into the ion source. If no field penetration occurs then the peak height of an ion will be zero at zero repeller volts and will increase rapidly to a maximum as the repeller field is increased. This maximum corresponds to all the ions formed in the section defined by the source slit being driven out of the ion source region and into the analyzer. As the repeller volts are increased still further no change in the maximum peak height should occur. This ideal case is represented in the figure shown below:

![Graph showing peak height vs. repeller voltage]

Peak height $\max$  
\[ \text{Repeller volts} \]
In the normal MS12 source (i.e. one with a source slit of 0.005") with an ion accelerating voltage of 8kV this behaviour does not occur. At zero repeller voltage the peak height is about 50% of the maximum. As the repeller volts are increased the peak height increases sharply to a maximum (at about 2v/cm). Further increase of repeller volts causes a sharp drop followed by a slow rise in peak height until a broad maximum is reached. The effect is illustrated below:

![Graph showing peak height against repeller volts]

This behaviour is common to most sector instruments when high ion accelerating potentials are used. Some workers (e.g. Henchman et al [88] and Birkinshaw [102]) suggest that this is a result of substantial field penetration. In the present work conditions were arranged so as to minimise the field penetration (0.001" source slit and 2kV ion accelerating potential). The plot of peak height (of $N_2O^+$) against repeller field is shown in Fig. 4.2. It can be seen that at zero repeller field very few ions are leaving the ion source. As the field is increased the peak height rises until a maximum is reached (at about 5v/cm). The peak height then falls as the field is increased levelling off to about 30% the maximum value at fields $\geq$ 24 volts/cm.

The fact that very few ions leave the ion source at zero repeller fields shows that penetration of the ion accelerating potential is negligible. No ready explanation for the appearance of a maximum (as opposed to a plateau in the ideal case) can be offered. It may be due to the apparently unusual ion optics associated with sector instruments.
Fig. 4.2 Variation of $\text{N}_2\text{O}^+$

Peak with Repeller Field.
(iii) Gas Handling System:

The gas handling system is shown in Fig. 4.3. Gases contained in the 500 ml volume are admitted to the reaction vessel through a glass-sinter molecular leak. The pressure in the volume was measured by an Atlas torr meter (type MAT 6103 MCT) which covered the range 0 to 20 torr in 3 ranges (0 to 2, 0 to 5 and 0 to 20 torr). This torr meter measures the absolute gas pressure by a diaphragm/capacitor arrangement and the reading is independent of the nature of the gas.

For the ion-molecule work mixtures of gases (at 10's of torr pressure) were made up in the 100 ml mixer using the mercury manometer to measure the pressure. The gases were allowed to mix thoroughly before being admitted to the 500 ml sample volume. It was found that during the course of a run (about 10 minutes) the pressure in the sample volume dropped by about 5%. The magnitude of the pressure drop was smaller than the inaccuracies of ion current measurement.

CALIBRATION OF SOURCE PRESSURE

(i) Method:

Ions are produced in the source by electron bombardment of gas molecules. For a given electron energy and ion current (I electron) the number of molecules ionized depends on the pressure of the gas (n molecules/cc.), the distance travelled by the electrons (taken as d the length of the repeller plate) and the ionization cross-section \( Q_1 \) of the gas. \( Q_1 \) is defined by

\[
\frac{I_{\text{ion}}}{I_{\text{electron}}}=n\ d\ Q_1 \quad (H)
\]

where \( I_{\text{ion}} \) is the current measured when all the ions formed by electrons traversing the length of the repeller plate (d) are collected at the
SAMPLE VOLUME.

GAS STORAGE.

MANOMETER.

PRE-MIXER.

TORR-METER.

Vacuum

Molecular
Leak.

SOURCE.

Fig: 4.3 Gas Handling System.

Fig: 4.4 Gas Pressure Calibration Circuit.
repeller. The technique for determining ion is a simple one and the circuit used is shown in Fig. 4.4.

The source H.T. and repeller circuits are switched off and disconnected. The source block is connected to earth. A variable negative voltage (supplied by a battery chain) is applied to the repeller plate, the current produced by the collection of positive ions formed by electron bombardment of the gas in the source develops a potential across a high value resistor (values of $10^9 \, \Omega$ and $2 \times 10^9 \, \Omega$ were used) which is measured by a Vibron 330 electrometer. With sample gas flowing through the source the negative potential applied to the repeller is increased until constant maximum voltage is recorded by the Vibron. When this maximum is reached it is assumed that all the positive ions formed in the source are being collected. The ion current this produced is calculated from the voltage by the usual Ohm's Law relationship. Thus since the electron current is known (10µA) the pressure of the gas may be obtained by substituting the known ionization cross-section of the sample gas into Equation H.

(ii) **Difficulties:**

Even with the source evacuated ($5 \times 10^{-8}$ torr) a current was measured by the Vibron. This current varied with the repeller potential, the electron energy and with the electron current, and in a number of instances it was much bigger than the ion current produced when gas was admitted to the source. In order to keep this residual current (due to space charge effects in the ion source) to a minimum, and at the same time produce enough ions to permit accurate measurement of the ion current, it was necessary to optimise the source conditions. All measurements were therefore made with 40 eV electrons with an electron beam intensity of 10µA. A small "back off" potential was applied to the vibron to
compensate for the residual current and thus allow measurement of the true ion current to be made.

It was also found that if the repeller was biased at too high a negative value an increase in the voltage measured, above the "constant" maximum, was observed in the voltage measured by the Vibron. This was probably caused by deflection of the electron beam by the negative repeller field.

(iii) Measurement of Ion Current:

The procedure adopted to measure the ion current was as follows:

a) the source was evacuated and the repeller set at a known negative voltage.

b) the residual current was "backed off" and a sample of gas at a known sample volume pressure (measured on the torr meter) was admitted to the source.

c) the ion current was measured and the cycle a) to c) was repeated at different repeller voltages with the same pressure of gas. A typical result is shown for nitrogen in Fig. 4.5c. It will be seen that the ion current rises steeply with repeller volts until a plateau is reached. The current remains constant until too high a repeller voltage is applied.

d) the source was then evacuated and the repeller set to the voltage corresponding to the centre of the plateau for the particular calibrant gas, and the residual current was "backed off" on the Vibron.

e) the ion current was then measured for a number of different gas pressures in the sample volume.

f) the whole process was repeated for each calibrating gas.
a). Variation of Ion Current with Repeller Bias

b). Ion Current vs. Pressure.

Fig: 4.5 Calibration of Source Pressure Using Nitrogen.
(iv) Results:

From Equation H (I ion/I electron = n d Q) it will be seen that if \( n \propto \) to pressure (P) of gas behind the leak then a plot of I ion against P will be a straight line. Fig. 4.5b shows the calibration for nitrogen, and similar straight lines were obtained for all the calibrant gases. From the slopes of these straight lines (given in Table 4.1) it is possible to calibrate the pressure in the sample volume (measured by the torr meter) with the number molecules/cc in the source using the published ionization cross-sections of the calibrant gases. The ionization cross-sections were obtained for 40eV electrons from tables published by Rapp and Englander - Golden [103]. Table 4.2 shows the calibration obtained for the different gases and also their cross sections for 40 eV electrons.

(v) Conclusion:

The rate at which a gas diffuses through the molecular leak into the source is proportional to the pressure drop across the leak and inversely proportional to the square root of its molecular weight. At the same time the rate at which a given pressure of gas is pumped out of the source is also inversely proportional to the square root of its molecular weight. To a first approximation, therefore, the number of molecules/cc of any gas in the source for the same pressure in the sample volume will be the same.

The calibrant gases used covered a large range of molecular weights and cross-sections. It will be seen from Table 4.2 that the calibration factor (molecules/cc·torr\(^{-1}\)) shows no trend with molecular weight, and therefore within the limits of experimental scatter the concentration of molecules in the source will be the same independent of the molecular weight. This is what was predicted. The fact that all the calibrating
Table 4.1  Slopes of Ion vs Pressure plots

<table>
<thead>
<tr>
<th>Gas</th>
<th>Source</th>
<th>Mol. Wt.</th>
<th>Slope $10^{-9}$ amp/torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>B.O.C.</td>
<td>2</td>
<td>0.520</td>
</tr>
<tr>
<td>D$_2$</td>
<td>Matheson</td>
<td>4</td>
<td>0.509</td>
</tr>
<tr>
<td>He</td>
<td>B.O.C.</td>
<td>4</td>
<td>0.094</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Air Products</td>
<td>16</td>
<td>1.63</td>
</tr>
<tr>
<td>N$_2$</td>
<td>B.O.C.</td>
<td>28</td>
<td>0.925</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>Air Products</td>
<td>28</td>
<td>1.88</td>
</tr>
<tr>
<td>O$_2$</td>
<td>B.O.C.</td>
<td>32</td>
<td>0.895</td>
</tr>
<tr>
<td>Ar</td>
<td>B.O.C.</td>
<td>40</td>
<td>1.39</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>B.O.C.</td>
<td>44</td>
<td>1.20</td>
</tr>
<tr>
<td>Kr</td>
<td>B.O.C.</td>
<td>84</td>
<td>1.90</td>
</tr>
<tr>
<td>Xe</td>
<td>B.O.C.</td>
<td>131</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Table 4.2  Calibration of Pressure behind Leak with number of molecules/cc in source.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Cross-section ($\text{Å}^2$)</th>
<th>Molecules cc$^{-1}$ torr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.984</td>
<td>2.87 x 10$^{11}$</td>
</tr>
<tr>
<td>D$_2$</td>
<td>0.996</td>
<td>2.78</td>
</tr>
<tr>
<td>He</td>
<td>0.195</td>
<td>2.62</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.43</td>
<td>2.58</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.79</td>
<td>2.81</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>5.11</td>
<td>2.00</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.67</td>
<td>2.98</td>
</tr>
<tr>
<td>Ar</td>
<td>2.72</td>
<td>2.77</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>2.63</td>
<td>2.48</td>
</tr>
<tr>
<td>Kr</td>
<td>3.97</td>
<td>2.60</td>
</tr>
<tr>
<td>Xe</td>
<td>5.09</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Average: 1 torr = 2.57 x 10$^{11}$ molecules cc$^{-1}$
gases gave good straight line plots of I ion against sample volume pressure is some justification of the calibration procedure.

The calibration factor for converting sample volume pressure to pressure in the source is

\[ 1 \text{ torr (sample volume)} = 2.57 \pm 0.40 \times 10^{11} \text{ molecules/cc} \]

The source temperature was 250°C and at this temperature 1 torr = \( 1.68 \times 10^{16} \text{ molecules/cc} \). Therefore the pressure in the source for 1 torr behind the leak is \( 1.52 \times 10^{-5} \) torr.

**ION MOLECULE REACTIONS:**

**EXPERIMENTAL RESULTS**

The gases used in these studies are described in Appendix 4.1 which contains an account of the preparation of hydrogen deuteride.

(1) **Introduction:**

For a simple ion molecule reaction of the type

\[ \text{N}_2\text{O}^+ + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H} \]

the phenomenological cross-section \( Q \) is defined by

\[ \frac{i_s}{i_p} = n \frac{1}{Q} \] (A)

and the Gioumousis-Stevenson theory predicts that \( Q \) is inversely proportional to the square root of the repeller voltage (\( \propto V^{-\frac{1}{2}} \)).

The method used to measure \( \frac{i_s}{i_p} \) for a given gas mixture was as follows:

a) the repeller voltage was set and the mass spectrometer tuned to the m/e 44 peak (\( \text{N}_2\text{O}^+ \) or \( \text{CO}_2^+ \)) and the signal intensity recorded \( (i_p) \)

b) the magnet was then tuned to the m/e 45 peak (\( \text{N}_2\text{OH}^+ \)) or the m/e 46 peak (\( \text{N}_2\text{OD}^+ \)) and the signal recorded \( (i_s) \).
c) the repeller volts were then increased, keeping the mass spectrometer tuned to m/e 45, and the signal recorded.

d) the mass spectrometer was then tuned to the 44 peak and the signal recorded.

The process was repeated until the whole experimental range of repeller fields was covered (i.e. E/1 from 1 to 21 v/cm). Throughout the course of a run the source focusing conditions and electron multiplier sensitivity was kept constant. For different mixtures the multiplier sensitivity was adjusted to maximise the signals obtained.

The experimentally measured $i_s/i_p$ ratios had to be corrected for the contribution to the m/e 45 and 46 peaks of the isotopic species of N$_2$O and CO$_2$. These contributions were determined experimentally and are:

For N$_2$O 45/44 = 0.76% and 46/44 = 0.20%

For CO$_2$ 45/44 = 1.16% and 46/44 = 0.40%

These average values were obtained from 20 separate determinations of 45/44 and 46/44 ratios. It was found that the individual values varied over a 10% range. This variation in isotopic contribution meant that the $i_s/i_p$ ratios could be as much as 40% in error when the contribution of the N$_2$OH$^+$ ion to m/e 45 peak was small.

Two different ion molecule reactions are possible when a mixture of N$_2$O/H$_2$ is subjected to ionising electrons

$$\text{N}_2\text{O}^+ + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H} \quad \text{(1)}$$

$$\text{H}_2^+ + \text{N}_2\text{O} \rightarrow \text{N}_2\text{OH}^+ + \text{H} \quad \text{(2)}$$

In both cases the products are the same. Both reactions were in fact detected (v. infra) and the extent of each of them was measured.

(ii) "Order" of Reaction:

Equation A shows that for a given repeller field $i_s/i_p \propto C$ pressure of neutral molecules in the source. Therefore if only the
reaction $\text{N}_2\text{O}^+ + \text{H}$ were occurring it would be expected that for a fixed concentration of $\text{N}_2\text{O}$ the $45/44$ peak ratio would vary linearly with hydrogen concentration. Conversely for a fixed concentration of hydrogen the $45/44$ ratio should remain constant with varying $\text{N}_2\text{O}$ concentration. Fig. 4.6a shows that $45/44$ varies linearly with hydrogen pressure for a fixed $\text{N}_2\text{O}$ pressure (5.12 x $10^{11}$ molecules/cc). It can be seen that the slope of $45/44$ vs $\text{H}_2$ pressure decreases with increasing repeller field. However Fig. 4.6b shows that $45/44$ is not constant with varying $\text{N}_2\text{O}$ pressure. The $i_s/i_p$ ratio increases with the increasing percentage of hydrogen in the gas mixture. One must therefore conclude that the reaction

$$\text{H}_2^+ + \text{N}_2\text{O} \rightarrow \text{N}_2\text{OH}^+ + \text{H}$$

is also occurring.

(iii) $i_s/i_p$ Ratios in $\text{N}_2\text{O}/\text{D}_2$ Mixtures of Fixed Composition:

From the results presented in the previous section one can see that the contribution of the isotopic $\text{N}_2\text{O}$ to the m/e 45 peak was at times much greater than the observed $\text{N}_2\text{OH}^+$ contribution. In order to minimise the errors introduced by the isotopic contribution in obtaining $\text{N}_2\text{OH}^+/\text{N}_2\text{O}^+$ ratios it was decided to use deuterium in place of hydrogen. The ion-molecule characteristics would be little changed. As the $\text{N}_2\text{O}$ isotopic contribution to the m/e 46 peak is about four times smaller than in the 45 peak's case it was hoped that better accuracy would be obtained in the measurement of the extent of ion-molecule reaction ($\text{N}_2\text{OD}^+/\text{N}_2\text{O}^+$). In order to achieve as large as possible $46/44$ peak ratios, mixtures in which deuterium was in excess were used.

It has been shown that both ion-molecule reactions are occurring concurrently.
Fig: 4.6 'Order' of $N_2O/H_2$ Ion-Molecule Reaction.
For reaction 3
\[ i_s = i_p n_{D_2} \frac{Q}{s} \]  \hspace{1cm} (I)

and for reaction 4
\[ i_{s'} = i_p n_{N_2O} \frac{Q'}{s'} \]  \hspace{1cm} (J)

where

Q and Q' are the cross sections of 3 and 4 respectively

\( i_s \) and \( i_s' \) are the secondary ion currents of 3 and 4 respectively

\( i_p \) and \( i_p' \) are the primary ion currents of 3 and 4 respectively

\( i_p' \) can be related to \( i_p \) by:
\[ i_p' = x a_i \frac{i_p}{p} \]

Where \( x \) = the number of times the deuterium concentration is greater than the \( N_2O \) concentration and \( s \) the ionization cross-section of deuterium divided by the ionization cross-section of nitrous oxide. Equation J becomes
\[ i_s' = x a_i \frac{i_p}{p} n_{N_2O} \frac{Q'}{s'} \]  \hspace{1cm} (K)

Adding (J) and (K)
\[ i_s + i_s' = i_p n_{D_2} \frac{Q}{s} + i_p x a_i n_{N_2O} \frac{Q'}{s'} \]  \hspace{1cm} (L)

Dividing both sides of Equation L by \( i_p \) one obtains the expression for the experimentally measured 46/44 peak ratios
\[ \frac{46}{44} = \frac{i_s + i_s'}{i_p} = n_{D_2} \frac{Q}{s} + x a_i n_{N_2O} \frac{Q'}{s'} \]  \hspace{1cm} (M)

However \( n_{N_2O} = x n_{D_2} \) and therefore Equation M becomes
\[ \frac{46}{44} = n_{D_2} \frac{1}{p} (Q + aQ') \]  \hspace{1cm} (N)

Experimental measurements were carried out to investigate the variation of 46/44 peak ratio with total pressure using 1:9, 1:4 and 1:2 \( N_2O/D_2 \).
mixtures the results are shown in Fig. 4.7 in which \(46/44\) peak ratios are plotted against total pressure (\(n_{\text{total}}\)). For a given mixture

\[ n_{D_2} = (\text{proportion of } D_2 \text{ in mixture}) \times n_{\text{total}} \]

It is therefore possible to obtain values for the overall phenomenological cross-section (\(Q+aQ'\)) from the slopes of the lines in Fig. 4.7 and the fraction of \(D_2\) in each mixture. The results are tabulated in Table 4.3. It can be seen that for a given repeller field the value of \(Q+aQ'\) is approximately the same for the different mixtures and that the overall cross-section decreases with increasing repeller volts (N.B. the term overall cross-section refers to the sum of \(Q+aQ'\)).

(iv) Reactions in \(N_2O/\text{HD Mixtures}:

The use of hydrogen deuteride in ion-molecule reaction systems was originally suggested by Klein and Friedman [104] as providing a means for studying translational-internal energy transfer processes in reactive collisions. For relatively fast reactant ions a hydrogen or deuterium atom is directly transferred. The isotope effect arises from the relative probabilities of forming the linear transition complexes

\[
N_2O - H - D^+ \\
\text{and } N_2O - D - H^+
\]

That a choice of transition complex is available (instead of assuming equal probabilities of formation) is explained by the fact that in hydrogen deuteride the centre of mass (\(c\)) does not coincide with the centre of polarizability (\(p\))

\[
\text{viz } H \quad \overset{p}{\text{\(c\)}} \quad \overset{\partial r}{D}
\]

as an ion approaches the HD molecule there will be a tendency for the molecule to orientate itself so that the hydrogen atom faces the on-
Fig 4.7 $\text{N}_2\text{O}/\text{D}_2$ Mixtures of Fixed Composition.
### Table 4.3  Overall Cross-sections for $N_2O/D_2$

<table>
<thead>
<tr>
<th>$N_2O:D_2$</th>
<th>$v$/cm</th>
<th>1</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td></td>
<td>48Å²</td>
<td>23Å²</td>
<td>12Å²</td>
</tr>
<tr>
<td>1:4</td>
<td></td>
<td>55</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>1:2</td>
<td></td>
<td>35</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>(Q+aQ')</td>
<td>46Å²</td>
<td>19Å²</td>
<td>11Å²</td>
</tr>
</tbody>
</table>

### Table 4.4  Overall Cross-Sections for $N_2O/HD$

<table>
<thead>
<tr>
<th>$N_2O:HD$</th>
<th>$v$/cm</th>
<th>1</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td></td>
<td>57Å²</td>
<td>-</td>
<td>15Å²</td>
</tr>
<tr>
<td>1:4</td>
<td></td>
<td>73</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>1:2</td>
<td></td>
<td>54</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>(Q+aQ')</td>
<td>61Å²</td>
<td>29Å²</td>
<td>13Å²</td>
</tr>
</tbody>
</table>

### Table 4.5  Overall Cross-sections for $CO_2$ Reactions

<table>
<thead>
<tr>
<th>$CO_2$</th>
<th>$v$/cm</th>
<th>1</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2/D_2$</td>
<td></td>
<td>223Å²</td>
<td>120Å²</td>
<td>48Å²</td>
</tr>
<tr>
<td>$CO_2/HD$</td>
<td></td>
<td>216</td>
<td>129</td>
<td>57</td>
</tr>
<tr>
<td>$HD/D_2$</td>
<td></td>
<td>0.97</td>
<td>1.06</td>
<td>1.20</td>
</tr>
<tr>
<td>$CO_2/N_2O$ for D$_2$</td>
<td>4.8</td>
<td>6.3</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>$CO_2/N_2O$ for HD</td>
<td>3.5</td>
<td>4.5</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>
coming ion \cite{105}. A preference will therefore be shown for the \( \text{N}_2\text{OH}^+ \) product. The isotope effect due to the formation of linear complex is given by \cite{104}
\[
\frac{k_H}{k_D} = \frac{(1 + \delta r/r)^2}{(1 - \delta r/r)^2}
\]
(0)
Where \( r \) is the Langevin radius of ion-molecule cross-section and \( \delta r \) the displacement of the centre of mass from the centre of polarizability. The kinetic energy dependence of the isotope effect comes via the energy dependence of the Langevin radius \( r \). At zero repeller volts the value of expression 0 is unity. As the ion energy increases (i.e. repeller field increases) the value of \( r \) decreases and \( k_H/k_D \) becomes greater than 1. A further isotope effect can be introduced when the unimolecular decomposition of a possible non linear complex is considered.

\[
\text{N}_2\text{O}^+ \xrightarrow{\text{H}} \text{H}^+ \text{D}^-
\]
Such complexes are more likely to be formed at low ion energies and will have the effect of decreasing the isotope effect predicted by Equation 0. This effect was observed by Klein and Friedman \cite{104} for rare gas/HD ion-molecule reactions where it was found that at low repeller fields the \( k_H/k_D \) ratio was < 1. In the case of \( \text{HD}^+ + \text{Ne} \) and \( \text{HD}^+ + \text{He} \) maxima were observed in the \( k_H/k_D \) vs. repeller field plots. These maxima were claimed by Klein and Friedman to demonstrate that kinetic energy - internal energy transfer was required within the transition complex before a reactive process could occur. Friedman \cite{71} suggests that such reactions will have much smaller cross-sections.

The data obtained on the intramolecular isotope effects in \( \text{N}_2\text{O}/\text{HD} \) mixtures was not sufficiently accurate to permit any but the most qualitative conclusions to be drawn (see Fig. 4.8). Fig. 4.8 shows the
Fig. 4.9 Isotope Effects in $N_2O/HD$.

1:9 Carbon Dioxide/Deuterium Mixtures.
$N_2O^+/N_2OD^+$ ratio plotted against repeller field for all $N_2O/HD$ mixtures. It can be seen that experimental scatter is appalling. The trend is for the $45/46$ peak ratio to increase with repeller field until a maximum (at about $10$ $v/cm$) is reached. The isotope effect then decreases. It should be pointed out that larger isotope effects than are commonly observed are found. (Friedman suggests that values ranging from slightly less than unity to two are to be expected [71]). The evaluation of the isotope effects are complicated by the fact that four reactions are occurring

\[
\begin{align*}
&N_2O^+ + HD \rightarrow N_2OH^+ + D \\
&N_2O^+ + HD \rightarrow N_2OD^+ + H \\
&HD^+ + N_2O \rightarrow N_2OH^+ + D \\
&HD^+ + N_2O \rightarrow N_2OD^+ + H
\end{align*}
\]

The fact that a maximum appears in Fig. 4.8 suggests that the reaction may involve kinetic energy - internal energy transfer. If such a transfer is taking place in the transition complex then it may explain why such a low reaction cross-section is observed.

It is of interest to note that the overall cross-section for $N_2O/HD$ reactions are somewhat larger than those obtained from $N_2O/D_2$ mixtures. They were obtained from plots of $i_s/i_p$ against total pressure in the manner described in section (iv). In this case $i_s/i_p$ is the sum of the m/e 45/44 and 46/44 peak ratios. The intermolecular isotope effect between $N_2O/D_2$ and $N_2O/HD$ reactions is about 1.3 ($Q_{HD}/Q_{D_2}$). The cross-sections obtained are shown in Table 4.4.

(v) $CO_2$ Ion-Molecule Reactions:

The data obtained on $CO_2$ ion-molecule systems was limited to 1:9 $CO_2/D_2$ and $CO_2/HD$ mixtures.
a) Overall Cross-Sections.

The method used for the determination is the same as used in sections (iii) and (iv). The results for the CO$_2$/D$_2$ mixture are shown graphically in Fig. 4.9 and the overall cross-sections obtained for both mixtures are shown in Table 4.5. It may be seen that the cross-sections for the CO$_2$ ion-molecule reactions are much greater than those for N$_2$O. Table 4.5 also shows the ratios of the overall cross-sections for the CO$_2$ and N$_2$O reactions. There is some scatter, but this is to be expected since the CO$_2$ data are not as extensive as the N$_2$O data. The average CO$_2$/N$_2$O reaction ratio from Table 4.5 is 4.7. This compares favourably with Fehsenfeld et al's [93] results for the reactions

\[
\text{CO}_2^+ + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}
\]

and

\[
\text{N}_2\text{O}^+ + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H}
\]

They obtained values for the bimolecular rate constant of $1.4 \times 10^9$ cm$^3$ mole$^{-1}$ sec$^{-1}$ for CO$_2^+ + \text{H}_2$ and $0.4 \times 10^9$ for N$_2$O$^+ + \text{H}$, a ratio CO$_2$/N$_2$O of 3.5.

Fehsenfeld et al [93] and Moran and Friedman [100] found that the rate constant for the CO$_2^+ + \text{H}_2$ reaction was in close agreement with that predicted by the Giauque-Sutton theory. It is therefore clear that in its simple form the G-S theory is not applicable to ion-molecule reactions involving N$_2$O and H$_2$.

b) Intramolecular Isotope Effects.

The variation of CO$_2$H$^+$/CO$_2$D$^+$ ratio with repeller field for 1:9 CO$_2$/HD mixtures is shown in Fig. 4.10. Experimental scatter is bad but not as great as in the case of the N$_2$O work. The dashed line represents the best line through the average values of all values obtained at each repeller setting. The solid line represents the results obtained by Moran and Friedman [100] for the CO$_2^+ + \text{HD}$ reactions. It can be seen that the results obtained in this work follow the same general trend as Moran and Friedman's data.
Fig: 4.10 Intramolecular Isotope Effects in CO₂/HD Mixtures.
The actual values of the isotope effects are however slightly higher. This may be due to the fact that in the present case two ion-molecule reactions (each with an isotope effect) are occurring, whereas in Moran and Friedman's system it was demonstrated that only $\text{CO}_2^+ + \text{HD}$ reaction occurred. It will be seen that in neither Moran and Friedman's data nor in the present data is a maximum in the plot of $k_H/k_D$ against repeller field observed.

(vi) Extent of Competing Reactions:

It has been shown that both possible ion molecule reactions occur when a mixture of $\text{N}_2\text{O}$ and hydrogen (or its isotopes) is subjected to electron bombardment.

\[
\text{i.e. } \text{N}_2\text{O}^+ + \text{D}_2 \rightarrow \text{N}_2\text{OD}^+ + \text{D} \quad (3)
\]
\[
\text{D}_2^+ + \text{N}_2\text{O} \rightarrow \text{N}_2\text{OD}^+ + \text{D} \quad (4)
\]

The ionization potentials of nitrous oxide and deuterium differ by about 2.5 eV. ($\text{N}_2\text{O} = 12.9$ eV; $\text{D}_2 = 15.4$ eV [106]). It should therefore be possible to observe a decrease in $i_s/i_p$ ratio as the energy of the ionizing electron beam is reduced to below the ionization potential of deuterium. Accordingly experiments were carried out to measure the ionization efficiency curves of $\text{N}_2\text{O}^+$, $\text{D}_2^+$ and the product of ion-molecule reaction $\text{N}_2\text{OD}^+$, at the same time the variation of $\text{N}_2\text{OD}^+/\text{N}_2\text{O}^+$ ratio with electron beam energy was measured at a repeller field of 3 v/cm for a 1:9 mixture of $\text{N}_2\text{O}/\text{D}_2$ at a pressure of $49 \times 10^{11}$ molecules/cc. The results are shown in Fig. 4.11a. In this figure the ionization efficiency curves are normalized at 50 eV electron beam energy. Also shown is the $46/44$ peak ratio plotted on the same electron energy scale. The presence of the two reactions is clearly demonstrated. It can be seen that a change in $46/44$ ratio occurs at about the appearance potential of deuterium, below and above this point the ratios remain approx-
immediately constant. The value of the $\frac{46/44}{46/44}$ ratio below the deuterium appearance potential divided by the ratio $\frac{46/44}{46/44}$ above the potential gives the relative extent of the $N_2O^+ + D_2$ reaction to the total ion-molecule reaction. For the $N_2O/D_2$ system this fraction is:

$$\frac{(N_2O^+ + D_2)}{\text{Total reaction}} = 0.79$$

The ionization potentials of $CO_2$ and deuterium differ by 1.6 eV ($CO_2 = 13.8$ eV and $D_2 = 15.4$ eV)\cite{106}. The same procedure may therefore be applied to the $CO_2/D_2$ system. Two determinations of the fraction of $CO_2^+ + D_2$ reaction were carried out at 3 V/cm repeller field and the results obtained agreed to within about 10% (0.67 and 0.60). To check the method and to see whether one or other of the reactions had an abnormal dependence on repeller field the experiments were repeated at a repeller field of 21 V/cm. The $(CO_2^+ + D_2)/(\text{Total reaction})$ ratio agreed within the experimental error to those obtained at 3 V/cm (0.61 at 21 V/cm). Therefore,

$$\frac{(CO_2^+ + D_2)}{\text{Total reaction}} = 0.63$$

It is concluded that under the experimental conditions employed, two concurrent ion molecule reactions are occurring in both the $N_2O/D_2$ and $CO_2/D_2$ systems. This disagrees with Moran and Friedman's result that only the reaction $CO_2^+ + HD$ occurred in the $CO_2/HD$ system \cite{100}.

One can obtain the cross-sections for the individual reactions

$N_2O^+(CO_2^+) + D_2 \rightarrow N_2OD^+(CO_2D^+) + D$

(cross section $Q$)

$D_2^+ + N_2O(CO_2) \rightarrow N_2OD^+(CO_2D^+) + D$

(cross section $Q'$)

from Equation \# which was derived in section (iii) for the two concurrent reactions.
\[ \frac{\text{46}}{\text{44}} \text{ peak ratio} = n_{D_2} \frac{1}{4} (Q + \alpha Q') \]  \hspace{1cm} (N)

and Equation I which defines the cross-section for the reaction

\[ \text{N}_2\text{O}^+(\text{CO}_2^+) + \text{D}_2 \text{ alone} \]

\[ \frac{\text{46}}{\text{44}} \text{ peak ratio} = n_{D_2} \frac{1}{4} Q \]  \hspace{1cm} (I)

It can be seen that the ratio of \( (\text{N}_2\text{O}^+ + \text{D}) \) reaction to total reaction is given by \( I \div N \)

\[ \frac{\text{N}_2\text{O}^+ + \text{D}_2}{\text{Total reaction}} = \frac{n_{D_2} \frac{1}{4} Q}{n_{D_2} \frac{1}{4} (Q + \alpha Q')} \]

Values of \( Q \) and \( \alpha Q' \) may therefore be calculated for both the \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) reactions from the overall cross-sections given in Tables 4.3, 4, and 5.

Values for \( Q' \) may be obtained using the published values for the ionization cross-sections of \( \text{D}_2, \text{N}_2\text{O} \) and \( \text{CO}_2 [103] \). It is assumed that the ionization cross-section of hydrogen deuteride is the same as that for deuterium. For 70 eV electrons \( \alpha = 0.285 \) for the \( \text{N}_2\text{O} \) reactions, and for \( \text{CO}_2 \) reactions \( \alpha = 0.305 \).

(vii) Evidence for \( E^{-\frac{1}{2}} \) dependence:

The Glauber-Stevenson theory predicts that the phenomenological cross-section \( (Q) \) will be dependent on \( \text{(kinetic energy of the ion)}^{-\frac{1}{2}} \).

The kinetic energy of an ion travelling a distance \( 1 \text{ cm} \) in a field \( E \text{ V/cm} \) is \( = (e 1 E) \) where \( e \) is the charge carried by the ion.

Therefore if one plots the \( i_s/i_p \) ratio against \( (1E)^{-\frac{1}{2}} \) a straight line should be obtained (since \( i_s/i_p \propto Q \)). Fig. 4.12 shows the \( \frac{46}{44} \) peak ratios for 1:9 \( \text{N}_2\text{O}/\text{D}_2 \) mixtures plotted against \( (\text{ion energy})^{-\frac{1}{2}} \). It can be seen that moderately good straight lines are obtained in the region \( 1 \text{ V/cm} \) to \( 7 \text{ V/cm} \), at higher fields there is a tendency for the \( i_s/i_p \) ratios to become constant. This is probably
Fig. 4.12 E^{-1/2} Dependence of N\textsubscript{2}O/D\textsubscript{2} Reactions.

Fig. 4.13 Dependence of Cross-Section on (Ion Energy)^{-1/2}
a result of the large experimental error in the measurement of $i_s/i_p$
in regions where the ion-molecule contribution to the 46 peak is very
small. It may therefore be concluded that the results obtained in the
repeller field region 1 v/cm to 7 v/cm may be used to calculate bi-
molecular rate constants ($k$) using the Gioumousis-Stevenson relationship:

$$k = \left(\frac{1 E}{2m}\right)^{\frac{1}{2}} Q$$

To confirm this finding the values for the overall cross-sections
for $N_2O/D_2$, $N_2O/HD$, $CO_2/D_2$ and $CO_2/HD$ mixtures were plotted against
$(1 E)^{\frac{1}{2}}$. As may be seen from Fig. 4.13 good straight lines are obtained.

**DISCUSSION**

(i) Comparison of Results with Gioumousis-Stevenson Theory:

A prerequisite for applying the Gioumousis-Stevenson theory to
an ion-molecule reaction is that the phenomenological cross-section
varies linearly with the (ion energy)$^{\frac{1}{2}}$. This has been observed to
occur in both $N_2O/hydrogen$ and $CO_2/hydrogen$ systems (Figs. 4.11 and 12).
The experimentally determined quantity is the sum of the individual
phenomenological cross-sections ($Q+aQ'$) at different repeller fields
for the concurrent reactions

$$AB^+ + X_2 \rightarrow \text{cross-section} = Q$$

$$X_2^+ + AB \rightarrow \text{cross-section} = Q'$$

where $AB$ is $N_2O$ or $CO_2$ and $X_2$ is $D_2$ or $HD$. The "a" term in ($Q+aQ'$) is
the ratio

$$\frac{\text{Ionization cross-section of } D_2^+ \text{ (or } HD^+)}{\text{Ionization cross-section of } N_2O^+ \text{ (or } CO_2^+)}$$

From the values of ionization cross-sections for $N_2O^+$, $CO_2^+$ and $D_2^+$
given by Rapp and Englander - Golden [103] the values of \( a \) are

\[
a \text{ for } \text{N}_2\text{O}/\text{D}_2 \text{ (and HD)} = 0.285 \\
a \text{ for } \text{CO}_2/\text{D}_2 \text{ (and HD)} = 0.309
\]

for 70 eV electrons.

The overall reaction cross-section \( (Q_R^o) \) may be obtained from the slope of plots of overall phenomenological cross-section \( (Q + aQ') \) against \((1/E)^{1/2}\) shown in Figs. 4.12 a and b. In order to obtain the theoretical overall reaction cross-section the reaction cross-sections for the individual reactions were calculated from the equation for the phenomenological cross-section given by the Gioumousis-Stevenson theory

\[
Q = 2\pi \left(2m \alpha e^2/\mu\right)^{1/2} (1/e \text{E} 1)^{1/2}
\]

and the relationship \( Q_R = Q (\text{E} 1)^{1/2} \)

i.e. \( Q_R = 2\pi (600 \text{ m} \alpha e/\mu)^{1/2} \)

The symbols are those defined in the previous section. For the equation to be dimensionally correct \( \alpha \) is in \( \text{cm}^3/\text{molecule} \).

\( \mu \) and \( m \) in grams
\( e \) in e.s.u. \((4.8 \times 10^{-10})\)

and the factor 300 is inserted to convert the experimental units of \( E \) (volts/cm) to e.s.u./cm. The dimensions of \( Q_R \) are \( \text{cm}^2 \text{ eV}^{1/2} \) (normally \( Q_R \) is expressed in \( \text{Å}^2 \text{ eV}^{1/2} \)). The average polarizabilities \( \alpha \) of the molecules \( \text{N}_2\text{O}, \text{CO}_2 \text{ and D}_2 \text{ (HD)} \) used are those given by Bottcher [101]. The theoretical overall reaction cross-sections (calculated from the individual reaction cross-sections), are compared with the experimental overall reaction cross-sections in Table 4.6.

It may be seen that good agreement between experiment and theory is obtained for the \( \text{CO}_2/\text{D}_2 \) and \( \text{CO}_2/\text{HD} \) systems. It is worth pointing out that the experimental value of \( Q_R^o \) for the \( \text{CO}_2/\text{HD} \) system is in good agreement with that obtained by Moran and Friedman [100] \((118 \text{ and } 108\text{Å}^2\text{ eV}^{1/2} \text{ respectively})\) and is a check on the validity of the experimental
Table 4.6 Overall Reaction Cross-sections

<table>
<thead>
<tr>
<th>Reaction System</th>
<th>$Q_R$</th>
<th>$Q_R'$</th>
<th>$aQ_R'$</th>
<th>$Q_R^\circ$</th>
<th>Experimental $Q_R^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2/D_2$</td>
<td>106</td>
<td>57.5</td>
<td>17.8</td>
<td>124</td>
<td>118</td>
</tr>
<tr>
<td>$\text{CO}_2/\text{HD}$</td>
<td>122</td>
<td>57.1</td>
<td>17.6</td>
<td>140</td>
<td>118</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}/D_2$</td>
<td>106</td>
<td>61.1</td>
<td>17.4</td>
<td>123</td>
<td>26.0</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}/\text{HD}$</td>
<td>122</td>
<td>60.9</td>
<td>17.4</td>
<td>139</td>
<td>27.1</td>
</tr>
<tr>
<td>$\text{CO}_2/\text{N}_2\text{O}$ for $\text{D}_2$</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>$\text{CO}_2/\text{N}_2\text{O}$ for $\text{HD}$</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td>4.3</td>
</tr>
</tbody>
</table>

Units are $\text{Å}^2 \text{eV}^{-1}$

$Q_R$ = cross-section for the reaction $\text{AB}^+ + \text{X}_2 \rightarrow \text{ABX}^+ + \text{X}$

$Q_R'$ = cross-section for the reaction $\text{X}_2^+ + \text{AB} \rightarrow \text{ABX}^+ + \text{X}$

$Q_R^\circ = (Q_R + aQ_R')$, the overall cross-section for the two reactions.

$a = \frac{\text{Ionization cross-section of } \text{X}_2^+}{\text{Ionization cross-section of } \text{AB}^+}$

$\text{AB} = \text{N}_2\text{O} \text{ or CO}_2$

$\text{X}_2 = \text{D}_2 \text{ or HD}$
technique and treatment of results used in this work. (Moran and Friedman corrected their experimental cross-section of 108Å² to allow for a secondary ion-molecule reaction which produced COH⁺ (and COD⁺) as a product. They showed that this was due to reactions involving CO⁺ and HD⁺. Their corrected cross-section was 12.4Å eV⁻¹ for the CO₂⁺/HD⁺ reactions alone which is slightly higher than the overall value found in this work).

In the nitrous oxide system, however, the overall cross-sections \( q_R \) are much smaller than those predicted by theory. This is contrary to expectation since nitrous oxide has a permanent dipole moment and hence the reaction cross-sections would be expected to be larger than those predicted by the Gioumousis-Stevenson theory (vide, their paper ref. 91). The ratio of the cross-sections of the CO₂ reactions to those of the N₂O reactions is 4.4. This is similar to the value of 3.5 found by Fehsenfeld, Schmeltekopf and Ferguson [93] for the reactions

\[
\text{CO}_2^+ + H_2 \rightarrow \text{CO}_2H^+ + H
\]

and \( N_2O^+ + H_2 \rightarrow N_2OH^+ + H \)

(ii) **Individual Reaction Cross-Sections and Rate Constants:**

That two concurrent reactions are occurring in both the N₂O and CO₂ systems is clearly shown in Fig. 4.11. For the N₂O case

\[
\begin{align*}
\text{N}_2\text{O}^+ + D_2 &\rightarrow \text{N}_2\text{OD}^+ + D \quad (3) \\
\text{D}_2^+ + \text{N}_2\text{O} &\rightarrow \text{N}_2\text{OD}^+ + D \quad (4)
\end{align*}
\]

\[
i_s/i_p \quad (\text{reaction} \ 3) = n_{D_2} \quad 1 \quad Q
\]

\[
i_s/i_p \quad (\text{reactions} \ 3 \ \text{and} \ 4) = n_{D_2} \quad 1 \quad (Q + aQ')
\]

\[
i_s/i_p \quad (i_s + i_s')/i_p = Q/(Q + aQ')
\]

The experimental value of \([i_s/i_p + (i_s + i_s')/i_p]\) is 0.79

\[
\therefore \quad Q/(Q + aQ') = 0.79
\]
For a given set of conditions \( Q \propto Q_R \) (the reaction cross-section) and
\[(Q + aQ) \propto Q_R^0 \) (the overall reaction cross-section) and hence
\[Q_R \left( \text{N}_2 \text{O}^+ + \text{D}_2 \right) = 0.79 Q_R^0 \) (both reactions).
Values for \( Q_R \) and \( Q_R' \) may therefore be calculated from the values of \( Q_R^0 \)
and \( a \). The values of \( Q_R \) and \( Q_R' \) for the \( \text{CO}_2/\text{D}_2 \) system are calculated
in a similar manner; the value \[ \frac{i_s / i_p}{i_s + i_s'} / i_p \] is 0.63 in this case.
Though no actual experiments were carried out to measure \[ \frac{i_s / i_p}{i_s + i_s'} / i_p \]
in the hydrogen deuteride reactions, approximate values for \( Q_R \) and \( Q_R' \) may be
obtained by assuming that the ratios \[ \frac{i_s / i_p}{i_s + i_s'} / i_p \] are the same as
those for deuterium. The values for the individual reaction cross-sections,
together with the theoretical values are given in Table 4.7.

The bimolecular rate constant \((k)\) may be obtained from the individual
reaction cross-sections \( (Q_R) \) by using the relationship
\[ k = \left( \frac{e}{600, \mu} \right) \frac{1}{2} Q_R \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]
with \( e \) in o.s.u. and \( \mu \) in grams. The experimental rate constant may be
compared with the one predicted by the Gioumousis-Stevenson theory which
gives
\[ k = 2\pi e \left( \frac{a}{\mu} \right) \frac{1}{2} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]
with \( a \) in cm\(^3\) molecule\(^{-1}\) and \( \mu \) in grams. The experimental and theoretical
rate constants for the individual reactions are shown in Table 4.7.

It may be seen that the agreement between experiment and theory is not
as good as was obtained in comparing the overall cross-sections for the \( \text{CO}_2 \)
reactions in Table 4.6. If the interpretation of the variation of \( i_s / i_p \)
ratios is correct (i.e. that the measured \[ \frac{i_s / i_p}{i_s + i_s'} / i_p \] ratio is
independent of gas pressure, repeller field and mixture composition) it
must be concluded that the agreement obtained by Moran and Friedman and
in this work between experimental cross-section and theoretical cross-
Table 4.7 Cross-sections and Rate Constants for Individual Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>a Reaction Cross Section</th>
<th>b Bimolecular Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exptl.</td>
<td>Theory</td>
</tr>
<tr>
<td>$\text{CO}_2^+ + \text{H}_2^+$</td>
<td>74.3</td>
<td>106</td>
</tr>
<tr>
<td>$\text{H}_2^+ + \text{CO}_2$</td>
<td>141</td>
<td>57.5</td>
</tr>
<tr>
<td>$\text{CO}_2^+ + \text{HD}$</td>
<td>74.3</td>
<td>122</td>
</tr>
<tr>
<td>$\text{HD}^+ + \text{CO}_2$</td>
<td>141</td>
<td>57.1</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}^+ + \text{H}_2$</td>
<td>20.5</td>
<td>106</td>
</tr>
<tr>
<td>$\text{H}_2^+ + \text{N}_2\text{O}$</td>
<td>19.3</td>
<td>61.1</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}^+ + \text{HD}$</td>
<td>21.4</td>
<td>122</td>
</tr>
<tr>
<td>$\text{HD}^+ + \text{N}_2\text{O}$</td>
<td>20.0</td>
<td>60.9</td>
</tr>
</tbody>
</table>

$\text{CO}_2^+ + \text{D}_2$  \hspace{1cm} 3.7

$\text{N}_2\text{O}^+ + \text{D}_2$

*a* Units in $\text{Å}^2 \text{eV}^{\frac{1}{2}}$

*b* Units in $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

*c* These values were obtained by inference

(see Discussion Section (ii) )
section for the \( \text{CO}_2/D_2(\text{HD}) \) system was fortuitous. (It can be seen in Table 4.7 that whilst the reaction cross-section for \( \text{CO}_2^+ + \text{HD} \) is lower than theoretical prediction, the reaction cross-section for \( \text{HD}^+ + \text{CO}_2 \) is considerably higher. The two effects approximately cancel in the calculation of \( Q_R^aQ_R = Q_R^o \). This conclusion is a tentative one, based as it is on only one mixture (1:9 \( \text{CO}_2/D_2 \) and one pressure; a more thorough investigation of the \( (i/a_i)p + (i/a_i')/i'p \) with different mixtures, pressure and repeller fields would be required to clarify the issue.

Support for the above interpretation appears in Fehsenfeld et al's paper [93]. They studied the reactions (among others)

\[
\begin{align*}
\text{CO}_2^+ + \text{H}_2 & \rightarrow \text{CO}_2\text{H}^+ + \text{H} \\
\text{N}_2\text{O}^+ + \text{H}_2 & \rightarrow \text{N}_2\text{OH}^+ + \text{H}
\end{align*}
\]

in a pulsed-discharge, flowing-afterglow reaction tube, a totally different environment from a mass spectrometer ion source. They obtained rate constants of

\[
\begin{align*}
k(\text{CO}_2^+ + \text{H}_2) &= 1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \\
k(\text{N}_2\text{O}^+ + \text{H}_2) &= 0.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}
\end{align*}
\]

If one assumes the Gioumousis-Stevenson relationship that

\[k \propto (1/\mu)^{1/2}\]

the rate constants for the analogous deuterium reactions may be calculated

i.e. \( k(D_2) = k(H_2) \times (\mu_{H_2}/\mu_{D_2})^{1/2} \)

which gives values of

\[
\begin{align*}
k(\text{CO}_2^+ + D_2) &= 0.73 \times 10^{9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \\
k(\text{N}_2\text{O}^+ + D_2) &= 0.21 \times 10^{9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}
\end{align*}
\]

These compare very favourably with values of 0.78 and 0.21 respectively obtained in the present work.

Moran and Friedman's rate constant for \( \text{CO}_2^+ + \text{HD} \) of \( 1.29 \times 10^{-9} \text{ cm}^3 \) molecule\(^{-1} \) sec\(^{-1}\) depended on two assumptions:
a) that the concurrent reaction $\text{HD}^+ + \text{CO}_2$ occurred to only a small extent and its contribution to the overall reaction cross-section $(Q_\text{R})$ was given by the ratio $[aQ'/(Q+aQ')]$. They calculated this from the theoretical reaction cross-sections for the individual reactions and from the ratio (a) of the relative ionization cross-sections for $\text{HD}^+$ and $\text{CO}_2^+$.

b) that their cross-section for $\text{CO}_2\text{H}^+$ formation fell short of the theoretical value because of an alternative reaction channel leading to $\text{CHO}^+$. They estimated the extent of this reaction and obtained a total reaction rate for the $\text{CO}_2^+ + \text{HD}$ reaction of 92% of the Gioumousis-Stevenson value.

Their first assumption relied on inspection of ionization efficiency curves for $\text{CO}_2\text{H}^+$ (and $\text{CO}_2\text{D}^+$), $\text{CO}_2^+$ and $\text{HD}^+$. They found that the curves for $\text{CO}_2\text{H}^+$ and $\text{CO}_2^+$ were similar and differed from the $\text{HD}^+$ curve. They deduced that $\text{CO}_2^+$ ions were the major ionic precursors of the $\text{CO}_2\text{H}^+$ reaction product with relatively minor contributions from $\text{HD}^+$ ions (as is predicted by theory). As can be seen from Fig. 4.11 the same effect is observed in both the $\text{CO}_2/\text{D}_2$ and $\text{N}_2\text{O}/\text{D}_2$ systems. However a study of the variation of $46/44$ peak height ratios with electron energy shows conclusively that the $\text{D}_2^+ + \text{CO}_2$ (or $\text{N}_2\text{O}$) reaction occurs to an appreciable extent.

The values of the rate constants for the individual reactions of $\text{CO}_2/\text{D}_2$ (HD) systems are not in good agreement with the G-S theory. It is felt that the agreement between overall experimental and theoretical cross-sections for $\text{CO}_2/\text{D}_2$ (HD) systems obtained both in this work and in that of Moran and Friedman may be fortuitous. If this is the case then neither the $\text{N}_2\text{O}/\text{D}_2$ system (which has rate constants much lower than theoretical prediction) nor the $\text{CO}_2/\text{D}_2$ system can be treated on purely electrostatic principles.
(iii) Tentative Explanations:

The analysis of results obtained in the study of ion-molecule reactions in the N$_2$O/hydrogen and CO$_2$/hydrogen systems has raised points which require further investigation. Problems requiring explanation are:

a) the observed discrepancy between the rates of reaction involving N$_2$O and D$_2$ (HD) and those predicted by theory,

b) the apparent anomaly between the good agreement with theory obtained for the overall reaction cross-sections of reactions in CO$_2$/D$_2$ and HD systems and the poor agreement with theory of the reaction cross-sections of the individual reactions.

The following explanations are provided as guidelines for possible further research. The symbol H$_2$ is taken in the following discussion as referring to all the isotopic species of hydrogen.

a) N$_2$O Ion-Molecule Reactions

The average polarizability of N$_2$O is higher than that of CO$_2$ (3.00 and 2.65 Å$^3$ respectively). Furthermore, nitrous oxide has a permanent dipole moment which would have the effect of increasing the ion-molecule interaction and thus giving cross-sections higher than those predicted by the Gioumousis-Stevenson theory. Ion-molecule reactions between nitrous oxide and H$_2$ would therefore be expected to occur at a faster rate than the analogous CO$_2$ reactions. The converse is found to be true. The rates of N$_2$O reactions are found to be substantially lower than those predicted both by theory and the analogous CO$_2$ reactions.

It has been demonstrated by Reuben [108] that the heat of formation of the CO$_2$H$^+$ ion in its linear form (O=C=O$^+$) is at least 40 kcal lower than $\Delta H_f$ for a pyramidal complex (H-C=O). He obtained this value from the appearance potentials of CO$_2$H$^+$ from acetic acid and formic acid (in both of which the CO$_2$H$^+$ ion would be expected to be linear), and from
methyl formate (which would be expected to yield a pyramidal \( \text{CO}_2\text{H}^+ \) ion). The appearance potentials and heats of formation of \( \text{CO}_2\text{H}^+ \) obtained by Reuben are shown in Table 4.8. If it is assumed in the light of Reuben's findings for \( \text{CO}_2\text{H}^+ \) that \( \text{N}_2\text{OH}^+ \) is also linear (there is insufficient thermochemical data to obtain values for \( \Delta H_f \text{N}_2\text{OH}^+ \)), on purely qualitative grounds it might be expected that the rate of reaction between \( \text{N}_2\text{O}^+ \) and \( \text{H}_2 \) (and \( \text{H}_2^+ + \text{H}_2\text{O} \)) would be one half that for \( \text{CO}_2 \). This conclusion may be visualized by considering that hydrogen can only attach itself to the oxygen in \( \text{N}_2\text{O} \), thus the orientations

\[
(\text{NNO})^+ \quad \text{---} \quad \text{H}_2
\]

and

\[
\text{H}_2^+ \quad \text{---} \quad \text{ONN}
\]

would lead to reaction whereas the orientations

\[
(\text{ONN})^+ \quad \text{---} \quad \text{H}_2
\]

and

\[
\text{H}_2^+ \quad \text{---} \quad \text{NNO}
\]

would not. In \( \text{CO}_2 \) reactions both orientations are equivalent. This argument may be thought of as introducing a steric factor analogous to the \( P \) factor in the collision theory of neutral-neutral reactions. However, this simple explanation would only reduce the rate to half that of the \( \text{CO}_2 \) reactions, whereas the experimental ratio is less than a quarter.

An alternative approach is to consider the possibility of kinetic energy - internal energy transfer in the transition complex before it breaks up. The transition complex may be considered to lie in a potential well in the saddle surface which defines the activated complex. The diagram shown below is a simple illustration of the point.
Table 4.8  Appearance Potentials and Heats of Formation of CO₂H⁺ (ex Reuben [108])

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔP</th>
<th>ΔHₚ</th>
<th>Structure of CO₂H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>13.72</td>
<td>179</td>
<td>O=C=O⁻H⁺</td>
</tr>
<tr>
<td>methyl formate</td>
<td>14.55</td>
<td>218</td>
<td>H-C⁻O⁺ / + O⁻</td>
</tr>
<tr>
<td>formic acid</td>
<td>12.2 to 12.5</td>
<td>156</td>
<td>O=C=O⁻H⁺</td>
</tr>
</tbody>
</table>

The discrepancy between ΔHₚ from acetic and formic acids is probably due to the COOH⁺ from acetic acid being formed with excess kinetic energy as would be expected on the basis of Stevenson's Rule [106].

Table 4.9  Polarizabilities (ex Bottcher [101]).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>α₁</th>
<th>α₂</th>
<th>α₃</th>
<th>α (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>0.55 Å³</td>
<td>0.96 Å³</td>
<td>0.96 Å³</td>
<td>0.832 Å³</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.10</td>
<td>1.93</td>
<td>1.93</td>
<td>2.65</td>
</tr>
<tr>
<td>N₂O</td>
<td>5.10</td>
<td>1.9</td>
<td>1.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Products will only be formed if the transition complex possesses sufficient energy to surmount the potential barrier (B). If more than this energy is available as internal energy in the reactants then for all practical purposes the reaction is "down-hill" and will proceed at every collision. If conversion of kinetic to internal energy is required, then the process is "up-hill" with a high probability of reflection back onto the valley. Consequently, processes which require kinetic to internal energy transfer would be expected to have much smaller reaction cross-sections (vide Friedman p.97 of Ref. 71).

A criterion for invoking the necessity for kinetic-internal energy transfer in an ion-molecule reaction has been shown by Klein and Friedman [104] to be the observation of a maximum in the plot of isotope ratio \( k_H/k_D \) against ion energy for reactions involving HD. Klein and Friedman observed such maxima in the reactions

\[
\text{HD}^+ + \text{He} \\
\text{and} \quad \text{HD}^+ + \text{Ne}
\]

and showed by theoretical calculation that these could only be accounted for by assuming that kinetic-internal energy transfer was a prerequisite for reaction. A maximum may be discerned in the plot of \( N_2\text{OH}^+/N_2\text{OD}^+ \) ratio against ion energy for the reaction system \( \text{N}_2\text{O}/\text{HD} \) (Fig. 4.8), whereas no maximum is observed in the \( \text{CO}_2/\text{HD} \) system which is shown to be in qualitative agreement with the isotope effect observed by Moren and Friedman. Even if it were feasible to calculate the potential energy surface for the \( N_2\text{OH}_2^+ \) transition complex the data in Fig. 4.8 are so scattered that quantitative prediction would be impossible. One may only say that there is some support for the conclusion that the formation of \( N_2\text{OH}^+ \) product ion from the \( N_2\text{OH}_2^+ \) transition state requires kinetic-internal energy transfer.
whilst the formation of $\text{CO}_2\text{H}^+$ from $\text{CO}_2\text{H}_2^+$ does not. If this is the case it would be an explanation why the $\text{N}_2\text{O}/\text{H}_2$ reactions are much slower than the $\text{CO}_2/\text{H}_2$ reactions.

b) $\text{CO}_2/\text{H}_2$ Ion-Molecule Reactions:

It was pointed out in Section (ii) of this discussion that Moran and Friedman's agreement between their experimental rate constant for $\text{CO}_2^+ + \text{HD}$ and that predicted by theory (and indeed agreement in this work between the experimental and theoretical values for $Q_r^0$) may be fortuitous.

The Gioumousis-Stevenson theory treats the neutral molecule as though it had isotropic polarizability. For a linear molecule the polarizability may be considered to be made up of three orthogonal components, one ($\alpha_1$) along the molecular axis and two ($\alpha_2, \alpha_3$) at right angles to the axis.

It is standard practice in the theoretical treatment of ion-molecule reactions to consider only the average polarizability $(\text{i.e. } \alpha_1 + \alpha_2 + \alpha_3/3)$ of the molecule. Table 4.9 shows that the three polarizability tensors can differ by appreciable amounts. If we consider the two reactions

$$
\text{CO}_2^+ + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H} \\
\text{H}_2^+ + \text{CO}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}
$$

and assume that the orientations

$$
\text{CO}_2^+ \quad \text{H - H} \\
\text{H}_2^+ \quad \text{O - C - O}
$$

are preferred then it is possible that the axial polarizability tensor ($\alpha_1$) of the neutral molecule is the one that plays the major part in determining the reaction cross-section. The effect of using only $\alpha_1$ in calculating the theoretical cross-sections on those given in Table 4.7 (these values of $Q_r$ were calculated from the average polarizability) will now be considered.
239.

For the reaction $\text{CO}_2^+ + \text{H}_2$ it can be seen that $\alpha_1 (\text{H}_2)$ is smaller than the average value and therefore the reaction cross-section would be expected to be smaller than that given by the theoretical $Q_R (\alpha \text{ average})$. This is indeed the case and $Q_R$ experimental is smaller than the theoretical value ($74.3 \text{ of } 106 \text{ A}^2 \text{ eV}^{-\frac{1}{2}}$). The theoretical cross-section (for $\text{CO}_2^+ + \text{D}_2$) may be modified to allow for the smaller value of $\alpha_1$ of $\alpha$ average.

$$Q_R (\alpha_1) = Q_R (\alpha \text{ average})(\alpha_1/\alpha \text{ average})^{\frac{1}{2}}$$

$$= 106 \left(\frac{0.55}{0.83}\right)^{\frac{1}{2}}$$

$$= 86.3 \text{ A}^2$$

This compares moderately well with the experimental value of $74.3 \text{ A}^2$.

The theoretical cross-section for the reaction $\text{D}_2^+ + \text{CO}_2$ may be treated in a similar way. In this case $\alpha_1 (\text{CO}_2)$ is larger than $\alpha$ average and hence, in agreement with experiment, the reaction cross-section would be expected to be larger than the value of $Q_R (\alpha \text{ average})$. The modified value of $Q_R = 71.9 \text{ A}^2$ is still smaller than the observed value of $141$.

It is obvious that some regard should be paid to the non-isotropic polarizability of molecules though it is difficult to say how much attention should be paid to the concept of "preferred" orientations. Indeed it is difficult to say whether orientation of molecules has any meaning in the treatment of ion-molecule collisions where the reactant ion is imagined as entering into a spiral orbit around the molecule if a reactive collision is to take place.

(iv) Summary:

Ion molecule reactions in $\text{N}_2\text{O}/\text{H}_2$, $\text{HD}$ and $\text{D}_2$, and $\text{CO}_2/\text{D}_2$ and $\text{HD}$ systems have been studied in a mass spectrometer ion source. It has been shown that two concurrent ion-molecule reactions take place in each
system. The reactions obey the theoretical linear dependence of phenomenological cross-section on (ion energy)$^{-1/2}$. The overall reaction cross-sections for CO$_2$/D$_2$ and HD systems are in agreement with those predicted by the Gioumousis-Stevenson theory (Table 4.5). The reaction cross-sections and bimolecular rate constants for the individual reactions

$$AB^+ + X_2 \rightarrow ABX^+ + X$$

and

$$X_2^+ + AB \rightarrow ABX^+ + X$$

where $AB = CO_2$ or N$_2$O and $X_2 = D_2$ or HD, have been obtained and compared with theory (Table 4.7).

Reactions involving N$_2$O and H$_2$ (HD, D$_2$) have reaction cross-sections much smaller than predicted by the Gioumousis-Stevenson theory. It is tentatively suggested that these reactions require kinetic-internal energy transfer in the transition state. This conclusion is based on the appearance of a maximum in the plot of the ratio of N$_2$OH$^+$/N$_2$OD$^+$ against ion energy.

The poor agreement between experiment and theory in the rate constants for the individual reactions in the CO$_2$/D$_2$ (HD) systems contrasts with the good agreement obtained between the overall reaction cross-sections. It is tentatively concluded that the non-isotropic character of the polarizability of the neutral molecule and possibly the orientations of the reactants should be taken into account.
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ABSTRACT

The work in this thesis deals with some aspects of the simple molecule, nitrous oxide. It is convenient to divide the work into four parts:

(i) Oxidation of Hydrogen in Nitrous Oxide

The reaction, in a static system, was followed by measuring $\text{N}_2\text{O}$ concentration by its absorption at 2200 $\mu$m. It was found that in the region of 560°C the reaction rate was between 500 and 1000 times as fast as $\text{N}_2\text{O}$ decomposition. The reaction may be considered in two parts:

1) a "high" pressure reaction which occurs at total pressures greater than 100 mm Hg and whose initial rate is given by:

$$\text{Initial rate (mm Hg/min)} = 1.37 \times 0.05 \times 10^{15} \exp(-62.5 \pm 2.1/RT) [\text{N}_2\text{O}][\text{H}_2]^{0.25}$$

where [N$_2$O] and [H$_2$] represents the pressure of N$_2$O and H$_2$ in mm Hg;

2) a "low" pressure reaction which occurs at total pressures less than 60 mm Hg and whose initial rate is given by:

$$\text{Initial rate (mm Hg/min)} = 0.26 \times 0.30 \times 10^{13} \exp(-62.5 \pm 2.1/RT) [\text{N}_2\text{O}]^2$$

The change from first to second order in nitrous oxide is caused by a change from gas phase chain termination (steps 5, 6, 7, below) to wall termination of the hydrogen atom chain carriers (step 8). The addition of inert gases (CO$_2$ and CF$_4$) extends the first order region to lower pressures.

To account for the fact that the observed rate of reaction is at least 100 times slower than that computed using known reactions and rate constants, an oxygen atom termination reaction, hitherto unreported, was added to the reaction mechanism.

viz. $\text{O} + \text{H}_2 + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ \hspace{1cm} (9)

A tentative value for the rate constant for this reaction was derived.

$$k_9 = 3.9 \times 10^{-31} \exp(4.5 \pm 2.0/RT) \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}.$$
The reaction mechanism proposed is

\[
\begin{align*}
N_2O & \rightarrow N_2 + O \quad (1) \\
O + H_2 + M & \rightarrow H_2O + M \quad (9) \\
O + H_2 & \rightarrow OH + H \quad (2) \\
H + N_2O & \rightarrow N_2 + OH \quad (3) \\
OH + H_2 & \rightarrow H_2O + H \quad (4) \\
H + OH + M & \rightarrow H_2O + M \quad (5) \\
H + OH + M & \rightarrow H_2O_2 + M \quad (6) \\
OH + OH + M & \rightarrow \frac{1}{2}(H_2O + O_2) \quad (7) \\
H & \rightarrow Wall \quad (8)
\end{align*}
\]

Nitric oxide inhibits the reaction and this effect is attributed to termination of the H and OH chain carriers by reaction with NO, rather than by oxygen atom removal. Oxygen catalyses the reaction in the initial stages but causes pronounced inhibition in the later stages. The initial catalysis is a result of the chain branching process \(H + O_2 \rightarrow OH + O\) and it is suggested that the inhibition is due to the formation of small amounts of nitric oxide (0.2 to 0.3%). An explanation is suggested for the minima in explosion limit vs temperature curves observed by workers investigating the explosive \(N_2O/H_2\) reaction. A small isotope effect is noticed when hydrogen is replaced by deuterium \((k_H/k_D \approx 2)\) which approaches unity at low pressures.

(ii) Oxidation of Carbon Monoxide in Nitrous Oxide

The \(N_2O/CO\) reaction at 700°C proceeds at about three times the rate of \(N_2O\) decomposition. It is accompanied by a blue chemiluminescence and the formation of small amounts of oxygen. The reaction was followed by measuring \(N_2O\) pressure spectroscopically, the production of oxygen manometrically and the intensity of the chemiluminescence at 4500 Å.
The reaction is first order in $N_2O$ and about 0.3 order in CO and has an activation energy of $59.7\pm1.5$ kcal. It is suggested that the increase in rate relative to the $N_2O$ decomposition is a result of water in 10's p.p.m. quantities initiating H and OH radical propagated reaction chains. The reaction is considered on the basis of CO, $N_2O$ and $H_2O$ competing for oxygen atoms made available by the decomposition of $N_2O$ and the proposed mechanism is:

**Initiation:**

1. $N_2O \rightarrow N_2O^+$ \hspace{1cm} (1)
2. $CO \rightarrow CO_2^{\neq} (3B_2, 1B_2)$ \hspace{1cm} (2)
3. $CO_2^{\neq} (1B_2) \rightarrow CO_2 (1\Sigma_g^+) + h\nu$ \hspace{1cm} (3)
4. $CO_2 (3B_2, 1B_2) + M \rightarrow CO_2 (1\Sigma_g^+) + M$ \hspace{1cm} (4)

**"Dry"**

5. $O + H_2O \rightarrow 2OH$ \hspace{1cm} (5)
6. $OH + CO \rightarrow CO_2 + H$ \hspace{1cm} (6)
7. $H + N_2O \rightarrow N_2 + OH$ \hspace{1cm} (7)
8. $H$ and $OH$ \rightarrow termination \hspace{1cm} (11)

**"Wet"**

In the system studied ($H_2O < 0.01\%$) it is suggested that the "wet" reaction contributed approximately $3/4$ of the $CO_2$ produced. It was found that the amount of oxygen formed varied from 0 to about 3% total reaction depending upon conditions (oxygen formation was favoured by high pressure and excess $N_2O$ in the reaction mixture). It was concluded that oxygen atom reaction with NO and NO$_2$ (reactions 6c and d) were rate determining for $O_2$ formation.

The chemiluminescence observed was found to be inversely proportional to total pressure and arises from radiation from electronically excited...
CO₂ in the \(^1B_2\) state to the ground electronic state. The rate constant for the collisional deactivation of \(^1B_2\) CO₂ has been shown to depend on the composition of reaction mixture and it was concluded that CO is a more efficient third body than N₂O. The ratio of the rates of radiative deactivation (3) to non-radiative deactivation (4) of \(^1B_2\) is of the order of unity.

(iii) **Temperature Dependence of the Absorption of N₂O in the Quartz Ultra-Violet.**

The continuous absorption of nitrous oxide between 1900 and 2800 Å has been studied from 20 to 680°C. The absorption coefficient, at any given wavelength, increases exponentially with temperature leading to apparent activation energies. It is proposed that the continuum is due to transitions from bending vibrationally excited ground state molecules to a bent repulsive upper state. It is suggested that the upper state is a \(^1A'\) state correlating with a \(^1B_2\) state of the isoelectronic CO₂ molecule. A small portion of the upper potential energy curve is derived. The excited \(^1A'\) state of N₂O is compared with the \(^2A_1\) ground state of N₂O₂.

[The \(^1A'\) state of N₂O only differs from the \(^2A_1\) state of N₂O₂ in that it has only one instead of two electrons in the penultimate (in energy) orbital]. From this comparison and the published data on the \(^1B_2\) state of CO₂ it is suggested that the \(^1A'\) state of N₂O has a bond angle lying between 122° and 134° and that the energy required to straighten it is between 22,000 and 10,000 cm\(^{-1}\).

(iv) **Ion-Molecule Reactions in N₂O/H₂ System**

Ion-Molecule Reactions in N₂O/H₂, HD and D₂, and CO₂/D₂ and HD systems have been studied in a mass spectrometer ion source. It was shown that two concurrent ion-molecule reactions take place in each system. The reactions obey the theoretical linear dependence of phenomenological cross-section on (ion energy)\(^{-\frac{1}{2}}\). The reaction cross-sections and
bimolecular rate constants for the individual reactions

\[ AB^+ + X_2 \rightarrow ABX^+ + X \]
\[ X_2^+ + AB \rightarrow ABX^+ + X \]

where \( AB = CO_2 \) or \( N_2O \) and \( X_2 = D_2 \) or HD, were obtained and compared with theory.

It was found that the overall reaction cross-sections for \( CO_2/D_2 \) and HD systems (i.e. the sum of both reactions) are in agreement with those predicted by the Gioumousis-Stevenson theory. The cross-sections for the analogous N\(_2\)O systems were found to be much smaller than predicted by the G-S theory. It is tentatively suggested, on the basis of the study of the intramolecular isotope effect in \( N_2O/HD \) systems, that the \( N_2O \) reactions require kinetic-internal energy transfer in the transition state before reaction can occur.

In contrast to the good agreement of the overall reaction cross-sections with theory in the \( CO_2 \) systems, it was found that the values for the individual reaction cross-sections did not agree with theory. It was tentatively concluded that the non-isotropic character of the polarizability of the neutral molecule and possibly the orientations of the reactants should be taken into account.
APPENDICES
APPENDIX 1.1
Summary of Runs for the $N_2O/H_2$ Reaction.

Headings used: $N_2O$ = initial pressure of $N_2O$, mm Hg.
$H_2$ = initial pressure of $H_2$, mm Hg.
$R$ = initial Rate, mm Hg/min.

i) Runs at 600°C.

<table>
<thead>
<tr>
<th>Run</th>
<th>$N_2O$</th>
<th>$H_2$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>154</td>
<td>None</td>
<td>$3.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>34</td>
<td>173</td>
<td>102</td>
<td>156.0</td>
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x Runs void as air had entered mixture.
### iii) Effect of Inert Gases

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*p pressure refers to deuterium*
vi) Effect of Nitric Oxide

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APPENDIX 1.2

Determination of Relative Rate Constants

The figure represents two reaction curves with reaction B slower than reaction A (due to substitution of deuterium for hydrogen, reduction in temperature, addition of an inhibitor etc.). The time (e.g. $t_A$ and $t_B$) taken for both reactions to reach the same stage of completion (e.g. $P_t$) is recorded over the whole reaction curve. A plot of the values of $t_A$ v.s. the values of $t_B$ will be a straight line if curves A and B are the same shape (i.e. are congruent, meaning that both reactions obey the same form of rate equation).

The slope of the line of $t_A$ v.s. $t_B$ is the ratio of the overall rate constants for the reactions (e.g. $k_B/k_A$).
APPENDIX 2.1

Summary of Runs for N₂O/CO Reaction

**Measurements used:**
- \( N₂O \) = Initial nitrous oxide pressure, mm Hg.
- \( CO \) = Initial carbon monoxide pressure, mm Hg.
- \( R₉N₂O \) = Initial rate of \( N₂O \) removal, mm Hg/min.
- \( R₉O₂ \) = Initial rate of \( O₂ \) production, mm Hg/min.
- \( G \) = Initial glow, \( 10^{-8} \) amp units.
- \( IG/CO \) = \((\text{Integral glow})/(\text{Rate of} \ CO₂ \text{ formation}) \times 10^{-8} \text{amp.min}²/\text{mm.Hg}\)

**i) Effect of \( H₂O \).**

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N₂O decomposition.
iii) Comparison of Chemiluminescence with \( \text{CO}_2 \) formation.

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v) Mass Spectrometric Analysis of Reaction Mixtures

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<td>50</td>
<td>15.3</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>49 to 51</td>
<td>100</td>
<td>196</td>
<td>20.3</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>159 to 143</td>
<td>151</td>
<td>151</td>
<td>26.5</td>
<td>2.7</td>
<td>Air leak</td>
</tr>
<tr>
<td>177 to 181</td>
<td>151</td>
<td>151</td>
<td>35.0</td>
<td>3.2</td>
<td>Successful (App. 2.2)</td>
</tr>
</tbody>
</table>
APPENDIX 2.2

Mass spectrometric analyses of N₂O/CO reaction mixtures.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time [min]</th>
<th>[N₂O]</th>
<th>ΔP</th>
<th>N₂O⁺</th>
<th>CO₂⁺</th>
<th>O₂⁺</th>
<th>NO⁺</th>
<th>N₂⁺</th>
<th>CO⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero</td>
<td>0.6</td>
<td>130</td>
<td>1.93</td>
<td>1230</td>
<td>204</td>
<td>8</td>
<td>159</td>
<td>215</td>
<td>1120</td>
</tr>
<tr>
<td>177</td>
<td>2.3</td>
<td>95</td>
<td>5.5</td>
<td>850</td>
<td>566</td>
<td>25</td>
<td>130</td>
<td>471</td>
<td>1000</td>
</tr>
<tr>
<td>178</td>
<td>5.4</td>
<td>62</td>
<td>10.0</td>
<td>654</td>
<td>593</td>
<td>44</td>
<td>93</td>
<td>247</td>
<td>675</td>
</tr>
<tr>
<td>179</td>
<td>10.4</td>
<td>30</td>
<td>13.1</td>
<td>544</td>
<td>963</td>
<td>56</td>
<td>88</td>
<td>Not recorded</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>14.6</td>
<td>20</td>
<td>13.5</td>
<td>380</td>
<td>1030</td>
<td>45</td>
<td>52</td>
<td>901</td>
<td>600</td>
</tr>
<tr>
<td>181</td>
<td>20.4</td>
<td>11</td>
<td>12.6</td>
<td>304</td>
<td>993</td>
<td>40</td>
<td>50</td>
<td>768</td>
<td>420</td>
</tr>
</tbody>
</table>

The table above gives the sample time (minutes), the pressure of N₂O and pressure change (mm Hg) and peak heights corresponding to the predominant ions. These values were obtained using a 1:1 N₂O/CO mixture at an initial pressure of 300 mm Hg. Two earlier attempts at analysis of reaction mixtures were not as successful in obtaining meaningful results. In both these cases it was impossible to achieve sufficient resolution to distinguish between N₂O⁺ and CO₂⁺, in one case a slight air leak during the course of the analyses prevented an estimation of oxygen.

The NO⁺/N₂O⁺ ratios are shown below. It can be seen that within experimental error there is no change in the ratio with reaction time.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time</th>
<th>NO⁺/N₂O⁺</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero</td>
<td>0.6</td>
<td>0.142</td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>2.3</td>
<td>0.153</td>
<td></td>
</tr>
<tr>
<td>178</td>
<td>5.4</td>
<td>0.142</td>
<td>0.150 ± 0.015</td>
</tr>
<tr>
<td>179</td>
<td>10.4</td>
<td>0.161</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>14.6</td>
<td>0.137</td>
<td></td>
</tr>
<tr>
<td>181</td>
<td>20.4</td>
<td>0.165</td>
<td></td>
</tr>
</tbody>
</table>
Order of $\text{N}_2\text{O/CO}$ reaction and irreproducibility encountered.

The plots of log (initial rate) vs log (initial pressure) are shown in Figs. a to g. The lines drawn are obtained from a least squares approximation. A chronological list of runs is shown below. An indication is given whether individual runs were faster (+) or slower (-) or the same (=) as the rate suggested by the least squares slopes of the individual order of reaction plots. Also shown are the points at which fresh carbon monoxide or nitrous oxide was prepared.
Fig: a to e.
Order w.r.t. CO.
Fig: f to j
Order w.r.t. N₂O.
<table>
<thead>
<tr>
<th>Run</th>
<th>N₂O</th>
<th>CO</th>
<th>Prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>7</td>
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<td></td>
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<tr>
<td>8</td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
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</tr>
<tr>
<td>18</td>
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<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
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<td></td>
</tr>
<tr>
<td>27</td>
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<td></td>
</tr>
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<td>28</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>29</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Order Plot**

**Gases**

- N₂O
- CO

**Water added**
APPENDIX 3.1

Determination of absorption coefficient in the presence of scattered light.

The figure above represents a typical plot of signal intensity versus nitrous oxide pressure. The scattered light contribution is considered constant and unknown. In order to obtain the true absorption coefficient it would be necessary to correct the measured...
intensities \((I_0, I_1, I_2 \text{ etc.)}\) for the scattered light contribution \(S\).

As pressure \(p_1\) the "true" Beer's Law relationship would be given by:

\[
\frac{I_1 - S}{I_0 - S} = \exp(-k p_1 \, d) \quad \ldots (1)
\]

Where \(k\) = absorption coefficient and \(d\) the light path.

Similarly at another pressure \(p_2\)

\[
\frac{I_2 - S}{I_0 - S} = \exp(-k p_2 \, d) \quad \ldots (2)
\]

If (1) is divided by (2)

\[
\frac{I_1 - S}{I_2 - S} = \exp[-kd (p_2 - p_1)] \quad \ldots (5)
\]

Provided that the pressure difference \((p_2 - p_1) = \Delta p\)

is a constant

\[
\frac{I_1 - S}{I_2 - S} = \text{constant } C \quad \ldots (4)
\]

for any pair of intensities and pressures.

Therefore,

\[
I_1 = C(I_2 - S) + S \quad \ldots (5)
\]

and plots of \(I_1\) against \(I_2\) would yield a straight line of slope \(C\) and intercept \((S - CS)\).

\[
\log_{10} C = \frac{k \, d \, \Delta p}{2.303}
\]

\[
\therefore \, k = \log_{10} \text{ slope, } 2.303 \times (d \cdot \Delta p)
\]
APPENDIX 4.1

Gases used in Ion-Molecule Reactions

Nitrous Oxide - B.O.C. anaesthetic grade
Carbon Dioxide - I.C.I. 99% pure
Hydrogen - B.O.C. standard grade
Deuterium - Matheson Co. C.P. grade 99.8%

Hydrogen deuteride was prepared using the method described by Fookson, Pomerantz and Rich [108] which is outlined below. The whole preparation was carried out on, and the HD obtained stored in, the gas handling system described in Section I of this thesis.

Lithium aluminium hydride (4 g) was added to n-butyl ether (80 ml), the operation being carried out in an N₂ filled dry box. The n-butyl ether had been dried over sodium wire and just before use was distilled from sodium to ensure perfect dryness. A slurry of LiAlH₄ in the ether was obtained. This slurry was contained in a two-necked 250 ml quickfit flask which was fitted with a magnetic stirrer. One neck of the flask was closed with a rubber spatula cap and the other was attached to a double surface reflux condenser. The flask and reflux condenser were then attached via a liquid air cold trap to the vacuum system.

The slurry was frozen in liquid air and the whole apparatus evacuated. The mixture was allowed to warm to room temperature with the vacuum switched off. The mixture was again frozen in liquid air and 3 ml of D₂O (I.C.I. 99.8% pure) was added from a syringe through the spatula cap. The mixture was allowed to melt and was stirred continuously. Under these conditions HD was evolved slowly. If the reaction mixture became too warm (signalled by the melting of frost collected round the sides of the flask) the reaction was slowed down by re-immersing the flask in liquid air.

After about 1 hour the reaction became very slow. The reaction...
mixture was frozen and a further 3 ml of D₂O added. This was repeated 1 hour later when 4 ml of D₂O was added. After about 3 hours 5 litres of HD at about 700 mm Hg pressure had been collected. The gas was stored and this was transferred to the mass spectrometer gas line when required.

Mass spectrometric analysis of the hydrogen deuteride showed that it was about 98% pure.