THE PYROLYSIS OF SOME AROMATIC HYDROCARBONS

by

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

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The work presented in this thesis was carried out at the London Research Station of the British Gas Corporation in collaboration with the Physical Chemistry Department of University of Surrey under the supervision of Dr. C.T. Brooks at the London Research Station and Dr. B.G. Reuben at the University of Surrey. I wish to say how grateful I am to Dr. Brooks and Dr. Reuben for all their help, friendship and encouragement.

I am grateful to the British Gas Corporation for allowing me to carry out the work in this thesis.

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

Mr. J. Williamson and Mr. T. Laker of the analytical section of the London Research Station for carrying out the mass spectroscopic and X-ray diffraction work.

S.I.R.A. for carrying out the electron microscopy work.

Dr. N.D. Parkyns and Mr. G.H. Rhodes of the London Research Station for helpful discussion of the work described here.

My wife, Kathy, and Miss Liz Caswell for the hard work and trouble that they have taken in the typing of the manuscript.

And finally to my wife for her patience and understanding while I was carrying out the work in this thesis.
ABSTRACT

The Pyrolysis of some Aromatic Hydrocarbons

The pyrolyses of benzene and ethyl benzene in a nitrogen carrier in a static system were investigated. Some high temperature/low residence time experiments were also performed with benzene in a flow system. Product analysis was by gas chromatography.

Between 913 and 1053K benzene pyrolyses by a free radical chain mechanism. Hydrogen and diphenyl are the major products. The rate expression

\[ \frac{d[H_2]}{dt} = 10^{9.83} \exp(-27,100/T) \left[ C_6H_6 \right]^{3/2} \text{ mole litre}^{-1} \text{ sec}^{-1} \]

applies between 952 and 1030K and may be explained by a simple five-step mechanism. At lower temperatures, the experimental activation energy is lower than that predicted by theory.

Above 1053K, the benzene ring opens and acetylene, ethylene, methane and solid carbon are produced. Many polynuclear hydrocarbons were found to be adsorbed on the carbon and their presence suggests a mechanism for carbon formation.

Pyrolysis of ethyl benzene gives hydrogen and styrene as the major products together with methane, toluene, ethylene, ethane and benzene plus traces of higher molecular weight hydrocarbons. The pyrolysis is a chain reaction with a chain length of the order of 10 initiated by

\[ C_6H_5C_2H_5 = C_6H_5CH_2 + CH_3 \]

for which

\[ k = 14.4 \exp(-35,300/T) \text{ sec}^{-1}. \]

This agrees well with previous work involving toluene and aniline carriers.
The results may be explained by a complex mechanism involving free radicals, \(\text{CH}_3\), \(\text{C}_6\text{H}_5\text{CH}_2\), \(\text{C}_6\text{H}_5\text{CHCH}_3\), \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\), \(\text{C}_2\text{H}_5\), \(\text{C}_6\text{H}_5\) and \(\text{H}\).

Termination seems to occur mainly by the disproportionation reaction:

\[2\text{C}_6\text{H}_5\text{CHCH}_3 = \text{C}_6\text{H}_5\text{CH}:\text{CH}_2 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5\]

For the reaction:

\[\text{C}_6\text{H}_5\text{CHCH}_3 = \text{C}_6\text{H}_5\text{CH}:\text{CH}_2 + \text{H}\]

a rate constant:

\[k = 10^{15.9} \exp (-26,200/T) \text{ sec}^{-1}\]

was deduced.
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**SECTION 4. OVERALL SUMMARY AND SUGGESTIONS**

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**REFERENCES**

**APPENDIX I**

Calculation of thermodynamic data by additivity and activation energies by BEBO methods.

**APPENDIX II**

Estimation of pre-exponential factors by Benson's methods

**APPENDIX III**

Heat of reaction calculation
NOTES.

1. In general diagrams and plates are included in the page immediately following reference to them in the text.

2. List of references are included at the end of section 4 and appendix 2.

3. C.G.S. units are used throughout this thesis and activation energies are quoted in calories mole\(^{-1}\). (1 cal = 4.18 Joules).

4. A line above a formulae represents a free radical

   e.g. \(\overline{\text{CH}_3}\) = methyl radical.

SOME COMMON TERMS USED IN THIS THESIS.

\[\begin{align*}
  k &= \text{rate constant.} \\
  A &= \text{pre-exponential factor.} \\
  E &= \text{activation energy.} \\
  T &= \text{Absolute temperature.} \\
  G^0 &= \text{Standard free energy.} \\
  K_p &= \text{Equilibrium constant.} \\
  S &= \text{entropy.}
\]
The work presented in this thesis deals with homogeneous gas phase hydrocarbon reactions which could possibly occur when fossilised fuels are turned into substitute natural gas. The thesis is divided into three sections.

Section one deals with the industrial significance of the work, and includes a brief description of the commercial processes.

The second section of the thesis deals with the pyrolysis of benzene both at relatively low temperatures, in which the ring remains largely intact and at higher temperatures, in which the ring opens and large quantities of carbon are formed. Benzene is an important feedstock constituent and reaction intermediate in these homogeneous gas making processes. Berthelot, over 100 years ago, observed hydrogen and diphenyl to be the major products at low temperatures and wrote that these products were, "rattachées à la benzine par des relations tres-simple". However, the kinetics and mechanism of this important reaction are still largely unknown. A considerable number of workers have studied the pyrolysis in the high temperature region but little agreement can be found regarding the reaction mechanism. In this section of the thesis, kinetics and mechanism of the low temperature pyrolysis are proposed and then extended to account for the experimental data obtained for the high temperature reaction. A brief study of the surface properties of the carbon produced is included and possible routes for its formation discussed.

Other industrially important pyrolysis reactions are the group involving the dealkylation of substituted benzenes. In the work discussed in section three the pyrolysis of ethyl benzene is chosen, since this aromatic compound also is thermally fairly stable in industrial gas making plant, and its presence may contribute to carbon formation via a styrene intermediate.
Previous studies of the pyrolysis of ethyl benzene have been carried out using the "toluene carrier technique" developed by Szwarc\textsuperscript{2}. This work considers the ethyl benzene pyrolysis in the absence of carriers. Kinetic data obtained are compared with the results obtained by carrier methods and from the results a reaction mechanism is proposed. A discussion of the consequences of the work in this thesis and its relevance to hydrogen processing of oils is included.
SECTION ONE

INDUSTRIAL BACKGROUND
In the last 30 years there has been a tremendous growth in the world's demand for energy. Demand in Western Europe and Japan has risen from 450 million tons of oil equivalent in 1950, of which the bulk was derived from coal, to 1300 million tons of oil equivalent in 1970 of which about two thirds was derived from crude oil and natural gas. This has recently been accompanied by a rapid increase in the price of the fuel.

Attempts to find cheaper feedstocks have resulted in interest in the heavier and less easily used ends of the oil barrel. Any process that can convert these fractions into a premium fuel such as methane is attractive. In the past, catalytic processes have been used for methane manufacture, but no catalytic process has been developed for the gasification of these heavy fractions. Homogeneous processes, which offer one solution to the problem, are being developed.

Thermal hydrogenation processes have been the subject of intensive research both in the U.K. and U.S.A., where the work of Linden et al.\(^4\) established conditions for the rapid breakdown of hydrocarbons to methane. British work however, took the effort a stage further, and Dent and his co-workers\(^5\) were able to develop full scale processes to achieve methane production from oil hydrogenation. Homogenous thermal hydrogenation processes are carried out in units called the gas recycle hydrogenator (GRH) and the fluidized bed hydrogenator (FBH). These plants are shown diagrammatically in fig. 1.1. Typical operating conditions and results have been summarised by Brooks and Thompson\(^6\) and their data are summarised in tables 1 and 2. In order to maximise methane formation and minimize side reactions attempts are made to optimise the stoichiometry of the reaction

\[
8C_{x\text{H}_y} + (16x - 4y)\text{H}_2 = 8x\text{CH}_4
\]
FIG: 1.1 Plant for the production of substitute natural gas by homogeneous processes.
where \( C_{xH_y} \) represents the average composition of the hydrocarbon feedstock.

To achieve this in the plant, at a pressure of 300 psi, a residence time of 15 seconds is employed. The plant is operated above 700°C so that the reaction can be sustained by exothermicity, but below 780°C to prevent carbon formation.

**The Gas Recycle Hydrogenator**

This plant is suitable for processing crude petroleum distillate fractions boiling up to about 326°C. The feedstock, which does not need to be free from sulphur compounds, is vaporized by heat exchange with hot product gas and mixed with preheated hydrogen rich gas. The exothermic hydrogenation reaction occurs in the specially designed vessel in which the temperature is controlled by the rapid recycling of reactants and product. Paraffins and naphthenes are decomposed to methane and ethane. Aromatics are dealkylated but the parent ring remains unbroken and is later separated as a purified aromatic condensate. After cooling, the product gas is hydrodesulphurised over nickel molybdate and zinc oxide before being scrubbed to remove condensate. Typical operating conditions and results are shown in table 1.

**The Fluidized Bed Hydrogenator**

This process will gasify crude oil, fuel oil, and a wide range of refinery fractions. The crude feedstock is preheated and atomized at the base of a bed of coke particles fluidized by a supply of preheated hydrogen rich gas. The fluidized bed recirculates within the reactor thereby effecting reaction temperature control and providing a receiver and support for the non-volatile content of the oil during hydrogenation.
Deposited carbon forms part of the burden which can be rejected if necessary during operation to maintain the bed depth. The hydrogenation reaction is exothermic and self-sustaining. As in the GRH, paraffins and naphthenes are decomposed to methane and ethane. Similarly aromatics are dealkylated but the parent ring remains unbroken and is separated as an aromatic condensate containing a high proportion of benzene with some toluene, xylene, naphthalene and higher polycyclics. Part or all of this aromatic product can be used as plant fuel. The gas is quench cooled and the high boiling condensate is separated. The gas is desulphurised with nickel molybdate and zinc oxide to yield pipe line quality gas. Typical operating conditions and results are shown in table two.
### TABLE 1

**TYPICAL CONDITIONS AND RESULTS OBTAINED IN A GAS RECYCLE HYDROGENATOR**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Naphtha LD170</th>
<th>Kerosine</th>
<th>Gas Oil</th>
</tr>
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<tr>
<td><strong>Operating Conditions</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pressure psig</td>
<td>900</td>
<td>305</td>
<td>305</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>725</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td><strong>Product Gas Composition</strong></td>
<td>% by Volume</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.2</td>
<td>6.8</td>
<td>7.5</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>0.8</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>2.1</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂</td>
<td>24.8</td>
<td>41.7</td>
<td>41.2</td>
</tr>
<tr>
<td>CH₄</td>
<td>47.1</td>
<td>31.3</td>
<td>29.6</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>24.3</td>
<td>15.3</td>
<td>16.3</td>
</tr>
<tr>
<td>N₂</td>
<td>1.0</td>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### TABLE 2

**TYPICAL CONDITIONS AND RESULTS OBTAINED IN A FLUIDISED BED HYDROGENATOR**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Algerian Crude</th>
<th>Middle East Crude</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating Conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure psig</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td><strong>Product Gas Composition</strong></td>
<td>% by Volume</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>CO</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>H₂</td>
<td>21.7</td>
<td>35.2</td>
</tr>
<tr>
<td>CH₄</td>
<td>57.5</td>
<td>48.2</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>18.3</td>
<td>13.9</td>
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</table>
SECTION TWO

THE PYROLYSIS OF BENZENE
INTRODUCTION

Benzene is the simplest aromatic hydrocarbon and has been widely studied. Many of its reactions are quite well understood from both a theoretical and an experimental viewpoint. Pyrolysis is an exception. Although various pyrolysis studies have been carried out the kinetics and mechanism of the reaction are still uncertain.

Apart from the intrinsic interest of the reaction mechanism, the pyrolysis has many industrial applications in connection with diphenyl production and carbon formation. Accordingly the reaction has been studied from both viewpoints. 1,7,8

Studies date back to Berthelot who found the principle products of decomposition to be diphenyl and hydrogen. This was confirmed some years later by Schultz 9,10 who suggested that small amounts of meta and para diphenyl benzenes were also formed. Much of the work during the early part of this century 11-19 was involved with identification of the reaction products. All workers agreed that hydrogen and diphenyl were the major products. Some investigators 19 found ortho diphenyl benzene but this was disputed by others.16

Probably the ortho diphenyl benzene was converted into triphenylene, although when Bachmann and Clarke 16 pyrolysed it they obtained diphenyl and carbon only.

Ring opening was a feature of reaction that held the attention of early workers. Bolton and co-workers 20 found an increase in methane yield as the temperature rose above 1023K, and attributed this to, "carbon to carbon decomposition of the benzene molecule." Kinney and Del Bel 21, however, suggested that "the methane is split out from the more or less randomly oriented condensed aromatic ring, characteristic of the first stages of carbon formation," i.e. the rings tend to shift into a graphite type structure. At reaction temperatures of 1073-1273K these workers 21
found traces of acetylene in contrast to the work of Zanetti and Egloff who found none. It was observed that carbon deposition was favoured by silica brick packing of the reaction vessel but that quartz and mullite packing increased the yield of diphenyl. Iley and Riley found three types of carbon deposited which resembled macrocrystalline graphite. Badger and Novotny in a detailed investigation identified diphenyl as the major product with significant amounts of para-diphenyl, meta-diphenyl benzene and triphenylene at reaction temperatures of 973K. Fluorene, phenanthrene and possibly ortho diphenyl benzene were also detected. Methane and ethylene were found in the exit gases.

Thus it appears that there are two distinct categories of reaction. The simplest case gives diphenyl and hydrogen

\[ 2C_6H_6 = (C_6H_5)_2 + H_2 \]

and a more complex reaction at higher temperatures, in excess of 1023K occurs, in which the benzene ring opens.

Pease and Morton studied the reaction in static and flow systems and suggested that it was a normal first order homogeneous gas reaction. At 903K 5% of the benzene decomposed giving equivalent amounts of hydrogen and diphenyl in the product gases.

On the other hand at reaction temperatures between 1023 and 1125K in a flow system Mead and Burke found the reaction to be heterogeneous and bimolecular. The reaction was strongly retarded by adsorption of products on the surface of the reaction vessel. Steel chips in the reaction vessel had a catalytic effect.
The rate equation: \[ \frac{dx}{dt} = \frac{k(a-x)^2}{x} \] (i)

where \( a \) = initial concentration

\( x \) = amount of decomposition

fitted the experimental data and an activation energy of 50,000 cals mole\(^{-1}\) was obtained.

Rudenko\(^{24-28}\) showed a heterogeneous reaction to occur on the surface of added quartz chips.

Slysh and Kinney\(^{29}\) showed that at 1200K in a flow system with helium as a carrier gas the reaction was first order with a rate constant of 20.6 sec\(^{-1}\). Residence times of between 4 and 112 milliseconds were obtained by the use of rapid flows through small bore tubes. Products consisted almost entirely of hydrogen, acetylene and diacetylene together with diphenyl. For first order reactions, pre-exponential factors of between \( 10^{14} \) and \( 10^{16} \) are typical. On this basis the rate constant of 20.6 sec\(^{-1}\) would correspond to an activation energy of 70,000 to 80,000 cals. mole\(^{-1}\).

As a result of a study of carbon film deposition in a flow system, Murphy, Palmer and Kinney\(^{30}\) obtained the rate expression (ii) for benzene decomposition.

\[ k = 5.60 \times 10^{16} \exp\left(-\frac{102,000}{RT}\text{ cal.}\right) \text{ sec}^{-1} \] (ii)

First order kinetics were obtained and a molecular mechanism was suggested.

Aten and Bauer\(^{31}\), in an attempt to ensure homogeneous reaction conditions, used a shock tube with a shock temperature in the neighbourhood of 1500K, and used initial rates of reaction in their calculations. They deduced the occurrence of a chain reaction with an overall activation energy of 40,000 cals. mole\(^{-1}\).
To account for this low value they proposed the following mechanism:

**Initiation:**
\[ C_6H_6 = C_6H_5 + H \]  
(1)

**Propagation:**
\[ C_6H_6 + H = C_6H_5 + H_2 \]  
(2)
\[ C_6H_5 = C_4H_3 + C_2H_2 \]  
(4)
\[ C_4H_3 = C_4H_2 + H \]  
(5)
\[ C_6H_6 + C_4H_3 = C_6H_5 + C_4H_4 \]  
(6)

**Companion Chain:**
\[ C_6H_5 = C_4H_4 + C_2H \]  
(7)
\[ C_6H_6 + C_2H = C_6H_5C_2H_2 \]  
(8)
\[ C_4H_4 = C_4H_2 + H_2 \]  
(9)

**Termination:**
\[ 2C_6H_5 = C_{12}H_{10} \]  
(3)
\[ 2C_4H_3 = C_8H_6 \]  
(10)
\[ C_6H_5 + C_4H_3 = C_{10}H_8 \]  
(11)

For termination via reaction 11 and by ignoring the companion chain they derived the rate expression (iii)

\[ - \frac{d[C_6H_6]}{dt} = \frac{k_4k_5}{k_{11}} + \left( \frac{2k_1}{k_{11}} + \frac{k_4k_6}{k_{11}} \right) [C_6H_6] \]  
(iii)

They proposed that \( E_4 = 83,000 \text{ cals mole}^{-1} \), \( E_6 = 22,000 \text{ cals mole}^{-1} \) and \( E_{11} = 0 \text{ cals mole}^{-1} \). Hence on this basis the apparent activation energy is \( (E_4 + E_6 - E_{11}) \) i.e. 105,000 cals mole\(^{-1}\).

This is approximately twice the observed value. If quadratic termination is considered (e.g. step 3) 52,500 cals mole\(^{-1}\) is predicted.

Hou and Palmer\(^{32}\) studied the pyrolysis at 1173 to 1523K with residence times from 20 to 250 m secs. in a conventional flow system. In order to explain their results, complex kinetics involving concurrent first and second order reactions were invoked. The first order reaction yielded the rate expression (iv)
k₁ = 10^{9.5} \exp (-51,000/RT) \text{ sec}^{-1} \quad \text{(iv)}

The reaction was assumed to occur via a chain mechanism similar to that proposed by Aten and Bauer. It was suggested that the low activation energy was a result of the stable phenyl radicals decomposing on the reaction vessel wall in a chain propagation step:\n
\[ \text{C}_6\text{H}_5 = \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \quad \text{(4)} \]

The second order contribution yielded the rate expression: \( k_2 = 10^{11.0} \exp(-40,000/RT) \text{ litre mole}^{-1} \text{ sec}^{-1} \) \quad \text{(v)}

This contribution was postulated to be the homogeneous bimolecular formation of diphenyl and hydrogen via a four-centre intermediate.

Fields and Meyerson pyrolysed monodeuterated benzene at 963K and observed significant scrambling of hydrogen and deuterium in the recovered benzene and product diphenyl. Their results are summarised in table one.

<table>
<thead>
<tr>
<th>No. of D Atoms</th>
<th>Rel. abundance</th>
<th>4.2-Sec. contact</th>
<th>21-Sec. contact</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzene</td>
<td>Diphenyl</td>
</tr>
<tr>
<td>0</td>
<td>10.5</td>
<td>7</td>
<td>27.1</td>
</tr>
<tr>
<td>1</td>
<td>84.5</td>
<td>31</td>
<td>52.6</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
<td>53</td>
<td>17.3</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>9</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>...</td>
<td>...</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>...</td>
<td>...</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The isotopic composition of the diphenyl produced corresponded to that of the benzene that had undergone exchange. They interpreted this as evidence for a molecular mechanism possibly via a phenylcyclohexadiene intermediate.
Reaction (12), however, can also lead to a random loss of 1 atom.

\[
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = \text{C}_{12}\text{H}_{10} + \text{H}
\]  
(12)

Several cannonical structures can be written for the intermediate radical.

\[
\text{e.g.}
\]

Their argument is therefore inconclusive.

Mar'yasin and Nabutovskii\(^{34}\) have carried out the pyrolysis of benzene in shock waves generating reaction conditions of 1400 to 2500K with 6 to 12 milliseconds residence times. Samples after reaction were automatically selected and analysed by gas-liquid chromatography. Gaseous products of hydrogen, methane, ethylene, vinylacetylene and diacetylene as well as carbon black were obtained. For the disappearance of benzene a second order rate equation was proposed and rate constants were calculated from expression (vi)

\[
k = 10^{15} \exp (-77,000/RT) \text{ litre mole}^{-1} \text{ sec.}^{-1}
\]

An abrupt increase in the amount of acetylene produced as the reaction temperature rose above 1750K was attributed to the start of the fragmentation of the benzene ring.

Asaba and Fujii\(^{35}\) recently used a shock tube to study the high temperature pyrolysis of benzene between 1400 and 1900K. The second order rate expression (vii) was obtained:

\[
k = 10^{9.5} \exp (-30,000/RT) \text{ litre mole}^{-1} \text{ sec.}^{-1}
\]

The previously postulated molecular mechanisms were questioned.
They showed that the reaction was promoted by methane. This was possibly due to attack on the benzene by hydrogen atoms produced in methane pyrolysis. This was considered evidence for a chain mechanism. Also, an induction period was observed in some photo-electric experiments. Although a complex chain was proposed, it consisted essentially of the following reactions.

Initiation: \[ \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \overline{\text{H}} \] (1)

Propagation: \[ \text{C}_6\text{H}_6 + \overline{\text{H}} = \text{C}_6\text{H}_5 + \text{H}_2 \] (2)

\[ \text{C}_6\text{H}_6 + \text{C}_6\text{H}_5 = \text{C}_{12}\text{H}_{10} + \overline{\text{H}} \] (12)

Termination: \[ \overline{\text{C}}_6\text{H}_5 = \overline{\text{C}}_6\text{H}_2 + \text{C}_2\text{H}_2 \] (4)

A stationary state approximation leads to the rate expression (viii)

\[-d[C_6H_6]/dt = 2k_1[C_6H_6] + 4k_1k_{12}/k_4[C_6H_6]^2 \] (viii)

Methods due to Benson\textsuperscript{36} were invoked to show that:

\[ 4k_1k_{12} = 10^{-3} \exp(-31,000/RT) \text{ litre mole}^{-1} \text{ sec}^{-1} \] (ix)

For long chains the \[ 2k_1[C_6H_6] \] contribution in expression (viii) can be ignored. Thus they suggested that agreement between expression (ix) and experiment was good.

In a study carried out concurrently with this work Louw and Lucas\textsuperscript{37} used a "tank flow reactor" system to establish the free radical nature of the reaction although the exact mechanism was not established.

Reaction order was found to be 3/2. The mechanism proposed was:

Initiation: \[ \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \overline{\text{H}} \] (1)

\[ 2\text{C}_6\text{H}_6 = \text{C}_6\text{H}_7 + \text{C}_6\text{H}_5 \] (13)

Propagation: \[ \overline{\text{H}} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_7 \] (14)

\[ \overline{\text{H}} + \text{C}_6\text{H}_6 = \text{H}_2 + \text{C}_6\text{H}_5 \] (2)

\[ \text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = \overline{\text{H}} + \text{C}_{12}\text{H}_{10} \] (12)

Termination: \[ \text{C}_6\text{H}_7 + \text{C}_6\text{H}_7 = 2\text{C}_6\text{H}_6 + \text{H}_2 \] (15)

\[ \overline{\text{C}}_6\text{H}_7 + \overline{\text{H}} = \text{C}_6\text{H}_6 + \text{H}_2 \] (16)
The above literature review leads to the following problems and conclusions.

(a) At temperatures above 1073K there is a wide variation in the results presented. A tenfold variation in reported rate is not exceptional. Results obtained are summarised in Fig.1.2.

(b) At these high temperatures ring opening occurs and large quantities of carbon are formed.

(c) There is little agreement on orders of reaction.

(d) Little evidence has been presented for the chain nature of the reaction or for the participation of atoms and radicals. Some investigators favour a molecular mechanism.

(e) Below 1073K where the reaction

\[ 2C_6H_6 = C_{12}H_{10} + H_2 \]

predominates few kinetic studies have been performed.

(f) There is a difference of opinion regarding the role of the surface in the reaction.

Table 1.1 summarises the kinetic data obtained to date.

In this work it is hoped to determine the nature of the low temperature reaction and describe the kinetics of diphenyl formation and benzene decomposition. Once this has been achieved, it may be possible to extend the work to higher temperatures and study the fragmentation of the benzene ring.
FIG. 1: Summary of benzene pyrolysis rate data

(Arrows indicate scale to be used.)

**Key**
- ○ Asaba & Fujii (ref. 35)
- ◯ Hou & Palmer (2nd order rate const.) (ref. 32)
- □ " " (1st " " " " ) ( " 32)
- ● Slysh & Kinney (corrected by Hou & Palmer (ref. 29)
- ◼ Murphy Palmer & Kinney (ref. 30)
- ● Hou & Palmer (corrected by Asaba & Fujii assuming $k = 10^{16.1} \exp(-98\text{ kcal}/\text{RT}) \text{ sec}^{-1}$)
- Line A from Mar'yasin & Nabutobskii (ref. 34)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Order</th>
<th>Activation energy (cals mole$^{-1}$)</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pease &amp; Morton (17)</td>
<td>1st order</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Meade &amp; Burk (18)</td>
<td>2nd order</td>
<td>50,000</td>
<td>...</td>
</tr>
<tr>
<td>Slysh &amp; Kinney (29)</td>
<td>1st order</td>
<td>80,000*</td>
<td>20.6</td>
</tr>
<tr>
<td>Murphy et al (30)</td>
<td>1st order</td>
<td>102,000</td>
<td>$5.60\times10^{16}\exp(-102000/RT)$</td>
</tr>
<tr>
<td>Aten &amp; Bauer (31)</td>
<td>...</td>
<td>40,000</td>
<td>...</td>
</tr>
<tr>
<td>Hou &amp; Palmer (32)</td>
<td>Mixed 1st order</td>
<td>51,000</td>
<td>$k_1=10^{9.5}\exp(-51000/RT)$</td>
</tr>
<tr>
<td></td>
<td>2nd order</td>
<td>40,000</td>
<td>$k_2=10^{11.0}\exp(-40000/RT)$</td>
</tr>
<tr>
<td>Maryasin and Nabutovskii (34)</td>
<td>2nd order</td>
<td>77,000</td>
<td>$10^{15.0}\exp(-77000/RT)$</td>
</tr>
<tr>
<td>Asaba &amp; Fujii (35)</td>
<td>2nd order</td>
<td>30,000</td>
<td>$10^{9.5}\exp(-30000/RT)$</td>
</tr>
<tr>
<td>Louw &amp; Lucas (37)</td>
<td>3/2 order</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Chambers et Al (38)</td>
<td>1st order</td>
<td>52,600</td>
<td>$10^{8.6}\exp(-52,600/RT)$</td>
</tr>
</tbody>
</table>

a. 1st order units: sec$^{-1}$

b. 2nd order units: litre mole$^{-1}$sec$^{-1}$

* Activation energy estimated from their results.
EXPERIMENTAL

The majority of the work described in this thesis was carried out in a static apparatus. It consisted of a vacuum line, sections of which were fitted with high vacuum stainless steel bellows valves. This made possible the study of the pyrolysis of relatively high boiling liquids.

Some experiments where a small residence time was required were carried out using a linear flow method.

The Static Apparatus

A general view of the apparatus together with a line diagram is shown in plate 1.

The apparatus consists of four sections.

a) a vacuum line
b) a gas handling system
c) a reaction vessel
d) a sampling and analytical system

a) Vacuum line

A conventional vacuum line, constructed from pyrex tubing was used. Vacuum was achieved by means of an Edwards ED75, two stage, rotary oil pump together with an Edwards E02 silicon oil diffusion pump. A trap, at liquid nitrogen temperatures, was incorporated between the pumping system and the vacuum line. This prevented back diffusion of pump oil and ensured an ultimate pressure in the system of less than \(10^{-4}\) torr, although a pressure of \(10^{-3}\) torr was considered acceptable for most work. Vacuum was measured using an Edwards Pirani gauge (C).

Globe (A) was used as a storage vessel in which gas mixtures were kept, or alternatively as a temporary storage vessel for gas mixtures that were to be introduced into the reaction vessel.
Plate 1. Diagram & general view of the static apparatus.
The mercury manometer (H) was used to calibrate the pressure transducer (F).

There were three gas inlets, labelled 1, 2 and 3. Each incorporated a trap, which could be cooled if necessary to facilitate further purification. Nitrogen was purified by passage through a tube containing copper turnings heated to 350°C by the furnace (B). This removed any traces of oxygen in the nitrogen.

A removable "cold finger" trap which could be maintained at liquid nitrogen temperature was incorporated between the vacuum line and the gas handling system. This was used to prevent contamination of the unheated glassware by reactant and products. The stop-cocks on the vacuum line were greased with Apiezon M grease. For some of the later runs with ethyl benzene the line was rebuilt with greaseless taps, containing teflon and neoprene "O" rings, manufactured by J. Young and Co. of Acton.

b) The gas handling system

The gas handling system is the section of the apparatus enclosed by the dotted line on plate 1. It was constructed of thin wall stainless steel tubing 1⁄4 inch o.d. Connection to the vacuum line was with a glass-to-metal Covar seal. The whole section could be heated to about 423K by heating tape.

The reactant liquid was stored in the pyrex reservoir (J) and connected to the system by a glass-to-metal seal.

Globe (D) was used for mixing and (E) for sampling. These were heated in an enclosure fitted with a fan to level out temperatures.

Mixture pressures were measured by the pressure transducer (F).
This pressure transducer was an E.M.I. (S.E.Laboratories Division) Type SE 180. The coils were encapsulated in epoxy resin. This enabled it to be used at temperatures up to 448K. The unit was controlled by a SE905 convertor box and the millivolt output measured by a Solartron digital voltmeter. A typical calibration graph is shown in Fig. 1:3(a). The system is capable of measuring pressure differences of 0.01 torr.

The taps on the gas handling system were Hoke series 4100 stainless steel bellows sealed valves and connections were made with Hoke Gyrolok \( \frac{1}{2} \)" stainless steel fittings. For leak tight operations (especially at high temperatures) sealing of the valve is achieved by a thin stainless steel bellows. One end of the bellows is sealed to the valve stem and the other to a fixed ring. The tapered regulating stem makes possible a limited degree of metering. Long lifetime and leak-free use was obtained from these taps, which only ceased to function properly when the valve seats became damaged and gas leaked across the seat.

c) The Reaction Vessels

Cylindrical clear silica reaction vessels, of the dimensions shown in Table 1:3 were used. Most experiments involved vessel A, the others being used to test for heterogenous behaviour.

**TABLE 1:3**

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
<th>Surface/Volume Ratio (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>60</td>
<td>200</td>
<td>0.077</td>
</tr>
<tr>
<td>B</td>
<td>45</td>
<td>200</td>
<td>0.100</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>200</td>
<td>0.143</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>200</td>
<td>0.205</td>
</tr>
<tr>
<td>E*</td>
<td>10</td>
<td>200</td>
<td>1.105</td>
</tr>
</tbody>
</table>

*Packed with \( \frac{1}{2} \)" thin wall silica tubes.*
FIG 1: 3a Typical transducer calibration plot

FIG 1: 3b Temperature pattern in furnace
Vessels were pretreated by washing successively with carbon tetrachloride, methanol, concentrated nitric acid and distilled water. Before use vessels were pumped for at least twenty four hours, at the reaction temperature.

The reaction vessel was housed in a tubular furnace 24ins long by 12ins diameter, manufactured by Carbolite Ltd. It had 3 windings each of which was wired in series and connected to a separate rheostat. An even temperature over the length of the reaction vessel could be achieved by adjustment of the current through the end windings. A typical temperature pattern is shown in Fig.1:3(b).

Temperature was controlled to within ± 0.5°C by an AEI platinum resistance thermometer controller and was measured with a chromel-alumel thermocouple attached to a Digitec, 0 to 40.00 mV range, digital voltmeter.

d) **Sampling and Analytical System**

After reaction, the reaction mixture was passed through a U-trap cooled with an acetone-cardice mixture, and into a gas chromatograph gas sampling loop. Gases were analysed directly. Liquid and solid products were trapped in the U tube which was constructed of very thin walled stainless steel. It was controlled by two Hoke stainless steel two way taps. The arrangement is shown in Fig.1:4(a).

For liquid and solid product analysis the taps were set so that carrier gas flowed through the U trap, down a thin walled stainless steel transfer line and through a "precolumn" of silicone gum rubber on chromasorb G, before entering the gas chromatograph. The U tube and transfer line were heated whilst the precolumn was cooled with an acetone-cardice mixture. Products were compressed to a small slug on the precolumn. On removal of the cold bath products were swept directly onto the column of the gas chromatograph.
FIG. 1:4a Product sampling system

FIG. 1:4b Dead space volume
This was a Perkin Elmer F11 fitted with a flame ionization detector.

A $\frac{1}{4}$" o.d. silicone oil/bentone on chromasorb W column was used for liquid product analysis. For polynuclear solid products a $\frac{1}{4}$" o.d. silicone gum rubber on chromasorb G column gave a more satisfactory separation. The oven temperature was 150°C and nitrogen carrier gas at 15 p.s.i. inlet pressure was used for both analysis.

Another Perkin Elmer F11 was used for gas analysis. The sample contained in a 50c.c. loop was injected into the chromatograph via a Loenco valve. A large volume loop could be used without peaks being smeared out because mixture pressures were usually 200 torr and never went above 400 torr. Nitrogen carrier at 35 p.s.i. then compressed the sample into a small slug which was separated on a 4 metre $\frac{1}{4}$" o.d. charcoal column. The oven temperature was 150°C. Hydrogen was analysed by a hot wire detector, but, for hydrocarbon gas analysis a flame ionisation detector in series with it was used.

Peak area measurements were made using a Honeywell electronic integrator.

**Some potential errors in the system**

i) The largest potential error in a static apparatus is that due to the dead space volume. This is the volume containing reactant which is not heated to the reaction temperature. In the system shown in figure 1:4b the dead space was made up of the inlet glass capillary (0.2c.c.), the metal system (0.5c.c.) and the volume of the transducer(0.5c.c.). Altogether, this comprises only 0.2% of the volume of a typical reaction vessel and was considered negligible.

ii) The error due to the time taken for the pressure and temperature of the reaction mixture to reach the equilibrium value was also thought to be negligible.
With the transducer on its most sensitive setting, equilibrium pressure was seen to be reached in a time of less than 0.5 seconds. This time is small compared with the residence times used of 30 seconds to 10 minutes.

iii) It is possible for the heat of reaction to be such that the temperature at the centre of the reaction vessel is different from the furnace temperature. Benzene pyrolysis is almost thermoneutral ($\Delta H = 3000 \text{ cals. mole}^{-1}$) and this effect is also negligible. These errors therefore were considered to have no observable effect on the pyrolysis and in future experiments and discussion were ignored.

**The Flow Apparatus**

A simple flow apparatus operating at atmospheric pressure was built to enable benzene pyrolysis at high temperatures and small residence times to be investigated. A line diagram of the system is shown in figure 1:5. Nitrogen was used as a carrier gas and its flow was controlled by a needle valve and measured on a Matheson rotameter (A) which was monitored by a soap bubble flowmeter (G).

Benzene was admitted to the system by a simple saturator device (B). This comprised two traps maintained at a constant temperature ($\pm 0.5^\circ C$) by a cold water bath. The nitrogen bubbled, via a sintered disc, through the liquid and introduced a known quantity of vapour into the system. This depended on the vapour pressure of benzene at the bath temperature.

Residence time was varied by alteration of the flow of nitrogen through the by-pass stream (2). Streams (1) and (2) were allowed to mix and then enter the reaction vessel (C).

For the runs in which the collection of large quantities of products was desired, operating conditions of the system were similar to those in the static apparatus.
Fig 1:5  Line diagram of the flow apparatus
Accordingly a furnace and reaction vessel of similar dimensions were employed.

In order to obtain small residence times a small furnace, shown diagrammatically in figure 1:6(a), was constructed using nichrome tape (12.57 ohms per yard) wound round a silica tube former. The whole was held in place with Autostick high temperature adhesive. A typical temperature profile is shown in figure 1:6(b). It is not good, but as precise kinetic parameters were not required it was considered adequate.

The accurate measurement of reaction temperatures of the order of 1173 to 1273K presented a problem. Radiation errors were minimized by use of a fine gauge (0.125 mm diameter) Pt/Pt13%Rh thermocouple. The gas stream temperature was measured prior to reaction. During reaction the thermocouple was removed. Plug flow was assumed for the calculation of residence times although laminar flow almost certainly occurred.

Solid and liquid products were collected in trap (D) which was maintained at -83°C by an acetone/solid carbon dioxide bath. Trap(E) was maintained at 0°C and prevented any carry-over of products into the gas sampling Loenco valve (F). Gases were analysed by the on-line gas chromatograph (H). Solid and liquid products were injected into a separate gas chromatograph. Some analyses were performed with an Edwards Chromato-Mass Spectrometer.

Gravimetric Apparatus used in Surface Measurements

The gravimetric apparatus was used for measurement of the surface of carbons deposited during pyrolysis. It is illustrated in Plate 2. The system shown in figures 1:7(a) and 1:7(b) has been described by Cutting and was built around a Cahn Electrobalance with nichrome hangdown wires and gold buckets. The Cahn balance operates on a null deflection principle and is capable of measuring mass changes of 10^-6 gm.
FIG. 1: 6a Furnace and controlling system for flow apparatus

FIG. 1: 6b Temperature profile of reactor
FIG. 1: 7a Gravimetric apparatus used for surface measurements

FIG. 1: 7b Diagrammatic representation of Cahn microbalance
ABOVE: General view of the balance and gas handling system.

LEFT: Close-up of the weighing section of the apparatus.

PLATE 2 Microbalance used for the surface measurements
A sample of approximately 40 mg mass was accurately weighed in the sample bucket. It was then counterbalanced with standard weights until the balance reading was a few milligrams above zero to allow for outgassing of the sample. The latter was warmed to 300°C and left overnight to outgas. An ultimate vacuum of below $10^{-5}$ torr was achieved. Doses of adsorbate were introduced into the balance and the increase in sample weight measured. A straight trace on the mass recorder indicated that equilibrium had been reached. Adsorbate pressure was measured on a Bell and Howell pressure transducer.

**Reactants Used In All Systems**

**Benzene**

Phillips research grade benzene was used. Purity was stated to be greater than 99.90 mol per cent. This was confirmed by gas chromatographic analysis. The main impurity was toluene.

Traces of oxygen can have a profound effect on free radical pyrolysis reactions and care was taken to ensure that the reagent was thoroughly degassed before use. On the static apparatus the sample was stored in a small glass bulb and frozen with liquid nitrogen. The bulb was allowed to warm up to room temperature and, as the solid melted, the dissolved air was pumped off. The procedure was repeated until no more air came off. This usually occurred after four degassings. The sample could then be warmed up to about 120°C and used in the static system in situ. In the flow system the sample was introduced into the saturator device and nitrogen bubbled through for 30 minutes before a run was started.

**Ethyl Benzene**

Phillips research grade, stated purity 99.92 mol per cent, ethyl benzene treated as above, was used.
Nitrogen

Cylinder nitrogen of white spot quality was used. Traces of oxygen were removed by passage over copper turnings at 300°C.

Nitric Oxide

Matheson 99.0% pure quality was used. The sample was purified by being frozen and pumped on as it warmed up. The nitric oxide was allowed to evaporate into an evacuated globe. Initial and final fractions, the latter containing a high proportion of nitrogen dioxide (m.p. -11.2°C), were rejected. This freezing - distillation procedure was repeated four times to ensure removal of any impurity.

Propylene

Phillips research grade propylene of purity 99.99 mole per cent was used without further purification. The freezing-distillation procedure described above was carried out several times to ensure that any air admitted during filling of the globe was removed.
THE LOW TEMPERATURE PYROLYSIS OF BENZENE

Procedure

The majority of the experiments described here were carried out using the static apparatus described earlier in this section. Gas and vapour mixtures were normally made up in the heated globe. In a typical experiment, forty torr of benzene were taken and nitrogen added until four hundred torr pressure was reached. When the mixture was admitted directly to the evacuated reaction vessel the total pressure dropped immediately to around three hundred torr. After a period of time the reaction mixture was removed from the vessel and the products of reaction sampled and analysed.

Some preliminary experiments

The object of these preliminary experiments was to establish some of the major facts of the pyrolysis and hence the working conditions for studying the reaction.

The conditions to be established are:

1. determination of a working temperature range,
2. effect of impurities on the reaction (particularly oxygen),
3. effect of vessel surfaces and type of reactor used,
4. effect of added "inert" gas on the reaction,
5. nature of the product distribution.

1. Product yield over a wide temperature range

A reaction mixture was made up and introduced into the reaction vessel from the mixing globe so as to give 31 torr benzene and 269 torr nitrogen in the vessel. The results obtained are shown in figure 2:1.
FIG. 2:1 Pyrolysis of 31 torr benzene; yield of hydrogen ○ and methane • after one minute.
Hydrogen is the major product and small quantities of methane are also formed. The methane can be formed by at least two routes.

Very small quantities can be formed by the decomposition of toluene impurity.

The opening of the benzene ring can lead to the formation of straight chain hydrocarbons. These can then be rapidly hydrogenated to methane.

The toluene impurity was shown previously to be very small. The research grade benzene was 99.90 mole per cent pure. Rate data for methane formation from toluene have been produced. The maximum methane expected from toluene impurity is $6 \times 10^{-4}$ torr after one minute residence time. Therefore, at temperatures in excess of 1033K ring opening must become significant, the apparent activation energy being 83,000 cal/mole. The low temperature pyrolysis must therefore, be studied above 883K, so that measurable quantities of product can be obtained, but below 1033K, to avoid significant ring opening.

Possible effects of small quantities of oxygen

The effect of small quantities of oxygen has been shown by Leathard and Purnell to be significant in the gas phase pyrolysis of paraffins. It is probable that this observed sensitising effect will hold true for aromatic hydrocarbon pyrolysis as well. If oxygen is present in the purified nitrogen, or air is dissolved in the aromatic hydrocarbon, then an effect will be observed on the product yield. Air was removed from the aromatic hydrocarbon by the process described earlier. Once all the air had been apparently removed a run was carried out. The observed rate of reaction was independent of the number of degassing cycles and suggests that oxygen is absent from the hydrocarbon. If air is present in the purified nitrogen then an effect on the product yield will be observed when varying amounts of this "nitrogen" are added to the reaction mixture.
The results shown in Figure 2.2(a) suggest that hydrogen yield is independent of added nitrogen. Mixtures of 0.46% oxygen in nitrogen and 0.041% oxygen in nitrogen were made up and the experiment repeated. A linear increase in hydrogen yield as shown in figure 2.2(b) was observed. This suggests that traces of oxygen are absent from the nitrogen diluent. The benzene and nitrogen were therefore used in subsequent experiments without any additional purification.

**Product distribution - the comparison of hydrogen and diphenyl yields**

Attempts to measure diphenyl yields in the static system presented two problems.

First, a calibration sample gave a different peak shape in the chromatograph from a product sample admitted via the heated transfer line.

Second, diphenyl yields were apparently slightly less than hydrogen yields. This could possibly be due to a loss of sample by adsorption on the transfer line, or to incomplete condensation of the sample in the cold trap.

At first sight, stoichiometry demands that hydrogen and diphenyl yields be equal. This was tested for in the simple flow system where collection of products was easier. The less volatile products were collected in a series of traps at -83°C over a two hour period. The gases passed through a sample loop of the gas chromatograph and were analysed immediately. The diphenyl was estimated separately by injection of a sample of the condensate into the chromatograph. The results in figure 2.3 show that the yields of hydrogen and diphenyl are equal, within experimental error. Some of the diphenyl must therefore, be lost in the sampling process in the static apparatus.

**The effect of surface**

The effect of vessel surface on the reaction was investigated by four different procedures.
FIG. 2:2 Effect of added oxygen on the pyrolysis of benzene.
FIG. 2:3  Yields of diphenyl \( \circ \) and hydrogen \( \bullet \) in a flow system with 1 minute residence time.
a) Alteration of the surface to volume ratio of the reaction vessel.
b) Alteration of the nature of the vessel's surface, e.g., salt and carbon coated vessels.
c) Pyrolysis in the presence of various amounts of inert gas whilst keeping a fixed amount of reactant.
d) Observation of the effect of different "inert" gases on diphenyl yield.

Before use, the vessels were treated by the method described in the experimental section.

a) Alteration of surface to volume ratio:

Reaction vessels A, B, C and D, diameters sixty, forty five, thirty, twenty mms and E, diameter fifty mm, but packed with silica tubes were used. A standard benzene pressure of thirty torr was used in these experiments. Figure 2:4(a) shows the results obtained at a reaction temperature of 960K.

b) Alteration of the vessel's surface:

Vessels of forty five mm diameter were coated with salt and carbon, and the experiments repeated. The points are also included on Figure 2:4(a). The carbon coating has little effect on reaction rate but a salt coating reduces it slightly.

c) Effect of added inert gas on hydrogen yield:

In this and all subsequent experiments reaction vessel A was used. Various pressures of nitrogen were added to a fixed 31 torr pressure of benzene. The results summarised in figure 2:4(b) show that product yield is independent of added nitrogen.

d) Effect of different inert gases on product yield:

Hydrogen yields were difficult to measure in the presence of inert gases other than nitrogen. Normally, hydrogen concentrations were measured on a gas chromatograph with a hot wire detector and nitrogen as a carrier.
FIG. 2: 4a Effect of change in surface/volume ratio on benzene pyrolysis
FIG. 2:4b Effect of added nitrogen on hydrogen yield from benzene pyrolysis

FIG. 2:4c Effect of added inert gas on diphenyl yield from benzene pyrolysis

○ argon, ● helium, ◇ nitrogen

reaction temp 953 K

reaction temp 913 K

reaction temp 968 K
Any inert gas other than nitrogen would appear as a large peak on the gas chromatograph and mask the relatively small hydrogen product peak. A possible solution is to use the inert gas as a carrier. This is satisfactory providing the thermal conductivities of the carrier and hydrogen are different. Hydrogen and helium have similar conductivities and a loss of sensitivity results. Therefore, the experiment was carried out by measurement of diphenyl yield.

Argon, helium and nitrogen were used as diluents and the experiment was carried out as described in (c) above. The results shown in figure 2:4(c) indicate that diphenyl yield is independent of the nature of the inert gas.

Surface can affect a chain reaction by promoting initiation or termination of chains. In the former case, free radicals are formed at the surface and released into the volume of the vessel. In the latter case, atoms or radicals are adsorbed at the surface and subsequently combine with further atoms or radicals from the gas phase. In both cases, the nature of the surface has a marked effect on the reaction rate and results tend to be irreproducible. The consistency of the results reported here suggests that heterogeneous effects are insignificant. At most, in a packed reaction vessel rate is reduced by one third. It is not uncommon for surface reactions to affect reaction rate by several orders of magnitude

All subsequent experiments were carried out in vessel A of diameter 60mm. High mixture pressures of 300 torr were used. Under these conditions the small heterogeneous effect was ignored.
Kinetic Experiments

The work was carried out in the 60 mm reaction vessel by the method described previously. The effects of variation of residence time, reactant pressure and temperature were measured so that the order of reaction and its activation energy could be established.

Effect of residence time

Hydrogen formation was measured after residence times between one and thirty minutes. The experiment was carried out at temperatures of 910K and 967K. The results are shown in figure 2:5. Results for diphenyl formation are also shown.

In all cases curves are slightly convex. In the early stages, however, they are acceptably close to linearity and the integrated rate of formation of product after four minutes residence time was usually taken as proportional to the initial rate of reaction.

Effect of benzene pressure

Benzene pressures from ten to fifty torr were used and the rate of reaction was measured by observation of both hydrogen and diphenyl yields. The results are shown in figure 2:6. The order of reaction was obtained by the Van't Hoff\(^4\) method; log (rate of product formation) was plotted against log (initial benzene concentration). The slope of the straight line graph yielded the reaction order. A least squares analysis of the data in figure 2:6 gave an order of 1.4 for diphenyl and 1.6 for hydrogen.

An alternative test for order is to use the integrated form of the rate equation. For first order reactions the integrated rate equation is:

\[
2.303 \log_{10} \left( \frac{a}{a-x} \right) = kt
\]
FIG. 2:5 Progress of reaction with time
○,●hydrogen, ●diphenyl yields
FIG. 2: 6a - Effect of change in benzene pressure on product yield in benzene pyrolysis (○ hydrogen, ● diphenyl)

FIG. 2: 6b - Log-log plots to determine reaction order. (○, ●, □) hydrogen, ● diphenyl
where $a =$ initial benzene concentration
$x =$ benzene consumed after time $t$.

Hence a plot of $\log_{10} (a-x)$ against time $t$ will yield a straight line.

If the order is $3/2$ then the integrated rate equation is:

$$2 (a-x)^{-\frac{1}{2}} - a^{-\frac{1}{2}} = kt$$  \hspace{1cm} (xi)

Hence a plot of $(a-x)^{-\frac{1}{2}}$ against time will be a straight line.

In this analysis, the data presented in figure 2:5 for reaction at $910K$ were used. Both 1st order and 3/2 order integrated rate expressions were plotted. The results are shown in figure 2:7. The curvature of the 1st order plot eliminates this possibility. The 3/2 plot yields a good straight line, confirming the previous approach.

The effect of temperature

So far the reaction has been studied with benzene concentration in pressure units (torr). This is valid as pressure is proportional to concentration at constant temperature as shown by expression (xii).

$$C \text{ (mole}^{-1} \text{ litre}^{-1}) = \frac{P \text{ (torr)}}{(760 \times R \times T)} \hspace{1cm} (xii)$$

where $R = 0.082$ litre atmos deg$^{-1}$ mole$^{-1}$
$T =$ temperature of reaction (K)

Thus for a non first order reaction where temperature is varied the assumption is no longer valid and concentration units must be used.

The temperature range over which reaction can conveniently be studied is limited. Below $873K$ the rate is too small to measure and above $1036K$ the ring opens and complicates the kinetics. The effect of temperature on the reaction was studied over this temperature range.

Application of the Arrhenius equation:

$$k = Ae^{-E/RT}$$  \hspace{1cm} (xiii)

yielded the plot shown in figure 2:8.
FIG. 2: Use of integrated rate equations to verify order.  
- 1st order case: $a = \text{initial benzene concentration}$  
- 0.3/2 order case: $x = \text{benzene consumed}$
FIG. 2: Arrhenius plot of hydrogen formed from benzene pyrolysis with an initial benzene concentration of $5.372 \times 10^{-4}$ mole litre$^{-1}$. Residence time 4 mins.
The line is slightly curved. If a straight line is assumed, an overall rate expression of

\[ k = 10^{8.2} \exp\left(-46,300/RT\right) \text{litre mole}^{-\frac{1}{2}} \text{sec}^{-1} \]  

(xiv)
is obtained. Over the temperature range 1036K to 952K the line is reasonably linear and the rate expression (xv) can be deduced.

\[ k = 10^{9.83} \exp\left(-53,800/RT\right) \text{litre mole}^{-\frac{1}{2}} \text{sec}^{-1} \]  

(xv)

**Preliminary Discussion on Reaction Mechanism**

Much of the disagreement concerns the reaction mechanism. Of the few workers who have investigated the low temperature reaction in which the benzene ring remains intact, Fields and Meyerson propose a molecular process, whereas Louw and Lucas favoured a free radical chain process.

The experimental results produced so far, suggest a free radical mechanism for the following reasons:

1. A molecular mechanism based on

\[ 2C_6H_6 = (C_6H_5)_2 + H_2 \]

would yield second order kinetics, whereas a free radical chain reaction could quite easily yield the experimentally observed three halves order kinetics.

2. Oxygen is more likely to affect a chain mechanism than a molecular one.

If a simple non chain radical process occurs then two feasible mechanisms can be envisaged. One involving first order initiation, the other second order initiation.

The first order initiation scheme comprises reactions (1), (2) and (3).

\[ C_6H_6 = C_6H_5 + H \]  

(1)

\[ H + C_6H_6 = C_6H_5 + H_2 \]  

(2)

\[ C_6H_5 + C_6H_5 = (C_6H_5)_2 \]  

(3)
These data are obtained by the least squares technique. Error limits are:

\[ k = 10^{8.2 \pm 0.2} \exp(-46,000 \pm 1,000/RT) \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1} \]

for expression (xiv) and

\[ k = 10^{9.83 \pm 0.4} \exp(-53,800 \pm 2,000/RT) \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1} \]

for expression (xv). Similar error limits apply to data presented later in the thesis.
Application of the stationary state approximation to this mechanism yielded the rate expression (xvi)

\[ \frac{d[H_2]}{dt} = k_1[C_6H_6] \]  

(xvi)

It is first order with an activation energy similar to the bond energy of the C-H bond in benzene. Latest recommended values put this as high as 110,000 cals mole\(^{-1}\). This is approximately double the experimental value. Thus the above simple mechanism is inadequate.

An alternative scheme comprises reactions\(1a, 3\) and \(4\):

\[ 2C_6H_6 = C_6H_5 + C_6H_7 \]  

(1a)

\[ C_6H_5 + C_6H_6 = (C_6H_5)_2 + H \]  

(3)

\[ H + C_6H_7 = C_6H_6 + H_2 \]  

(4)

and second order kinetics are predicted.

\[ \frac{d[H_2]}{dt} = k_{1a} [C_6H_6]^2 \]  

(xvii)

Low and Lucas have suggested the rate expression(xviii) for reaction \(1a\).

\[ \ln k_{1a} = 11.5 - 84,000/RT \text{ litre mole}^{-1} \text{ sec}^{-1} \]  

(xviii)

So these data also are not consistent with the experimental results.

Therefore, if a free radical mechanism is to be invoked, other chain carrying steps must be sought.

**Investigations into the chain nature of the reaction**

Evidence for chains can be obtained from the effect of inhibitors, although the nature of the distribution of secondary products can also yield information.

**The effect of inhibitors**

Reaction chain length, which is often of the order of hundreds, is a dominant factor in determining the rate of a chain reaction. Thus the addition of an inhibitor, which reacts with any of the chain carriers in such a way as to terminate the chains prematurely, will cause the rate to be reduced. Often a limiting value is reached.
This was originally interpreted by Hinshelwood and co-workers\textsuperscript{44}, as implying concurrent free radical and molecular mechanisms in alkane pyrolysis systems. The inhibitor completely suppressed the free radical mechanism, leaving the molecular mechanism only. It is now believed that both the uninhibited and inhibited pyrolyses occur exclusively via a free radical mechanism. The inhibited reaction is a complex modification of the uninhibited pyrolysis. Evidence for this is summarised by Purnell and Quinn\textsuperscript{45}.

Even though a limiting value to the inhibited rate cannot be taken to show a molecular process, occurrence of inhibition must be regarded as good evidence for a free radical process. Both propylene and nitric oxide were used to test for a chain reaction in the benzene system. Figure 2:9 shows the results obtained. With nitric oxide results similar to those obtained by Hinshelwood and his co-workers\textsuperscript{44} for alkanes are obtained. With propylene the results are more confused. After reaching a limiting value, when one torr of propylene is present, the rate of hydrogen formation starts to increase.

Inhibition was further investigated by addition of nitric oxide at different reaction temperatures. The results are shown in figure 2:10. In this graph the results are presented as per cent inhibition against added nitric oxide.

\[
\text{Per cent inhibition} = \frac{(R_o - R_1)}{R_o} \times 100 \quad (xix)
\]

where \(R_o\) = Uninhibited rate of hydrogen production

\(R_1\) = Inhibited rate of hydrogen production

At lower temperatures inhibition approaches 100%.

The formation of secondary products

The formation of solid products other than diphenyl was investigated with the aid of gas chromatography and chromato-mass spectrometry.
FIG. 2: 9 Inhibition of benzene pyrolysis by nitric oxide, propylene at 966K

FIG. 2: 10 Inhibition of benzene pyrolysis by nitric oxide at various reaction temperatures
Three small peaks were observed. Para and meta terphenyls were positively identified. The third peak although not positively identified was assumed to be triphenylene.

If the secondary products are formed in a ratio that is independent of reaction time then product formation occurs simultaneously and not consecutively.

i.e. for a first order reaction

\[
\begin{array}{c}
A \\
\frac{k_B}{k_C} \downarrow \\
B \\
\frac{k_B}{k_C} \\
C
\end{array}
\]

then \( \frac{dx}{dt} = k_B (a-x) + k_C (a-x) \) (xx)

where \( k_B \) and \( k_C \) are the rate constants of the two side reactions.

Therefore, on integration

\[
k_B + k_C = \frac{1}{t} \ln \frac{a}{(a-x)} \quad (xxi)
\]

and the reaction as a whole behaves as first order.

Table 4 shows the ratios of peak area obtained for the three products for various residence times.

**TABLE 2:4**

<table>
<thead>
<tr>
<th>Residence Time (mins)</th>
<th>Ratio of Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>triphenylene</td>
</tr>
<tr>
<td>9</td>
<td>1.6</td>
</tr>
<tr>
<td>4.5</td>
<td>1.4</td>
</tr>
<tr>
<td>18</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Thus the ratio of concentration of the secondary products is independent of time. This suggests that they are formed via a common intermediate (possibly a free radical). This simple test was first described by Wegscheider

**Effect of added hydrogen**

Benzene was pyrolysed in the presence of various amounts of hydrogen. Thirty torr of benzene were taken and total pressure was kept constant at 300 torr by interchange of hydrogen with nitrogen. The effect on diphenyl yield was observed. Figure 2:11 shows the results obtained. Diphenyl formation decreases with increasing hydrogen pressure until a limiting value is reached. This suggests that the system is approaching equilibrium. At equilibrium

\[
\Delta G^o = \Delta G^o \text{ products} - \Delta G^o \text{ reactants} \quad (xxii)
\]

at 1000K it can be shown from the data given in appendix 1 that

\[
\Delta G^o = 4,580 \text{ cals mole}^{-1}
\]

also

\[
\Delta G^o = -RT \ln K_p \quad (xxiii)
\]

Thus the equilibrium constant, \(K_p\), is 0.1 at 1000K.

This means that under ideal conditions thirty torr of benzene will dissociate into 5.8 torr of hydrogen and 5.8 torr of diphenyl.

When 300 torr of hydrogen is present 0.3 torr of diphenyl formed is predicted.

Addition of 300 torr of hydrogen reduces the diphenyl yield by a factor of 2.7. Diphenyl production in the absence of hydrogen is of the order of 0.6 torr; therefore, the observed yield when 300 torr of hydrogen is present is quite close to the equilibrium value of 0.3 torr.

Thus in the absence of hydrogen the system is operation under conditions far removed from equilibrium, and decrease in diphenyl yield with increase in hydrogen concentration is a consequence of the system approaching equilibrium.
FIG. 2:11 Effect of added hydrogen on diphenyl yield from benzene pyrolysis at 966K.
DISCUSSION

In the previous part evidence for a free radical chain mechanism was presented and preliminary ideas on a possible mechanism were suggested.

A summary of the evidence is:

1. Reaction order is about 1.5.
2. The activation energy is low compared with the strength of the C-H bond.
3. Added oxygen has a profound effect on the rate of reaction.
4. Inhibitors reduce the rate in a way similar to their action in alkane pyrolysis.
5. Wegscheider's test suggests that secondary products are formed simultaneously from the same intermediate.

Possible reaction mechanisms

There are two possible modes of initiation

a) Unimolecular

\[ C_6H_6 = C_6H_5 + H \]  \hspace{1cm} (1)

first suggested by Aten and Bauer\(^{31}\).

b) Bimolecular

\[ 2C_6H_6 = C_6H_5 + C_6H_7 \]  \hspace{1cm} (1a)

first suggested by Louw and Lucas\(^{37}\).

a) Mechanism involving 1st order initiation

A mechanism involving the steps 1, 2 and 3

\[ C_6H_6 = C_6H_5 + H \]  \hspace{1cm} (1)

\[ \overline{H} + C_6H_6 = C_6H_5 + H_2 \]  \hspace{1cm} (2)

\[ 2C_6H_5 = (C_6H_5)_2 \]  \hspace{1cm} (3)

has already been discussed, and predicts first order kinetics which do not fit the experimental results.
If the chain propagating step (5) proposed by Asaba and Fujii

\[
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)_2 + \overline{\text{H}}
\]  

(5)
is included then the expression (xxiv) for hydrogen production can be derived.

\[
d[H_2]/dt = k_5 (k_1/k_3)^{1/2} [C_6H_6]^{3/2} + k_1 [C_6H_6]
\]  

(xxiv)

If long chains exist then

\[
k_5 (k_1/k_3)^{1/2} [C_6H_6]^{3/2} \gg k_1 [C_6H_6]
\]  

(xxv)

and the rate expression simplifies to (xxvi)

\[
d[H_2]/dt = k_5 (k_1/k_3)^{1/2} [C_6H_6]^{3/2}
\]  

(xxvi)

The expression (xxvi) is of the correct order and at first sight seems reasonable.

A test of the fit of the derived expression is to estimate the activation energy and compare it with the experimentally obtained value.

Estimation of activation energy:

The activation energy of the postulated initiation stage (1) must be of the order of the bond dissociation energy C-H in benzene. Recently this has been the subject of controversy. For many years a value of 102,000 cal mol\(^{-1}\) was accepted. The value is now considered to be low and the most recent value is 110,000 ±2 cal mol\(^{-1}\). Table 5 lists some of the published data.
TABLE 2:5
DATA FOR C,H,-H BOND ENERGY IN BENZENE

<table>
<thead>
<tr>
<th>(C,H,-H) Bond Energy</th>
<th>Source and Reference</th>
<th>Date of Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>102,000</td>
<td>Szwarc &amp; Williams</td>
<td>47 1952</td>
</tr>
<tr>
<td>107,000</td>
<td>Kandel</td>
<td>48 1954</td>
</tr>
<tr>
<td>102,000</td>
<td>Duncan &amp; Trotmann-Dickenson</td>
<td>49 1962</td>
</tr>
<tr>
<td>99,000</td>
<td>Fields &amp; Franklin</td>
<td>50 1954</td>
</tr>
<tr>
<td>104,000</td>
<td>Fielding &amp; Pritchard</td>
<td>51 1962</td>
</tr>
<tr>
<td>112,000</td>
<td>Rogers,Golden &amp; Benson</td>
<td>52 1967</td>
</tr>
<tr>
<td>109,000</td>
<td>Szilagyi &amp; Berces</td>
<td>53 1970</td>
</tr>
<tr>
<td>110,000</td>
<td>Chamberlain &amp; Whittle</td>
<td>43 1971</td>
</tr>
</tbody>
</table>

Reaction (3) is a radical recombination process and its activation energy can be assumed to be zero, although a small negative value is possible.

Calculation of the activation energy of reaction (5) presents more of a problem. Established procedures such as the REBO method are basically for hydrogen atom transfer reactions, although the method has been extended to include some other atom transfer reactions.

Alfassi and Benson have recently devised a simple empirical method for estimating activation energies for atom transfer reactions, which although not strictly applicable, was applied, faute de mieux, to reaction (5). The method applies only to exothermic reactions. If a reaction is endothermic the back reaction must be considered. Using Benson's additivity rules it can be shown (Appendix 1) that reaction (5) is slightly exothermic with $\Delta H^{\circ}_{1000K} = -694$ cals mole$^{-1}$. 
The activation energy is predicted as 5,500 cals mole\(^{-1}\). (Details of the method are listed in Appendix 1). This is in good agreement with a recently measured value\(^{72}\) of 4,000 cals mole\(^{-1}\). The measured value is used in subsequent discussion.

The overall activation energy predicted by the mechanism is \(E_5 + (E_1 - E_3)/2\) i.e. 59,000 cals mole\(^{-1}\); a value slightly higher than that of 53,000 cals mole\(^{-1}\) obtained experimentally. It seems possible that some other contribution to the mechanism may be taking place. It is difficult to envisage any other homogeneous process involving first order initiation that will lead to three halves order kinetics. Consideration of second order initiation processes, however, reveals other possibilities.

b) Mechanism involving second order initiation.

The only second order initiation possible is reaction (1a).

\[
2C_6H_6 \rightarrow C_6H_5 + C_6H_7
\]  

(1a)

Goldfinger, Niclause and Letort\(^{32}\) have proposed empirical rules for predicting termination reactions from the overall order and the order of the initiation reaction. They say that, for second order initiation and three halves order overall, simple termination reactions must involve \(\beta\mu\) radicals. A \(\beta\) radical is one involved in a bimolecular propagating step and a \(\mu\) radical is one involved in a unimolecular propagating step. The rules also state that if termination reactions involve a third body then \(\beta\beta\) radicals are involved in termination, for three halves order.
In benzene pyrolysis the only radical that can decompose in a unimolecular step is C$_6$H$_7$.

\[ \text{C}_6\text{H}_7 = \text{C}_6\text{H}_5 + \text{H}_2 \]  \hspace{1cm} (6)

If C$_6$H$_5$ radicals decompose ring opening occurs. Experiment shows this to be insignificant below 1053K.

Termination is thus

\[ \text{C}_6\text{H}_7 + \text{H} = \text{C}_6\text{H}_6 + \text{H}_2 \]  \hspace{1cm} (7)

or

\[ \text{C}_6\text{H}_7 + \text{C}_6\text{H}_5 = 2\text{C}_6\text{H}_6 \]  \hspace{1cm} (-1a)

Reaction (-1a) is the reverse of the proposed initiation stage. Termination via this reaction is discussed later.

The rules propose that an alternative chain termination reaction is with $\text{H}_2$ radicals and a third body. The only radicals or atoms in the system with few enough degrees of freedom to require a third body in termination are hydrogen atoms. Therefore reaction 8 is a possible termination reaction

\[ \text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M} \]  \hspace{1cm} (8)

However, experimental evidence on the effect of added inert gas suggests the absence of a third body such as nitrogen taking part in the reaction. Also compared with C$_6$H$_7$ or C$_6$H$_5$ radicals hydrogen atoms are very reactive and the relative concentration is likely to be low. Thus termination via reaction 8 can be discounted as a major termination step and termination via reaction 7 is the only possibility considered. Propagation reactions in the mechanism will include reactions 2 and 5 as well as reaction 6.
Reaction 2, however, may not be a simple abstraction reaction
\[ \text{H} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H}_2 \]  
(2)

The parallel addition reaction 9 may also occur
\[ \text{H} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_7 \]  
(9)

In recent years evidence has accumulated to show that addition reactions readily occur at low temperatures. The high bond energy of the C-H bond in benzene is responsible. Charles and Whittle\(^73\) have shown that addition readily occurs with CF\(_3\) radicals in the temperature range 297\(^0\)K - 359\(^0\)K. Chamberlain and Whittle\(^43\), however, have shown that above 413\(^0\)K genuine hydrogen abstraction takes place.

At low temperatures hydrogen atoms readily add to benzene via reaction 9 and Yang\(^74\) has obtained a rate constant of
\[ k = 10^{10} \exp\left(-4,000/RT\right) \text{ litre mole}^{-1} \text{ sec}^{-1} \]  
(xxvii)

Kim, Lee, Bananno and Timmins\(^75\) have more recently obtained a value of
\[ k = 6 \times 10^9 \exp\left(-2700/RT\right) \text{ litre mole}^{-1} \text{ sec}^{-1} \]  
(xxviii)

The work was at low temperatures but Benson and Shaw\(^76\) have shown that the addition reaction (9) readily occurs at temperatures as high as 664 K.
\[ \text{H} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_7 \]  
(9)

It is therefore possible that the addition reaction takes place in the pyrolysis reaction as well.
Rate Data for Addition and Abstraction Reactions (9) and (2)

a) The Abstraction Reaction (2):

For this reaction the activation energy can readily be estimated by both the bond energy bond order (BEBO)\(^{54}\) and the Alfassi\(^{55}\) and Benson methods. From the calculations in Appendix 1 (b) the BEBO method yields a value of 16,000 cals mole\(^{-1}\) whereas Alfassi and Benson's method yields a value of 11,700 cals mole\(^{-1}\). As the BEBO method uses data completely outside the field of kinetics an average value of 14,500 cals mole\(^{-1}\) weighted towards the BEBO result was taken. The BEBO method has been extended to give A Factors and a value of \(10^{11.8}\) litre mole\(^{-1}\) was calculated\(^{77}\) for reaction (2). In recent years Benson\(^{36}\) has devised methods for obtaining A the pre-exponential factor from thermodynamic data obtained by group additivity and statistical mechanical considerations. Thus if entropies of activation can be calculated then the A factor can be estimated from the transition state expression (xxix).

\[
A = \text{(h)} \left( \frac{e^{\frac{\Delta S^\ddagger}{R}}} {ekT} \right) \tag{xxix}
\]

\(\Delta S^\ddagger\) is the entropy change in forming the transition state complex.

From the data listed in Appendix 2 a value of \(10^{11.6}\) litre mole\(^{-1}\) sec\(^{-1}\) was obtained.
TABLE 2:6
CALCULATED RATE DATA FOR ABSTRACTION REACTION (2).

<table>
<thead>
<tr>
<th>Activation Energy (cals mole(^{-1}))</th>
<th>A Factor (litre mole(^{-1}) sec(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(*16,000)</td>
<td>(10^{11.8}) (10^{11.6})</td>
<td>This Work.</td>
</tr>
<tr>
<td>(*11,700)</td>
<td>(10^{11.7}) (10^{11.6})</td>
<td>Asaba &amp; Fujii(^{29})</td>
</tr>
<tr>
<td>7,900</td>
<td>(10^{11.7}) (10^{10.0})</td>
<td>Louw &amp; Lucas(^{31})</td>
</tr>
<tr>
<td>13,000</td>
<td>(10^{10.0})</td>
<td></td>
</tr>
</tbody>
</table>

\*BEBO Method
\*Alfassi and Benson Method.

b) Addition Reaction:

Kim, Lee Bonanno and Timmins\(^{75}\) have measured the rate of the addition reaction and they propose a value of \(k = 10^{10.0} \exp(-2,700)/RT\) litre mole\(^{-1}\) sec\(^{-1}\).

Competition between Addition and Abstraction.

A plot of the calculated rate constants for reactions (2) and (9) is shown in Figure 2:12. Thus even at the high temperatures of this pyrolysis, addition can occur. Probably abstraction is a more complex process involving addition initially followed by decomposition of the adduct radical

\[
\begin{align*}
\tilde{H} + C_6H_6 &= C_6H_7 \\
C_6H_7 &= C_6H_5 + H_2
\end{align*}
\]  

(9)  
(6)

This has no effect on the first order initiation mechanism as \(C_6H_7\) and hence hydrogen are produced only in reactions (9) and (6).
FIG. 2:12 Comparison of rate constants for (o) H atom addition and (●) H atom abstraction reactions with benzene.
With the second order scheme, however, $\text{C}_6\text{H}_7$ is also produced in the initiation stage and hence the kinetics are affected.

The revised mechanism now becomes

$$2\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{C}_6\text{H}_7 \quad (1a)$$
$$\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)_2 + \text{H} \quad (5)$$
$$\text{H} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_7 \quad (9)$$
$$\text{C}_6\text{H}_7 = \text{C}_6\text{H}_5 + \text{H}_2 \quad (6)$$
$$\text{H} + \text{C}_6\text{H}_7 = \text{C}_6\text{H}_6 + \text{H}_2 \quad (7)$$

and this is essentially the mechanism proposed by Louw and Lucas.\(^{37}\)

From this a rate expression for hydrogen production of

$$\frac{d[H_2]}{dt} = 2k_{1a}[\text{C}_6\text{H}_6]^2 + \left(\frac{2k_{1a}k_6k_9}{k_7}\right)^{1/2}\left[\text{C}_6\text{H}_6\right]^{3/2} \quad (xxx)$$

can be obtained. For long chains

$$2k_{1a}[\text{C}_6\text{H}_6]^2 \ll \left(\frac{2k_{1a}k_6k_9}{k_7}\right)^{1/2}\left[\text{C}_6\text{H}_6\right]^{3/2} \quad (xxxi)$$

and the expression simplifies to

$$\frac{d[H_2]}{dt} = \left(\frac{2k_{1a}k_6k_9}{k_7}\right)^{1/2}[\text{C}_6\text{H}_6]^{3/2} \quad (xxxii)$$

For the above an approximate activation energy is $(E_{1a} + E_6 + E_9)/2$ as $E_7$ can be assumed to be zero.

Data for the initiation reaction (1a) have been proposed by Louw and Lucas as

$$\log k_1 = 11.5 - \frac{(84,000/RT)}{\text{litre mole}^{-1} \text{ sec}^{-1}} \quad (xviii)$$

A lower limit of $E_6$ can be estimated from Louw and Lucas data to be about 33,000 cals mole$^{-1}$ and from Kim et al’s work $E_9 = 2,700$ cals mole$^{-1}$. Thus the overall activation energy obtained by the above considerations is 61,000 cals mole$^{-1}$. Again this value is slightly higher than that obtained experimentally.
Estimation of Rate Data.

Calculation of A factors have been made for most of the reactions involved in the scheme and full details are included in Appendix 2. Table 2:7 lists a summary of the results obtained together with rate data proposed by other workers.

TABLE 2:7
RATE DATA FOR REACTIONS INVOLVED IN BENZENE PYROLYSIS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log A Factor</th>
<th>Activation Energy (cals mole(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H})</td>
<td>15.7</td>
<td>110,000</td>
<td>This Work</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5 + \text{H} \rightarrow (\text{C}_6\text{H}_5)_2 + \text{H})</td>
<td>16.0</td>
<td>110,000</td>
<td>Louw &amp; Lucas 37</td>
</tr>
<tr>
<td></td>
<td>14.9</td>
<td>105,000</td>
<td>Asaba &amp; Fujii 35</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_5)_2 + \text{H})</td>
<td>8.4</td>
<td>5,500</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>4,000</td>
<td>P. Gibbs 72</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>10,500</td>
<td>Asaba &amp; Fujii 35</td>
</tr>
<tr>
<td>(\text{H} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 + \text{H}_2)</td>
<td>11.6</td>
<td>12,500</td>
<td>This Work</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5 = (\text{C}_6\text{H}_5)_2)</td>
<td>10.0</td>
<td>13,000</td>
<td>Louw &amp; Lucas 37</td>
</tr>
<tr>
<td></td>
<td>11.7</td>
<td>8,000</td>
<td>Asaba &amp; Fujii 35</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_7 + \text{H} \rightarrow \text{C}_6\text{H}_6 + \text{H}_2)</td>
<td>9.2</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>(2\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{C}_6\text{H}_7)</td>
<td>11.5</td>
<td>84,000</td>
<td>Louw &amp; Lucas 37</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_7 = \text{C}_6\text{H}_5 + \text{H}_2)</td>
<td>13.0</td>
<td>33,000</td>
<td>Derived from Louw &amp; Lucas 37</td>
</tr>
</tbody>
</table>

Units of 1st order sec\(^{-1}\). Units of 2nd order litre mole\(^{-1}\) sec\(^{-1}\).
Competition between the two Mechanisms.

Both mechanisms outlined give solutions which can approximately describe the observed experimental results. For first order initiation reaction (1) let the rate of reaction = $R_1$; then

$$R_1 = k_1 [C_6H_6]$$

(xvi)

For second order initiation reaction (1a) let $R_{1a}$ = the rate of reaction.

.$$R_{1a} = k_{1a} [C_6H_6]^2$$

(xvii)

If the benzene concentration is $5.372 \times 10^{-4}$ moles litre$^{-1}$ then it follows that

$$\log R_1 = 12.4 \text{ moles litre}^{-1} \text{ sec}^{-1}$$

$$\log R_{1a} = 12.1 \text{ moles litre}^{-1} \text{ sec}^{-1}$$

Thus both types of initiation have approximately the same rate and it is impossible to differentiate between them on this basis.

Further examination of the proposed mechanisms.

The rate expression (xxiv)

$$R = \frac{d[H_2]}{dt} = k_1 [C_6H_6] + k_5 (k_1/k_3)^{1/2} [C_6H_6]^{3/2} \quad (xxiv)$$

was derived earlier. On dividing by $[C_6H_6]$ concentration the expression becomes

$$R/[C_6H_6] = k_1 + k_5 (k_1/k_3)^{1/2} [C_6H_6]^{1/2} \quad (xxxiii)$$

Therefore, for a given set of conditions a plot of $R/[C_6H_6]$ against $[C_6H_6]^{1/2}$ is a straight line with an intercept equal to $k_1$. If the data are plotted at different temperatures a value for $E_1$ can be obtained.
Figure 2:13 shows that the data fit a straight line. The intercept is very close to the origin and demonstrates that long chains exist i.e. initiation is very small compared with propagation. Data for \( k_1 \) cannot however, be obtained because of this very small value of the intercept. The results are insensitive to \( k_1 \) and the intercept varies randomly around the origin. For second order initiation the rate expression (xxx)

\[
R_2 = \frac{d[H_2]}{dt} = 2k_{1a}[C_6H_6]^2 + \frac{(2k_{1a}k_6k_9)}{k_7}[C_6H_6]^{3/2}
\]

was developed.

On dividing by \( [C_6H_6]^2 \) the expression becomes:

\[
\frac{R_2}{[C_6H_6]^2} = 2k_{1a} + \frac{(2k_{1a}k_6k_9)}{k_7}[C_6H_6]^{-1/2}
\]

A plot of \( \frac{R_2}{[C_6H_6]^2} \) against \( [C_6H_6]^{-1/2} \) will yield a straight line plot similar to above.

**Comparison of Derived Rate Expressions with Experiment.**

From the data listed in table 2-7, theoretical values of the rate of hydrogen production can be obtained for the several proposed mechanisms.

For the first order initiation mechanism:

\[
\frac{d[H_2]}{dt} = 10^{11.6} \exp\left(-59,000/RT\right)[C_6H_6]^{3/2} \text{ mole litre}^{-1} \text{ sec}^{-1}
\]

For the second order initiation mechanism (a simplified version of that proposed by Low and Lucas\(^{31}\))

\[
\frac{d[H_2]}{dt} = 10^{12.2} \exp\left(-61,000/RT\right)[C_6H_6]^{3/2} \text{ mole litre}^{-1} \text{ sec}^{-1}
\]

The second order initiation reaction mechanism as proposed by Low and Lucas\(^{31}\) comprises \( 1a, 9, -9, 2, 5 \) and \( 7 \).
FIG. 2: Function plot to test the proposed mechanism (involving 1st order initiation) for benzene pyrolysis.
For this \( \frac{d[H_2]}{dT} = k_2 \frac{k_{1a} \sqrt{k_6}}{k_9 k_7} [C_6H_6]^{3/2} \) (xxxvii) if long chains exist.

Using their data

\[
\frac{d[H_2]}{dT} = 10^{13.8} \exp \left( -67,000/RT \right) [C_6H_6]^{3/2} \text{ mole litre}^{-1} \text{ sec}^{-1} \]  

This value is far removed from observed experimentally in this work, which was:

\[
\frac{d[H_2]}{dT} = 10^{9.83} \exp \left( -53,800/RT \right) [C_6H_6]^{3/2} \text{ mole litre}^{-1} \text{ sec}^{-1} \]  

For the working benzene concentration of \( 5.372 \times 10^{-4} \) mole litre\(^{-1} \) an Arrhenius plot was obtained for the various expressions. The results are shown in figure 2:14. The mechanism with 1st order initiation agrees best with experiment although the predicted activation energy at low temperatures is too high. The rate data obtained from the mechanism proposed by Louw and Lucas are not in such good agreement. Thus the mechanism that best describes the experimental data at temperatures between 973 K and 1023 K is:

\[
\begin{align*}
C_6H_6 & \rightarrow \overline{C}_6H_5 + \overline{H} \quad (1) \\
\overline{C}_6H_5 + C_6H_6 & \rightarrow (C_6H_5)_2 + \overline{H} \quad (5) \\
\overline{H} + C_6H_6 & \rightarrow \overline{C}_6H_7 \quad (9) \\
\overline{C}_6H_7 & \rightarrow \overline{C}_6H_5 + H_2 \quad (6) \\
2\overline{C}_6H_5 & \rightarrow (C_6H_5)_2 \quad (3)
\end{align*}
\]

At lower temperatures the Arrhenius plot deviates from linearity and a rate constant of

\[
k = 10^{8.2} \exp \left( -46,300/RT \right) \text{ mole litre sec}^{-1} \]  

was obtained over the full temperature range.
FIG. 2:14 Comparison of derived rate expressions with experiment for a benzene conc. of $5.372 \times 10^{-4}$ mole litre$^{-1}$ and a residence time of 4 mins.
One explanation of this might be a catalytic effect on the surface of the reaction vessel which reduces the apparent activation energy. Little effect of surface on rate was observed so this must be ruled out.

An alternative explanation may be termination by reaction (-la)

\[ \text{C}_6\text{H}_5 + \text{C}_6\text{H}_7 = 2\text{C}_6\text{H}_6 \]  

(-la)

Inclusion of the reaction in the 1st order initiation scheme does not yield \( \frac{3}{2} \) order kinetics, and thus it can be ruled out. Inclusion of (-la) in the 2nd order initiation scheme does, however, yield \( \frac{3}{2} \) order kinetics and a rate expression of

\[ \frac{d[H_2]}{dt} = \frac{(2k_{\text{la}}k_5k_6/k_{\text{la}})^{\frac{1}{2}} [C_6H_6]^{3/2}}{\text{mole}^{-1/2} \text{ litre}^{-1} \text{ sec}^{-1}} \]  

(\text{xxxix})

is obtained, which yields an activation energy of 60,000 cals mole\(^{-1}\). Thus this will not explain the curvature of the plot either. So far no satisfactory explanation has been found.
FURTHER REACTIONS OF BENZENE AT HIGHER TEMPERATURES

Mechanisms for diphenyl and hydrogen formation were proposed and discussed earlier. The results reported in figure 2:1 (page 35) show that no major gaseous products other than methane and hydrogen are formed. It is difficult to envisage a mechanism by which methane can be formed above 953K other than ring opening followed by hydrogenation. A carbon balance indicates that methane cannot be the only product of ring opening. Some carbon must appear in another form. In the static apparatus, it appeared as soot, and as the temperature was increased above 1073K the reaction vessel rapidly became blocked. This factor made studies of methane formation in the static apparatus impossible. The pyrolysis was therefore carried out in a flow system where much shorter residence times of the order of 0.1 sec were possible.

The following experiments were performed using the flow apparatus.

The effect of temperature and residence time on product yields

With an average residence time of 0.1 sec the pyrolysis reaction was carried out over the temperature range of 1053K to 1243K. The gaseous product yields are shown in figure 2:15. Hydrogen is still the major product, about ten times more abundant by volume than the next major constituent, but its distribution is altered considerably. Acetylene is now an important product, and ethylene is also detected. Methane formation appeared to be less, relative to the other products, than was found in the static apparatus. This effect suggests the acetylene is formed in a primary process and ethylene and methane are formed in secondary reactions with the excess hydrogen.

A possible sequence is

$\text{H}_2 \rightarrow \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_4 \rightarrow 2\text{CH}_4$
FIG. 2: Pyrolysis of benzene in a flow reactor at relatively high temperatures and ~0.1 sec. residence time.
If ethylene and methane result from the hydrogenation of acetylene then the pyrolysis of benzene in the presence of deuterium should yield deuterium substituted ethylene and methane. Accordingly benzene was pyrolysed in the presence of deuterium and the gaseous products analysed on a mass spectrometer. m/e peaks at 19, 20, and 30, 31 were observed, which suggest the presence of CD$_3$H and CD$_4$, and C$_2$D$_2$H$_2$ and C$_2$D$_3$H. This conclusion assumes negligible hydrogen - deuterium exchange. In a further experiment, however, benzene-d$_6$ was pyrolysed in the presence of hydrogen. The condensate obtained was analysed for various substituted benzene products. The results in figure 2:16 show that scrambling does occur and the conclusions from the previous experiment must be regarded as tentative.

The effect of pressure on acetylene yield

Benzene pressure was varied by alteration of the flow through the saturator device. The total flow and hence residence time was kept constant by passage of nitrogen through the by-pass. The results for a reaction temperature of 1067K are shown in figure 2:17. The open circles show data obtained for acetylene alone. A log-log plot yields an order of 0.3. If methane and ethylene are formed from acetylene then a correction for the formation of these products must be made. The filled circles show this plot. In this case a log-log plot yields an order of 0.5.

The activation energy for acetylene formation

Accurate determination of the activation energy is more difficult than the above pressure dependency experiment. Radiation errors and the lack of a temperature plateau across the furnace make temperature measurement extremely difficult. However, an approximate Arrhenius plot yielded an activation energy of about 50,000 cal/mole$^{-1}$. As this value is lower than that for the low temperature reaction it must be suspect.
FIG. 2:16. Hydrogen scrambling between hydrogen and benzene-d₆
FIG. 2.16 Effect of benzene concentration change on product yield from benzene pyrolysis at 1167K.
If acetylene is a primary reaction product then possible additional reactions in the basic scheme are

\[ \begin{align*}
\text{C}_6\text{H}_5 & = \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \\
\text{C}_4\text{H}_3 + \text{C}_6\text{H}_6 & = \text{C}_4\text{H}_4 + \text{C}_6\text{H}_5
\end{align*} \]  

Rate expressions for hydrogen and acetylene production are

\[ \begin{align*}
\frac{d[H_2]}{dt} & = k_5 \frac{(k_1/k_3)^{1/2} [C_6H_6]^{3/2} + k_1 [C_6H_6]}{} \\
\frac{d[C_2H_2]}{dt} & = k_7 \frac{(k_1/k_3)^{1/2} [C_6H_6]^{1/2}}{}
\end{align*} \]

Thus the order of acetylene production is predicted to be one half, with an activation energy of \((\frac{1}{2}E_1 - \frac{1}{2}E_3) + E_7\). 

\(E_1\) has been established as 110,000 cals mole\(^{-1}\) and \(E_3\) for the termination reaction will be about zero. Estimation of \(E_7\) presents more of a problem. Asaba and Fujii\(^{35}\) have suggested a value of 83,000 cals mole\(^{-1}\) which is similar to the heat of reaction. With this value, an activation energy of acetylene formation of about 138,000 cals mole\(^{-1}\) is predicted. The experimental value of 50,000 cals mole\(^{-1}\) is very different. At the higher end of the temperature range, large quantities of carbon are formed. Both benzene and acetylene are known carbon precursors and the yield of acetylene measured at this end could be wildly in error. As stated earlier the experiments conducted in the flow apparatus are only semi-quantitative. For accurate data another system must be employed and the small reaction times possible in shock tubes suggest this as a possible solution.

**The formation of carbonaceous solids (soot)**

Soot formation from the pyrolysis of gases is an important industrial process, and there is a vast literature on the subject. Cullis and Palmer\(^{57}\) have produced a comprehensive review up to 1964.
Work up to 1971 has been reviewed by Mueller. In the Gas Industry, soot is an unwelcome product in hydrogenation processes. Its precursor is likely to be the aromatic content of the oil. This part of the thesis describes the formation and properties of soot from benzene pyrolysis at relatively high temperatures between 1173K to 1273K.

When benzene is pyrolysed in this range carbon is readily formed. Two distinct types can be identified:

i) a shiny lustrous type formed on the surface of the reaction vessel

ii) a fluffy type formed at the reaction vessel exit.

Plate 3 shows scanning electron microscope photographs of the two types of carbon. The photograph of the deposit in the reaction vessel tells little of its method of formation. That of the deposit at the exit shows it to be built up of spherical droplets. A mechanism where gas phase molecules \( \rightarrow \) bigger molecules \( \rightarrow \) liquids \( \rightarrow \) droplets which then pyrolyse may be operating.

The lustrous carbon from the reaction vessel wall was shown by X-ray diffraction to be poorly crystalline with carbon of crystallite size 15 to 20 Å.

Chemical analysis gave 98.8% carbon present which if the remainder is assumed to be hydrogen corresponds to a C:H ratio of approximately 7:1. This carbon is virtually graphite.

The carbon at the reaction vessel exit, in contrast, did not give an X-ray diffraction pattern, indicating that it is non-graphitic and amorphous. Chemical analysis showed the carbon content to be 94.3%. This corresponds to a C:H ratio of 1.6:1. The sooty carbon resembled typical pyrolytic carbons and is formed in much greater yield than the lustrous carbon.
Carbon inside reactor

Carbon at reactor exit

Electron micrographs of carbon deposited.

PLATE 3
Future experiments and discussions are thus restricted to this carbon.
The graphitic carbon may of course be formed via a route involving the
fluffy carbon as an intermediate.

**Surface properties of the carbon**

The surface chemistry of the carbon was investigated by adsorption
studies with the microbalance discussed in part II of this section.
Initially nitrogen adsorption at 77K was investigated. The resulting
isotherm is shown in figure 2:17.

The surface area was calculated by the B.E.T. equation.

\[
p/w(p_o-p) = \frac{1}{X_m} c + \frac{(c-1)}{X_m} c(p/p_o)
\]

where \( p \) = adsorbate pressure

\( p_o \) = saturated vapour pressure of adsorbate

\( X_m \) = monolayer capacity

\( c \) = constant

\( w \) = mass of gas (or vapour adsorbed)

A plot of \( p/w (p_o-p) \) against relative pressure \( p/p_o \) will give a straight
line with \( X_m = 1/\text{gradient} + \text{intercept} \)

Hence surface area = \( (X_m \times N \times A_m \times 10^{-20})/M \) \( \text{metre}^2\text{gm}^{-1} \)

where \( N \) = Avogadro's number

\( A_m \) = cross sectional area of the adsorbate molecule \( \text{Å}^2 \)

\( M \) = gram molecular weight of adsorbate

In recent years there have been criticisms of the B.E.T. equation but
in spite of this, the method is still widely used as a comparative method
for surface areas.

In these experiments benzene was used as well as nitrogen as an
adsorbate.
FIG. 2:17 Nitrogen adsorption isotherm at 77K on carbon produced from benzene pyrolysis.

FIG. 2:18 Benzene adsorption isotherm at 299K on carbon produced from benzene pyrolysis.
The isotherm is shown in figure 2.18. The surface area of the nitrogen molecule was taken as 16.2 Å² and that for benzene as 40 Å². This value is described by Gregg and Sing as the usual value and is somewhat higher than the value of 30.5 Å² derived from the density of the pure liquid. Application of the B.E.T. equation over the range \( p/p_0 = 0 \) to 0.3 yielded surface areas of 12.9 metre² gm⁻¹ with nitrogen as an adsorbate and 11.6 metre² gm⁻¹ with benzene. The nitrogen isotherm is a typical type I isotherm as described by Langmuir.

Type I behaviour can be the result of:

a) chemisorption, or

b) physical adsorption by a microporous solid

As the isotherm is reversible i.e. the desorption isotherm follows that for the adsorption isotherm case (a) can be ruled out and the adsorption can be attributed to micropores of diameter less than 10 Å. On addition of a dose of nitrogen, pore filling takes place to give a monolayer. Multilayer formation is not possible as the external area of the sample is small. Enhanced adsorption often occurs and this gives rise to B.E.T. areas that are too high. The enhanced adsorption is due to overlap of the potential fields on opposite sides of the pore resulting in an attractive force on the nitrogen molecule.

The external surface area of the sample can be measured from an electron microscope photograph. The carbon sample was embedded in epoxy resin and sectioned. Plate 4 shows the results obtained at x 6,000 and x 20,000 magnification. A typical radius of a particle in the x 20,000 photograph is 3.75 x 10⁻⁵ cm. If the density of the soot is equal to that of graphite i.e. 2.25 gm cc⁻¹ then the external surface area of the sample is 4.0 metre² gm⁻¹. This is in agreement with the previous hypothesis, and indicates the presence of micropores.
PLATE 4 Electron micrographs of the carbon formed during the pyrolysis of benzene.
The isosteric heat of adsorption of benzene on the soot

Isosteric heats of adsorption are obtained from a study of adsorption isosteres. The amount of gas adsorbed is kept constant and the adsorbate measured for various temperatures.

Application of the Clapyron Clausius equation:

\[
\frac{d\ln p}{dt} = \frac{\Delta H_{\text{ads}}}{RT}
\]

where \( p \) = adsorbate pressure

\( T \) = absolute temperature

\( \Delta H_{\text{ads}} \) = isosteric heat of adsorption

yields the heat of adsorption.

In practice adsorption isotherms are measured at various temperatures (286K to 340K). For a constant value of amount adsorbed the corresponding pressure is read off the isotherm. A Van't Hoff plot of \( \log p \) against \( 1/T(K^{-1}) \) will then be a straight line of slope \( \Delta H_{\text{ads}} \). For a coverage of 0.003 mg per mg of sample the plot is shown in figure 2:19. The slope yields an isosteric heat of adsorption of about 8,000 cal mole\(^{-1}\). This is approximately the same as the latent heat of evaporation. Benzene, therefore is only physically adsorbed on the carbon. This suggests that the carbon laid down on the vessel walls is inert and will not enhance chain initiation or chain destruction.

Mass spectrometric analysis of the soot

This experiment was carried out on a Varian Mat 311A mass spectrometer coupled to an on-line data system. A carbon sample was prepared by passage of benzene through the tubular flow reactor, at a reaction temperature of about 1223K. The sample was collected from the tube exit. It was introduced into the mass spectrometer via a direct insertion probe at 433K. Figure 2:20 shows the resulting spectrum. As little fragmentation occurs the peaks are generally molecular ion peaks.
FIG. 2: Temperature dependence of benzene adsorption on carbon produced from benzene pyrolysis.
FIG. 2:20 Mass spectrum of carbon from benzene pyrolysis
Molecular formulae can be obtained by accurate mass measurements. The mass of the unknown peak is compared with that of a reference compound. By this technique the mass to four decimal places can be found; thus it is possible to distinguish between compounds of the same molecular mass and obtain a molecular formula. Table 2:8 shows the results for three major peaks.

**TABLE 2:8**

<table>
<thead>
<tr>
<th>Peak (m/z)</th>
<th>Formula</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>276.0939</td>
<td>C_{22}H_{12}</td>
<td>276.0944</td>
</tr>
<tr>
<td>302.1097</td>
<td>C_{24}H_{14}</td>
<td>302.1095</td>
</tr>
<tr>
<td>304.1248</td>
<td>C_{24}H_{16}</td>
<td>302.1252</td>
</tr>
</tbody>
</table>

From these data it is possible to draw up a table of possible structures for each peak. This is shown in table 2:9.

Further spectra were obtained by a technique of selective ion monitoring. The sample was introduced by the direct insertion probe and heated by a programme from 313K to 773K in 500 seconds. The line 5 on figure 2:21 shows that the sample is made up of two major constituents.

The m/e peaks of 57, 302 and 378 were then scanned and the results also shown in figure 2:21. Temperatures for maximum intensity of these peaks are 333K, 433K and 573K respectively. The spectra run at these temperatures are shown in figure 2:22.

The soot is composed of two types of compound. The major portion is aromatic.
### Table 2:9

**Some Possible Compounds Found in the Soot Formed from the High Temperature Pyrolysis of Benzene**

<table>
<thead>
<tr>
<th>m/e</th>
<th>Possible Structure</th>
<th>Amount Relative to 302 Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>154</td>
<td>diphenyl</td>
<td>17</td>
</tr>
<tr>
<td>178</td>
<td>phenanthrene, anthracene</td>
<td>15</td>
</tr>
<tr>
<td>202</td>
<td>pyrene, benzobiphenylene, fluoranthrene</td>
<td>12</td>
</tr>
<tr>
<td>228</td>
<td>triphenylene, chrysene, benzenophenanthrene tetraphene</td>
<td>12</td>
</tr>
<tr>
<td>230</td>
<td>terphenyl</td>
<td>12</td>
</tr>
<tr>
<td>252</td>
<td>perylene, benzopyrene</td>
<td>7</td>
</tr>
<tr>
<td>276</td>
<td>anthracene, benzenopyrene, phenylene-pyrene</td>
<td>28</td>
</tr>
<tr>
<td>278</td>
<td>benzoanthracene, picene, pentacene</td>
<td>10</td>
</tr>
<tr>
<td>300</td>
<td>coronene</td>
<td>25</td>
</tr>
<tr>
<td>302</td>
<td>benzenopyrenes, dibenzenopyrenes</td>
<td>100</td>
</tr>
<tr>
<td>304</td>
<td>tetraphenylene, dihydrodibenzotetracene</td>
<td>43</td>
</tr>
<tr>
<td>326</td>
<td>dibenzenopyrenes, peropyrene, rubicene</td>
<td>12</td>
</tr>
<tr>
<td>328</td>
<td>hexahelicene, dibenzochrysene</td>
<td>4</td>
</tr>
<tr>
<td>382</td>
<td>quinquiphényl</td>
<td>7</td>
</tr>
</tbody>
</table>
FIG. 2:21 Selective ion monitoring of ions m/e 57, 302, 378
FIG. 2: Mass spectra of the soot at various probe temperatures

probe temperature 60°C

probe temperature 160°C

probe temperature 300°C
Polycyclic and compounds composing benzene rings linked head to tail, up to sexiphenyl, are in this group. A smaller but still significant type is comprised of straight chain paraffinic compounds as indicated in spectrum (a) of figure 2:22.

**Structure and mechanism of the soot formation**

The work described so far in this section shows that the soot is amorphous with a carbon to hydrogen ratio of 1.4:1. It appears at the reaction vessel exit as small spheres of $3.75 \times 10^{-5} \text{cm}$ radius. They are of low surface area and contain micropores. Benzene is only physically adsorbed. Chemically the soot is complex and mass spectrometric analysis indicates formation via both polymerisation and fragmentation mechanisms.

Numerous theories of carbon formation have been proposed. The major ones are summarised by Cullis and Palmer. Recently Graham, Homer and Rosenfeld have produced evidence that at a high temperature in a shock tube (1600 to 2300K) aromatics produce soot by two routes. These are either condensation reactions in which the molecules retain their aromatic character or an indirect route by which the molecule decomposes into small non-aromatic species before any soot is formed.

![Diagram](A) condensation $\rightarrow$ soot

![Diagram](B) fragmentation $\rightarrow$ soot

$$\begin{array}{c}
\text{CH}_x \\
\text{C}_2\text{H}_x \\
\text{C}_3\text{H}_x
\end{array}$$
They also conclude that route A is six times faster than route B at 1750 to 1800 K.
The experiments in this thesis are in accord with this theory and it is possible to build up a detailed scheme for the condensation reaction mechanism, for the compounds identified in the soot.
The formation of triphenylene is well known.

![Reaction Scheme]

This reaction can be used as a model for the formation of other polynuclear compounds found in the soot.

![Reaction Schemes]

1,2,6,7 dibenzopyrene

tetrabenzanthracene
Similarly a dibenzopicene can be built up from p-terphenyl.

\[
\begin{array}{c}
\text{p-terphenyl} + \text{benzene} \rightarrow \\
\text{dibenzopicene}
\end{array}
\]

The compound can now dehydrogenate to give:

Although not detected (most probably due to evaporation of the polynuclear compounds on the mass spectrometer probe at too low a temperature) it is highly possible that hexaperibenzocoronene is present. A similar synthesis as described above is possible.
This compound has been synthesised by Clar and Stephen. It is insoluble in all known solvents and does not melt at temperatures below 760°C. To all intents and purposes it and compounds similar to it can be regarded as carbon. This 'carbon' can quite easily be built up from relatively simple compounds. Another interesting feature is the presence of quinquiphenyl and sexiphenyl.

Sexiphenyl has a melting point of about 380°C which suggests that carbon can be built up quite quickly via this route also. Of course the complete mechanism is not as simple as described, since compounds based on tetraphenylene can also be built up.
Route (2) involves the ring opening mechanism possible via reaction

\[ \text{C}_6\text{H}_5 = \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \]  

(4)

The \( \text{C}_4\text{H}_3 \) can then perhaps add on to an already formed ring and build-up can occur this way.

A cross combination of both reactions can yield compounds such as coronene.

Thus, in aromatic pyrolysis experiments, soot may well be formed by the above condensation mechanism. A fragmentation route can also occur.

Further work, perhaps with shock tubes, would be required to establish the detailed mechanism of the high temperature pyrolysis.
SECTION THREE

THE PYROLYSIS OF ETHYL BENZENE
In a recent paper on paraffin pyrolysis Bradley commented, "Genuine progress in this field has been rather slow and erratic."

The previous section on benzene pyrolysis suggests that in the field of aromatic pyrolysis by comparison, progress has been even slower. This is also true of dealkylation studies of ethyl benzene. Although kinetic studies date back to Szwarc's work in 1949, no full mechanism for the pyrolysis of ethyl benzene in the absence of carriers has been proposed. Szwarc suggested that the reaction could be described by a free radical chain mechanism. Initiation occurred by fission of the aliphatic C-C bond to yield benzyl and methyl radicals.

\[
C_6H_5CH_2CH_3 = C_6H_5CH + CH_3 \quad (1)
\]

This was followed by the propagation reactions:

\[
\begin{align*}
\text{CH}_3 + C_6H_5CH_2CH_3 & = CH_4 + C_6H_5CHCH_3 \\
\text{CH}_3 + C_6H_5CH_2CH_3 & = CH_4 + C_6H_5CH_2CH_2 \\
\text{C}_6H_5CHCH & = \text{H} + C_6H_5CH_2 \\
\text{H} + C_6H_5CH_2 & = \text{H}_2 + C_6H_5CHCH_2 \\
\text{H} + C_6H_5CH_2 & = \text{H}_2 + C_6H_5CHCH_3 \\
\text{H} + C_6H_5CH & = C_6H_6 + C_2H_5 \\
\text{H} + C_6H_5CH & = CH_4 + C_6H_5CH_2 \\
C_2H_5 + C_6H_5CH_2 & = C_2H_6 + C_6H_5CHCH_2 \\
C_2H_5 + C_6H_5CH_2 & = C_2H_6 + C_6H_5CHCH_3 \quad (8a)
\end{align*}
\]

Possible chain termination processes were

\[
\begin{align*}
\text{H} + C_6H_5CH_2 & = C_6H_5CH_3 \\
2C_2H_5 & = C_2H_4 + C_2H_6 \\
\text{H} + \text{H} + \text{M} & = \text{H}_2 + \text{M} \quad (10a)
\end{align*}
\]
The prime object of Szwarc's work was to obtain an accurate value for the aliphatic C–C bond energy in the ethyl benzene side chain. No proof of the mechanism was proposed. In fact Szwarc suggested that as the chain process is complicated, it is unsuitable for an exact study and proposed a technique employing excess toluene as a carrier. Thus the reaction was modified to

\[
\begin{align*}
\ce{C6H5C2H5} &\rightarrow \ce{C6H5CH2} + \ce{CH3} \\
\ce{C6H5CH3} + \ce{CH3} &\rightarrow \ce{C6H5CH2} + \ce{CH4} \\
2\ce{C6H5CH2} &\rightarrow \ce{(C6H5CH2)2}
\end{align*}
\]

The excess toluene suppressed the chain by reacting with the methyl radicals produced by ethyl benzene dissociation. Reaction 11 is very rapid, hence the rate of methane appearance is a measure of the rate of dissociation of the ethyl benzene. Thus Szwarc was able to obtain a rate constant given by

\[
\log_{10} k \ (\text{sec}) = 13.0 - \frac{63,000}{2.303RT}
\]

from his results in a plug flow reactor. The activation energy was taken to be the C–C bond energy. The carrier method in one form or another has been widely used in subsequent investigations.

Estban, Kerr and Trotman-Dickenson used aniline as a carrier in a plug flow apparatus. They were investigating the heat of formation of the benzyl radicals formed in ethyl benzene pyrolysis. Aniline was considered a better carrier than toluene because it was unlikely to yield hydrocarbon side products. It is stable at the pyrolysis temperature and there is no sign of induced decomposition. The first order rate constants for ethyl benzene decomposition were calculated from the methane formed which was assumed to come from the sequence of reactions

\[
\begin{align*}
\ce{C6H5CH3} &\rightarrow \ce{C6H5CH2} + \ce{CH3} \\
\ce{CH3} + \ce{C6H5NH2} &\rightarrow \ce{CH4} + \ce{C6H5NH}
\end{align*}
\]
The aniline radical was assumed to dimerize or polymerize. The amount of ethane detected was small and the recombination of methyl radicals was disregarded. Hydrogen found was assumed to come from the molecular decomposition of ethyl benzene into hydrogen and styrene. Although no volatile nitrogeneous products were observed, decomposition of the aniline radical could not be eliminated. Formation of ethylene and benzene were also considered to be via a molecular decomposition. Methane formation was regarded as the only significant process and a rate constant given by

$$\log_{10} k \text{ (sec}^{-1}) = 14.6 - 70,000/2.303RT$$

was obtained.

Crowne, Grigulis and Throse\textsuperscript{1166} used a stirred flow reactor to study the pyrolysis in the presence of a toluene carrier. Their findings show that the experimental first order is dependent on the pressure of toluene and that the rate of methane production falls with a reduction in carrier pressure for a given partial pressure of reactant. Because there was a high concentration of benzyl radicals the reverse of reaction 1 was thought to be significant.

$$\text{CH}_3 + \text{C}_6\text{H}_5' \rightarrow 2 \text{C}_6\text{H}_5\text{CH}$$

An uncorrected value for the rate constant of

$$\log_{10} k \text{ (sec}^{-1}) = 13.1 - 62,200/2.303RT$$

for reaction (1) was obtained. The value was corrected with the help of rate data obtained by Kominar, Jacko and Price\textsuperscript{68} for reaction (1).

$$\log_{10} k \text{ (litre mole}^{-1}\text{sec}^{-1}) = 8.2 - 200/2.303RT$$

Clarke and Price\textsuperscript{67} have carried out a detailed investigation with a toluene carrier and have suggested that the pyrolysis occurs at 910 to 1089K by three main reactions.
\[
\begin{align*}
C_6H_5C_2H_5 &= C_6H_5CH_2 + CH_3 \quad (1) \\
C_6H_5C_2H_5 &= C_6H_6 + C_2H_4 \quad (12) \\
C_6H_5C_2H_5 &= C_6H_5C_2H_3 + H_2 \quad (13)
\end{align*}
\]

For the initiation reaction (1) a rate constant of

\[
\log_{10} k \text{ (sec}^{-1}) = 14.7 - 70,100/2.303 RT \quad (v)
\]

was obtained.

They showed that at the lowest end of the temperature range negligible corrections for the reverse of reaction 1 were necessary. At 1025K 35% decomposition occurs and they suggest that about 15% of ethyl benzene undergoing decomposition would be expected to be regenerated. They consider a correction of 2,000 to 3,000 cals. mole\(^{-1}\) on the activation energy to be sufficient. Experiments showed ethylene yield to be surface dependent but in a conditioned quartz vessel a rate constant of

\[
\log_{10} k \text{ (sec}^{-1}) = 9.06 - 51,700/2.303 RT \quad (iv)
\]

for reaction 12 was obtained. In most experiments, benzene yield was found to be higher that that of ethylene, although the authors state that the accuracy of the benzene results are open to question.

A rate constant for reaction 13 of

\[
\log_{10} k \text{ (sec}^{-1}) = 12.7 - 64,000/2.303 RT
\]

was obtained from the styrene yield.

Experiments without a carrier gas, have been performed by Lee and Oliver\(^{69}\), who used a flow reactor. For reaction temperatures between 848 and 880K they found orders of reaction 0.8 for benzene formation and 1.1 for toluene formation. Styrene order, however, varied between one at low temperatures and zero at higher temperatures. No reaction mechanism was proposed.
Hausmann and King\textsuperscript{70} repeated these experiments with and without traces of oxygen present. They used an unusual coiled reactor of 1 metre length. Residence time was varied from 0.06 sec to 0.17 sec and temperature from 863 to 923K. In the absence of oxygen, the order of reaction with respect to styrene was found to be one half. A rate expression of

$$\frac{d\text{[styrene]}}{dt} = k_2 \left[ \frac{C_6H_5C_2H_5}{2} \right]^{1/2}$$

(viii)

where

$$k_2 = 10^{15} \exp\left(\frac{-70,000}{RT}\right) \text{mole}^{-1/2} \text{litre}^{1/2} \text{sec}^{-1}$$

(ix)

was proposed. Considerable scatter on their Arrhenius plot makes the value unreliable. The following chain mechanism was proposed.

$$C_6H_5C_2H_5 = C_6H_5CH_2 + CH_3$$

(1)

$$CH_3 + C_6H_5C_2H_5 = C_6H_5CHCH_3 + CH_4$$

(2a)

$$C_6H_5CHCH_3 = C_6H_5CHCH_2 + H$$

(5)

$$H + C_6H_5C_2H_5 = C_6H_6CHCH_3 + H_2$$

(6a)

$$2C_6H_5CHCH_3 = \text{various products}$$

(10c)

The benzyl radical $C_6H_5CH_2$ was assumed to be unreactive and hence reactions involving it were not included. For long chains the expression (x) was found to be consistent with the experimental results.

$$\frac{d\text{[styrene]}}{dt} = (k_2k_5^2/k_{10c})^{1/2} \left[ \frac{C_6H_5C_2H_5}{2} \right]^{1/2}$$

(x)

Additional steps to account for ethane, ethylene, and benzene were suggested. Polynuclear hydrocarbons can be formed as secondary products in the pyrolysis and Badger and Spotswood\textsuperscript{71} have carried out a detailed non-kinetic study. Compounds identified include phenanthrene, naphthalene, diphenyl and dibenzyl.

This review shows that the bulk of the kinetic studies have been carried out with carrier techniques in flow systems. As better experimental techniques became available the limitations of these processes became apparent.
Molecular processes which seem unlikely were proposed to account for hydrogen, ethane, benzene and styrene formation. If the carrier does not completely suppress the chain (as is often the case with nitric oxide and propylene inhibition) then the additional chain products will be observed. The dependence of reaction on toluene pressure shows that this carrier is not completely 'inert'.

For a complete investigation in which a reaction mechanism can be proposed it is desirable that the pyrolysis be done in the absence of carriers. Hausmann and King have attempted this in a flow system but their results are incomplete.

Modern methods enable accurate results to be obtained for vapours in a static system. The original objections to non carrier techniques, proposed by Szwarc, no longer apply. Gas chromatography enables speedy and accurate product analysis and stainless steel bellows sealed taps enable vapours to be handled.

The work discussed here uses the static system described earlier and sets out (a) to confirm that the rate data obtained for the initiation reaction by carrier techniques applies to the system in the absence of carrier and (b) to obtain a more complete reaction mechanism for the reaction.
Introduction

These experiments were carried out with the static apparatus and similar procedures to those described earlier. Gas and vapour mixtures were made up in a heated globe. In a typical experiment, about 40 torr of ethyl benzene was taken and nitrogen added until 400 torr pressure was reached. When the reaction mixture was admitted to the evacuated reaction vessel, the total pressure dropped to around 300 torr. The exact pressure was determined by a previous calibration. After a period of time, usually four minutes, the reaction mixture was removed from the vessel and the products of reaction sampled and analysed.

Preliminary Observations

Literature cited previously in this section indicates that the major products of reaction are hydrogen and styrene. To minimize side reactions and secondary product formation, the reaction was studied at low conversions. A typical experiment at 783K with four minutes residence time gave about 3% conversion. Table 3.1 shows the product distribution for the decomposition of thirty torr of ethyl benzene under these conditions.

<table>
<thead>
<tr>
<th>Product</th>
<th>Partial Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.5</td>
</tr>
<tr>
<td>Methane</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.07</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.08</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Product Analysis

Analysis was carried out by gas chromatography. Gaseous products were easily separated on a charcoal column and accurate peak area measurements were made with an electronic integrator. With columns suitable for liquid product analysis an order of elution of benzene, toluene, ethyl benzene and styrene was obtained. Thus a relatively small styrene peak was eluted on the tail of a very large ethyl benzene peak. In most experiments ethyl benzene overloaded the column. The best separation was found with a silicone oil/bentone column but it was impossible to measure the peak area accurately with the integrator, for styrene. A planimeter gave greater accuracy but the method is very time consuming and the tedium can lead to errors. An alternative procedure is to cut out the peaks and weigh them. The method gave good consistent results and was used to estimate styrene formation. A typical calibration graph is shown in figure 3:1.

Effect of varying residence times

Experiments were carried out with a precisely measured pressure of about 30 torr of ethyl benzene, a reaction temperature of 788K and residence times of two to ten minutes. The effect on gaseous product yield is shown in figure 3:2. In all cases a straight line passing through the origin can be drawn, so the rate after any time can be equated to the initial rate. In practice, subsequent experiments were carried out with a residence time of four minutes and the overall rate after this time was taken as equal to the initial rate.

The effect of added nitrogen

About 30 torr of ethyl benzene was taken and between 100 and 400 torr of nitrogen added.
FIG. 3:1 Typical styrene calibration graph
FIG. 3:2 Progress of ethyl benzene pyrolysis reaction with time.
With a reaction temperature of 788K and a residence time of four minutes, the effect of nitrogen pressure on the pyrolysis product yield was observed. Results obtained for gaseous and liquid product yield are shown in figure 3:3. Of the gaseous products, methane, hydrogen and ethane remain unaffected by increase in nitrogen concentration but a 60% increase in ethylene yield is seen. As ethane and ethylene are probably formed via the same intermediate a corresponding decrease in ethane yield would be expected. Of the liquid products little effect is seen although benzene yield decreases as nitrogen concentration is increased.

Effect of surface/volume ratio on product yield

Leathard and Purnell\(^40\) have discussed the role of the surface in pyrolysis reactions. Rate can easily be affected by several orders of magnitude. To test for the effect on ethyl benzene pyrolysis, experiments were carried out in a reaction vessel packed with silica tubes. Total surface to volume ratio was 1.105 mm\(^{-1}\). The results were compared with those obtained in the usual reaction vessel of surface to volume ratio 0.077 mm\(^{-1}\). Table 3:2 shows the results for a run at a reaction temperature of 792K with a four minute residence time and an ethyl benzene concentration of 34 torr.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield/Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Packed</td>
</tr>
<tr>
<td>methane</td>
<td>0.075</td>
</tr>
<tr>
<td>hydrogen</td>
<td>0.52</td>
</tr>
<tr>
<td>ethylene</td>
<td>0.095</td>
</tr>
<tr>
<td>ethane</td>
<td>0.075</td>
</tr>
</tbody>
</table>

**Table 3:2**

**EFFECT OF VARYING SURFACE/VOLUME RATIO ON THE ETHYL BENZENE PYROLYSIS**
FIG. 3:3 Effect of added nitrogen on ethyl benzene pyrolysis.
Effect of nitrogen pressure on reaction in the packed vessel

Nitrogen pressure was varied from 100 to 450 torr. The results are shown in figure 3:4. Results are very similar to those in the unpacked vessel although, there is a small effect on ethane yield as would be expected. In subsequent experiments with the 60 mm diameter reaction vessel surface effects were considered small and ignored.

The effect of pressure on the reaction

Dependence of rate on pressure was investigated at 719K and a residence time of four minutes. Ethyl benzene pressure was varied from 10 to 45 torr. The results are shown in figure 3:5 for both gaseous and liquid products. Order of reaction with respect to each product was obtained from graphs of \( \log_{10} \) (ethyl benzene) vs \( \log_{10} \) (product). The results are tabulated below in table 3:3.

**TABLE 3:3**

**ORDER OF REACTION WITH RESPECT TO EACH PRODUCT**

<table>
<thead>
<tr>
<th>Product</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>0.65</td>
</tr>
<tr>
<td>methane</td>
<td>1.0</td>
</tr>
<tr>
<td>toluene</td>
<td>1.0</td>
</tr>
<tr>
<td>ethylene</td>
<td>0.9</td>
</tr>
<tr>
<td>ethane</td>
<td>1.1</td>
</tr>
<tr>
<td>styrene</td>
<td>0.65</td>
</tr>
<tr>
<td>benzene</td>
<td>1.0</td>
</tr>
</tbody>
</table>
FIG. 3:4 Effect of added nitrogen on ethyl benzene pyrolysis in a packed reaction vessel.

- Hydrogen yield (torr)
- Methane yield (torr)
- Ethylene yield (torr)
- Ethane yield (torr)
FIG. 3: Effect of change in ethyl benzene pressure on product yield in ethyl benzene pyrolysis. (hydrogen, styrene, benzene, methane and toluene yields)
FIG. 3:5b Effect of change in ethyl benzene pressure on product yield in ethyl benzene pyrolysis. (ethylene and ethane yields)
The formation of higher molecular weight products

Three different techniques were used to determine the nature of higher molecular weight products which were produced in the reaction. These were:

a) gas liquid chromatography
b) mass spectrometry
c) infra red spectroscopy

a) gas liquid chromatography:

Liquid and solid products for analysis were collected in the trap of the static apparatus shown in plate 1 in the experimental section. Several runs were carried out under normal conditions of 773K reaction temperature, four minutes residence time and thirty torr ethyl benzene, so that a measurable quantity of product could be collected.

0.5 μl of the sample thus collected was injected into a gas chromatograph equipped with a silicone gum rubber column and a flame ionisation detector. Oven temperature was held at 150°C for 12 minutes and then temperature-programmed to 200°C at 8°C per minute. The resulting chromatogram is shown in figure 3:6. A reference mixture was run and the position of these compounds is shown for comparison. The chromatograph suggests that a mixture of polynuclear compounds is formed and no one compound predominates. In the absence of a more powerful gas chromatograph and suitable standard compounds, this method of analysis was not pursued further.

b) mass spectrometry:

Samples for the mass spectrometer were prepared by the dropping of ethyl benzene at 3 mls of liquid per hour from a syringe into a stream of nitrogen in a flow system set up for the experiment.
FIG. 3: Gas chromatograph of the solid products obtained from the pyrolysis of ethyl benzene.
Approximately two minutes residence time was allowed. Products were collected in cold trap at -85°C. Two samples were prepared; one at relatively high conversions with a reaction temperature of 833K and the other at very low conversions with a reaction temperature of 778K.

Products from high conversions:

Before examination, the sample was distilled at 413K in a simple apparatus, to concentrate the higher molecular weight products. Both the residue and the distillate were examined on the Varian mass spectrometer described earlier. Electron impact mass spectra of the residue were obtained at 50°C and 300°C with a variable temperature probe. These spectra are shown in figures 3:7a and 3:7b. The spectrum at 50°C shows few higher molecular weight peaks above \( m/e = 250 \). The most prominent peak is at \( m/e = 178 \) which probably corresponds to anthracene or phenanthrene.

The spectrum at probe temperature 300°C shows that most of the lower molecular weight components have been distilled off, leaving mainly the higher molecular weight trace components. Even so \( m/e = 178 \) remains the base peak. A large number of compounds of molecular weights 128 to 502 were found. Table 3:4a lists them together with some possible structures. In table 3:4b some molecular formulae obtained from accurate mass measurements are listed.

The distillate was also examined by electron impact. The sample was introduced into the source via a reference inlet system at 170°C. The spectrum in figure 3:8 shows the major components to be benzene, styrene, ethyl benzene, naphthalene and diphenyl.
mass spectra of:
products of reaction at high conversion

FIG. 3:7a Electron impact spectrum of the distillation residue from ethyl benzene pyrolysis using variable-temperature probe at 50°C

FIG. 3:7b Electron impact spectrum of the distillation residue from ethyl benzene pyrolysis using the variable-temperature probe at 300°C
### Table 3:4a

Solid compounds found by mass spectrophotometric analysis of the residue from the pyrolysis of ethyl benzene at high conversions

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>ZRI</th>
<th>Compound (other isomeric forms are possible)</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>5</td>
<td>naphthalene</td>
</tr>
<tr>
<td>142</td>
<td>trace</td>
<td>methyl naphthalene</td>
</tr>
<tr>
<td>152</td>
<td>11</td>
<td>diphenylene</td>
</tr>
<tr>
<td>154</td>
<td>4</td>
<td>diphenyl</td>
</tr>
<tr>
<td>166</td>
<td>5</td>
<td>fluorene</td>
</tr>
<tr>
<td>168</td>
<td>2</td>
<td>diphenyl methane</td>
</tr>
<tr>
<td>178</td>
<td>100</td>
<td>anthracene</td>
</tr>
<tr>
<td>180</td>
<td>20</td>
<td>stilbene</td>
</tr>
<tr>
<td>192</td>
<td>14</td>
<td>methyl anthracene</td>
</tr>
<tr>
<td>194</td>
<td>2</td>
<td>ethyl fluorene</td>
</tr>
<tr>
<td>202</td>
<td>26</td>
<td>pyrene</td>
</tr>
<tr>
<td>204</td>
<td>29</td>
<td>ethyl cyclopentacenaphthylenene</td>
</tr>
<tr>
<td>206</td>
<td>5</td>
<td>ethyl anthracene</td>
</tr>
<tr>
<td>216</td>
<td>4</td>
<td>methyl pyrene</td>
</tr>
<tr>
<td>228</td>
<td>4</td>
<td>chrysene</td>
</tr>
<tr>
<td>230</td>
<td>5</td>
<td>p-terphenyl</td>
</tr>
<tr>
<td>232</td>
<td>10</td>
<td>benzopyrene</td>
</tr>
<tr>
<td>234</td>
<td>17</td>
<td>dinaphthylalkanes</td>
</tr>
<tr>
<td>278</td>
<td>9</td>
<td>benzochrysenes</td>
</tr>
<tr>
<td>280</td>
<td>6</td>
<td>ethyl perylenes</td>
</tr>
<tr>
<td>300</td>
<td>trace</td>
<td>coronene</td>
</tr>
<tr>
<td>302</td>
<td>2</td>
<td>benzoperylenes</td>
</tr>
<tr>
<td>304</td>
<td>2</td>
<td>tetraphenylenes</td>
</tr>
<tr>
<td>330</td>
<td>3</td>
<td>methyl benzonaphthoperinaphthenes</td>
</tr>
<tr>
<td>342</td>
<td>trace</td>
<td>methyl dibenzo chrysene</td>
</tr>
<tr>
<td>350</td>
<td>trace</td>
<td>pyreno-pyrene</td>
</tr>
<tr>
<td>378</td>
<td>trace</td>
<td>dibenzo picenes</td>
</tr>
<tr>
<td>380</td>
<td>trace</td>
<td>ethyl benzochrysenes</td>
</tr>
<tr>
<td>402</td>
<td>trace</td>
<td>tetra benzopyrene</td>
</tr>
<tr>
<td>502</td>
<td>trace</td>
<td>benzanthracenopyrene</td>
</tr>
</tbody>
</table>

### Table 3:4b

Examples of components of residue from ethyl benzene pyrolysis identified by high resolution impact mass spectrometry

<table>
<thead>
<tr>
<th>Nominal mass</th>
<th>Accurate mass (measured)</th>
<th>molecular formula</th>
<th>Possible compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>142</td>
<td>142.0770</td>
<td>C_{11}H_{10}</td>
<td>methyl naphthalene</td>
</tr>
<tr>
<td>154</td>
<td>154.0739</td>
<td>C_{12}H_{10}</td>
<td>diphenyl</td>
</tr>
<tr>
<td>166</td>
<td>166.0782</td>
<td>C_{13}H_{10}</td>
<td>fluorene</td>
</tr>
<tr>
<td>168</td>
<td>168.0939</td>
<td>C_{13}H_{12}</td>
<td>diphenyl methane</td>
</tr>
<tr>
<td>178</td>
<td>178.0782</td>
<td>C_{14}H_{10}</td>
<td>anthracene</td>
</tr>
<tr>
<td>180</td>
<td>180.0939</td>
<td>C_{14}H_{12}</td>
<td>stilbene</td>
</tr>
<tr>
<td>192</td>
<td>192.0939</td>
<td>C_{15}H_{12}</td>
<td>methyl anthracene</td>
</tr>
<tr>
<td>194</td>
<td>194.1095</td>
<td>C_{15}H_{14}</td>
<td>ethyl fluorene</td>
</tr>
<tr>
<td>202</td>
<td>202.0783</td>
<td>C_{16}H_{10}</td>
<td>pyrene</td>
</tr>
<tr>
<td>204</td>
<td>204.0939</td>
<td>C_{16}H_{12}</td>
<td>ethylcyclopentacenaphthylenene</td>
</tr>
<tr>
<td>206</td>
<td>206.1096</td>
<td>C_{16}H_{14}</td>
<td>ethyl anthracene</td>
</tr>
<tr>
<td>216</td>
<td>216.0938</td>
<td>C_{17}H_{12}</td>
<td>methyl pyrene</td>
</tr>
</tbody>
</table>
FIG. 3:8 Electron impact mass spectrum of the distillate from ethyl benzene pyrolysis at high conversion.
Products from low conversion:

These products were examined with techniques similar to those for the high conversion sample. Initially only ethyl benzene and styrene were found. The sample was then concentrated down by distillation so that only a few microlitres of the high boiling portion remained. This sample was introduced into the mass spectrometer. The resulting spectrum is shown in figure 3:9. In this case the major peak other than ethyl benzene is at m/e 210. Peaks marked □ are from straight chain alkanes. These could be from impurities in the original ethyl benzene or background from the pump oil. A sample of the original ethyl benzene was treated as above and showed similar peaks confirming the presence of alkane impurities.

The compound of molecular weight 210 is present in the reaction mixture in only fractions of a percent.

A possible structure is:

\[
\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3
\]

This compound is, however, only one of a number of possible isomers e.g.

\[
\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3
\]

and

\[
\text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 : \text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\]

\[
\text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 : \text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\]

\[
\text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 : \text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\]

\[
\text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 : \text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\]
FIG. 3:9  Mass spectrum of products from ethyl benzene pyrolysis at low conversions.
Chromato-mass spectrometry

A Perkin Elmer F11 gas chromatograph was connected to an Edwards ED mass spectrometer. A sample of the reaction mixture was injected into the chromatograph, and as the compounds were eluted, they were admitted via a heated transfer line to the mass spectrometer. A large number of secondary products were shown to be present. Some of the major components are listed in table 3:5.

**TABLE 3:5**

SECONDARY PRODUCTS FOUND BY CHROMATO-MASS SPECTROMETRY

<table>
<thead>
<tr>
<th>Order of elution</th>
<th>Compound identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>methyl ethyl benzene</td>
</tr>
<tr>
<td>2</td>
<td>3 phenyl prop-1-ene</td>
</tr>
<tr>
<td>3</td>
<td>isomer of 1</td>
</tr>
<tr>
<td>4</td>
<td>isomer of 1</td>
</tr>
<tr>
<td>5</td>
<td>methyl styrene</td>
</tr>
<tr>
<td>6</td>
<td>sec-butyl benzene</td>
</tr>
<tr>
<td>7</td>
<td>isomer of 5</td>
</tr>
<tr>
<td>8</td>
<td>indene</td>
</tr>
<tr>
<td>9</td>
<td>1-phenyl but 1-ene</td>
</tr>
<tr>
<td>10</td>
<td>methyl indene</td>
</tr>
<tr>
<td>11</td>
<td>tetrahydronaphthalene</td>
</tr>
<tr>
<td>12</td>
<td>naphthalene</td>
</tr>
</tbody>
</table>

Infra red analysis

A sample of the products mixture was spotted on a thin layer chromatography plate and the chromatogram run in chloroform. A number of products were separated. The largest spot was scraped off and the infra red spectrum taken. It is shown as line A in figure 3:10.
A sample of the liquid and solid products mixture was then spotted on a rock salt plate, and the liquid evaporated. An infrared spectrum was run and the results are given in figure 3:10 (line B).

Both spectra are typical of a substituted aromatic with peaks around 900 and 1,100 cm\(^{-1}\). Little other information can be obtained.

**Summary of data on higher molecular weight products**

The higher molecular weight solid products are principally aromatic. Even at relatively low conversions the mixture produced is complex. However, at low conversions, a possible chain termination product of molecular weight 210, is observed. At high conversions anthracene (or phenanthrene) is found to predominate. This must be formed by some secondary reaction.

**The effect of temperature on reaction**

The reaction temperature was varied between 768 and 808K. Thirty torr of ethyl benzene was used and a residence time of four minutes was employed. The activation energy was obtained from the Arrhenius plot of log (product yield or rate constant) against reciprocal temperature. The results are summarised in figures 3:11 (a) to 3:11 (f).

**Preliminary analysis and interpretation of results**

(a) Methane and toluene yields:

Methane is formed in a first order process and is related to ethyl benzene concentration by expression (xi)

\[
d[CH_4]/dt = k_{methane} [ethyl benzene]\]

where \(k_{methane}\) is the first order rate constant for this process. If \(\Delta CH_4\) moles litre\(^{-1}\) is the concentration of methane after a time \(\Delta t\) seconds then

\[
k_{methane} = [CH_4]/\Delta t [ethyl benzene] \text{ (sec}^{-1})\]

(xi)

(xii)
**FIG. 3:10** Infrared spectrum of solid products from ethyl benzene pyrolysis.
Thus a plot of \( \log(k_{\text{methane}}) \) against \( 1/T \) \( \text{K}^{-1} \) will yield the activation energy and pre-exponential factor for the process.

A similar expression can be derived for toluene yield. The Arrhenius plots are shown in figure 3:11(a). Both toluene yield and methane yield lie on the same line. Rate expressions (xiii) and (xiv) were obtained for methane and toluene yields respectively:

\[
\begin{align*}
  k_{\text{methane}} &= 10^{14.48} \exp(-70,300/RT) \text{sec}^{-1} \\
  k_{\text{toluene}} &= 10^{14.35} \exp(-69,800/RT) \text{sec}^{-1}
\end{align*}
\]  

Hydrogen and styrene yields:

The data obtained were expressed for a constant ethyl benzene concentration of \( 6.05 \times 10^{-4} \) mole litre\(^{-1} \). This enabled an Arrhenius plot of \( \log_{10} \) product mole litre\(^{-1} \) against reciprocal temperature (K\(^{-1} \)) to be obtained. The results are shown in figure 3:11 (b) and (c) yielding activation energies of 91,000 cals mole\(^{-1} \) and 86,900 cals mole\(^{-1} \). Thus combining this with the pressure dependency results, hydrogen and styrene are formed according to the rate expressions (xv) and (xvi).

\[
\begin{align*}
  \frac{d[H_2]}{dt} &= 10^{19.89} \exp(-90,300/RT)[C_6H_5C_2H_5]^{0.65} \text{mole litre}^{-1}\text{sec}^{-1} \ (xv) \\
  \frac{d[\text{styrene}]}{dt} &= 10^{18.2} \exp(-86,000/RT)[C_6H_5C_2H_5]^{0.65} \text{mole litre}^{-1}\text{sec}^{-1} \ (xvi)
\end{align*}
\]

Ethane and ethylene yields:

Ethane is formed in a process with an order of 1.1, whereas ethylene is formed in a process with an order of 0.9. Arrhenius plots of \( \log k_{\text{product}} \) against inverse temperature (K\(^{-1} \)) were drawn. The results are shown in figures 3:11 (d) and 3:11 (e). The slopes of the graphs yield activation energies of 93,300 mole litre\(^{-1} \) for ethane formation and 97,000 mole litre\(^{-1} \) for ethylene formation.

To summarise:

\[
\begin{align*}
  \frac{d[C_2H_6]}{dt} &= 10^{21.08} \exp(-93,300/RT)[C_6H_5C_2H_5]^{1.1} \text{mole litre}^{-1}\text{sec}^{-1} \ (xvii) \\
  \frac{d[C_2H_4]}{dt} &= 10^{21.48} \exp(-97,000/RT)[C_6H_5C_2H_5]^{0.9} \text{mole litre}^{-1}\text{sec}^{-1} \ (xviii)
\end{align*}
\]
FIG. 3: 11a Arrhenius plot for o methane, • toluene formation from the pyrolysis of ethyl benzene.
**FIG. 3:11b** Arrhenius plot for hydrogen formation from the pyrolysis of ethyl benzene with an ethyl benzene conc. of $6.05 \times 10^{-4}$ mole litre$^{-1}$.

**FIG. 3:11c** Arrhenius plot for styrene formation from ethyl benzene pyrolysis. Yield after four mins; ethyl benzene conc $6.05 \times 10^{-4}$ mole litre$^{-1}$. 
FIG. 3: 11d Arrhenius plot for ethylene formation from ethyl benzene pyrolysis.

FIG. 3: 11e Arrhenius plot for ethane formation from ethyl benzene pyrolysis.
FIG. 3: Arrhenius plot for benzene formation from ethyl benzene pyrolysis.
Benzene yield:

Benzene is formed in a first order process. The rate constant $k_{\text{benzene}}$ was obtained by the same procedure as that described for the rate constant $k_{\text{methane}}$. Log $k_{\text{benzene}}$ was plotted against $1/T (K^{-1})$. The rate expression (xix) was obtained from the results shown in figure 3:11(g).

$$k_{\text{benzene}} = 10^{16.59} \exp(-76,900/RRT) \text{sec}^{-1}$$ (xix)

Table 3:6 summarises the activation energies and orders obtained by these methods.

### TABLE 3:6

**APPARENT ACTIVATION ENERGIES AND ORDERS OBTAINED FOR PRODUCTS OF ETHYL BENZENE PYROLYSIS**

<table>
<thead>
<tr>
<th>Product</th>
<th>Apparent activation energy (cals mole$^{-1}$)</th>
<th>Order w.r.t. ethyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>90,300</td>
<td>0.65</td>
</tr>
<tr>
<td>methane</td>
<td>70,000</td>
<td>1.0</td>
</tr>
<tr>
<td>toluene</td>
<td>69,000</td>
<td>1.0</td>
</tr>
<tr>
<td>ethylene</td>
<td>97,000</td>
<td>1.1</td>
</tr>
<tr>
<td>ethane</td>
<td>93,300</td>
<td>0.9</td>
</tr>
<tr>
<td>styrene</td>
<td>86,000</td>
<td>0.65</td>
</tr>
<tr>
<td>benzene</td>
<td>76,900</td>
<td>1.0</td>
</tr>
</tbody>
</table>
DETAILLED DISCUSSION OF EXPERIMENTAL RESULTS.

Introduction

In this work, at low conversions, a large number of secondary products such as the methyl ethyl benzenes and the methyl styrenes were formed. These products could arise from free radical attack on reactants and primary products such as styrene, and the presence of methyl and ethyl radicals seems likely. This is in agreement with the carrier studies by previous workers.

To account for the presence of ethylene and ethane in the products from their carrier experiments, Clark and Price \(^ {67}\) have suggested concurrent free radical and molecular processes. The argument against such processes is now well established, and pyrolyses are thought to proceed by either one mechanism or the other. As no evidence for molecular reactions was found in this work, the discussion presented here is limited to free radical processes. It is convenient to consider the initiation, propagation and termination stages in turn.

Initiation

Initiation in a free radical chain process usually occurs via the rupture of the weakest bond in the molecule. In the case of ethyl benzene the two most likely processes are:

\[
\begin{align*}
C_6H_5CH_2CH_3 & = C_6H_5CH_2 + CH_3 \quad (1) \\
C_6H_5C_2H_H & = C_6H_5C_2H_4 + H \quad (1a)
\end{align*}
\]

The C – C bond energy in the ethyl side chain has been estimated by Kominar, Jacko and Price \(^ {68}\) as 70,500 cals mole\(^{-1}\). The H – H bond energy is similar to that for H – H in ethane and this is published as 98,000 cals mole\(^{-1}\).

Initiation process (1) is thus more probable. In the previous section, removal of a hydrogen atom from the ring was discussed and shown to be about 110,000 cals mole\(^{-1}\) endothermic. Initiation via this process is thus discounted.
If initiation is via reaction 1 then methyl and benzyl radicals will be formed by a first order reaction in equal yields. Their amounts can be estimated from methane and toluene which are formed by reactions (2) and (3)

\[
\text{CH}_3 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{C}_2\text{H}_4 + \text{CH}_4 \quad (2)
\]
\[
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{C}_2\text{H}_4 + \text{C}_6\text{H}_5\text{CH}_3 \quad (3)
\]

Rate expressions (i), (ii) were obtained for methane and toluene formation.

\[
k_{\text{methane}} = 10^{14.48} \exp \left( \frac{-70,300}{RT} \right) \text{sec}^{-1} \quad (i)
\]
\[
k_{\text{toluene}} = 10^{14.35} \exp \left( \frac{-69,800}{RT} \right) \text{sec}^{-1} \quad (ii)
\]

These values are identical within experimental error and may be taken as the rate constant for the initiation process. It compares well with the results of previous carrier studies. (see table 3.7)

<table>
<thead>
<tr>
<th>A factor (sec(^{-1}))</th>
<th>Activation energy (cals mole(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.0</td>
<td>63,200</td>
<td>64</td>
</tr>
<tr>
<td>14.6</td>
<td>70,100</td>
<td>65</td>
</tr>
<tr>
<td>13.1</td>
<td>62,200</td>
<td>66</td>
</tr>
<tr>
<td>14.7</td>
<td>69,200</td>
<td>66'</td>
</tr>
<tr>
<td>14.7</td>
<td>70,100</td>
<td>67</td>
</tr>
<tr>
<td>14.9</td>
<td>69,000</td>
<td>68</td>
</tr>
<tr>
<td>14.4</td>
<td>70,100</td>
<td>This work</td>
</tr>
</tbody>
</table>

* uncorrected value

' corrected value
In further discussion the initiation reaction is therefore taken to be (1) with the rate constant $k_1 = 10^{14.4} \exp \left( -70,100/RT \right) \sec^{-1}$

**Propagation Reactions.**

The reaction mechanism cannot be simple because it must account for all the major reaction products i.e. styrene, hydrogen, methane, toluene, ethane, ethylene and benzene. The concentration time curves for these products are linear at low conversions and they are therefore assumed to be primary products. Szwarc has proposed a scheme comprising reactions (2), (2a), (5), (6), (6a), (6b), (6c).

\[
\begin{align*}
\text{CH}_3 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{CH}_4 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 \\
\text{CH}_3 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{CH}_4 + \text{C}_6\text{H}_5\text{CH} \text{CH}_3 \\
\text{C}_6\text{H}_5\text{CHCH}_3 &= \text{H} + \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 \\
\text{H} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{H}_2 \\
\text{H} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{C}_6\text{H}_5\text{CHCH}_3 + \text{H}_2 \\
\text{H} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 \\
\text{H} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 &= \text{C}_6\text{H}_5\text{CH}_2 + \text{CH}_4
\end{align*}
\]

Reaction (6c) is probably insignificant because the data obtained in this work for the initiation reaction are similar to those obtained by other workers in carrier studies in which the chain was suppressed by the addition of toluene. In the subsequent discussion it is ignored. The other reactions seem reasonable. Szwarc reported a chain length of about 15 to 20. The ratio Initiation Rate/Overall Rate, in this work, suggested a chain length of just over 10.
Formation of toluene and methane in equal amounts suggests the need for reactions (3) and (3a) in which case the benzyl radical is more reactive than was proposed by Szwarc.

\[
\begin{align*}
C_6H_5CH_2 + C_6H_5C_2H_5 &= C_6H_5CH_2CH_2 + C_6H_5CH_3 \quad (3) \\
C_6H_5CH_2 + C_6H_5C_2H_5 &= C_6H_5CHCH_3 + C_6H_5CH_3 \quad (3a)
\end{align*}
\]

The decomposition of \( C_6H_5CHCH_3 \) to hydrogen atoms and styrene in reaction (5) was proposed to account for styrene formation. The radical \( C_6H_5CH_2CH_2 \) might similarly react as in reaction (4) to give ethylene

\[
C_6H_5CH_2CH_2 = C_6H_5 + C_2H_4 \quad (4)
\]

If phenyl radicals are present, an alternative source of benzene could be:

\[
\begin{align*}
C_6H_5 + C_6H_5C_2H_5 &= C_6H_6 + C_6H_5CH_2CH_2 \quad (7) \\
C_6H_5 + C_6H_5C_2H_5 &= C_6H_6 + C_6H_5CHCH_3 \quad (7a)
\end{align*}
\]

Ethane, the remaining product, can be formed by attack of an ethyl radical on ethyl benzene:

\[
\begin{align*}
C_2H_5 + C_6H_5C_2H_5 &= C_6H_5CH_2CH_2 + C_2H_6 \quad (8) \\
C_2H_5 + C_6H_5C_2H_5 &= C_6H_5CHCH_3 + C_2H_6 \quad (8a)
\end{align*}
\]

Experiments with added nitrogen show ethylene formation to be dependent on nitrogen concentration. Lin & Back have shown that the unimolecular decomposition reaction (9) of ethyl radicals is in its pressure dependent region under the conditions of this pyrolysis, and this may account for the dependence.

\[
C_2H_5 + (M) = C_2H_4 + H + (M) \quad (9)
\]
The mechanism, therefore, is made up of a number of cycles. The major cycle yields hydrogen and styrene and this accounts for 90% of the reaction products. Benzene and ethylene are formed in another cycle whilst ethane is formed in a third cycle. In addition some ethylene is formed separately by the decomposition of ethyl radicals Fig. 3.12 represents the scheme diagrammatically.

To summarise, the simplest series of propagation reactions that can account for the observed products is shown below:

\[
\begin{align*}
\text{CH}_3 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{CH}_4 & (2) \\
\text{CH}_3 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_4 & (2a) \\
\text{C}_6\text{H}_5\text{CH}_2 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_3 & (3) \\
\text{C}_6\text{H}_5\text{CH}_2 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_4\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_3 & (3a) \\
\text{C}_6\text{H}_5\text{CH}_2 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5 + \text{C}_2\text{H}_4 & (4) \\
\text{C}_6\text{H}_5\text{CH}_3 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{H} + \text{C}_6\text{H}_5\text{CH}_2 & (5) \\
\text{H} &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{H}_2 & (6) \\
\text{H} &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_3 + \text{H}_2 & (6a) \\
\text{H} &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5 + \text{C}_2\text{H}_6 & (6b) \\
\text{C}_6\text{H}_5 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_6 & (7) \\
\text{C}_6\text{H}_5 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_6 & (7a) \\
\text{C}_2\text{H}_5 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_6 & (8) \\
\text{C}_2\text{H}_5 &+ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_2\text{H}_6 & (8a) \\
\text{C}_2\text{H}_5 &+ \text{M} = \text{H} + \text{C}_2\text{H}_4 + \text{M} & (9)
\end{align*}
\]
FIG. 3:12 Diagrammatic representation of the suggested ethyl benzene pyrolysis mechanism.

NOTE
Diagram shows cyclical nature of the propagation reactions. Molecules are given as names, free radicals as formulae and dots represent collision processes. The hydrogen – chlorine reaction would be represented as:

- Hydrogen chloride
- H
- Chlorine
- Hydrogen
Termination Reactions.

The free radicals assumed to be involved in the reaction are $\text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2, \text{C}_2\text{H}_5$ plus possibly some polycyclic radicals.

These radicals can be involved in three kinds of chain termination reactions if we ignore wall processes which seem to be insignificant.

(a) Recombination of similar free radicals, e.g.

$$\text{H} + \text{H} + \text{M} = \text{H}_2 + (\text{M}) \quad (10a)$$

$$2 \text{C}_6\text{H}_5\text{C}_2\text{H}_4 = (\text{C}_6\text{H}_5\text{C}_2\text{H}_4)_2 \quad (10b)$$

(b) Recombination of dissimilar radicals (cross combination), e.g.

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{H} = \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \quad (10c)$$

(c) Disproportionation reactions e.g.

$$2 \text{C}_6\text{H}_5\text{C}_2\text{H}_4 = \text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{C}_2\text{H}_3 \quad (10)$$

For nitrogen as the inert gas, the rate constant for reaction (10a)

$$\text{H} + \text{H} + \text{M} = \text{H}_2 + (\text{M}) \quad (10a)$$

is

$$k = 10^{9.6} \text{ litre}^2 \text{ mole}^{-2} \text{ sec}^{-1}$$

which when 300 torr of nitrogen present at 783K corresponds to a pseudo second order rate constant of

$$k = 10^{7.4} \text{ litre mole}^{-1} \text{ sec}^{-1}$$

whereas for $2 \text{C}_2\text{H}_5 = \text{C}_2\text{H}_6$

$$k = 10^{10.4} \text{ litre mole}^{-1} \text{ sec}^{-1} \quad (10d)$$

For large radicals Benson suggests a typical value for recombination of $10^{9.8 \pm 0.5} \text{ litre mole}^{-1} \text{ sec}^{-1}$.

As cross combination reactions involve large radicals the rate constant for this group of reactions will be similar to Benson's typical value.
Large radicals are generally less reactive than small radicals and hence achieve the highest intermediate concentration. Furthermore the reaction

$$\text{H} + \text{H} + (M) = \text{H}_2 + (M)$$  \hspace{1cm} (10a)

is third order. Therefore it is unlikely to be significant. Reactions involving \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3\) or \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\) are more probable. \(\text{C}_6\text{H}_5\text{CH}_3\) is a secondary free radical whereas \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\) is primary. \(\text{C}_5\text{H}_5\text{CH}_3\) is therefore likely to achieve higher intermediate concentrations. Also the isomerisation reaction (11) may occur.

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 = \text{C}_6\text{H}_5\text{CH}_3$$  \hspace{1cm} (11)

The chain length of the reaction is little more than 10 and if termination involves recombination to give products different from the reactants or chain-reaction products then there should be little difficulty in detecting them. No butane was observed and therefore

$$2 \text{C}_2\text{H}_5 = \text{C}_4\text{H}_{10}$$  \hspace{1cm} (10d)

can be discounted.

Similarly polynuclear association products should have been observed if termination involved recombination of large radicals. Small quantities were found, but quantities were much smaller than the methane and toluene initiation products yield. If rate of initiation = rate of termination, then the yield of termination products should equal the yield of methane and toluene from the initiation reaction.

Thus termination by disproportionation is more likely e.g.

$$2 \text{C}_6\text{H}_5\text{CH}_3 = \text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{C}_2\text{H}_3$$  \hspace{1cm} (10)
although the cross combination reaction

$$H + C_6H_5CH CH_3 = C_6H_5C_2H_5 \quad (10c)$$
cannot be ruled out at this stage.

**Simplified Scheme.**

Hydrogen and styrene comprise 90% of the reaction products. If only formation of these products is considered, then a mechanism comprising reactions 1, 2, 4, 5 and 7 together with a termination reaction can be written

$$C_6H_5C_2H_5 = CH_3 + C_6H_5CH_2 \quad (1)$$

$$CH_3 + C_6H_5C_2H_5 = C_6H_5CH CH_3 + CH_4 \quad (2)$$

$$C_6H_5CH_2 + C_6H_5C_2H_5 = C_6H_5CH CH_3 + C_6H_5CH_3 \quad (4)$$

$$C_6H_5CH CH_3 = C_6H_5CH CH_3 + H \quad (5)$$

$$H + C_6H_5C_2H_5 = C_6H_5CH CH_3 + H_2 \quad (7)$$

The simplified scheme ignores the presence of ethyl radicals and any termination reactions involving them. This is reasonable as butane is not an observed reaction product.

Suppose that the termination reaction is:

$$2 C_6H_5CH CH_3 = C_6H_5C_2H_5 + C_6H_5CH:CH_2 \quad (10)$$

then the rate equation (xx) for styrene formation is obtained:

$$d [C_6H_5CH:CH_2] / dt = 2k_1 [C_6H_5C_2H_5] + k_5 (k_1 / k_{10}) \frac{1}{2} [C_6H_5C_2H_5] \frac{1}{2} \quad (xx)$$

Thus:

$$\frac{d [C_6H_5CH:CH_2]}{[C_6H_5C_2H_5]} / dt = 2k_1 + k_5 (k_1 / k_{10}) \frac{1}{2} [C_6H_5C_2H_5]^{-\frac{1}{2}} \quad (xxi)$$

a plot of rate of styrene formation/ethyl benzene against (ethyl benzene)\(^{-\frac{1}{2}}\) should be a straight line with the intercept equal to 2k_1.
Figure 3.13 shows that this is approximately true. $2k_1 = 19.42 \times 10^{-8}$ sec$^{-1}$. The least squares intercept is $2.5 \times 10^{-5}$ sec$^{-1}$, but there is considerable scatter and a slight redrawing of the line would give a much smaller value. The rate expression (x) is made up of an initiation term $2k_1 [C_6H_5C_2H_5]$ and a propagation term $k_5 (k_1/k_{10})^{1/4} [C_6H_6C_2H_5]^{1/2}$. If $2k_1 [C_6H_5C_2H_5]$ is assumed to be small compared with $k_5 (k_1/k_{10})^{1/4} [C_6H_6C_2H_5]^{1/2}$ then the rate expression (xxii) results

$$d[C_6H_5CH:CH_2]/dt = k_5 (k_1/k_{10})^{1/4} [C_6H_6C_2H_5]^{1/2}$$  \hspace{1cm} (xxii)

Thus, for styrene formation, half order kinetics are predicted. In fact, the chain length is about 10, so the initiation term will be about $1/10$ of the propagation term, and an order slightly greater than 0.5 is predicted. Experiment shows a value of about 0.65. Also the predicted activation energy is $(E_5 + \frac{1}{4} E_1 - \frac{1}{4} E_{10})$. $E_{10}$ is the activation energy for the termination reaction and is approximately zero. $E_1$ is the activation energy for the initiation reaction and experiment has shown this to be 70,100 cals mole$^{-1}$. $E_5$ is the activation energy for reaction 5. Thermochemical calculation (Appendix 3) shows that this has a value of about 50,000 cals mole$^{-1}$. Thus the overall activation energy is predicted as 85,800 cals mole$^{-1}$. The experimental value for styrene formation was 87,000 cals mole$^{-1}$ and therefore agreement is reasonable. Work described later in this section develops the argument more fully.

**Hydrogen Formation.**

The expression

$$d[H_2]/dt = k_5 (k_1/k_{10})^{1/4} [C_6H_5C_2H_5]^{1/2}$$  \hspace{1cm} (xxiii)

can be obtained for hydrogen formation.
FIG. 3:13 Function plot to test simplified ethyl benzene pyrolysis mechanism.
Reaction order for hydrogen production is 0.65 and an activation energy of about 90,000 cals mole\(^{-1}\) was obtained. Once again agreement is reasonable with the predicted values 0.5 and 85,800 cals mole\(^{-1}\).

The alternative termination process is cross combination between H atoms and \(\text{C}_6\text{H}_5\text{CH}-\text{CH}_3\) radicals. If this occurs exclusively then the rate expression (xxiv) can be deduced and first order kinetics are predicted for hydrogen production:

\[
d[H_2]/dt = \frac{k_1}{2}(1 + \frac{4k_7k_5}{k_1k_{10c}})^{\frac{1}{2}} [\text{C}_6\text{H}_5\text{C}_2\text{H}_3] \quad (\text{xxiv})
\]

An order of magnitude calculation can be made for the ratio \(4k_7k_5/k_1k_{10c}\).

Reaction (7) is bimolecular and a typical bimolecular rate constant would be of the order of \(10^{12} \exp (-10,000/RT)\) mole litre\(^{-1}\) sec\(^{-1}\). Reaction (5) is unimolecular and a typical value for this would be of the order of \(10^{16} \exp (-50,000/RT)\) sec\(^{-1}\). \(k_1\) has been measured as \(10^{14} \exp (-70,300/RT)\) sec\(^{-1}\) and using Benson's suggestion \(k_{10}\) is \(10^9.8\) mole litre\(^{-1}\) sec\(^{-1}\). Thus the expression \(4k_7k_5/k_1k_{10}\) has an approximate value of \(2.5 \times 10^7\). This is greatly in excess of one, hence the rate equation (xxiv) simplifies to

\[
d[H_2]/dt = \frac{(k_7k_5k_1)^{\frac{1}{2}}}{k_{10c}[\text{C}_6\text{H}_5\text{C}_2\text{H}_3]} \quad (\text{xxv})
\]

First order kinetics are predicted together with an activation energy of 65,000 cals mole\(^{-1}\). The experimental activation energy for hydrogen production is 90,000 cals mole\(^{-1}\). This is considerably higher than the predicted value. Furthermore this mechanism predicts first order kinetics for the production of hydrogen whereas the experimental value is 0.65.
Experiment therefore favours termination by the disproportionation reaction 10.

\[
2 \overset{\cdot}\text{C}_6\text{H}_5\text{CHCH}_3 = \text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{C}_2\text{H}_3 \quad (10)
\]

Hausmann and King\textsuperscript{70} have considered termination to proceed via reaction

\[
2 \overset{\cdot}\text{C}_6\text{H}_5\text{CHCH}_3 = (\text{C}_6\text{H}_5\text{CHCH}_3)_2
\]

This accounted for their experimentally observed 0.5 order for styrene formation although reaction (10) will also account for it. They did not, however, identify a product of molecular weight 210. Lee and Oliver\textsuperscript{69} reported that the order for styrene formation varied between one at low temperatures and zero at high temperatures. Hausmann & King\textsuperscript{70} found no evidence for this in their work. The work described here was deliberately carried out at low conversions and low temperatures so that side reactions would be kept to a minimum. With these conditions a small amount of product 210 molecular weight was found but not in sufficient quantity to be considered as a major termination product.

The variable order behaviour observed by Lee and Oliver\textsuperscript{69} could possibly arise from the formation of styrene polymers at higher temperatures.

**Summary.**

This work and some previous work are consistent with a mechanism involving termination via reaction (10a). Termination via reaction (10c) cannot be completely ruled out. Nonetheless, if inserted, it yields much too low an activation energy compared with experiment. The following points can now be made.
First order rate constants for methane and toluene yields suggest initiation via reaction 1.

\[ C_6H_5C_2H_5 = C_6H_5CH_2 + CH_3 \] (1)

for which the rate constant is

\[ k = 10^{14.4} \exp(-70,100/RT) \text{ sec}^{-1}. \]

Reactions (2) to (9) are the major propagation steps.

Termination is probably via the disproportionation reaction (10).

Analysis of the mechanism in full.

(a) Comparison of ethane and hydrogen yields.

The above conclusions show that to a first approximation the reaction can be described by a mechanism in which hydrogen and styrene are the only products formed by propagation reactions.

If all the proposed propagation reactions are included to account for ethane and ethylene products as well then the scheme comprising reactions 2 to 9 given earlier must be used.

From this, rate expressions (xxvi) and (xxvii) can be derived for hydrogen and ethane formation.

\[ \frac{d[H_2]}{dt} = (k_6 + k_{6a}) [H] [C_6H_5C_2H_5] \] (xxvi)

\[ \frac{d[C_2H_5]}{dt} = (k_8 + k_{8a}) [C_2H_5] [C_6H_5C_2H_5] \] (xxvii)

These can be combined to give expression (xxviii)

\[ \frac{d[H_2]}{dt} \quad (k_6 + k_{6a}) [H] \] (xxviii)

\[ \frac{d[C_2H_6]}{dt} \quad (k_8 + k_{8a}) [C_2H_5] \]

This can be developed via the stationary state approximation to give (xxix)

\[ \frac{d[H_2]}{dt} = (k_6 + k_{6a}) + (k_6 + k_{6a}) (k_9) [C_6H_5C_2H_5]^{-1} \] (xxix)

\[ \frac{d[C_2H_6]}{dt} = k_{6b} \quad (k_8 + k_{8a}) (k_{6b}) \]
A plot of \( \frac{d[H_2]/dt}{d[C_2H_6]/dt} \) against \([C_6H_5C_2H_5]\) should yield a straight line with an intercept of \((k_6 + k_{6a})/k_{6b}\) and a gradient of \((k_6 + k_{6a}) k_9/(k_8 + k_{8a}) k_{6b}\).

Figure 3: 14 shows that this holds true for a number of temperatures between 758 and 945K.

The ratio of gradient to intercept will give a value for \(k_9/(k_8 + k_{8a})\). Thus an Arrhenius plot of log (gradient/intercept) against inverse temperature will yield an activation energy and pre-exponential factor for this ratio of rate constants. However, a small error in value of the intercept has a large effect on the function (gradient/intercept) and leads to a meaningless plot. A more productive approach is to plot log (gradient) against inverse temperature to yield Arrhenius parameters for the function \((k_6 + k_{6a}) k_9/(k_8 + k_{8a}) k_{6b}\). The plot is shown in figure 3:15. It yields a value of 11,300 ± 2,800 cals mole\(^{-1}\) for the activation energy. This is equal to \(E_{(6 + 6a)} + E_9 - E_{(8 + 8a)} - E_{6b}\). The scattered intercepts in figure 3.14 suggest that \(E_{(6 + 6a)} - E_{6b}\) is approximately zero. If so, \(E_9 - E_{(8 + 8a)} \approx 11,300\) cals mole\(^{-1}\) Arrhenius parameters for reaction 9 are well documented. Lin and Back's experiments 78 lead to the expression (xxx) for reaction 9.

\[
k_\infty = 10^{13.6} \exp - 38,000 \text{ (cals mole}\ ^{-1}\)/RT sec\(^{-1}\) (xxx)
\]

\(k_\infty\) is the true unimolecular rate constant above the high pressure limit. Arrhenius parameters for the ethane-forming reactions 8 and 8a are more difficult to obtain.
FIG. 3:14 Comparison of hydrogen and ethane yields from ethyl benzene pyrolysis at various temperatures.
FIG. 3:15 Arrhenius plot for the function $\left[\left(\frac{k_6 + k_{6a}}{k_8 + k_{8a}}\right) / \left(\frac{k_9}{k_{6b}}\right)\right]$ derived from ethyl benzene pyrolysis.
Very little data for abstraction reactions by ethyl radicals is reported in the literature although there is a wealth of information for reactions involving methyl radicals. In general these reactions have rate constants of the order

\[ k = 10^9 \exp(-11,000/RT) \text{ litre mole}^{-1} \text{ sec}^{-1}. \]

The reaction of ethyl radicals with hydrogen

\[ \text{C}_2\text{H}_5 + \text{H}_2 = \text{C}_2\text{H}_6 + \text{H} \]

has Arrhenius parameters of

\[ k = 10^{-8.96} \exp(-14,100/RT) \text{ litre mole}^{-1} \text{ sec}^{-1}. \]

Thus, by analogy, the activation energy for reactions 8 and 8a may be about 14,100 cals mole\(^{-1}\). This means that the estimate of \( E_9 - E(8 + 8a) \) is 23,900 cals mole\(^{-1}\) compared with the experimental value of about 11,200 cals mole\(^{-1}\). Lin and Back have shown that reaction (9)

\[ \text{C}_2\text{H}_5 + (M) = \text{C}_2\text{H}_4 + \text{H} + (M) \quad (9) \]

is in its pressure dependent region at all pressures below 1 atmos. The work described in this thesis was carried out at 300 torr and hence if reaction (9) participates in the mechanism then it is in its pressure dependent region. Lin and Back have reported an activation energy of 32,400 cals mole\(^{-1}\) for the bimolecular limit of reaction (9). If this value is chosen for the activation energy of reaction 9 then the activation energy for the function \( E_9 - E(8 + 8a) \) is (32,400-14,100) cals mole\(^{-1}\) i.e. 18,200 cals mole\(^{-1}\). Agreement between this and the experimental value is better but still only moderate.
The rate of styrene formation.

Styrene is only formed in the reactions 5 and 10 discussed in the simple mechanism. Hence the rate equation derived there still holds true for the mechanism as a whole.

Hence
\[ \frac{d[\text{styrene}]}{dt} = k_5 \left( \frac{k_1}{k_{10}} \right)^\frac{1}{2} \left[ C_6H_5C_2H_5 \right]^\frac{1}{2} \quad (\text{xxii}) \]

Previous discussion showed this to be reasonable. If a value for the termination reaction rate constant \( k_{10} \) is assumed then it is possible to estimate a value for the rate constant of reaction 5.

\[ C_6H_5CHCH_3 = H + C_6H_5CH:CH_2 \quad (5) \]

Now \( k_{\text{styrene}} = k_5 \left( \frac{k_1}{k_{10}} \right) \) \quad (\text{xxxi})

Thus by rearrangement and substitution in the Arrhenius equation, expression (\text{xxxii}) is obtained for \( k_5 \)

\[ k_5 = A_{\text{styrene}} \left( \frac{A_{10}}{A_1} \right)^\frac{1}{2} \exp \left( -\frac{E_{\text{styrene}}}{2} \frac{E_1}{RT} \right) \sec^{-1} \quad (\text{xxxii}) \]

The rate data for reaction (1) have already been accurately measured and those for styrene formation can be obtained experimentally. If a value can be estimated for the termination reaction (10) then an estimate can be made for \( k_5 \). Benson\textsuperscript{36} has discussed termination reactions involving large radicals and suggests that a typical value for the pre-exponential factor in recombination reactions is

\[ 10^{9.8} \pm 0.5 \ \text{litre mole}^{-1} \ \text{sec}^{-1} \]

Now \( k_1 = 10^{14.4} \ \exp \left( -70,100/RT \right) \ \text{sec}^{-1} \)

and \( k_{\text{styrene}} = 10^{18.2} \ \exp \left( -87,00/RT \right) \ \text{mole}^{-\frac{1}{2}} \ \text{litre}^{\frac{1}{2}} \ \text{sec}^{-1} \)

if styrene yield is assumed to be half order.
Thus $k_5 = 10^{15.9} \exp\left(-52,000/RT\right) \text{sec}^{-1}$. (xxxiii).

Now for analogous reaction for ethyl radical decomposition (9)

$$\ce{C_2H_5} \quad = \quad \ce{C_2H_4 + H} \quad (9)$$

Lin and Back suggest the rate expression for $k_\infty$, the limiting high pressure unimolecular rate constant, of

$$k_\infty = 10^{13.6} \exp\left(-38,000/RT\right) \text{sec}^{-1}. \quad (\text{xxx})$$

The activation energy estimated for reaction (5) is some 14,000 cals mole$^{-1}$ above that for reaction 9. The radical $\ce{C_6H_5CHCH_3}$ is however resonance stabilized

\[
\text{i.e.} \quad \ce{CHCH_3} \quad \leftrightarrow \quad \ce{CHCH_3CH} \quad \leftrightarrow \quad \ce{CHCH_3CHCH_3}
\]

The resonance energy of this radical is about 12,000 cals mole$^{-1}$. The activation energy of reaction 5 will thus be approximately 12,000 cals mole$^{-1}$ higher than that for reaction 9. Hence the derived value for $E_5$ is reasonable. Thermochemical calculation yields a value of about 50,000 cals mole$^{-1}$.

**Hydrogen Yield.**

The derivation of an expression for hydrogen yield is more complicated. Hydrogen is produced by reactions 6 and 6a.

$$\ce{H + C_6H_5C_2H_5} \quad = \quad \ce{C_6H_5CH_2CH_2} \quad + \quad \ce{H_2} \quad (6)$$

$$\ce{H + C_6H_5C_2H_5} \quad = \quad \ce{C_6H_5CHCH_3} \quad + \quad \ce{H_2} \quad (6a)$$

These reactions compete with reaction 6b.

$$\ce{H + C_6H_5C_2H_5} \quad = \quad \ce{C_2H_5} \quad + \quad \ce{C_6H_6} \quad (6b)$$
It is possible to derive an equation (xxxiv) which expresses this

\[
d[H_2] = \frac{(k_6 + k_{6a})[C_6H_5C_2H_5]^1 (k_1/k_{10})^1 \Theta}{(k_6 + k_{6a} + k_{6b})^0 + k_9k_{6b}}
\]

where \( \Theta = (k_8 + k_{8a})[C_6H_6C_2H_5] + k_9 \)

If \( k_{6b} \ll (k_6 + k_{6a}) \) then the expression becomes

\[
d[H_2]/dt = k_5(k_1/k_{10})^1 [C_6H_6C_2H_5]^1
\]

This is identical with the equation derived in the simple mechanism and is also similar to that derived for styrene production. To a first approximation this simplifying assumption is valid. Reactions 6 and 6a lead to hydrogen whereas reaction 6b leads to benzene and ethyl radicals. The ethyl radicals in turn yield ethane and ethylene via reactions 8, 8a and 9. Reactions 8 and 8a are the only sources of ethane and it occurs at a level an order of magnitude less than that of hydrogen. A reaction order for hydrogen formation of about a half is predicted. The activation energy of the process will be similar to that for styrene formation. Experiment confirms both these conclusions. The simplified expression (xxiii) for hydrogen formation is identical with that derived for styrene yield. Thus to within an order of magnitude a value for the rate constant for reaction (5) can be isolated by a similar procedure to that earlier described.

Now \( k_{H_2} = 10^{19.89} \exp(-90,300/RT) \) mole \(^{0.5}\) litre \(^{0.5}\) sec \(^{-1}\) (xxxv)

if hydrogen formation is assumed to be half order.
Thus using the data for $k_1$ and $k_{10}$ given earlier

$$k_5 = 10^{16.5} \exp (-55,000/RT) \text{ sec}^{-1}$$

(zzxvi)

The value is similar to that derived from styrene yield, as would be expected from the fact that hydrogen and styrene yields were identical.

**Ethane Yield.**

The expression for ethane yield is:

$$\frac{d[C_2H_6]}{dt} = \frac{(k_8 + k_{8a}) [C_6H_5C_2H_5]^{3/2} k_{6b} k_5 (k_1/k_{10})^{1/2}}{(k_6 + k_{6a} + k_{6b}) \Theta + k_9 k_{6b}}$$

where $\Theta = ((k_8 + k_{8a}) [C_6H_5C_2H_5] + k_9)$

An order of three halves is predicted, if $k_9 >> (k_8 + k_{8a}) [C_6H_5C_2H_5]$.

If the reverse is true and $k_9$ is small then

$$\frac{d[C_2H_6]}{dt} = \frac{k_{6b} k_5 (k_1/k_{10})^{1/2} [C_6H_5C_2H_5]^{1/2}}{(k_6 + k_{6a} + k_{6b})}$$

(zzxvi)

and an order of one half is predicted. This does not agree with the experimental value of 1.1 and suggests that the two terms are of similar magnitude and a considerable quantity of ethane is produced via reaction 9.

$$C_2H_5 + (M) = C_2H_4 + \overset{\cdot}{H} + (M)$$

(9)

It confirms the need for the inclusion of reaction 9 in the reaction scheme.
Summary of proposed mechanism and rate data obtained.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2^* + \text{CH}_3 & (1) \\
\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{CH}_4 & (2) \\
\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{CH}_4 & (2a) \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_3 & (3) \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{C}_6\text{H}_5\text{CH}_3 & (3a) \\
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 & = \text{C}_6\text{H}_5 + \text{C}_2\text{H}_4 & (4) \\
\text{C}_6\text{H}_5\text{CHCH}_3 & = \text{H} + \text{C}_6\text{H}_5\text{CH}:\text{CH}_2 & (5) \\
\text{H} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{H}_2 & (6) \\
\text{H} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{H}_2 & (6a) \\
\text{H} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_2\text{H}_5 + \text{C}_6\text{H}_6 & (6b) \\
\text{C}_6\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_6 & (7) \\
\text{C}_6\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{C}_6\text{H}_6 & (7a) \\
\text{C}_2\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_6 & (8) \\
\text{C}_2\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{C}_2\text{H}_6 & (8a) \\
\text{C}_2\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{H} + \text{C}_6\text{H}_5\text{CH}:\text{CH}_2 & (9) \\
\text{C}_2\text{H}_5 & + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{C}_6\text{H}_6 & (10)
\end{align*}
\]

In deriving this mechanism it is assumed that -

(1) There are no secondary reactions at low conversions.

(2) Abstraction from the benzene ring does not occur.

(3) Surface reactions are unimportant.

(4) The only sources of methane and toluene are via the initiation reaction.
An examination of the proposed mechanism shows it to agree well with experiment. All the major products have been shown to be produced via chain carrying steps and not via secondary reactions. From the mechanism, a number of rate constants have been derived. Rate expressions (xiii), (xiv) for the initiation reaction (1) have been derived.

\[ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2 + \text{CH}_3 \]  
\[ k_1 = 10^{14.48} \exp \left( -70,300/RT \right) \text{sec}^{-1} \]  (xiii)

based on methane yield and

\[ k_1 = 10^{14.35} \exp \left( -69,800/RT \right) \text{sec}^{-1} \]  (xiv)

based on toluene yield. These expressions agree with data obtained from carrier techniques.

For reaction 5 the rate expression (xxxiii) was obtained

\[ \text{C}_6\text{H}_5\text{CHCH}_3 = \text{H} + \text{C}_6\text{H}_5\text{CH:CH}_2 \]  
\[ k_5 = 10^{15.9} \exp \left( -52,000/RT \right) \text{sec}^{-1} \]  (xxxiii)

Rate expressions for hydrogen, styrene, ethane, ethylene and benzene yields have also been obtained.
SECTION FOUR

OVERALL SUMMARY AND SUGGESTIONS

FUTURE WORK
Until recently most studies of benzene pyrolysis had been carried out in the high temperature region of the reaction where both diphenyl formation and ring fission occur. Little agreement could be found between the rate data obtained by different sets of workers.

In section II of this thesis the mechanism for the low temperature pyrolysis of benzene has been developed. The results show that a free radical chain mechanism takes place, and hydrogen was shown to be formed according to the relation (i).

\[
\frac{d[H_2]}{dt} = 10^{9.83} \exp(53,800/RT) \left[ \frac{[C_6H_6]}{mole \ litre^{-1} \ sec^{-1}} \right]^{3/2} (i)
\]

The mechanism below accounts reasonably well for the observed kinetics of diphenyl and hydrogen formation:

\[
C_6H_6 = C_6H_5 + H' \quad (1)
\]

\[
C_6H_5 + C_6H_6 = (C_6H_5)_2 + H \quad (5)
\]

\[
H + C_6H_6 = C_6H_7 \quad (9)
\]

\[
C_6H_7 = C_6H_5 + H_2 \quad (6)
\]

\[
2C_6H_5 = (C_6H_5)_2 \quad (3)
\]

At the lowest temperatures, the experimental Arrhenius plot curves away from that predicted by the theory. Preliminary experiments with different surface-to-volume ratio reaction vessels failed to reveal a significant effect. At most rate, was reduced by 30%. The change in surface/volume ratio would have caused a change of rate of an order of magnitude had heterogeneous reactions been important. Further study is necessary to establish the reason for the low activation at low temperatures. A full study of the surface effects may prove useful.
In predicting the overall rate equation for benzene pyrolysis, estimates were made of the pre-exponential factors and activation energies of the individual elementary reactions. Little experimental work has been done on the reaction (3).

\[ \text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)^2 + \text{H} \]  
(3)

and rate data obtained by Trotmann-Dickenson and Steacie, and Kretch and Price, for reaction (10) have been disputed by Benson and others.

\[ \text{CH}_3 + \text{C}_6\text{H}_6 = \text{CH}_4 + \text{C}_6\text{H}_5 \]  
(10)

Further work to establish the rate parameters for these abstraction reactions is necessary.

The extension of the work to the benzene pyrolysis reaction at higher temperatures was inconclusive. More sophisticated apparatus than available for this work is necessary. However, acetylene appears to be an important product. Carbon is formed in large quantities.

The work here suggests possible routes to carbon formation. The early stages of reaction, however, were not satisfactorily defined. Shock tube studies might yield valuable information.

In Part III of the thesis, the pyrolysis of ethyl benzene was considered. The large number of reaction products suggests the complex mechanism shown below:

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CH}_2 + \text{CH}_3 \]  
(1)

\[ \text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{CH}_4 \]  
(2)

\[ \text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{CH}_4 \]  
(2a)

\[ \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_3 \]  
(3)

\[ \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CHCH}_3 + \text{C}_6\text{H}_5\text{CH}_3 \]  
(3a)

\[ \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 = \text{C}_6\text{H}_5 + \text{C}_2\text{H}_4 \]  
(4)
\[
\begin{align*}
C_6H_5CHCH_3 & = \text{H} + C_6H_5CH:CH_2 \\
H + C_6H_5CH_2CH_3 & = C_6H_5CH_2CH_2 + \text{H}_2 \\
H + C_6H_5CH_2CH_3 & = C_6H_5CHCH_3 + \text{H}_2 \\
H + C_6H_5CH_2CH_3 & = \text{C}_2H_5 + C_6H_6 \\
C_6H_5 + C_6H_5CH_2CH_3 & = C_6H_5CH_2CH_2 + C_6H_6 \\
C_6H_5 + C_6H_5CH_2CH_3 & = C_6H_5CHCH_3 + C_6H_6 \\
C_2H_5 + C_6H_5CH_2CH_3 & = C_6H_5CH_2CH_2 + C_2H_6 \\
C_2H_5 + C_6H_5C_2H_3 & = C_6H_5CHCH_3 + C_2H_6 \\
C_2H_5 + \text{(M)} & = \text{H} + C_2H_4 + \text{(M)} \\
2C_6H_5C_2H_4 & = C_6H_5CH_2CH_3 + C_6H_5CH:CH_2
\end{align*}
\]

Rate data for the initiation reaction of
\[ k = 14.4 \exp(-70,300/RT) \text{ sec}^{-1} \]
agrees with those of previous workers who used aniline or toluene carrier techniques.

For reaction (5) rate data of
\[ k = 10^{15.9} \exp(-52,000/RT) \text{ sec}^{-1} \]
was derived.

The predicted kinetics from the mechanism were shown to be compatible with those found experimentally.

In this work conversions were kept low and no attempt was made to study the reaction at higher temperatures where carbon is formed. Some preliminary experiments showed that polycyclic aromatic compounds can be formed relatively easily from ethyl benzene. The role of ethyl benzene in carbon formation is another area in which little is known.

The kinetics of the pyrolysis of \text{n}-propyl benzene and the xylenes in the absence of carriers was another area in which little work has been published.
There is little point, however, in going any further up the homolo-
gous series as the work then becomes a study of the chemistry of the
side chain, and is likely to be similar to that of the corresponding
alkanes which have been thoroughly investigated.

**The relevance of the work to the gas industry.**

In G.R.H. and F.B.H. processes a large number of pyrolysis reactions
occur. A small but important constituent of the feedstock comprises
aromatic compounds. These aromatic compounds will react in the manner
described in this thesis. In order to obtain a fuller understanding of
the process, reaction modelling studies are undertaken. The rate data
obtained in this thesis will be of use in these modelling studies. In
turn it may be possible to predict conditions under which greater efficiency
of plant operation will occur.

An unwelcome product in F.B.H. Processes is carbon. The work in
this thesis suggests that this carbon is formed via aromatic compounds
and a mechanism for its production can be postulated. By applying the
results found in this thesis it may be possible to minimise and possibly
eliminate this carbon forming process.
### References

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<tbody>
<tr>
<td>No.</td>
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<td>36</td>
<td>S.W. Benson</td>
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<td>E.S. Swinbourne</td>
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<tr>
<td>60</td>
<td>S.J. Gregg &amp; I.S.W. Sing</td>
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</table>
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A. Calculation of Thermodynamic and Kinetic Data for Reaction (5)

\[
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)_2 + \text{H} \quad (5)
\]

\[H_F = 78.0 \quad 19.8 \quad 42.9 \quad 52.1 \text{ k cals mole}^{-1}\]

(i) Estimation of heat of reaction at 1000K.

\[\Delta H^\circ_{298} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}} \]

\[\Delta H^\circ_{298} = -2,000 \text{ cals mole}^{-1}\]

\[\text{Now } \Delta H^\circ_{1000} = \Delta H^\circ_{298} + \Delta C_p^\circ \text{ (mean) } (T - T_0)\]

|| molecule or radical | \(\text{Cp}^\circ\) gibbs mole\(^{-1}\) | \(\text{Cp}^\circ_m\) gibbs mole\(^{-1}\) |
|-----------------|-----------------|-----------------|
|                 | \(298^\circ\text{C}\) | \(1000^\circ\text{C}\) |                 |
| \text{C}_6\text{H}_5 | 18.8            | 47.0            | 38.0            |
| \text{C}_6\text{H}_6 | 19.4            | 50.5            | 40.0            |
| \(\text{C}_6\text{H}_5\)_2 | 39.1           | 96.1            | 76.0            |
| \text{H}          | 5.0             | 5.0             | 5.0             |

*Variation of \(\text{Cp}^\circ\) with temperature is not linear and \(\text{Cp}^\circ\) mean tends to be nearer the high value.

\[\Delta C_p \text{ mean} = 3.0 \text{ gibbs mole}^{-1}\]

\[\Delta H^\circ_{1000} = -694 \text{ cals mole}^{-1}\]

Estimation of activation energy by Benson and Affassi\(^3\) method.

The method assigns additive contributions to \(E\) by the end groups \(\text{C}_6\text{H}_5\) and \(\text{H}\). The effect of the transferred group is neglected.
Both the arithmetic mean and geometric mean values are considered, where $X$ and $F$ represent the respective end group contributions.

**Arithmetic Mean.**
The end group contribution for H atoms is tabulated but the value for $C_6H_5$ is not known. This can be obtained from a reaction of known activation energy. The most reliable data is probably that of Chamberlain and Whittle for the reaction

$$\text{CF}_3 + H - C_6H_5 = \text{CF}_3H + C_6H_5$$

For this reaction the experimental activation energy is 9,100 cals mole$^{-1}$ and $\Delta H^o_{298} = 3,900$ cals mole$^{-1}$.

As the method only applies to exothermic reactions the back reaction must be used.

$$E_{\text{back}} = X_{\text{CF}_3} + X_{C_6H_5}$$

where $X$ represents the end group contribution.

$$5.2 = 4.1 + X_{C_6H_5}$$

$$X_{C_6H_5} = 1.1 \text{ k cals mole}^{-1}$$

and $X_H = 4.7 \text{ k cals mole}^{-1}$ from tables

For reaction (5)

$$E_{\text{calc}} = X_{C_6H_5} + X_H$$

$$= (1.1 + 4.7) \text{ k cals mole}^{-1}$$

$$= 5,800 \text{ cals mole}^{-1}$$

**Geometric Mean**

Similarly the end group $F_{C_6H_5}$ can be calculated

$$FC_6H_5 = 1.76 \text{ cals mole}^{-1}$$

and $F_H = 3.0 \text{ cals mole}^{-1}$ from tables
For reaction 5

\[ E_{\text{calc}} = 1.76 \times 3.0 \text{ k cals mole}^{-1} \]
\[ = 5,300 \text{ cals mole}^{-1} \]

B. Calculation of the activation energy for the reaction by BEBO method\textsuperscript{4} for reaction (2).

\[ \text{H} + C_6H_6 = C_6H_5 + H_2 \quad \Delta H^0_{298} = 6,100 \text{ cals mole}^{-1} \]  

Basic data

<table>
<thead>
<tr>
<th>( D_e ) (cals mole(^{-1}))</th>
<th>( r_o (\text{Å}) )</th>
<th>( \beta (\text{Å}) )</th>
<th>( p )</th>
</tr>
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<tbody>
<tr>
<td>( C_6H_5 - \text{H} )</td>
<td>114,000</td>
<td>1.08</td>
<td>1.93</td>
</tr>
<tr>
<td>( \text{H} - \text{H} )</td>
<td>109,400</td>
<td>0.74</td>
<td>1.94</td>
</tr>
</tbody>
</table>

\( D_e = \) dissociation energy measured from the bottom of the potential energy well.

\( r_o = \) internuclear distance

\( \beta = \) Parameter from the Morse function

\( p = \) empirical relationship between bond order, bond energy and length.

Data above for \( \text{H} - \text{H} \) bonds is listed by Johnson and Parr\textsuperscript{4}.

For \( C_6H_5 - \text{H}, p \) is obtained from the empirical relationship

\[ p = 0.26 \ln \left( \frac{D_8}{E_x} \right) \frac{r_x - r_s}{D_8} \]

where

\( D_8 = C_6H_5 - \text{H} \) bond energy.

\( E_x = \) depth of the Lennard Jones potential of Noble gas analogue.

\( r_x = \) internuclear distance of the noble gas analogue.
Now for C₆H₅ - H, Dₜ = 110,000 cals mole⁻¹ and Johnson lists Ne - He as the noble gas analogue where

\[ E_\alpha = 38.0 \text{ cals.} \]
\[ r_\alpha = 2.99. \]

Hence \( p = 1.084 \)

\( \beta \) is estimated from the Morse function

\[ \beta = w \sqrt{\frac{2 \pi \hbar}{c D_e}} \]

where \( w \) is the vibrational frequency of the

\( \text{C}_6\text{H}_5 - \text{H} \) bond (cm⁻¹)

\( c \) is velocity of light (cm sec⁻¹)

\( m \) is reduced mass (gm)

\( D_e \) is measured in cm⁻¹

\( h \) is Planck's constant (ergs secs)

Now \( w = 3070 \text{ cm}^{-1} \)
\( D_e = 45,600 \text{ cm}^{-1} \)

hence \( \beta = 1.74 A^{-1} \)

For the general equation

\[ A + H - R = A - H + R. \]

The BEBO expression states

\[ E_{AHR} = D_1(1 - n^{P1}) - D_2 (1 - n)^{P2} + D_3 B (n - n^2)^{0.26\beta_3} \]

where 1, 2, 3 refer to the single bonds H - R, A - H and A - R respectively.

\( n \) is the bond order

\[ B = 0.5 \exp \left[ -\beta_3 (r_0, 1 + r_0, 2 - r_{0,3}) \right] \]

By substituting the above data

\[ B = 0.137 \]
The activation energy for the reaction corresponds to the maximum value of the potential energy $E$.

For the reaction
\[ \text{H} + C_6H_6 = C_6H_5 + \text{H}_2 \]
this corresponds to a value of $n = 0.41$
where $E = 16,000 \text{ cal mole}^{-1}$.

Benson and Alfassi Method\(^3\) for Reaction
\[ \text{H} + \text{H} - C_6H_5 = \text{H} - H + C_6H_5. \]
The basic data for this reaction were calculated in part A of this Appendix.

(a) Arithmetic Mean
\[
\begin{align*}
X_H &= 4.7 \\
X_{C_6H_5} &= 1.1
\end{align*}
\]
\[ E_{\text{calc}} = 4.7 + 1.1 (+ \text{endothermicity of the reaction}) = 5.8 + 6.1 \text{ kcal mole}^{-1} = 11,900 \text{ cal mole}^{-1} \]

(b) Geometric Mean
\[
\begin{align*}
F_H &= 3.0 \\
F_{C_6H_5} &= 1.76
\end{align*}
\]
\[ E_{\text{calc}} = 1.76 \times 3.00 + (\text{endothermicity}) \text{ kcal mole}^{-1} = 11,400 \text{ cal mole}^{-1} \]
APPENDIX 2

Estimation of Pre-exponential Factors.

If basic thermodynamic data for reactant molecules and the transition state can be estimated then it is possible to obtain a value for the pre-exponential or "A" factor from the transition state theory expression

\[ A = \left( \frac{e^{\frac{\Delta S^\pm}{R}}}{T} \right) e \]

The method is that outlined by Benson in his book 'Thermochemical Kinetics'. The thermochemistry data used here is either listed there or estimated by the bond additivity rules described there.

**TABLE 1. THERMOCHEMICAL DATA FROM REFS (1)(2)**

<table>
<thead>
<tr>
<th>Group</th>
<th>( H^0 ) kcal mole(^{-1} )</th>
<th>( S^0 ) gibbs mole(^{-1} )</th>
<th>( C_P ) at 298(^{\circ})K gibbs mole(^{-1} )</th>
<th>( C_P ) at 1000(^{\circ})K gibbs mole(^{-1} )</th>
</tr>
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<tr>
<td>( C_6H_6 )</td>
<td>19.8</td>
<td>64.3</td>
<td>19.4</td>
<td>50.5</td>
</tr>
<tr>
<td>((C_6H_5)_2)</td>
<td>42.9</td>
<td>93.9</td>
<td>39.0</td>
<td>96.0</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>0</td>
<td>31.2</td>
<td>6.90</td>
<td>7.2</td>
</tr>
<tr>
<td>( H )</td>
<td>52.1</td>
<td>27.4</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>( C_6H_5 )</td>
<td>78.0</td>
<td>69.4</td>
<td>18.8</td>
<td>47.0</td>
</tr>
</tbody>
</table>

A. Reaction.

\[ H + C_6H_6 = [H ---- H ---- C_6H_5] = \overline{C_6H_5} + H_2 \]

Method.

1. An estimation of the lower limit for the entropy of the transition state is made by comparison with that of a model compound.
2. Structural differences are considered so that a value for the entropy of the transition state may be estimated.

3. Overall entropy change may be obtained from

\[ \Delta S^\dagger = S^0_{\text{Transition State}} - S^0_{\text{Ground State}} \]

**Calculation.**

Consider the contributions to the entropy in turn using benzene as a model compound.

(i) **Translation.**

\[ \Delta S = \frac{3}{2} R \ln \left( \frac{M_{C_6H_6}}{M_{C_6H_7}} \right) = 0. \]

(ii) **Rotation.**

Similarly the entropy change will be small.

(iii) **Symmetry.**

This will lead to a large contribution.

Benzene has 6 \( C_2 \) axes and therefore the symmetry number

\[ \sigma = 6 \times 2. \]

(Benson defines the symmetry number as the total number of independent permutations of identical atoms or groups in a molecule that can be arrived at by simple rigid rotations of the entire molecule.)

The transition state has only 1\( C_2 \) axis and thus \( \sigma = 2 \)

\[ \therefore \text{Entropy difference} = R \ln 6. \]
(iv) Spin.

Addition of an atom leads to a change in spin.

\[ \text{Entropy difference} = R \ln 2. \]

\[ S_{C_6H_7}^0 \neq S_{C_6H_6}^0 + R \ln 6 + R \ln 2. \]

Now \( \Delta S^{\text{sp}} = S_{C_6H_7}^0 - S_{C_6H_6}^0 \)

\[ \Delta S^{\text{sp}} \gg -S_H^0 + R \ln 12 \quad (1) \]

At 1000 K

\[ S_H^{(1000)} = S_H^{(298)} + (C_p^0) \ln 1000/298 \]

\[ S_H^0 = -27.4 + 6.1 \quad \text{Mean } C_p = 5.0 \text{ gibbs mole}^{-1} \]

Substituting in (1)

\[ \Delta S^{\text{sp}} \gg 28.6 \text{ gibbs mole}. \]

This is with a standard state of 1 atmosphere and molarity units are required. Add \( R \ln (eRT) \) where \( R \) outside the logarithm is in units of calories mole\(^{-1}\) and \( R \) inside the logarithm is in units of litre atmos. deg\(^{-1}\) mole\(^{-1}\).

\[ \Delta S^{\text{sp}} \gg -29.6 + 11.1 \text{ gibbs mole}^{-1} \]

\[ > -17.5 \text{ gibbs mole}^{-1} \]

\[ \Lambda = \frac{(eRT)^{\Delta S^+}}{h} e^{\Delta S^+/R} \]

\[ > 10^{13.7} e^{-17.5/R} \]

\[ > 10^{10.9} \]
The above analysis has not taken account of the additional \( \text{H.H.C} \) bending vibrations with frequencies of about 400 cm\(^{-1}\) which exist in the transition state

\[
A = 10^{10.9} 10^{0.7} \text{litre mole}^{-1} \text{sec}^{-1}
\]

\[
= 10^{11.6} \text{litre mole}^{-1} \text{sec}^{-1}.
\]

Reaction \( \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H} \).

Consider entropy changes in forming transition state.

Assume \( [\text{C}_6\text{H}_5 \cdots \cdots \text{H}]^+ \) is the transition state.

Translation entropy changes are small.

Similarly as the extension of the \( \text{C} \cdots \cdots \text{H} \) bond will not appreciably affect the moment of inertia, changes in rotational entropy are small.

Symmetry will however be affected

\( \sigma \) for benzene = 12

but when a bond is elongated the symmetry is reduced to \( 1\text{C}_2 \) axis

\( \therefore \sigma \) for transition state = 2

\( \therefore \Delta S^\#_{\text{symmetry}} = 6 \text{ gibbs mole}^{-1} = 3.56 \text{ gibbs mole}^{-1} \)

The other major change is in the weakening of the bending modes of vibration.

In forming the transition state

the one \( \text{C}_B \cdots \text{H} \) stretching frequency is lost

and the two \( \text{C}_B \cdots \text{C}_B \cdots \text{H} \) bending modes are modified to

two \( \text{C}_B \cdots \text{C}_B \cdots \text{H} \) bending modes.
Consider the total vibrational entropy in benzene and the transition state in turn.

In Benzene.

$C_B - H$ stretch is at $\sim 3100 \text{ cm}^{-1}$ and this leads to an $S^0$ contribution at $1000^\circ K$ of 0.1 gibbs mole$^{-1}$.

$C_B - C_B - H$ bends occur at $\sim 1150 \text{ cm}^{-1}$ and this leads to an $S^0$ contribution of 1.2 gibbs mole$^{-1}$

\[ \text{Total contribution} = 2.4 \text{ gibbs mole}^{-1} \]

\[ \text{Total entropy of vibration concerned in benzene} = 2.5 \text{ gibbs mole}^{-1} \]

Benson suggests that in this type of reaction the formation of the transition state results in a reduction of the bending modes to about $1/5$ of their original values.

$C - C \sim H$ bending modes occur at $\sim 230 \text{ cm}^{-1}$

\[ \text{S}^0 \text{ contribution} = 4.2 \text{ gibbs mole}^{-1} \]

As 2 modes are affected contribution = 8.4 gibbs mole$^{-1}$.

\[ \text{Total change in vibrational entropy} = (8.4 - 2.5) \text{ gibbs mole}^{-1} \]

\[ = 5.9 \text{ gibbs mole}^{-1} \]

As the $\pi$-electron system is largely unaffected entropy changes due to possible resonance changes were ignored.

\[ \text{Total entropy change in forming transition state} = (3.6 + 5.9) \text{ gibbs mole}^{-1}. \]
\[ \Delta S^\pm /R \]

\[
\therefore \quad \Lambda = \frac{\text{e}^{\text{ckT}}}{h} e^{9.5/R}
\]

\[ = 10^{15.7} \text{sec}^{-1} \text{ at } 1000^\circ \text{K.} \]

**Reaction.**

\[ \text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5) + \text{H}. \]

The \( A \) factor for this reaction can be estimated by the lower limit method by comparison of the entropy of the transition state with that of a model compound such as diphenyl. Assume the transition state to be

![Transition State Diagram](image)

Then

**Translation and rotational** entropy changes can be ignored as the addition of a light hydrogen atom will have little effect on overall mass or moment of inertia.

**Symmetry** changes however occur. If diphenyl is assumed to be planar it has 3\( C_2 \) axes

\[
\therefore \sigma = 8.
\]

The transition state has only 1\( C_2 \) axis.

\[
\therefore \sigma = 2.
\]

**Entropy difference** = \( R \& n \) 4 gibbs mole\(^{-1} \).
Spins of the transition state and model compound are different.

Entropy difference = Rln 2.

\[ S^{0+} > S^{0}_{(C_6H_5)_2} + Rln 4 + Rln 2. \]

Now \( \Delta S^{0+} > S^{0+} - S^{0}_{C_6H_6} - S^{0}_{C_6H_5} \)

\[ \Delta S^{0+} > S^{0}_{(C_6H_5)_2} + Rln 8 - S^{0}_{C_6H_6} - S^{0}_{C_6H_5} \]

This is the lower limit.

The value can be improved by considering the vibrational differences.

In the transition state there is a C----C----H bend added. Benson suggested these bends have a frequency of 800 cm\(^{-1}\) and this leads to a contribution of 1.8 gibbs mole\(^{-1}\).

\[ \Delta S^{0+} = S^{0}_{(C_6H_5)_2} + Rln 8 + 1.8 - S^{0}_{C_6H_6} - S^{0}_{C_6H_5} \]

At 1000K

\[ \Delta S^{0+} = (186.5 - 113.0 - 115.0 + 4.1 + 1.8) \text{ gibbs mole}^{-1} = -35.6 \text{ gibbs mole}^{-1}. \]

This is with a standard state of 1 atmos. For a bimolecular gas reaction Rln (eRT) must be added to convert to molarity units.

\[ \Delta S^{0+} = -24.5 \text{ gibbs mole}^{-1} \]

\[ A = \frac{e^{kT}}{h} \frac{\Delta S^{+}}{R} \]

\[ = 10^{8.3} \text{ litre mole}^{-1} \text{ sec}^{-1} \]
Termination Reaction.

\[
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5 = (\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5)
\]

The entropy of this reaction can be estimated by the model compound technique.

Consider diphenyl as a model compound.

Translational differences are virtually nil.

Spin and symmetry of the transition state and the model compound are the same. Entropy will be unaffected.

Major differences occur however in vibrational entropy.

Vibrational frequencies affected in diphenyl are

(i) C-C stretching at 1000 cm\(^{-1}\).

(ii) 4C\(_B\) - C\(_B\) - C vibrations at 420 cm\(^{-1}\).

In forming the transition state the C - C is lost and 4C\(_B\) - C\(_B\) - C stretching frequencies become

4C\(_B\) - C\(_B\) ----C frequencies.

Benson suggests that C\(_B\) - C\(_B\) ----C bend = \(\frac{1}{5}\) C\(_B\) - C\(_B\) - C.

Entropy difference due to vibration between diphenyl and transition state = -(4 x 5.9) + 1.4 + (4 x 3.1)

= -9.8 gibbs mole\(^{-1}\).

Now consider rotational changes.

These can be divided into internal and external rotations.

(a) External.

\[
\Delta S^+_{\text{rot}} = \frac{R}{2} \ln \frac{I_B}{I_A}
\]

where \(I_B\) is the moment of inertia of the complex and \(I_A\) is moment of inertia in the ground state.
\[ \Delta S_{\text{rot}} = R/2 \ln x^2 \] where \( x \) = extension of the C - C bond.

If \( x = 2.5 \)

\[ \Delta S^\neq = 1.7 \text{ gibbs mole}^{-1} \]

Now consider internal rotation.

In forming the transition state the barrier to rotation in Ph-Ph is reduced. This will lead to a contribution.

1. Estimate moment of inertia of each Phenyl radical i.e.

\[ I_{\text{Ph}} \xrightarrow{c} \infty \]

\[ I = \sigma \cdot m \cdot r \cdot \sin (180-\theta)^2 \]

where \( \sigma \) = internal symmetry number.

\( m \) = mass

\( r \) = bond length

\( \theta \) = bond angle

\[ I = 2 \times 77 \times 1.45 \]

\[ = 223 \text{ amu} \cdot \text{Å}^2 \]

Reduced Moment

of Intertia = \( \frac{I_A \cdot I_B}{I_A + I_B} \)

2. Estimate the Rotational Partition Function for Diphenyl.

\[ Q_f = \frac{3.6}{\sigma} \left[ \frac{I_R \cdot T}{100} \right]^{\frac{1}{2}} \]

\( \sigma \) = internal symmetry

\( = 4 \)

\( T \) = Temperature

\[ Q_f = 42.5 \]
3. In the transition state there is free rotation but in the ground state rotation is hindered. Benson suggests that there is a barrier height (\(V\)) of 2.2 k cals mole\(^{-1}\).

Lewis and Randalls tabulate values of the decrease in entropy (\(S_f^0 - S_h^0\)) of the free rotor as a function of the barrier height (expressed as \(\frac{V}{RT}\)) and the partition function (expressed as \(\frac{1}{Q_f}\)). This is in fact the entropy change due to internal rotation in forming the transition state

\[
\frac{1}{Q_f} = 0.023
\]

\[
\frac{V}{RT} = 1.11.
\]

internal rotational entropy difference between complex and diphenyl = 0.1 gibbs mole\(^{-1}\).

Now consider total entropy of the complex

\[
S^\pm = (S_{\text{diphenyl}} + 9.8 + 1.7 + 0.1) \text{ gibbs mole}^{-1}
\]

\[
\Delta S^\pm = S^o - 2S_{C_6H_5}^o
\]

\[
= S_{\text{diphenyl}}^o + 11.6 - 2S_{C_6H_5}^o
\]

\[
= 31.9 \text{ gibbs mole}^{-1}
\]

Now reaction is bimolecular and A factor must have units of litre mole\(^{-1}\) sec\(^{-1}\) • Add R\(\Delta T\) (eRT)

\[
\Delta S^\pm = -20.8 \text{ gibbs mole}^{-1}
\]

\[
A = \left[ \frac{e^{kT}}{h} \right] e^{\frac{\Delta S^\pm}{R}}
\]

\[
= 10^{13.7} \times 10^{-4.5} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]

\[
= 10^{9.2} \text{ litre mole}^{-1} \text{ sec}^{-1}
\]
Appendix 3

Estimation of heat of reaction for reaction (5)

\[
\text{C}_6\text{H}_5\text{CHCH}_3 = \text{C}_6\text{H}_5\text{CH:CH}_2 + \text{H} \quad (5)
\]

**THERMOCHEMICAL DATA**

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta H^\circ \text{cals mole}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>( \text{C}_6\text{H}_5\text{CHCH}_3 )</td>
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<td>( \text{C}_6\text{H}_5\text{CHCH}_2 )</td>
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<td>( \text{H} )</td>
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</tr>
</tbody>
</table>

\[
\Delta H^\circ = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}} = 49,000 \text{ cals mole}^{-1}
\]
References.


