STUDIES IN THE THERMAL DECOMPOSITIONS OF ISOMERIC PENTANES

by

JOHN CHRYSOCHOOS

Dipl. of Chem. (Athens) 1957

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

in the Department of Chemistry

We accept this thesis as conforming to the required standard.

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1962
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia, Vancouver 8, Canada.

Date 9-5-1962
An investigation has been made of the pyrolysis of n-pentane, isopentane and neo-pentane in a static system at temperatures near 500°C. Both uninhibited and inhibited reactions were investigated. Of principal concern has been the effect of variation of initial pressure of hydrocarbon on the decomposition products for the uninhibited reaction. The effect of variation in surface-to-volume ratio on rates and on the distribution of the products has been also a point of concern. Structural effects on rates as well as the variation of energy of activation and frequency factors with pressure have been considered of importance. Investigations of orders of reaction provide information as far as the mechanism is concerned. As a final point the most important task for the uninhibited reaction was a mechanism explaining the results obtained, and offering logical reasons for the similarities and differences between the isomeric pentanes.

For the inhibited reaction the points of principal concern considered have been: the effect of nitric oxide on the product distribution; the effect of packing on both rates and products, the behavior of NO. The investigation has as a main purpose to determine whether the role of nitric oxide as an inhibitor involves homogeneous or heterogeneous reactions. Whether NO was consumed or not was also an important question. As a final point a mechanism is also
II

proposed for inhibited reactions which accounts for the experimental results and attempts to give a logical explanation of the inhibition phenomenon.
ACKNOWLEDGEMENTS

The present investigation in the thermal decomposition of isomeric pentanes, has been made as a partial fulfilment of the requirements for the M.Sc. degree, under the general supervision of Dr. W.A. Bryce, to whom the author is greatly indebted for his advice in both the experimental work and the writing of this thesis. The author is also indebted to the University of British Columbia for the offered assistantship during the completion of the present study. He is also greatly indebted to Mrs. Zell for the valuable facilities she offered to him for the use of infra-red instruments in her laboratory.

April, 1962.
# Table of Contents

## Preface

## Introduction

## Chapter I

The Uninhibited decomposition ........................................ 2
Heterogeneous Reaction ............................................. 7
The Inhibited Reaction ............................................... 11

## Experimental

## Chapter II

Materials and methods .................................................. 24
Gas chromatographic equipment ........................................ 25
Detector ................................................................. 25
Infra Red Analysis ..................................................... 25
The pyrolysis apparatus ............................................... 26
Reaction vessel and furnace .......................................... 26
Description of a typical experiment .................................. 28

## Results

## Chapter III

Uninhibited pyrolysis ................................................... 33
Rates of reaction ....................................................... 33
Rates of reaction for isopentane ..................................... 36
Variation of rate with collision frequencies ....................... 36
The effect of packing for isopentane ................................. 40
Rates for n-pentane .................................................... 42
The effect of packing .................................................. 42
Rates for neo-pentane .................................................. 42
The effect of Packing .................................................. 42
Order of reaction ....................................................... 46
Order of reaction for n-pentane ...................................... 46
Effect of packing for n-pentane ...................................... 46
Order of reaction for isopentane ..................................... 46
Order of reaction for neo-pentane ................................... 50
Effect of packing ....................................................... 50
Energy of activation and frequency factors ......................... 50
- n-pentane ............................................................. 52
- isopentane ............................................................. 53
- neopentane ........................................................... 54
Analytical results for .................................................. 55
- isopentane ............................................................. 55
- n-pentane ............................................................. 56
- neo-pentane .......................................................... 56
Variation of the product with
- time .............................................................. 56
- initial pressure .................................................. 58

Variation of product ratios with
- time .............................................................. 58
- initial pressure .................................................. 63

Variation of $C_2H_4/C_2H_6$ with pressure ......................... 63

The effect of packing ............................................. 71

Variation of $i-C_4H_8/C_3H_6$ with pressure ......................... 75

The effect of chain branching on rate ............................ 77

Inhibited reaction .................................................. 79

Nitric oxidized concentration for the fully inhibited reaction for
- isopentane ....................................................... 79
- $n$-pentane ....................................................... 83
- neo-pentane ...................................................... 83

Variation of products with time .................................... 84

Variation of the decomposition products with $P(NO)$ as $S/V$ ratio ................................................. 99

Variation of product ratios with $P(NO)$ and $S/V$.................. 103
- variation of $C_2H_4/C_2H_6$ ..................................... 103
- variation of $CH_4/C_2H_6$ ........................................ 103
- variation of $C_2H_4+C_2H_6/C_3H_6$ ............................. 103
- variation of $C_2H_4+C_2H_6/C_4H_8$ ............................. 110
- variation of $CH_4/C_2H_4$ with $P(NO)$ .......................... 110
- variation of $C_2H_6/C_2H_5NO$ with $P(NO)$ ..................... 110
- variation of $i-C_4H_8/C_3H_6$ ................................. 110

consumption of Nitric oxide ...................................... 110

DISCUSSION

CHAPTER IV

Uninhibited decomposition ............................................. 118
- isopentane ....................................................... 118

The overall mechanism for isopentane .............................. 126
- $n$-pentane ....................................................... 128

The overall mechanism for $n$-pentane .............................. 132
- neo-pentane ...................................................... 133

Inhibited decompositions ........................................... 138
- isopentane ....................................................... 139
- $n$-pentane ....................................................... 149
- neo-pentane ...................................................... 151

CHAPTER V

Kinetic laws the thermal decomposition of isopentane .......... 153

Uninhibited reaction ................................................. 153

Inhibited reaction .................................................. 162
References .................................................. 164

Appendix I
Calculation of activation energies and frequency factors for n-, iso, and neo-pentane ............... 170

Appendix II
Analytical balance for the decomposition products of n-pentane ........................................ 173
<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Variation of $E_A$ and $A$ with $P_1$ for n-pentane</td>
<td>53</td>
</tr>
<tr>
<td>II Variation of $E_A$ and $A$ with $P_1$ for isopentane</td>
<td>53</td>
</tr>
<tr>
<td>III Variation of $E_A$ with $P_2$ for neo-pentane</td>
<td>54</td>
</tr>
<tr>
<td>IV Analytical results for isopentane</td>
<td>55</td>
</tr>
<tr>
<td>VI Variation of the products of decomposition of isopentane with time</td>
<td>58</td>
</tr>
<tr>
<td>VII Variation of product ratios with time</td>
<td>62</td>
</tr>
<tr>
<td>VIII Variation of $C_2H_4/C_2H_5$ with pressure and temperature</td>
<td>75</td>
</tr>
<tr>
<td>IX Variation of $C_3H_6$ /$C_4H_8$, $\sum C_2/C_3H_6$, $\sum C_2/1-C_4H_8$ ratios with pressure for n-pentane</td>
<td>77</td>
</tr>
<tr>
<td>X Variation of $P$ with time for various $P_{NO}$ for neo-pentane</td>
<td>84</td>
</tr>
<tr>
<td>XI Consumption of NO</td>
<td>117</td>
</tr>
<tr>
<td>XII Analytical results for isopentane. Inhibited and uninhibited reaction</td>
<td>139</td>
</tr>
<tr>
<td>XIII Variation of $C_2H_4/C_2H_5NO$ with NO</td>
<td>142</td>
</tr>
<tr>
<td>XIV Rate constants for various pressures and temperatures for isopentane</td>
<td>170</td>
</tr>
<tr>
<td>XV $E_A$ and $A$ for isopentane</td>
<td>170</td>
</tr>
<tr>
<td>XVI Rate constants for various pressures and temperatures for n-pentane</td>
<td>172</td>
</tr>
<tr>
<td>XVII $E_A$ and $A$ for n-pentane</td>
<td>172</td>
</tr>
<tr>
<td>XVIII Rate constants for various pressures and temperatures for neo-pentane</td>
<td>172</td>
</tr>
<tr>
<td>XIX $E_A$ for neo-pentane</td>
<td>172</td>
</tr>
<tr>
<td>XX Analytical results for n-pentane</td>
<td>173</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Variation of energy with the reaction coordinate</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Variation of potential energy with the reaction coordinate for a unimolecular reaction</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Schematic outline of thermal decomposition apparatus</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Furnace heater circuit</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>Chromatogram of the products on HMPA column</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Chromatogram of the products on silica gel column</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>Variation of pressure with time for isomeric pentanes</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>Variation of the rate (dp/dt) with time at various values of P_1 for isopentane</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>Variation of K overall with init. pressure for isopentane</td>
<td>37</td>
</tr>
<tr>
<td>10</td>
<td>Variation of initial rate with pressure for isopentane</td>
<td>38</td>
</tr>
<tr>
<td>11</td>
<td>R_P vs Z_1/Z_14 (collision numbers) for isopentane</td>
<td>39</td>
</tr>
<tr>
<td>12</td>
<td>k overall vs P_2 for packed and unpacked vessel for isopentane</td>
<td>41</td>
</tr>
<tr>
<td>13</td>
<td>Variation of R_P with initial pressure for n-pentane</td>
<td>43</td>
</tr>
<tr>
<td>14</td>
<td>Effect of packing on initial rate for n-pentane</td>
<td>44</td>
</tr>
<tr>
<td>15</td>
<td>R_P vs P_2 for neo-pentane</td>
<td>45</td>
</tr>
<tr>
<td>16</td>
<td>Order of reaction for unpacked vessel for n-pentane</td>
<td>47</td>
</tr>
<tr>
<td>17</td>
<td>Order of reaction in packed and unpacked vessels for n-pentane</td>
<td>48</td>
</tr>
<tr>
<td>18</td>
<td>Order of reaction for isopentane</td>
<td>49</td>
</tr>
<tr>
<td>19</td>
<td>Order of reaction for neo-pentane</td>
<td>51</td>
</tr>
<tr>
<td>20</td>
<td>Product yield in mole.% vs time for n-pentane</td>
<td>57</td>
</tr>
<tr>
<td>21</td>
<td>Product yield in mole.% vs initial pressure for n-pentane</td>
<td>59</td>
</tr>
<tr>
<td>22a</td>
<td>Variation of decomposition products with pressure for iso-pentane</td>
<td>60</td>
</tr>
<tr>
<td>22b</td>
<td>Variation of the products with initial pressure for iso-pentane</td>
<td>61</td>
</tr>
<tr>
<td>23</td>
<td>Variation of C_2H_6/C_2H_4 ratio with time for n-pentane</td>
<td>66</td>
</tr>
<tr>
<td>24</td>
<td>Variation of CH_4/C_2H_6 ratio with P_1 at various temperatures for isopentane</td>
<td>67</td>
</tr>
<tr>
<td>25</td>
<td>CH_4/C_2H_6 vs P initial for n-pentane</td>
<td>68</td>
</tr>
<tr>
<td>26</td>
<td>Variation of C_2H_4/C_2H_6 with P_1 at various temperatures for isopentane</td>
<td>69</td>
</tr>
<tr>
<td>27</td>
<td>Variation of C_2H_4/C_2H_6 ratio with P_1 for n- and isopentane</td>
<td>70</td>
</tr>
<tr>
<td>28</td>
<td>Effect of packing on the C_2H_4/C_2H_6 ratio at various pressures for n-pentane</td>
<td>72</td>
</tr>
<tr>
<td>29</td>
<td>Effect of packing on the C_2H_4/C_2H_6 ratio at various pressures for iso-pentane</td>
<td>73</td>
</tr>
<tr>
<td>29b</td>
<td>Influence of packing on the variation of C_2H_4/C_2H_6 with P_1 for n-pentane</td>
<td>74</td>
</tr>
</tbody>
</table>
30. Variation of i-C$_4$H$_8$/C$_3$H$_6$ ratio with initial pressure for variation values for T, for isopentane ...... 76
31. Structural effect of isomeric pentanes on the initial rate ........................................... 78
32. Rate (initial) vs PNO in unpacked reaction for iso­pentane ........................................... 80
33. K overall vs PNO at various S/V ratios for isopentane ........................................ 81
34. Effect of PNO on rate (overall) for n-pentane; packed vessel ....................................... 82
35. Neo-pentane k over vs PNO .................................................. 85
36. Yield of C$_2$H$_5$NO and C$_2$H$_6$ with time for isopentane; fully inhibited reaction; S/V 2.5 .......................... 86
37. C$_2$H$_4$ vs time at various S/V ratios and different PNO for isopentane; fully inhibited reaction ... 87
38. i-C$_4$H$_8$ vs time at different PNO for isopentane ..................... 88
39. Product yield vs time in the fully inhibited reaction for isopentane .................................. 89
40. Yield of C$_2$H$_6$ vs time at various S/V ratios and PNO for isopentane; fully inhibited reaction ... 90
41. Product yield vs PNO for n-pentane ........................................... 92
42. Effect of NO in the products of C$_3$H$_6$ at various S/V ratios for isopentane ..................... 93
43. i-C$_4$H$_8$ vs PNO in packed and unpacked vessels for isopentane ......................................... 94
44. Product yield vs PNO for neo-pentane ........................................... 95
45. C$_2$H$_6$ vs PNO at various S/V ratios for isopentane ..................... 96
46. CH$_4$ vs PNO at various S/V ratios for isopentane ..................... 97
47. Yield of C$_2$H$_4$ vs PNO at various S/V ratios for isopentane .......................... 98
48. C$_2$H$_5$NO vs PNO for isopentane ........................................... 102
49. C$_2$H$_4$/C$_2$H$_6$ vs PNO for isopentane ........................................... 104
50. C$_2$H$_4$/C$_2$H$_6$ vs PNO at various S/V ratios for isopentane. 105
51. CH$_4$/C$_2$H$_6$ vs PNO for n-pentane ........................................... 106
52. CH$_4$/C$_2$H$_6$ vs PNO at various S/V ratios for isopentane .......................... 107
53. CH$_4$/C$_2$H$_6$ vs PNO for n-pentane ........................................... 108
54. C$_2$H$_4$/C$_2$H$_6$/C$_3$H$_6$ vs PNO for n- and isopentane .... 109
55. C$_2$H$_4$/C$_2$H$_6$/C$_4$H$_8$ vs PNO for n- and isopentane .... 111
56. CH$_4$/C$_2$H$_4$ vs PNO for n-pentane ........................................... 112
57. C$_2$H$_6$/C$_2$H$_5$NO vs PNO at various reaction extent for isopentane .......................... 113
58. i-C$_4$H$_8$/C$_3$H$_6$ vs PNO at various S/V ratios for isopentane .......................... 114
59. NO consumption vs PNO for isopentane .......................... 116
PREFACE

The present study, is divided into three main sections: introduction, experimental and discussion. The introduction provides a historical survey of the subject. The experimental, which consists of two chapters, II and III, deals with the description of the apparatus and materials and the experimental results. In the third section, consisting of two chapters IV and V, mechanisms and kinetic laws are proposed to explain the experimental results. Each chapter is divided into two main divisions, one dealing with the uninhibited decomposition and the other with the inhibited reaction, and each division into three more subdivisions, dealing with isopentane, n-pentane and neo-pentane respectively.

April, 1962.
CHAPTER I

INTRODUCTION

The thermal decomposition of hydrocarbons has been subject of investigation for several decades. The existence of free radicals was proved in many of these decompositions by the Paneth metallic mirror technique \((1,2,3,4)\) as well as by mass spectrometric methods \((5,6,7,8)\). It is also well known that the decomposition of several hydrocarbons is accelerated by methyl radical \((9,10)\) as well as by some traces of impurities such as \(O_2\) etc. \((11,12,13)\). Rice was the first to treat the decomposition of a simple paraffin, \(C_2H_6\) as a free radical mechanism \((14)\). The Rice-Hertzfeld mechanisms along with the alternative proposed by Wühle and Theilé \((15)\) formed the basis for the investigation of thermal decomposition of hydrocarbons.

Most of these decompositions show common characteristics. A marked feature is the chain nature of the mechanism as well as the phenomenon of inhibition. The rate of decomposition of almost all of them is reduced by several inhibitors of which the most important are nitric oxide, propylene and \(C_4H_8\). The inhibition by NO was discovered and exhaustively investigated by Hinshelwood and his co-workers for \(C_5\) hydrocarbons. They compared the effect of NO and \(C_3H_6\) and found that the same inhibition is attained if the relative concentrations of \(NO/C_3H_6\) is 1/12, which means, NO is 12 times more effective than propylene \((16)\). Stepukhovitz has compared quantitatively the action of isobutylene and
propylene for several hydrocarbons (17,18,19) and found that the same limiting rate is always reached for these two inhibitors.

I. The Uninhibited decomposition

In the normal decomposition, the main problem arising is the nature of the mechanism, and of course an examination of the chain reaction is first of all necessary. It has been known for a long time that the majority of gas-phase reactions involve considerable activation energy in the range from 30 - 50 KCal/Mole. On correlating the activation energy $E_A$ with the energy barrier $E_0$ and the heat of reaction (20), it was found that these quantities were not related. Every molecular decomposition proceeds through a transition state (Fig. 1) and for exothermic reactions

$$E_A = E_0 + q,$$

but for endothermic reactions $E = E_0$

For free radical reaction $E_0 = A - a|q|$ where $A$ is a constant quantity approximately 11 KCal/Mole., slightly dependent on the type of the reaction and, $a$, is another constant approximately 0.25 (20). Polanyi and Evans (21) found the existence of a formula for exothermic reactions $\Delta E_0 = -a|q|$. The relationship between these symbols is given in (Fig. 1). Whether the reaction is a molecular or a free radical mechanism can now be discussed. Consider the reaction

$$A + B \rightarrow C$$

The rate is $R_{\text{molec.}} = k [A][B]$ where $k$ is a bimolecular rate constant. Hence $R_{\text{molec.}} = 10^{10} e^{-E/RT} [A] [B]$ (20) when $10^{10}$
is the preexponential factor for the bimolecular reaction. Supposing that the above reaction proceeds through a free radical process

\[ \begin{align*}
R_1 + B &\rightarrow M_1 + R_2 \\
R_2 + A &\rightarrow M_2 + R_1
\end{align*} \tag{1} \tag{2} \text{ etc.}\]

where \( R_1 \) and \( R_2 \) are radicals produced from \( A \), and \( M_1, M_2 \) are molecules, we get:

\[ R_{\text{chain}} = k_1 [R_1][B] = k_2 [R_2][A] \approx 10^{-10} e^{-E_1/RT} [R_1][B] \]

where \( E_1 \) is the activation energy for the step with the lowest rate. Then by forming the ratio

\[ \gamma = \frac{R_{\text{molec}}}{R_{\text{chains}}} = \frac{[A][B]}{[R_1]} \frac{10^{-10} e^{-E/RT}}{10^{-10} e^{-E_1/RT}} = \left[ \frac{[R_1]}{[R_1]} e^{\frac{E_1-E_A}{RT}} \right] \]

(1)

The concentration of \( R_1 \) is calculated by the ratio of the rate of formation over the rate of disappearance. If \( I \) is the intensity of light for a photoinitiated reaction

\[ A \xrightarrow{I} R_1 + R_2 \tag{2} \]

\[ R_1 + R_1 \rightarrow M_2 \tag{3} \]

so \( I = K_3 [R_1]^2 \) or

\[ [R_1] = \left( \frac{I}{K_3} \right)^{\frac{1}{2}} \]

Substituting in (1) we get

\[ \gamma = \left[ \frac{[A]}{[R_1]} \right] e^{\frac{E_1-E_A}{RT}} = [A] \left( \frac{K_3}{I} \right)^{\frac{1}{2}} e^{\frac{E_1-E_A}{RT}} \]

For molecular reaction \( E_A \) is high around 40 KCal/Mole. For chains reaction \( E_1 \) is small around 5-10 KCal/Mole. so
\[ \chi = \left[ A \right] \left( \frac{K_3}{1} \right)^{\frac{1}{2}} e^{-\frac{35000}{RT}} \]. I varies from \(10^{12} \sim 10^{15}\) and 

\(K_3\) is usually very much less than unity. 

Hence \(\chi > \left[ A \right] \left( \frac{10^{15}}{1} \right)^{\frac{1}{2}} e^{-\frac{35000}{RT}}\)

Values of \(\chi\), under normal conditions vary from \(10^{-4} \sim 10^{-6}\) for hydrocarbons decomposition (20). Thus reaction in the gas phases proceed much more through a chain mechanism than by the molecular mechanism.

In the case of

\[ \text{Br}_2 + H_2 \rightarrow 2 \text{BrH} \quad \chi = 0.1 \text{ while for} \]

\[ \text{J}_2 + H_2 \rightarrow 2 \text{TH} \quad \chi = 2 \cdot 10^2 \quad \text{i.e. the main process is a molecular process.} \]

In a chain type mechanism three stages are distinct. Initiation, propagation and termination. In thermal decomposition of hydrocarbons, initiation can take place through a C-C split, provided that \(D(C-C)\) is less than \(D(C-H)\). This reaction can take place either unimolecularly or bimolecularly. Reactants proceed to products through an activated complex.

In \(A \leftrightarrow B\) we can follow the scheme (22)

\[ A \rightleftharpoons B \]

The reaction will take place through two excited states, with \(E^*\) greater than that required for the reaction. The potential energy of such a system is given in (Fig. 2). The frequency factor can be considered as a criterion for the evidence of a unimolecular reaction. It usually has a value
around $10^{13}$ sec. for these reactions. This corresponds approximately to the frequency of the bond breaking. In the case of radical decomposition it is assumed that the pre-exponential factor does not vary much from those of the molecules. For bimolecular reaction the pre-exponential factor is close to the number of collisions per cm$^3$/sec. and has an average value $A=10^{-10}$ cm$^3$/sec. Actually $A=P$, where $P$ is the steric factor, found by several workers to be $10^{-3}-10^{-4}$ for hydrocarbons. By comparing a unimolecular decomposition with a bimolecular one, of the same activation energy we get

$$R_1/R_2 = 10^{13}e^{-E_1/RT} n/10^{-10}e^{-E_1/RT} n^2 = 10^{23} 1/n$$

$n$ is the number of molecules per cm$^3=10^{19}$

Thus $R_1/R_2<10^{4}$ and $R_1=10^{4}R_2$. The unimolecular reaction is much more preferred than the bimolecular process. The unimolecular initiation process will thus be of major importance in this study.

A molecule can split into radicals either by passing through an activated complex unimolecularly, or by colliding with other molecules, bimolecularly. Unimolecular reaction is favored at lower pressures where energy loss by collisions is low. In these cases molecules can use all their kinetic energy and pass the energy barrier leading to decomposition. Heterogeneous phenomena will be important since the energy needed for a heterogeneous reaction is lower than that for homogeneous.
Heterogeneous reactions

Heterogeneous initiation was first studied by TRIFONOV (23) for the reaction

\[ \text{Cl}_2 + \text{H}_2 \xrightarrow{\text{photocatalysis}} 2 \text{ClH} \]

for vessels with different diameter. At low pressures and low diameters (14, 27 mm) he found the ratio of the rates

\[ \frac{R_2}{R_1} \propto \frac{d_2^2}{d_1^2} \]

which relates the ratio of the rates to the rates of diffusion to the vessel. At higher pressures, dependence of observed rates on diameters was still, but at higher diameters no regularity existed. The rates are higher for larger surface because less energy is needed. The heat of reaction is given by

\[ \Delta H = D(C-C) - Q \]

where \( D(C-C) \) is the bond dissociation energy and \( Q \) the heat of adsorption.

Chaykin (20) using the concept of differential calorimetry by which one can measure the heat of reaction by a differential thermocouple both in the center of the vessel and on the wall, proved that generation and termination of the chain take place on the walls in the thermal reaction.

\[ \text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl} \]

The hypothesis of heterogeneous - homogeneous catalysis first proposed by POLYAKOV (24), found application to the investigation of oxidation reactions. The catalysis depends on both the nature of the wall and the nature of the compound.
Actually the probability for the capture of a radical or atom by a surface site was found by several workers (25-26, to be 27,28) to be between $10^{-5}$ and 1.

In the case of wall reactions SEMENOV (20) discusses the possibilities of bond termination between the free radical or atom and the unbalanced charge of the surface. He correlates the magnitude of heterogeneous reaction with the required energy for electron transfer in the surface with formation of a surface with unbalanced charges. If $u$ is the potential energy of such a surface then homogeneous initiation is favored if $u$ is more than $D(C-C)$ and heterogeneous is favored if $u$ is less than $D(C-C)$. Heterogeneous initiation, even if not marked, at least appears to promote the initiation action of impurities. POLTORAK and VOEVODSKII (29) proved that acceleration in the cracking of propane at low pressures by oxygen strongly depends on the pretreatment of the vessel.

Many workers have tried to show the existence or not of wall effects in hydrocarbon decomposition. Many results are contradictory. In most of them the same basic error has been made. They used two different vessels, of the same size one packed and the other unpacked. But it is not the size of the important factor, but the number of active centers. It is possible that this difference some times is so important that, packing may merely equalize the number of centers. LAIDLER and WOJCIECHOWSKII (30,31) tried to show
surface effect in ethane decompositions with negative results. They found rates to be a little decreased by an increase in S/V ratios. PURNELL AND QUINN (32) found no effect for different wall coatings for n-butane. In contrast with the above authors WALL AND MOORE (33) in the mixed pyrolysis of C_2H_6 and C_2D_6, following the results by mass spectrographic analysis, have found evidence of catalysis by the surface for packed vessel. This work along with the studies of the Russian investigators mentioned above are in contrast with the previously mentioned. To determine whether or not there is wall effect was one of the main tasks of this present work.

Initiation taking place on the wall is expected to increase rates more at low pressures than at high pressures. But termination on the walls is expected to favor more high pressures than low, because for the high pressure, the chain length is larger than at low pressures. As far as the propagation is concerned it can take place by three main mechanisms:

Substitution reaction: \[ R_1 + R_2 R_3 \rightarrow R_1 R_2^+ R_3 \] (a)

decomposition of radicals: \[ R A_1 A_2 \rightarrow R + A_1 = A_2 \] (b)

and isomerization reaction: \[ CH_3CHCH_3 \rightarrow CH_3CHCH_2 \] (c)

Reaction (b) and (c) are unimolecular and (a) bimolecular.

For reaction (a) the activation energy can be given as

\[ E_A = \Delta H_f(R_1 R_2) + \Delta H_f(R_3) - \Delta H_f(R_1) - \Delta H_f(R_1 R_3) \]

Enthalpies of formation as well as heat capacities are well
known for molecules but not for radicals. **Tàccitly** we use the values of $\Delta H_f$ for radicals, found for lower temperatures, assuming they remain the same, or that, we can calculate them, by using the literature and Voevodskii's empirical formula (33).

$$D(C-H)_{\text{prim.}} = D(C-H)_{\text{sec.}} + B = D(C-H)_{\text{tert.}} + 2B$$

This method would be followed in connection with thermochemical data and dissociation energies found experimentally to calculate activation energies for individual steps in the proposed mechanism.

For reaction (b) more than one mode of decomposition can be accepted. The choice between them is a function of their activation energies, frequency factors, etc. Their relatives probabilities commonly are based on product analysis. Methyl and ethyl radical are likely to be present in the reaction vessel in significant amounts, since the energy of activation in these decompositions is small. Isomerizations as in reaction (c) are very important, as far as the most favorable angle of attack is concerned. Rough quantum mechanical calculations (20) lead to the qualitative result that the attack on a 6-bond is more favorable when the approaching radical and the bond attacked are collinear. These calculations indicate that twice as much energy is required for perpendicular attack as for a linear attack. In the case of a $\pi$-bond, a direction perpendicular to the bond axis is the most favorable. In isomerization reactions, which differ from real decomposition, one of the $\sigma$ electrons, combines from C-H or from C-C bond shifts and forms a pair
with the free valence electron, forming a new π - bond. At the same time the σ-bond is ruptured and the molecule assumes the most favorable configuration for the attack. The problem of isomerization of free radicals, as common property, has been discussed (34,35). Isomerization processes will be considered as important in the following study.

The inhibited reaction

As we have seen before, the decomposition of hydrocarbons follow a free radical mechanism. The composition of the products is a function of the chain length which is given by the relative importance of the propagation against the termination steps. For this reason the product distribution should be a function of pressure since the chain length depends on pressure also. The recombination of radicals can cause the interruption of the chain. The longer the chain the higher the rate because propagation reactions are very fast, having low activation energies, while the initiation is rather slow. The interruption of a chain can be done not only by radical recombinations but also by other ways. The capture of the propagating radical by an inhibitor inevitably stops the chain. As inhibitors we use either molecules which are radicals in themselves such as NO with an unpaired electron, or compounds such as olefins. The inhibition by olefins is often termed self-inhibition, since these compounds appear in the products, and their effect is obvious, from the shape of either pressure-time curves or the behavior of products with time.
Nitric oxide in slight amounts suppresses markedly the rate of reaction, and after that a limiting rate is attained. The nature of the residual reaction was a point of controversy, for many years, and even now it cannot be said that is completely known. One point that is established is that for each hydrocarbon there exists under certain conditions, a definite limiting inhibited rate of decomposition, depending only on the addition of sufficient amount of inhibitor, but independent of the nature of the latter. A thorough investigation of the inhibition for all hydrocarbons under the same experimental conditions could give information on whether inhibition is related to the nature of the hydrocarbon to the conditions of the experiment. Hinshelwood and his co-worker's supposed that chain reaction disappears completely and that residual reaction is simply a molecular reaction.(36).

Studying the inhibition of butane by NO they proposed the following scheme.

\[
\begin{align*}
\text{C}_4\text{H}_10 & \xrightleftharpoons[k_1]{k_1} 2 \text{R} \quad \text{(a)} \\
\text{R} + \text{C}_4\text{H}_10 & \xrightarrow{k_2} \text{R + products} \quad \text{(b)} \\
2 \text{R} & \xrightarrow{k_3} \text{x} \quad \text{(c)} \\
\text{R} + \text{NO} & \xrightarrow{k_4} \text{S} \quad \text{(d)} \\
\text{S} & \xrightarrow{k_5} \text{R} + \text{NO} \quad \text{(e)}
\end{align*}
\]

If (d) and (c) come into equilibrium at once then they will not affect the stationary concentration of R and no inhibitory effect will be observed. This has been also assumed by ECHOLS and PEASE (37) for the later stages of the reaction, when inhibition is no longer effective. Why this equilibrium should occur in the later stages and not in the beginning is
open to question. But Hinshelwood adds another step for the beginning of the reaction to explain the inhibition. He assumes that S is destroyed irreversibly and the rate differs only by a constant by this addition from that obtained if reaction (d) is also irreversible. If equilibrium is attained slowly there is some explanation of the inhibition on the beginning but still the problem is not clear. Our hypothesis that at maximum inhibition the complex S, regenerates radicals as fast as it destroys them, is considered invalid, since addition of more NO should have some effect on the amount S and of course on inhibition, but this is not found to be the case.

The solution of the above set of equation is given by ECHOLS and PEASE (37) as follows:

\[
d[R]/dt = k_1 [C_4H_{10}] - k_3 [R] - k_4 [R][NO] + k_5 [S] = 0 \quad (1)
\]

\[
[R] = k_1 [C_4H_{10}] + k_5 [S] / k_3 + k_4 [NO] \quad (2)
\]

\[
d[S]/dt = k_4 [R][NO] - k_5 [S] \quad (3)
\]

but S is not stationary so solving (3) and using (2) we get

\[
d[S]/dt = k_4 \left( k_1 [C_4H_{10}] + k_5 [S] / k_3 + k_4 [NO] \right) - k_5 [S]
\]

Hence \[S\] = \[
\frac{k_1 k_4 [C_4H_{10}][NO]}{k_3 k_5} \left( 1 - e^{-k_3 k_5 t / k_3 + k_4 [NO]} \right)
\]

and substituting (4) back into (2) we get

\[
[R] = k_1 [C_4H_{10}] / k_3 + k_4 [NO] + k_1 k_4 [C_4H_{10}][NO] / k_3 (k_3 + k_4 [NO]) \left( 1 - e^{-k_3 k_5 t / k_3 + k_4 [NO]} \right)
\]

From (5) at \(t = 0\) \[R\] = \[
\frac{k_1 [C_4H_{10}]}{k_3 + k_4 [NO]}
\]
Thus the concentration of $R$ is dependent upon the concentration of NO.

At larger values of $t$

$$R = k_1 \frac{[C_4H_{10}]}{k_3}$$

(7)

Immediately two questions arise.

From equation (6) the concentration of $R$ is always decreasing by increased NO which means that the more NO we add the more abrupt is the reduction in $R$. No limiting rate can be considered in that case and even if we suppose that the total concentration of $R$ is suppressed by considerable amount the mechanism does not explain why more radicals are not generated.

Also, assumption of a long reaction time as an explanation of the limiting reaction rate is uncertain. On the basis of these ideas Hinshelwood introduced the concept of the apparent chain length. This chain length was assumed to be given by the ratio

$$\text{rate in the absence of inhibitor} / \text{rate in the presence of maximum amount of inhibitor}$$

The formula is based on the hypothesis that all chains are suppressed by NO and the residual reaction is a molecular one. However chain lengths were found by other methods to be much longer than those predicted by the above formula. For inhibited reaction chain length was also found to be a function of pressure (38). By calling the rate of uninhibited reaction $\tau_0$, the rate of the fully inhibited $\tau_{\infty}$ and $\tau$ the rate for any NO concentration the ratio

$$\tau - \tau_0 / \tau_{\infty}$$

plotted against $P(\text{NO})$ gives
the limiting concentration in NO as does also the simple plot of \( \frac{P_{\text{init.}}}{P_{\text{NO}}} \). Hinshelwood and his school, attach much importance in the variation of this ratio, with NO by connecting the variation of chain length with NO concentration, but little information comes from these relationships so far as the real nature of inhibition is concerned. They found (39) that

\[
\tau - \tau_\infty = \left( \gamma [\text{NO}]^2 + 1 \right)^{\frac{1}{2}} \gamma [\text{NO}]
\]

where \( \gamma \) is a constant different for different hydrocarbons. Hinshelwood, trying to explain the fact that the products appear to be identical in the normal and fully inhibited decomposition suggested that two separate free radical mechanisms might occur simultaneously, one suppressed by NO and the other remaining (40). This hypothesis is arbitrary. The property of chains is to be suppressed and there is no obvious reason as to why one chain reaction should be suppressed and the other not. The second hypothesis which comes from the Rice-Herzfeld mechanism has been used by several workers and has common points with the previous one. As a general mechanism, the following is proposed:

\[
\begin{align*}
M_1 & \rightarrow R_1 + R_2 \\
R_1 + M_1 & \rightarrow R_1^H + R_2 \\
R_2 & \rightarrow R_1 + M_2 \\
R_1 + R_2 & \rightarrow M_3 \\
R_1 + \text{NO} & \rightarrow \text{Products} \\
R_2 + \text{NO} & \rightarrow \text{Products}
\end{align*}
\]
To solve such a system we need some simplifications. Two possibilities exist. Chains can be broken either by $R_1$ or by $R_2$. If they are broken by $R_2$

$$M_1 \rightarrow R_1 + R_2$$  \hspace{1cm} (1)

$$R + M_1 \rightarrow R_1 H + R_2$$ \hspace{1cm} (2)

$$R_2 \rightarrow R_1 + M_2$$  \hspace{1cm} (3)

$$R_1 + R_2 \rightarrow R_1 R_2$$ \hspace{1cm} (4)

$$R_2 + NO \rightarrow \text{Products}$$ \hspace{1cm} (6)

$$M_1 \rightarrow \text{Products}$$ \hspace{1cm} (9)

This case was examined in detail by Hobbs (41) with the following results, assuming the steady state:

$$\frac{d[R_1]}{dt} = k_1 [M_1] + k_3 [R_2] - k_2 [R_1][M_1] - k_4 [R_1][R_2] = 0$$

$$\frac{d[R_2]}{dt} = k_1 [M_1] + k_2 [M_1][R_1] - k_3 [R_2] - k_4 [R_1][R_2] - k_6 [R_2][NO] = 0$$

Where

$$[R_1] = \frac{k_2 k_6 [NO] + \left( k_2 k_6 [NO]\right)^2 + 8 k_2 k_4 (k_1 k_6 NO + 2 k_1 k_3)^3}{4 k_2 k_4}$$

Reaction (1) is considered negligible in comparison with reaction (2)

$$\text{rate} = k_9 [N_1] + k_2 [R_1][M_1]$$

and by using the value for the concentrate of $R_1$ from the previous formula we get for the rate
rate = \frac{k[\text{NO}]}{\sqrt{2}} \left( \frac{k_2k_6[\text{NO}]}{k_1k_6[\text{NO}]} \right)^2 + \frac{8k_2k_4}{2k_1k_3} k_2k_6[\text{NO}]

where, \text{rate}_0 = \frac{k[\text{NO}]}{\sqrt{2}} \left( \frac{k_2k_6[\text{NO}]}{k_1k_6[\text{NO}]} \right)^2

and \text{rate}_\infty = k[\text{NO}]

Hence \text{rate} - \text{rate}_0 = \left( a[\text{NO}] + B[\text{NO}] + 1 \right)^{1/2} - a[\text{NO}]

where a, and b are the combinations of various values of k.

The second case, which suggests that chains are broken by R_1 has been investigated by HORBS AND HINSHELWOOD (42) and led to a relation analogous to the above

\text{rate} - \text{rate}_0 = (1 + \gamma^2[\text{NO}])^{1/2} - \gamma[\text{NO}]

In these two cases stationary state conditions were assumed and this is open to question. The concentration NO must remain the same, i.e. no consumption, and the nature of the radical involved requires consumption of NO.

TOMSON and NEISSNEZ (43) photographed the absorption spectrum of mixtures of NO with organic components during decomposition. Other workers (44,45) proved the existence of \text{CH}_2\text{NO} and \text{CH}_2\equiv\text{NOH}, in products of decomposition in the presence of NO. The formation of HNO is considered probable (46) and that NO reacts with some radicals must be considered as certain.

The most critical point arising from the above suggestions is the following. Is the residual reaction a molecular one or not? First of all the products are considered to
to be identical for both inhibited and non-inhibited reaction. Poltorak found identity in the products of cracking of $C_3H_8$, but from his table it is obvious that some variation exists in his results although he presents results for only the uninhibited and fully inhibited reaction. Hinshelwood ascribes this supposed identity to be a coincidence. In contrast with Hinshelwood, Rice and Rolley (47) as well as Golanskii (48) use the hypothesis that molecules capable of ending chains are at the same time able to regenerate them. The explanation makes molecular reaction improbable but it is not entirely satisfactory by itself. Why does the same inhibited rate exist for different inhibitors? A direct attempt to check the idea of the molecular reaction was made by Wall and Moore (43). They decomposed thermally a mixture of $C_2H_6$ and $C_2D_6$ in both the absence of NO and in the presence of 2.5% NO. They found identical products and among them $H_2$, $D_2$ and HD. For the uninhibited reaction this is logical but for the inhibited reaction if a molecular one takes place HD would not be expected. Unfortunately, they did not extend the investigation over a broad range of NO pressures, and Hinshelwood questioned the result, since insufficient $H(\text{NO})$ was used (50). But according to the work of Hinshelwood himself it is obvious that maximum inhibition is attained very quickly and for a small amount of NO, so even if NO was not sufficient in WALL and MOORE'S experiment the products ought to be different and especially the amount of HD highly reduced for the inhibited reaction. Poltorak and Voevodskii tried to clarify this
work (29). They studied pyrolysis of C\textsubscript{2}H\textsubscript{6} in the presence of D\textsubscript{2}. The exchange of D\textsubscript{2} could give information about the chain mechanism. A lack of exchange could validate the molecular reaction. Exchange of D was found in both uninhibited and inhibited reaction. Rice and Varnerin (51) completed the previous results by decomposing C\textsubscript{2}D\textsubscript{6} in the presence of CH\textsubscript{4}. The CH\textsubscript{3}D/CH\textsubscript{4} ratio was found to be identical in both inhibited and uninhibited reaction.

From the above information the problem of molecular reaction seems to be excluded. The problem of the identity of the products remains. Recent efforts to explain inhibition and limiting rates has been made by Voevodskii (52) and Voevodskii and Poltorak (29). They tried to correlate heterogeneous phenomena with inhibition. They postulate the existence of irreversible decomposition processes on the wall. They showed that initial rate in the presence of small amounts of O\textsubscript{2}, strongly depends on the state of the surface. They treated the vessel with HF to increase the effect of the surface, and finally decomposed C\textsubscript{3}H\textsubscript{8} in such a vessel in the presence of small amounts of O\textsubscript{2}. For low pressures they found acceleration. Similarly they found reduced effect of NO in vessels with active centers. By covering the surface with several oxides, they found similar results. The treatment of the surface may not have been the most effective. The active surface might have been increased but might have been decreased as well. And no information about the S/V
ratio is given. Voevodskii questioning the coincidence that a molecular reaction and a chain could give the same products introduced the suggestion that decomposition might be initiated and terminated on the walls. This leads to a reversal of ideas on inhibition, since the limiting $P(NO)$ might be related with the vessel and not to the hydrocarbons. The limiting pressure of $P(NO)$ has been always given as percent of the hydrocarbon. At the same time Voevodskii accepts the existence of two heterogeneous chain initiations, one reversible and one irreversible but this looks arbitrary and without much validity. A conclusion of Voevodskii's is that no effect is expected at higher pressure, which does not agree with the concept of heterogeneous termination.

Recently some new material from a theoretical point of view have been presented by Laidler and Wochichowskii (53). This material is related to the inhibited reaction of $C_2H_6$, a hydrocarbon exhaustively investigated, but it is rather hard to apply to more complicated systems. A free radical mechanism is proposed involving the participation of inhibitor molecules. The inhibitor can react in some $H -$ abstraction reactions such as

$$C_2H_6 + HNO \rightarrow C_2H_5 + HNO$$

Chain termination may also involve

$$C_2H_5 + HNO \rightarrow C_2H_6 + NO$$

These ideas applied to $C_2H_6$ thermal decomposition give the mechanism:-
The rate is expressed as:

$$\text{rate} = \frac{(k_1 k_2 k_3 k_{-4}/k_{-1} k_4)^{1/2} [C_2H_6]}{[C_2H_6]}$$

This mechanism leads to first order kinetics as found experimentally (54,55).

The activation energy of dissociation of HNO is 44 KCal/Mole, which leads to an activation energy for reaction (1) of 56 KCal/Mole.

$$E = \frac{1}{2} \left( E_1 + E_2 + E_3 + E_4 - E_{-1} - E_4 \right) = \frac{1}{2} \left( 56 + 40 + 10 + 44 - 0 - 0 \right) = 75 \text{ value}$$

which is near the experimental value of 74 kCal/Mole.

For inhibited decomposition the initial rate has been shown to have an order of $3/2$ and this is explained by the addition to the above set of reactions of the reaction

$$H + HNO \xrightarrow{k_6} H_2 + NO$$
Hence: \( \text{rate} = k_3 \left( \frac{k_1 k_{-4}}{k_4 k_b} \right)^{\frac{1}{2}} \left[ C_2H_5 \right]^{-3/2} \)

An initiation like the above can be considered as reasonable for systems like \( C_2H_5 \) or \( CH_4 \) with high activation energy, but little help seems to come from that point for more complex systems.

The appearance of catalysis by NO, in high NO concentrations, in the decomposition of \( CH_3COCH_3 \), provides some support for reaction (1). But in the case of \( CH_3COCH_3 \) the H-atoms are highly activated and abstraction reaction requires lower energy.

**Résumé.** The following results, involving controversies, are provided from all previous investigations:

1. The nature of the inhibition, heterogeneous or homogeneous.
2. The effect of the \( P_{NO} \) on the products.
3. The effect of S/V ratio on the products and rates and
4. The mechanism of both inhibited and uninhibited reaction.

An investigation of these problems was the main objective of the present study. The extensive use of analytical results should provide reliable data. The use of the same vessel for both packed and unpacked systems would
eliminate possible effects of surfaces between vessels of the same S/V ratio. The investigation was extended to all the isomeric pentanes, to determine the possible effect of the structure of the hydrocarbons on the decomposition mechanism.
CHAPTER II

EXPERIMENTAL

Materials and Methods

1) Hydrocarbons

The hydrocarbons used were liquids (n-pentane, and isopentane) and gases (neopentane and all the C\textsubscript{1}-C\textsubscript{4} hydrocarbons which were used to calibrate gas chromatography and infra-red spectra). All these hydrocarbons were from Research grades of Phillips Petroleum Company, Bartlesville, Oklahoma, U.S.A. and their purity as supplied varied from 99.5 - 99.9%. For further purification successive distillations were used, from trap-to-trap, using two temperatures, -196° C, lig. N\textsubscript{2}, so that traces of volatile compounds like H\textsubscript{2} etc. were removed, and -78° C, (solid CO\textsubscript{2} and methanol, so that less volatile compounds were kept in solid condition). The hydrocarbons were finally stored in globes on the vacuum system.

2) Nitric oxide

Nitric oxide was supplied in a cylinder by the Matheson Company, East Rutherford, N.Y., in gas phase. By successive the trap-to-trap distillation nitric oxide was purified from more volatile impurities by condensing it at -196° C and from NO\textsubscript{2} which was kept in solid state at -78° C. Special care was paid to its purification, because impurities like NO\textsubscript{2}, affect markedly the decomposition of hydrocarbons generates traces of O\textsubscript{2} at high pressures.

3) Mercury dimethyl H_g(\text{CH}_3)_2

A standard sample from the American Petroleum Institute
Pittsburgh, Penn., was used. It was not purified further.

Gas Chromatographic Equipment

Columns

Two different columns were used in the analysis of all products. The first was a silica gel 60/80 mesh column, 2 meters long, used for the analysis of $C_1$-$C_2$ hydrocarbons and inorganic gases. The other column used for $C_2$-$C_6$ compounds was a 30% HMPA (Hexo-methyl phosphoramide) on 60/80 mesh column pack, obtained from Fisher Scientific Company. The container was $\frac{3}{4}$" copper tubing 3 meters long.

Detector

For the gas chromatography a thermal conductivity detector was used, designed by Ryce et al. The cell current was always kept at 90 mA. Cell temperature and recorder sensitivity were constant for the whole investigation, at $44^\circ$ C and 1 mv respectively. The sensitivity corresponding to 1 mv was the maximum possible. The sensitivity was checked day by day, using a sample of air. By keeping the cell temperature, column temperature and cell current strictly constant, the sensitivity was kept constant within the limits of experimental error. This was important for the reproducibility of the analytical results. The temperature of the columns were kept constant, $0^\circ$ C and $34^\circ$ C for HMPA and silica gel respectively.

Infra-red analysis

For the identification of the products, infra-red spectra were taken for all products, on a Perkin Elmer Model 21 instrument. The spectra of all compounds were taken in the region of 650-4000 cm$^{-1}$. 
The gaseous sample was kept in a glass cell with NaCl windows polished time by time to remove any deposited compounds. The cell was evacuated to about $10^{-4}$ mm and it was possible to maintain the vacuum for 5-6 hours. Pycene cement was used to seal the NaCl windows into the cell. By comparing the infra-red spectra of the products with the spectra of individual compounds and especially for absorption bands in the finger print region, 1300-650 cm$^{-1}$, the products were identified.

**The Pyrolysis Apparatus**

**The vacuum system**

The apparatus used was a conventional static vacuum system shown schematically in Fig. 3. The hydrocarbons being studied were stored in globes, G, and could be admitted to the quartz reaction vessel, V, through a stopcock, $S_1$. The pressure in the reaction vessel could be read on a monometer, M. Samples for gas chromatographic analysis were withdrawn into a sample pipette, P, through stopcock $S_2$. A Toepler pump, B, was used to transfer all hydrocarbons into the stirring vessel, K, driven by a magnetic stirring motor, for premixing where necessary. The globes were filled by freezing the hydrocarbons from cylinder into a trap $T_1$, from which air was removed. Trap-to-trap distillation from $T_1$ to $T_2$ could be used for further purification where necessary. Liquid compounds were transferred to the globes, by freezing into a cold-finger, I.

**Reaction vessel and furnace**

The reaction vessel consisted of a cylindrical quartz vessel with a volume around 300 cm$^3$. It was placed in a brass cylinder wound with heating wire and covered with cement. Several inches of
FIG. 3 SCHEMATIC OUTLINE OF THERMAL DECOMPOSITION APPARATUS—Front Sit
vermiculite provided thermal insulation. The furnace was modified so that, the reaction vessel was removable, by removal of its upper section. A quartz capillary tube connected the reaction vessel with the vacuum system. A variable voltage was supplied to the heating element of the furnace by means of a controlled power supply, shown in Fig. 4. Two chromel-alumel thermocouples were placed in drill-holes one in the cover of the furnace at half the length and on the lid. A Honeywell Electronic Millivolt controller was used to control the temperature within one degree at 500°C.

The reaction products were withdrawn after pyrolysis and were analysed on the HMPA and silica gel columns and by I.R. for their identifications. In Fig. 5 and 6 typical gas chromatograms are shown. The spectra of individual hydrocarbons, as used for the identification of the products are given in Appendix IV.

Description of typical experiment

After pumping the reaction vessel, mixing system and pre-expansion volume to a "black vacuum", the substance being used to be pyrolysed was admitted to the mixing system. The pressure was measured before the entrance of the compound into the mixing system, so constant pressure could be used. In the case of inhibited decomposition, the preceding procedure, was performed first for the inhibitor which was used in relatively small amounts. The apparatus was pumped down again, and the hydrocarbon was admitted to the vacuum system. By the same procedure, the hydrocarbon, was pushed into the mixing system, where an homogeneous mixture was formed. The partial pressures of each species has been pre-
FIG. 4  FURNACE HEATER CIRCUIT
Fig. 5: Chromatogram with HMPA 30% 60/80 column of product mixture for inhibited decomposition of isopentane.
Fig. 6: Chromatogram with silica gel 60/80 column of product mixture for inhibited decomposition of isopentane.
measured, before it entered the mixing system. The pressure of hydrocarbon was kept constant while the inhibitor varied. After the evacuation of the system, the mixture was admitted into the reaction vessel. A manometer directly connected with the reaction vessel, was used to measure the initial pressure, the final pressure, and the variation of pressure with the time. After the desired extent of decomposition, the products were expanded from the reaction vessel to an evacuated flask which was connected through a two-way trap with both the vacuum system and the reaction vessel. The sample in the evacuated flask was used for the analysis. The gas chromatography apparatus was evacuated to a less degree than that of the reaction vessel. By using a Toepler in the case of small pressures of samples the whole sample could be used for analysis. Silica column, used for analysis of C<sub>1</sub>-C<sub>2</sub> compounds and after that it was heated, to 150° so compounds like C<sub>3</sub>-C<sub>5</sub> hydrocarbons, and NO<sub>2</sub>, which were kept in the column, were removed, and the column was keeping its efficiency. Helium was used as carrier gas, and the temperature of the cell and column was always above the maximum possible room temperature, to avoid any effect. The helium was purified by a system of two charcoal traps, and two traps of CaCl<sub>2</sub>. A reducing valve could regulate the available pressure. The flow rate was kept constant for each column, so that effects due to different absorption were avoided.
CHAPTER III

RESULTS

I) Uninhibited pyrolyses

The pyrolyses of the isomeric compounds isopentane, n-pentane and neo-pentane were done at temperatures near $500^\circ$ C. The following investigations were made for the uninhibited or normal decomposition.

i) The effect of variation in initial pressure of hydrocarbon on the rates and on product distribution for constant extent of reaction.

ii) The effect of variation in extent of reaction on product distribution for constant initial pressure of hydrocarbon.

iii) The effect of variation in surface to volume ratio in the vessel on rate of reaction and on product distribution at various temperatures.

A) Rates of Reaction

The pressure-time curves (Fig. 7) do not have a sigmoid shape but show that reaction rates fall after a certain reaction time. This can be attributed to self-inhibition by the products. Pyrolysis at different pressures showed the same feature but in varying degrees. Isopentane, neopentane, and n-pentane have curves of similar shape. A plot for isopentane of $\frac{dp}{dt}$ for both overall rate $R(\text{over})$, and initial rate, $(H)$, against time for various pressures (Fig. 8) shows a sharp reduction with time for the higher pressures, but the reduction is very slight for the lower pressures. Rates were calculated from pressure measurements and not from analytical results. It has been established by other workers (Hinshelwood etc.)
Fig. 7: Variation of pressure with time for isomeric pentanes.
Fig. 8: Variation of rate \((dp/dt)\) with time for various values of \(P_4\) for isopentane.
that pressure measurements give an accurate measure of reaction rates in paraffin pyrolysis. This method was chosen because of its convenience and because it gives a more uniform rate curve. Both overall and initial rates were used in calculating rate constants, energy of activation and frequency factors. The variation of rate with pressure was measured for pressures ranging from 10 to 200 mm at several temperatures.

**A.1: Isopentane**

In the case of isopentane the plot of overall rate against initial pressure, $P_i$ was linear for pressures ranging from 100 to 40 mm (Fig. 9). Some curvature was observed at higher pressures. At lower pressures the relationship

$$\text{Rate (overall)} = aP_i$$

is obeyed, while for high pressures the relationship becomes

$$\text{Rate (overall)} = aP_i + bP_i^2.$$  

Pyrolysis at four different temperatures from 502 to 530° gave curves of similar shape. Extrapolation of the linear portion shows that the curves diverge from linearity very rapidly as pressure increases. Partington et al.\(^{(57)}\) attribute this increase to a simple kinetic factor, indicated by the second expression for Rate(overall) given above. This relationship indicates that second order mechanisms are more important at higher pressures. The plots of $R_i$ against $P_i$ are approximately linear (Fig. 10).  

**Variation of rate with collision frequencies**

A correlation of reaction rates with collision frequencies $Z_i$ at each pressure used has been attempted in Fig. 11. $R_i$ is
Fig. 9: Variation of $R_{overall}$ with initial pressure for isopentane.
Fig. 10: Variation of initial rate with pressure for isopentane.
plotted against $Z_1/Z_{14}$ mm, 14 mm being the lowest pressure at which decomposition was done. The curve shows an irregular portion. The ratio of collision number $Z_1/Z_{14}$ was found to be given directly by the pressures ratio $P_1^2/P_{14}^2$. The rate at lower pressures appears to be enhanced relative to $Z_1/Z_{14}$. Then an almost horizontal region, is followed by a regular increase of rate at higher pressures. The lower portion indicates that at low pressures the rates predicted by collisional processes are much lower than the experimental rates. Heterogeneous initiation may be responsible for the enhanced rate, since the required energy of activation is less for the heterogeneous than for the homogeneous reaction. At high pressures both heterogeneous and homogeneous processes will occur. At low pressures, inelastic collisions take place on the walls, leading to decomposition of molecule, while the collision which takes place in the gas phase, are largely elastic at low pressures. The available energy in these collisions is transferred more to the translational mode than to the vibrational mode, so that the energy for decomposition of molecule is insufficient.

**The effect of packing**

To evaluate the effect on rate of packing the vessel was packed with quartz rods, so that the surface to volume ratio of 1.2 for the empty vessel became 2.5. The temperature used, was low, 490° C, so that, the regular reaction would be slow and any increase due to the packing would be marked. The overall rate was increased for both low and high pressures but increase was greater for high pressures. (Fig. 12). The increase in rate can be explained only on the assumption of heterogeneous initiation and termination.
Fig. 12: $R_{overall}$ VS $P_1$ for packed and unpacked vessel for isopentane.
For higher pressures longer chains exist due to higher concentrations, and consequently termination is suppressed, but not for lower pressures. However heterogeneous initiation affects reaction at both low and high pressures. The net result is that packing promotes decomposition at higher pressures to a greater extent than at lower pressures.

**A 2 : n-pentane**

A plot of initial rate against initial pressure is given in Fig. 13. The variation of initial rates with pressure is similar to that for isopentane.

**Effect of packing**

By increasing the packing by a factor of 3, with pyrex tubes, no regular effect was observed (Fig. 14). Lack of sufficient data is an obvious disadvantage in this connection. The temperature used was rather high, $520^\circ C$, it might be that in such a temperature wall effects are less important. It is also possible that the pyrex packing provided a much lower surface concentration of active centres than that provided by the quartz packing used in the isopentane experiments.

**A 3 : neopentane**

A plot of initial rates against pressures for neopentane is given in Fig. 15. It is very similar to the corresponding figures for n-pentane and isopentane.

**Effect of packing**

By increasing the packing by a factor of 3, with pyrex tubes, no regular effect was observed. Some irregularities appeared in higher pressures where packing appeared to slow down the rate.
Fig. 13: Variation of $R_1$ with initial pressure for $n$-pentane
Fig. 14: Effect of packing on initial rate for n-pentane.
Fig. 15: $R_4$ VS $P_1$ for neo-pentane
In the most cases the, Δp-time variation was the same for both packed and unpacked vessel. Lack of sufficient data is the main point in this section too.

**B. Order of reaction**

Some irregularities were found in the reaction orders which were more marked as one goes from n-pentane to neo-pentane. These irregularities seem to be a function of the branching in the hydrocarbon molecule. Orders were obtained by plotting log (dP/dt) against log (P_i) that is by using the common rate equation dP/dt = kP^n. Evaluations of log dP/dt for all compounds are given in appendix III.

**B.1: n-pentane**

The order of reaction calculated for three different temperatures was found to be unity (Fig. 16). Thus the decomposition of n-pentane seems to follow a first order mechanism for the pressure range 10 to 150 mm.

**Effect of packing**

By increasing the surface to volume ratio by a factor of approximately 3, with pyrex tubes, the order for the packed reaction vessel was increased to 3/2 (Fig. 17). These results were obtained by using only one series with a packed vessel and thus cannot be considered as completely reliable.

**B.2: Isopentane**

Some irregularities in order were observed for isopentane (Fig. 18). For three different temperatures a value of n = 1.12 was found, which agrees with the concept of first order decomposition but the points are rather scattered. The curve seems rather to consist of two parts, one for low pressures with n = 1 and another for higher pressures with n > 1 (∼ 3/2).
Fig. 16: Order of reaction for unpacked vessel for n-pentane.
Fig. 17: Order in packed and unpacked vessels for n-pentane.

\[ \log(R_1) \]

\[ \log(P_1) \]

- S/V = 3
- S/V = 1

\[ T = 519^\circ \]

\[ \Delta P = 20\% \]
Fig. 18: Order of reaction for isopentane.
B 3: Neopentane

In the third and more branched isomeric pentane the above irregularity is more marked. (Fig. 19). The overall order is approximately unity but a division at low pressures into n-1 and at higher pressures into n = 3/2 is apparent. Two different temperatures were used. Some second order effects might be caused by collisional factors characteristic of higher pressures. (see chapt.IV).

Effect of packing

One series only of runs was used as was in the case of n-pentane. There was no effect of packing on the overall reaction order. The order was again unity but the curve has the same shape as for the unpacked vessel, with a slightly higher slope (Fig. 19).

C: Energy of activation and frequency factors

Energies of activation and frequency factors were calculated from the Arrhenius equation. The formula

\[ E = 2.303 \left( \frac{T_1 T_2}{T_2 - T_1} \right) \log \left( \frac{K_2}{K_1} \right) \text{K cal/mol} \]

was used. Similarly A was calculated from the expression \( K = A e^{-E_A/RT} \). Details of these calculations are given in appendix II. Energies of activation as well as frequency factors showed a variation with pressure reaching a limiting lower value at high pressures. The \( E_A \) falls as the pressure increases. Such a variation with pressure was found by other worker (58) for 2 and 3-methyl pentanes. One common point in all isomeric pentanes is that the frequency factors for the lower pressure range agrees with the expected value for unimolecular reaction, \( A = 10^{13} \text{ sec}^{-1} \). Neopentane shows irregularities as far as this value is concerned. In the above case
Fig. 19: Order of reaction for neo-pentane.
we expect that, unimolecular decomposition should be predominant for low pressures and should also participate at higher pressures. Provided that collisions are rare at lower pressures, molecules retain their collisional energy, so they can easily reach the higher values required for a unimolecular reaction. Wall effects in such cases are very important because the required energy is reduced by an amount approximately of that equal to the adsorption energy. If D is the dissociation (C-C) energy, and Q is the adsorption heat, which is a function of the nature of the surface then the required energy for decomposition is 
\[ E_{(\text{heterog})} = D - Q. \]

Several workers have used these concepts of unimolecular and bimolecular decomposition in both phases, correlating the variation of \( E_A \) with the pressure, and trying to find support, from this variation of \( E_A \). Cundall and Palmer (59) studying the isomerization of cis-butene-2 found analogous variation of \( E_A \). At low pressures a complete unimolecular reaction appears to take place. For higher pressures they found side reactions and wall effects. Rabinovitch and Mitchell (60) found the same variation for the above isomerization.

**Cl : n-pentane**

Overall rates were used to calculate rate constants by drawing tangents to the Rate (overall) VS \( P_1 \) curves at two temperatures only. A greater variation in temperature was not used because exact values for activation energies were not sought (given by other workers). The variation with the pressure was the major interest. The results are tabulated in Table I.
Table I

Variation of $E_A$ and $A$ with $P_1$ for n-pentane

<table>
<thead>
<tr>
<th>Initial pressure mm</th>
<th>activation energy K cal/mole</th>
<th>frequency factor sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>66.5</td>
<td>$3.08 \times 10^{13}$</td>
</tr>
<tr>
<td>20</td>
<td>66.5</td>
<td>$3.08 \times 10^{13}$</td>
</tr>
<tr>
<td>30</td>
<td>66.5</td>
<td>$3.08 \times 10^{13}$</td>
</tr>
<tr>
<td>50</td>
<td>66.5</td>
<td>$1.67 \times 10^{12}$</td>
</tr>
<tr>
<td>100</td>
<td>56.5</td>
<td>$1.1 \times 10^{11}$</td>
</tr>
<tr>
<td>120</td>
<td>55.5</td>
<td>$8.6 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Average values are not to be used because they are considered as meaningless. The $E_A$ determined by Hinshelwood et al. (58) ranged from $65.8 \text{ K cal}$ at 50 mm to $63.7 \text{ K cal}$ at 100 mm. Frey and Hepp (61) give the following expression for the rate constant.

$$K = 2.5 \times 10^{13} e^{-61.200/RT} \text{ sec}^{-1}$$

C 9: Isopentane

In the case of isopentane three different temperatures were used. A similar variation of $E_A$ and $A$ with initial pressure was found as for n-pentane. The results are given in Table II.

Table II

Variation of $E_A$ and $A$ with $P_1$ for isopentane

<table>
<thead>
<tr>
<th>Initial pressure mm</th>
<th>activation energy K cal/mole</th>
<th>frequency factor sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>64.1</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
<tr>
<td>20</td>
<td>64.1</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
<tr>
<td>30</td>
<td>64.1</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
<tr>
<td>40</td>
<td>64.1</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
<tr>
<td>50</td>
<td>64.5</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
</tbody>
</table>

....cont.
(Table II cont.)

<table>
<thead>
<tr>
<th>Initial pressure mm</th>
<th>activation energy K cal/mole</th>
<th>frequency factor $\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>59.1</td>
<td>$1.9 \times 10^{12}$</td>
</tr>
<tr>
<td>100</td>
<td>55.6</td>
<td>$2.23 \times 10^{11}$</td>
</tr>
<tr>
<td>150</td>
<td>56.8</td>
<td>$3.82 \times 10^{11}$</td>
</tr>
<tr>
<td>200</td>
<td>56.3</td>
<td>$3.17 \times 10^{11}$</td>
</tr>
</tbody>
</table>

The $E_A$'s determined by Hinshelwood et al (62) varied from 67.8 K cal at 8.45 mm to 70 (average) K cal at 50-400 mm. The rate expression given by Frey and Hepp (61) for isopentane is

$$K = 7.9 \times 10^{12} e^{-58600/RT} \text{ sec}^{-1}.$$  

**C 3: neo-pentane**

Neo-pentane was insufficiently studied. Energies of activation are not very reliable. Values of $A$ show very low values. For low pressure, for instance $A \approx 10^{11}$ and is still lower for higher pressure. The lack of sufficient data unable us to make any comment for this peculiarity. In any case the accuracy of the values of $A$, is a function of the accuracy of the values $E_A$. A variation of $E_A$ with the pressure is again profound. Results are given in Table III.

**Table III**

<table>
<thead>
<tr>
<th>Initial pressure mm</th>
<th>energy of activation K cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>57</td>
</tr>
<tr>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>30</td>
<td>57</td>
</tr>
<tr>
<td>40</td>
<td>57</td>
</tr>
<tr>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>100</td>
<td>47.5</td>
</tr>
</tbody>
</table>
D. Analytical results

The products of decomposition were analysed by gas chromatography, by using a silica gel 60/80 column for C₁-C₂, hydrocarbons, Nitric oxide, etc. and HMPA column for C₃-C₅ hydrocarbons. Identification was completed where necessary by infra-red spectroscopic analysis.

**D1: Isopentane**

The main products in isopentane decomposition are CH₄, i-C₄H₈ and C₃H₆.

C₂H₆ and C₂H₄ are formed in lower amounts.

C₃H₈ was detected only in traces and it was measurable only for high pressures and high temperatures. By increasing both the pressure and the temperature some traces of cis-butene-2 were found by I.R. analysis. The trans isomer was not detected. The high temperature of the reaction provides a highly energetic medium which favors the formation of the cis-isomer. Hydrogen was detected in trace amounts only and at very high temperatures and pressures. The I.R. Spectra confirmed the identification of CH₄, C₂H₄, C₃H₆, i-C₄H₈, and cis-butene-2 but they didn't give any unique characteristic peak for C₂H₆ and C₃H₈. A complete mass balance was obtained as is shown by the analytical results given in Table IV.

**TABLE IV**

<table>
<thead>
<tr>
<th>Products</th>
<th>P₁=50 mm.T=510°C. P₁=73 mm.T=510°C. P₁=100 mm.T=510°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P/P=0.415</td>
</tr>
<tr>
<td>i-C₅H₁₂</td>
<td>47.1</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>18.1</td>
</tr>
<tr>
<td>i-C₄H₈</td>
<td>10.3</td>
</tr>
<tr>
<td>CH₄</td>
<td>19.1</td>
</tr>
</tbody>
</table>
The main products again appear to be CH₄, C₂H₆, 1-C₄H₈, C₂H₆ and C₂H₄ with small amounts of H₂. Some traces of cis-butene-2 were found for higher pressures and temperatures by only I.R. spectroscopy. C₂H₆ and C₂H₄ are increased in comparison with the corresponding amount in isopentane. The main difference with isopentane is the production of 1-butene and not iso-butene. Mass balance for the analysis of the products is given in appendix H.

D 3: Neo-pentane

Two main products appeared in neo-pentane pyrolysis: CH₄ and i-C₄H₈; C₃H₆ in very small amounts. C₄H₁₀ was not checked, because neo-pentane had nearly the same elution time, so if there was any butane it was masked by the neo-pentane peak. Hydrogen was not analysed. Some very slight traces of C₂ compounds appeared sometimes. The characteristic predominance of CH₄ and i-C₄H₈ over the other products suggest a different decomposition mechanism from those of the other two pentanes.

E: The variation of products

1) Variation of the products with time

The variation of the products with time for a given P₁ was measured at intervals for a given time period up to 1 hour.

Results were obtained in detail for n-pentane only; these results are presented in Fig. 20 for n-pentane.
PIR. 20: Product yield in mole % V5 time for n-pentane.

Decomposition products in mole %

Time (min)

1. C₇H₈
2. C₆H₆
3. C₅H₆
4. C₄H₈
5. C₃H₆
6. C₂H₆
The yields of \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \) follow a nearly linear relation with time, while those for \( \text{C}_3\text{H}_6 \) and \( 1-\text{C}_4\text{H}_8 \) have more curvature. The production of \( \text{C}_2\text{H}_6 \) increases markedly with time to a nearly limiting value. Corresponding results for isopentane are given in tables VI.

**Table VI**

Variation of the products of decomposition of isopentane with time

<table>
<thead>
<tr>
<th>time min</th>
<th>( \text{CH}_4 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_2\text{H}_6 )</th>
<th>( \text{C}_3\text{H}_6 )</th>
<th>( 1-\text{C}_4\text{H}_8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>7.5</td>
<td>1.39</td>
<td>1.04</td>
<td>11.4</td>
<td>7.6</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.4</td>
<td>13.4</td>
</tr>
<tr>
<td>120</td>
<td>13.3</td>
<td>2.98</td>
<td>2.46</td>
<td>25</td>
<td>15.6</td>
</tr>
</tbody>
</table>

2) The variation of individual products with \( P_1 \)

The complete variation of products was investigated with pressure in both isopentane and n-pentane. In n-pentane \( \text{C}_3\text{H}_6 \) increases steadily, \( 1-\text{C}_4\text{H}_8 \) is nearly constant, while \( \text{CH}_4, \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) show increase in the beginning and then reach a limiting value Fig. 21. For the isopentane series the situation is different. \( \text{C}_3\text{H}_6 \) and \( 1-\text{C}_4\text{H}_8 \) show a slight but constant increase. \( \text{C}_2\text{H}_6 \) increases steadily and \( \text{C}_2\text{H}_4 \) falls in the beginning and then reaches a limiting value. \( \text{CH}_4 \) increases but not so rapidly as \( \text{C}_2\text{H}_4 \) Fig. 22.a,b

3) Variation of product ratio with time

The ratios: \( \frac{\text{C}_2\text{H}_4}{\text{C}_2\text{H}_6}, \frac{\sum \text{C}_2}{\text{C}_3\text{H}_6}, \frac{\sum \text{C}_2}{1-\text{C}_4\text{H}_8}, \frac{\text{C}_3\text{H}_6}{1-\text{C}_4\text{H}_8}, \frac{\text{CH}_4}{\text{C}_2\text{H}_4}, \frac{\text{CH}_4}{\text{C}_2\text{H}_6} \) were obtained as a function of time for different experimental conditions. The results are given in table VII for different initial pressures of n-pentane at \( 509^\circ \text{C} \).
Fig. 21: Product yield in mole % VS initial pressure for n-pentane.
Fig. 22a: Variation of the decomposition products with initial pressure for isopentane.
Fig. 22b: Variation of the product with initial pressure for isopentane.
### Table VII

Variation of product ratios with time

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$C_2H_4/C_2H_6$</th>
<th>$\Sigma C_2/\Sigma C_3H_6$</th>
<th>$\Sigma C_2/1-C_4H_8$</th>
<th>$C_3H_6/1-C_4H_8$</th>
<th>$CH_4/C_2H_4$</th>
<th>$CH_4/C_2H_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.41</td>
<td>1.41</td>
<td>5</td>
<td>3.55</td>
<td>1.93</td>
<td>0.79</td>
</tr>
<tr>
<td>13</td>
<td>0.68</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.34</td>
</tr>
<tr>
<td>17</td>
<td>0.59</td>
<td>0.8</td>
<td>4.5</td>
<td>5.3</td>
<td>0.72</td>
<td>0.42</td>
</tr>
<tr>
<td>27</td>
<td>0.49</td>
<td>0.875</td>
<td>-</td>
<td>-</td>
<td>0.765</td>
<td>0.37</td>
</tr>
<tr>
<td>36</td>
<td>0.66</td>
<td>0.870</td>
<td>3.46</td>
<td>4</td>
<td>0.874</td>
<td>0.58</td>
</tr>
<tr>
<td>44</td>
<td>0.685</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
<td>0.666</td>
</tr>
<tr>
<td>55</td>
<td>0.78</td>
<td>0.932</td>
<td>4.25</td>
<td>4.6</td>
<td>0.85</td>
<td>0.573</td>
</tr>
</tbody>
</table>

**Pn-pentane = 76 ± 1mm**  
$T = 509^\circ C$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$C_2H_4/C_2H_6$</th>
<th>$\Sigma C_2/\Sigma C_3H_6$</th>
<th>$\Sigma C_2/1-C_4H_8$</th>
<th>$C_3H_6/1-C_4H_8$</th>
<th>$CH_4/C_2H_4$</th>
<th>$CH_4/C_2H_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-</td>
<td>1.02</td>
<td>3.3</td>
<td>3.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0.66</td>
<td>0.97</td>
<td>3.1</td>
<td>3.21</td>
<td>1.02</td>
<td>0.67</td>
</tr>
<tr>
<td>15</td>
<td>0.91</td>
<td>1.1</td>
<td>3.4</td>
<td>3.08</td>
<td>0.347</td>
<td>0.318</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>1.03</td>
<td>3.2</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>32</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.815</td>
<td>0.542</td>
</tr>
<tr>
<td>38</td>
<td>0.73</td>
<td>0.9</td>
<td>-</td>
<td>4.08</td>
<td>0.65</td>
<td>0.46</td>
</tr>
<tr>
<td>49</td>
<td>-</td>
<td>1.07</td>
<td>3.64</td>
<td>3.76</td>
<td>1.19</td>
<td>0.592</td>
</tr>
<tr>
<td>60</td>
<td>0.85</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>0.94</td>
<td>0.795</td>
</tr>
</tbody>
</table>

**Pn-pentane = 100 ± 1mm**  
$T = 509^\circ C$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$C_2H_4/C_2H_6$</th>
<th>$\Sigma C_2/\Sigma C_3H_6$</th>
<th>$\Sigma C_2/1-C_4H_8$</th>
<th>$C_3H_6/1-C_4H_8$</th>
<th>$CH_4/C_2H_4$</th>
<th>$CH_4/C_2H_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.61</td>
<td>1.66</td>
<td>-</td>
<td>-</td>
<td>0.98</td>
<td>0.6</td>
</tr>
<tr>
<td>19</td>
<td>0.71</td>
<td>1.21</td>
<td>6.08</td>
<td>5</td>
<td>0.72</td>
<td>0.515</td>
</tr>
<tr>
<td>25</td>
<td>0.76</td>
<td>1.13</td>
<td>4.25</td>
<td>3.78</td>
<td>0.744</td>
<td>0.556</td>
</tr>
<tr>
<td>31</td>
<td>0.71</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>0.83</td>
<td>0.582</td>
</tr>
<tr>
<td>45</td>
<td>0.75</td>
<td>1.23</td>
<td>4.37</td>
<td>4.30</td>
<td>0.9</td>
<td>0.67</td>
</tr>
<tr>
<td>55</td>
<td>-</td>
<td>1.07</td>
<td>4.65</td>
<td>4.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>65</td>
<td>0.89</td>
<td>1.13</td>
<td>5.25</td>
<td>4.62</td>
<td>0.815</td>
<td>0.715</td>
</tr>
</tbody>
</table>

**Pn-pentane = 57 ± 1mm**  
$T = 509^\circ C$
From the above table we see that the ratio $C_2H_4/C_2H_6$ increases regularly with time. This regular variation is more clearly shown in Fig. 23. The conclusion is that the more extensive the reaction the greater the production of $C_2H_4$ relative to $C_2H_6$ and $CH_4$. The ratios $C_2/C_3H_6$ and $C_2/1-C_4H_8$ seem to be approximately constant. This means that the mechanism leading to $C_3$ and $C_4$ products on one hand and to $C_2$ products on the other, is not affected by the extent of the reaction. Since, as will be shown, the latter two ratios are unaffected by variation of pressure, it means that the mechanism leading to the formation of these products vary with temperature only.

4) The variation of product ratios with $P_1$

1) $CH_4/C_2H_6$ ratio: The variation of $CH_4/C_2H_6$ with $P_1$ is similar in both isopentane and n-pentane decomposition but it is much more marked in isopentane where in the pressure range 30-200 mm the ratio falls by a factor of nearly 2. (Fig. 24.) In n-pentane for the same range of pressure the fall is approximately 1.5. (Fig. 25.) This difference is explained by the fact that in n-pentane $C_2H_6$ appears as a main product. So an increase of pressure has less influence on it than in isopentane (see chapter IV.) Neo-pentane did not give any information about this ratio since $C_2H_6$ could not be detected in the products of the pyrolysis.

II) The variation of $C_2H_4/C_2H_6$ with pressure

The variation of this ratio with pressure for both cases was similar to that above Fig. 26 and Fig. 27. The variation is again more marked for isopentane changing by a factor greater than 2
Fig. 23: Variation of $\frac{\text{C}_2\text{H}_6}{\text{C}_2\text{H}_4}$ ratio with time for n-pentane.
Fig. 24: Variation of CH₄/C₂H₆ with P₁ at various temperatures for isopentane.
Fig. 25: $\frac{CH_4}{C_2H_6}$ VS P, init. for n-pent.
Fig. 26: Variation of $\frac{C_2H_4}{C_2H_6}$ with $P_1$ at various temperatures for isopentane.
Fig. 27: Variation of $\frac{C_2H_4}{C_2H_6}$ ratio with $P_1$ for n- and iso-pentane.
while for n-pentane the ratio falls by a little less than a factor of 2. The variation was similar at each of several temperatures. In the case of n-pentane only two different temperatures were used, since 4 different isothermals in the case of isopentane removed any doubt about the validity of this change; neopentane is not included, due to the lack of analytical results.

**The effect of packing**

The variation of $C_2H_4/C_2H_6$ with pressure was compared for packed and unpacked vessel, in both n-pentane and isopentane. For n-pentane the unpacked vessel was packed with pyrex tubes to change the $s/v$ ratio by a factor of nearly 3, and in the case of isopentane, the vessel was packed with quartz rods to change the $s/v$ ratio by a factor of approximately 2.5. In both cases no marked effect was in the ratios found. Points fall near a common curve which could be considered as valid for both packed and unpacked vessel Fig. 28 and 29. At first sight it seems that either packing does not affect $C_2H_4$ and $C_2H_6$ or it affects both of them to the same extent. The problem will be examined in detail in the inhibited reaction. The variation of $C_2H_4/C_2H_6$ with temperature for constant pressure and with pressure for constant temperature is given in the following table.
Fig. 28: effect of packing on the $\frac{C_2H_4}{C_2H_6}$ ratio for various pressures for $n$-pentane.
Fig. 29: Effect of packing on $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio at various pressures for isopentane.
Fig. 29a: Influence of packing on the variation of $\frac{C_2H_4}{C_2H_6}$ with $P_1$ for n-pentane.
Table VIII
Variation of \( \frac{C_2H_4}{C_2H_6} \) with pressure and temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Pressure mm</th>
<th>490°</th>
<th>502</th>
<th>509</th>
<th>519</th>
<th>529</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-</td>
<td>1.55</td>
<td>1.5</td>
<td>2.31</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>1.47</td>
<td>1.8</td>
<td>1.88</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2 ?</td>
<td>1.63</td>
<td>1.28</td>
<td>1.76</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1.2</td>
<td>1.42</td>
<td>1.26</td>
<td>1</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.32</td>
<td>1.28</td>
<td>1.64</td>
<td>1.09</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.69</td>
<td>1.05</td>
<td>1</td>
<td>0.89</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>0.92</td>
<td>1.32</td>
<td>0.82</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>

For 30 and 40 mm pressure there is a regular increase of \( \frac{C_2H_4}{C_2H_6} \) with temperatures, while for other pressures the values remain around a constant value, different for every pressure. Higher pressures seem to have more effect than higher temperatures, so no regular variation is observed with temperature for higher pressures.

111) The variation of \( \frac{i-C_4H_8}{C_2H_6} \) ratio with pressure

This ratio was available only for isopentane. No marked effect of pressure on it is observed and the curves show a very slight increase Fig. 30. \( C_3H_6 \) and \( i-C_4H_8 \) seem to be produced mainly by the primary process which is unaffected by pressure in contrast with \( C_2H_6 \) and \( C_2H_4 \) which might be produced in secondary processes more than in primary. In the case of n-pentane, the variation of the ratios \( \frac{C_3H_8}{i-C_4H_8}, \frac{\Sigma C_2/C_3H_6}{C_2H_6} \) and \( \frac{\Sigma C_2}{i-C_4H_8} \) with pressure indicates that \( C_3H_6 \) and \( i-C_4H_8 \) as well as \( C_2 \) compounds come from processes which are unaffected by pressure.
Fig. 30: Variation of $1$-$C_4H_8/C_3H_6$ ratio with initial pressure for various values of $T$ for isopentane.
The values of these ratios at various pressures appear in the following table.

Table IX

<table>
<thead>
<tr>
<th>Pn-pentane (mm)</th>
<th>C₃H₆/1-C₄H₈</th>
<th>∑ C₂/C₃H₆</th>
<th>∑ C₂/1-C₄H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>2.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>46</td>
<td>3.33</td>
<td>1.05</td>
<td>3.5</td>
</tr>
<tr>
<td>70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>98</td>
<td>3.9</td>
<td>1.38</td>
<td>5.4</td>
</tr>
<tr>
<td>150</td>
<td>3.4</td>
<td>1.13</td>
<td>3.86</td>
</tr>
<tr>
<td>203</td>
<td>3.9</td>
<td>1.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

F: Effect of chain branching on rate

The effect of the structure in the decomposition of hydrocarbons is attempted in Fig. 31. The initial rates of the three isomeric compounds obtained under the same experimental conditions, are plotted VS P₁₂. The more the branching, the lower the rate. This is in agreement with relative data given by various investigators (118, 119, 120) for the oxidation of paraffins. This problem is approached in chapter 4, from a more theoretical point of view. The difference in effect can be attributed partially to a statistical base. Normal pentane with 6 primary and 6 secondary hydrogens is more vulnerable to the abstraction of H by a radical than isopentane with 1 tertiary, 2 secondary and 9 primary, and much more than neo-pentane with 12 primary hydrogens. The size of the molecule is one more important factor, as far as collisions are
Fig. 31: Structural effect of isomeric pentanes on the initial rate.
concerned. The importance of molecular size and the collisional area is explained in chapter IV

II) Inhibited reaction

The thermal decomposition of all isomeric pentanes is inhibited by NO, yet differences appear from member to member. Inhibition in n-pentane decomposition has been investigated sufficiently by various workers in the past. In normal inhibition the rate falls rapidly for a small amount of NO and finally, approaches a limiting value. By adding more and more nitric oxide no more inhibition is observed. A slight acceleration occurs at higher nitric oxide pressures. The necessary amount of NO to reach the limiting rate, has been found by other investigators to be about 10% of the hydrocarbon.

A: Nitric oxide concentration for the fully inhibited reaction

1: Isopentane

The effect of NO was examined at different pressures of the hydrocarbon, to determine whether the limiting $P_{NO}$ is related to the hydrocarbon pressure. In Fig. 32, the initial rate is plotted against $P_{NO}$. A common limit at $P_{NO}$ 10 mm appears at all three pressures, or at least it is apparent that the limiting pressure of NO is independent of the partial pressure of hydrocarbon. To determine whether or not the limiting $P_{NO}$ is a function of the surface-to-volume ratio for the vessel, the latter was repacked twice so that the S/V ratio was increased from 1.2 to 2.5 and then 5.0. By using constant amounts of hydrocarbon (101 ± 1 mm) the change of the rate with $P_{NO}$ was examined. A shift of the limit to higher values appeared with increasing packing Fig. 33. For the three
Fig. 32: Rate (initial) VS P(NO) in unpacked reaction for isooctane.
Fig. 33: \( R_{\text{overall}} \) vs. \( P(\text{NO}) \) at various S/V ratios for isopentane.
Fig. 34: Effect of $P_{NO}$ on rate (overall) for n-pentane: packed vessel.

$P_{n\text{pentane}} = 102 \pm 2 \text{ mm}$

$T = 519^\circ \text{ C}$

$\Delta P = 20\% \quad S/\sqrt{V} = 3.0$
different S/V ratios the limit was approximately 10, 13, and 15 mm respectively. These numbers are not absolute, but what is obvious is that the following inequality holds.

\[ \lim P_{N0}(S/V = 1.2) < \lim P_{N0}(S/V = 2.5) < \lim P_{N0}(S/V = 5.0) \]

This indicates clearly the relationship of the inhibition process to the surface-area of the reaction vessel and shows the importance of heterogeneity in the overall inhibition.

II 1 N-pentane

In normal pentane no comparison like the above was made, because the limiting \( P_{NO} \) for decomposition was considered as well known from previous work, to be 10 mm. The vessel was packed until the S/V ratio became approximately 3. The change of the overall rate against \( P_{NO} \) is given in Fig. 34 which indicates, but not positively, that \( \lim P_{NO}(\text{unpacked vessel}) \leq \lim P_{NO}(\text{packed}) \).

The fact that the vessel was packed with pyrex tubes and not quartz rods, might be an explanation of the reduced surface effect as compared with isopentane. The surface activity of these two packings may not be the same.

III) Neo-pentane

Neo-pentane show differences from the other two members of the series. Nitric oxide has no significant effect on the initial rate of decomposition of neo-pentane. There may be in fact an accelerating rather than inhibition. The experiments done were insufficient to estimate this effect with certainty. These results are given in Table X.v.
Table XI

Variation of $\Delta P$ with time for various $P_{NO}$ for neo-pentane

$P_{neo-pent)} = 76 \pm 1 \text{ mm} \quad T=540^\circ \text{C}$

<table>
<thead>
<tr>
<th>time (min)</th>
<th>$P_{NO0}$ (mm)</th>
<th>$P_{NO1}$ (mm)</th>
<th>$P_{NO7}$ (mm)</th>
<th>$P_{NO10}$ (mm)</th>
<th>$P_{NO13}$ (mm)</th>
<th>$P_{NO19}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>3</td>
<td>1.5</td>
<td>3</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>3.5</td>
<td>2</td>
<td>3.5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
<td>5</td>
<td>3.5</td>
<td>5</td>
<td>4.5</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>7.5</td>
<td>5.5</td>
<td>7</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

If decomposition is extended to some 20% of the initial pressure, the overall rate shows a distinct inhibition. For two different pressures of neo-pentane, 75 and 100 mm the limiting pressure of NO appears to be fixed at 10 mm. By packing the vessel with pyrex tubes so that $S/V$ rate is changed by a factor of nearly 3, the limit was shifted to approximately 12 mm, an effect similar to that found for isopentane Fig. 35.

B) Variation of products with time

The variation of product distribution with the time was investigated for the fully inhibited reaction for isopentane Fig. 36-41. The percentage of each product in the reaction mixture varied linearly with time, in contrast with the uninhibited reaction. Assuming that a fully inhibited decomposition occurred in the latter case, this difference can be explained, by
Fig. 35  Neopentane : $R_{overall}$ vs. $P(NO)$
Fig. 36: Yield of $\text{C}_2\text{H}_5\text{NO}$ and $\text{C}_2\text{H}_6$ with time for isopentane; fully inhibited reaction at $519^\circ \text{C}$.

- $P$ Isop = 100±1 (mm)
- $P$ NO = 25 (mm)
- $T = 519^\circ \text{C}$
Fig. 37: $C_2H_4$ VS time at various S/V ratios and different P(NO) for isopentane. Fully inhibited reaction.
Fig. 38: 1-\text{C}_4\text{H}_8$ vs time at different P(NO) for isopentane.
Product yield VS time in the fully inhibited reaction for isopentane.

Fig. 39:

P_NO = 2.5 (mm)

T = 519°C

P_isopent = 101 ± 1 (mm)
Fig. 40: Yield of C$_2$H$_6$ VS time at various S/V ratios and P(NO) for isopentane. Fully inhibited reaction.
assuming that, in the inhibited reaction the effects of heterogeneity were completely counterbalanced by the NO so the reaction followed a homogeneous mechanism, while in the uninhibited reaction heterogeneous effects participated with the homogeneous reaction.

By using high pressures of inhibitor, a nitroso compound was detected, and its identification has been attempted by its I.R. spectrum. It gave an absorption peak at 695-700 cm\(^{-1}\). Literature data on I.R. spectra \(^{(63)}\) gave an absorption peak at 690-695 for all nitroso compounds. A second line of evidence was obtained from the fact that, the unknown substance was eluted from the silica gel column in which all hydrocarbons but C\(_1\)-C\(_2\) and their derivatives are retained. The substance appears to be either CH\(_3\)NO or C\(_2\)H\(_5\)NO. CH\(_3\)NO was excluded by pyrolysing \(\text{Hg}(\text{CH}_3)_2\) in the presence of NO. Analysis of the products on a silica gel column gave no peak at an elution time corresponding to that of the unknown compound. It is assumed that this substance is C\(_2\)H\(_5\)NO.

C\(_2\)H\(_5\)NO is much more stable thermally than CH\(_3\)NO and its presence is more reasonable at the temperature used in the present study. In Fig. 36 the variation of this assumed C\(_2\)H\(_5\)NO with time is compared with that of C\(_2\)H\(_6\). At the beginning of the reaction C\(_2\)H\(_5\)NO is favoured and C\(_2\)H\(_6\) appears in small amounts. As the extent of reaction increases, C\(_2\)H\(_5\)NO increases very slowly, while C\(_2\)H\(_6\) increases very rapidly. The instability of C\(_2\)H\(_5\)NO does not allow it to increase markedly with time. The actual increase of C\(_2\)H\(_5\)NO is by a factor of 1.5 over the time of reaction while C\(_2\)H\(_6\) for the same period is increased by a factor at least 9.
Fig. 41: Product yield vs. $P(\text{NO})$ for $n$-pentane.

$T = 529^\circ C$

$P_{1-n\text{-pentane}} = 130 \pm 2 \text{mm}$

$P = 20\%$
Fig. 42: Effect of NO in the production of $C_3H_6$ at various S/V ratios for isopentane.
Fig. 43: I-C₄H₈ VS P(NO) in packed and unpacked vessel for isopentane.
Fig. 44: product yield vs P(NO) for neo-pentane.
Fig. 45: C₂H₆ VS P(NO) at various S/V ratios for isopentane.
Fig. 46: CH₄ VS P(NO) at various S/V ratios for isopentane.
Fig. 47: Yield of C$_2$H$_4$ vs. P(NC) at various S/V ratios for isopentane.
In Fig. 37 the variation of \( C_2H_4 \) with time at various S/V ratios and \( P_{NO} \) is shown. At constant reaction time the effect of NO and surface is obvious. The curve corresponding to higher packing is not strictly a straight line because the \( P_{NO} \) used (15 mm) is exactly the limiting pressure for this S/V ratio.

In Fig. 38 and 39 the variations with time of \( 1-C_4H_8, C_3H_6 \) and \( CH_4 \) are presented. At constant hydrocarbon concentration and constant \( P_{NO} \) and S/V ratio, for all products except \( C_2H_6 \) (Fig. 40) the equation holds

\[
\frac{d(\text{products})}{dt} = K \text{ (constant)}
\]

In reality \( P_{NO} \) does not remain constant, as will be shown later on. There appears to be a close relationship between the production of \( C_2H_6 \) and the consumption of NO. \( C_2H_6 \) and \( C_2H_2NO \) appear to be formed in competing reactions. \( C_2H_6 \) is favoured as the reaction is extended.

C) Variation of the decomposition products with NO and surface-to-volume ratio

Previous workers postulated that the product distributions with the inhibited and uninhibited decomposition were identical. A careful analysis in the present work, by gas chromatography, of more than 1000 samples obtained from pyrolysis under different conditions, from partially or fully inhibited decompositions, proves that this is not the case. The concentrations of most products were found to be dependent upon the NO pressure and reached a limiting value when the NO pressure exceeded approximately 15 mm for all isomers (Fig. 41-47). The products are in general the same for both the inhibited and uninhibited decomposition, but with some differences. The yield of saturated hydrocarbon is reduced with the increasing of \( P_{NO} \). Some differences are encountered for the three pentanes
as well as some similarities. $C_3H_6$ is decreased with $P_{NO}$ in the case of n-pentane while it is independent of $P_{NO}$ in iso-pentane. Fig. 41 and 42. $C_4H_8$ is decreased in both n-pentane and iso-pentane but increases rapidly with $P_{NO}$ for neopentane (Fig. 41, 43, 44). A catalytic effect of NO on the production of 1-$C_4H_8$ is observed in neo-pentane. A common feature for all isomeric pentane is that $C_2H_6$ decreases with increasing $P_{NO}$ and that $C_2H_4$ and $CH_4$ increase proportionally with $P_{NO}$ (Fig. 43, 45, 46 and 47). The yield of $C_3H_6$ from isopentane (Fig. 42) appears independent of both $P_{NO}$ and S/V ratio while 1-$C_4H_8$ appears independent of S/V ratio but slightly dependent on $P_{NO}$. Both NO and packing seem to have no effect on the main mode of decomposition. In (Fig. 45), the dependence of $C_2H_6$ on both $P_{NO}$ and S/V ratio is presented. $C_2H_6$ decreases slowly with $P_{NO}$ reaching a limiting value, after the $P_{NO}$ passes the value for full inhibition. The variation is clear for both packed and unpacked vessel. Packing seems to favour $C_2H_6$ highly. An increase of S/V ratio by a factor of approximately 2, nearly doubles the yield of $C_2H_6$. The addition of NO was extended to some 25 mm, nearly 2.5 times the limiting value to see whether a limiting value of $C_2H_6$ is reached. The yield of $C_2H_4$ increases with $P_{NO}$ to a limiting value at high $P_{NO}$ (Fig. 47). An increase by a factor of nearly 1.5 is observed for both packed and unpacked vessel. Higher S/V ratios favour the yield of $C_2H_6$ more than $C_2H_4$. A change in S/V ratio of 5 causes a change in $C_2H_4$ of a factor of approximately 2, half of the corresponding effect for $C_2H_6$. The variation of $CH_4$ is shown in (Fig. 46) with both $P_{NO}$ and S/V ratio $CH_4$, line $C_2H_4$, increases
with $P_{NO}$, for both packed and unpacked vessels reaching also a limiting value for higher $P_{NO}$. The effect on $CH_4$ is less marked than for $CH_4$. Higher S/V ratios favour the yield of $CH_4$ but not as much as in the case of $C_2H_4$ and $C_2H_6$. As a final point comes the increasing surface area, which favours the product formation in the following sequence

$$C_2H_6 \rightarrow C_2H_4 \rightarrow CH_4 \rightarrow C_3H_6 \rightarrow 1-C_4H_8$$

no effect

Increasing the $P_{NO}$ favours the reaction products in the sequence

$$C_2H_4 \rightarrow CH_4 \rightarrow 1-C_4H_8 \rightarrow C_3H_6$$

$C_2H_6$ formation is reduced by NO. In Fig. 44 the variation of $1-C_4H_8$ and $CH_4$ with $P_{NO}$ is shown for neo-pentane. Both products appear to increase but the increase is more marked in the case of $1-C_4H_8$. It increases by a factor at least 2, while $CH_4$ changes very slightly. A peculiar point is that in spite of the fact that $P_{NO}$ passes its limiting value, for full inhibition, $1-C_4H_8$ continue to increase regularly. Thus $1-C_4H_8$ must result, not from a free radical reaction, which is subject to inhibition, but from another process such as molecular splitting unaffected by NO.

In (Fig. 48) the variation of $C_2H_5NO$ with NO is shown for isopentane. An attempt was made to increase the yield of $C_2H_5NO$ by greatly increasing the NO pressure up to 75 mm. $C_2H_5NO$ is favoured by increased $P_{NO}$ but not proportionately. This failure to promote $C_2H_5NO$ formation significantly can be attributed to the instability of $C_2H_5NO$ at the temperatures of $500^\circ C$ and higher.
D) Variation of product ratios with \( P_{NO} \) and S/V

I) Variation of \( \frac{C_2H_4}{C_2H_6} \) with \( P_{NO} \) and S/V ratio

The change of the \( \frac{C_2H_4}{C_2H_6} \) ratio was considered as the most important ratio since it indicated directly a different behaviour of both saturated and unsaturated products with \( P_{NO} \). This variation is similar for both n-pentane and isopentane (Fig. 49, 50, 51). In both cases the ratio changes by a factor of nearly 2 and reaches a limiting value when \( P_{NO} \) exceeds its limiting pressure. The variation of \( \frac{C_2H_4}{C_2H_6} \) with both \( P_{NO} \) and S/V ratio is very important because it gives an indication in the inhibited reaction of the importance of heterogeneous processes. The ratio shows a variation with \( P_{NO} \) similar in kind, but differing in magnitude for three different values of S/V (Fig. 50). For constant \( P_{NO} \) the \( \frac{C_2H_4}{C_2H_6} \) ratio is reciprocally proportional to S/V ratio. This behaviour indicates that increased surface favours \( C_2H_6 \) to a greater extent than \( C_2H_4 \).

II) Variation of \( \frac{CH_4}{C_2H_6} \)

In both n-pentane and isopentane \( \frac{CH_4}{C_2H_6} \) is significantly increased by increasing \( P_{NO} \) (Fig. 52 and 53). In the case of isopentane the variation of \( \frac{CH_4}{C_2H_6} \) ratio is reduced as the S/V ratio increases. at constant \( P_{NO} \). This is another indication that increased surface, for constant \( P_{NO} \), favours highly the formation of \( C_2H_6 \).

III) Variation of \( \frac{C_2H_4+C_2H_6}{C_3H_6} \) with \( P_{NO} \)

Variation in \( P_{NO} \) affects only slightly the ratio \( \frac{C_2H_4+C_2H_6}{C_3H_6} \) (Fig. 54) for n-pentane. The ratio increases slightly with \( P_{NO} \). In contrast to iso-pentane the ratio is constant for isopentane.
Fig. 49: C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} VS P(NO)\% for isopentane.
Fig. 50: $\frac{C_2H_4}{C_2H_6}$ vs $P(\text{NO})$ at various S/V ratios for isopentane.
Fig. 51: $\frac{C_2H_4}{C_2H_6}$ VS $P(NO)$ for n-pentane.

$T = 529^\circ C$

$P_n$ n-pentane = 130 ± 2 (mm)
Fig. 52: $\text{CH}_4/\text{C}_2\text{H}_6$ VS P(NO) at various S/V ratios for isopentane.
T = 529°C
P, n-C₅H₁₂ = 130±2 (mm)

FIG. 53: CH₄/C₂H₆ VS P(NO) for n-pentane.
Fig. 54: (C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6})/C\textsubscript{2}H\textsubscript{6} VS P(NO) for \textit{n}-pentane and isopentane.
IV) Variation of $\frac{C_2H_4 + C_2H_6}{C_4H_8}$ with $P_{NO}$

The variation of $\frac{C_2H_4 + C_2H_6}{C_4H_8}$ changes slowly with $P_{NO}$ for both isopentane and n-pentane (Fig. 55). $C_4H_8$ is of course different in these two cases, $1-C_4H_8$ in n-pentane and $i-C_4H_8$ in isopentane. This difference is unimportant because both products are a consequence of a $CH_2-C_4H_9$ primary decomposition.

V) Variation of $CH_4/C_2H_4$ with $P_{NO}$

The ratio was examined only for the n-pentane series. It increased very slightly with $P_{NO}$ (Fig. 56) in contrast with the rapid change of both $C_2H_4/C_2H_6$ and $CH_4/C_2H_6$. It appears that NO favours both $CH_4$ so that the ratios remain nearly constant.

VI) Variation of $C_2H_6/C_{2H5NO}$ with NO

This ratio was examined for $P_{NO} > P_{NO}$ (limiting) because for lower $P_{NO}$ $C_{2H5NO}$ is not detected. By increasing the $P_{NO}$ to high values formation of $C_2H_5NO$ is accelerated but steadily reaches a limiting value (Fig. 57). It is rather improbable that more NO does not give rise to the formation of more $C_2H_5NO$, but the concentration of $C_2H_5NO$ appears to reach a steady state. For higher extent of decomposition ($\Delta P 30\%$), the decrease in the ratio i.e. the formation of $C_2H_5NO$, is more pronounced. This nitroso-compound was detected with n-pentane.

VII) Variation of $i-C_4H_8/C_2H_6$ with $P_{NO}$ and S/V ratio

This ratio, which was examined only with isopentane, decreases significantly with $P_{NO}$, but no regular variations were observed with S/V ratio (Fig. 58).

E) Consumption of NO

In previous studies, NO, was either reported to be slightly
Fig. 55: \( \frac{(\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)}{\text{C}_4\text{H}_8} \) VS \( P(\text{NO}) \) for n- and iso-pentane.
Fig. 57: \( \frac{C_2H_6}{C_2H_5NO} \) vs \( P(\text{NO}) \) at various reaction extent for isopentane.
Fig. 58: \( \frac{1-C_4H_8}{C_3H_6} \) vs. \( P(\text{NO}) \) at various \( S/V \) ratios for isopentane.
consumed, or not consumed at all. The chemical analysis used for NO were liable to considerable error, since NO is very unstable in the presence of $O_2$. In the present study, a very careful estimation of NO was attempted for all pyrolysis, by gas chromatography, using a silical gel column. The fact that NO was consumed has been established for high concentrations of NO (Fig. 59). The analytical results for NO pressures below 8 mm are not reliable. 20-40% of the nitric oxide used was found to be consumed in many cases. Some of this consumption may be due to traces of $O_2$. However, the results clearly show that the consumption of NO increases with increasing $P_{NO}$, and decreases with increasing $S/V$ ratios. For small concentrations of NO, the consumption would thus be low. Above the limiting NO pressure the consumption increases rapidly. For higher $S/V$ ratios consumption is lower. Thus, NO consumption, is not a simple linear function of initial $P_{NO}$. For $P_{NO} \leq P_{NO}$ (limiting), NO seems to be less active while for $P_{NO} \geq P_{NO}$ (limiting) it is consumed rapidly.

The fact that increasing the surface, reduces the consumption, means that NO is retained on the surface and consequently protected from being consumed. After the complete covering of the active centers of the surface, NO establishes a dynamic equilibrium with molecules in the gas phase, being subject to consumption, much more than those held on the surface. In a number of experiments, the extent of decomposition was increased from 15 to 30%. A slight increase in NO consumption occurred. The consumption of NO for various initial pressures of NO, and for a $\Delta P=20\%$ is given in table XI.
Fig. 59: NO consumption vs. P(NO) for isopentane.
Table XI
Consumption of NO% of the $P_{NO}$ $\Delta P = 20\%$

<table>
<thead>
<tr>
<th>$P_{NO}$ mm</th>
<th>Consumption %</th>
<th>$P_{NO}$ mm</th>
<th>Consumption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>29</td>
<td>4.7</td>
<td>36</td>
</tr>
<tr>
<td>1.4</td>
<td>27</td>
<td>5.1</td>
<td>32.8</td>
</tr>
<tr>
<td>5.1</td>
<td>51 (?)</td>
<td>5</td>
<td>34.3</td>
</tr>
<tr>
<td>10</td>
<td>16.6</td>
<td>7.45</td>
<td>34.8</td>
</tr>
<tr>
<td>12</td>
<td>43</td>
<td>8.1</td>
<td>28.9</td>
</tr>
<tr>
<td>8.5</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.72</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.43</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER IV

DISCUSSION

A. Uninhibited Reaction

A great deal of work has been done in the past on the pyrolysis of the pentanes and especially of n-pentane. In spite of this, relatively little is known about the mechanisms of these reactions. The lack of sufficient experimental data is a common feature of the kinetics of decomposition of higher hydrocarbons.

Investigations of the decomposition products of n-pentane and iso-pentane were done by Frey and Hepp (61) in 1933.

They proved the following rate expressions for the two hydrocarbons.

\[ n\text{-pentane: } k = 2.5 \times 10^{13} e^{-61.200/RT} \]
\[ iso\text{-pentane: } k = 7.9 \times 10^{12} e^{-58.600/RT} \]

These values should be in general agreement with the present results if one refers to an average energy of activation. Whether or not one can use average values for \( E_A \) for the whole pressure range, where different modes of reaction might take place, is open to question. The decomposition proceeds through a free radical mechanism, as it was proved by Rice et al (64-65). The mechanisms of the uninhibited decomposition of the three isomeric pentanes will be discussed.

I. Isopentane

The decomposition of isopentane involves a free
radical process, as has been shown by the action of inhibitors. A significant point, open to question is whether homogeneous initiation of the radical reaction, or heterogeneous initiation is predominant. At low pressures, as we have shown before, molecules can accumulate energy without collisional deactivations, and hence can pass the energy barrier for unimolecular reaction. If the reaction is initiated on the walls, the required energy is diminished. The surface possesses active centers, formed during the production of the vessel. The number of centers vary with the method of production of the vessel, but they may be still formed during the reaction at high temperature. According to PARAVANO (66), physical and chemical changes take place, in a number of semi-conductors and certain oxides at higher temperatures. An equilibrium is attained for dislocations or migrations of elements from the interior to the surface, leading to a heterogeneous surface. On such a surface with active centers, molecules with an excess of free valencies, unsaturated hydrocarbons and free radicals, can be held, where they are subject to collisions with other molecules. These molecules are not strongly attached but they attain a dynamic equilibrium following the laws of adsorption. On such a surface a molecule of hydrocarbon can dissociate, thus causing an initiation reaction. At low pressures, where homogeneous initiation through binary collisions is negligible, heterogeneous initiation must be considered as the predominant process, except for higher temperatures, where the available energy is high enough to enable unimolecular decomposition to occur. For ethane the difference between D(C-C) and D(C-H) is nearly
20 KCal/Mole (20). It is obvious that for higher hydrocarbons some variation in this difference occurs, but the greater part of difference remains. From Semenov's data (20) we get the following values:

\[
\begin{align*}
D(\text{C}_3\text{H}_7-\text{CH}_3) &= 79 \text{ KCal/Mole} \\
D(\text{i-C}_3\text{H}_7-\text{CH}_3) &= 74 \text{ KCal/Mole (?)}
\end{align*}
\]

The production of a radical, from a CH$_3$ group joined to a secondary carbon atom, will thus be favored as an initiation reaction:

\[
\text{CH}_3-\text{CH-CH}_2\text{-CH}_3 \xrightarrow{\text{homog. or heterog.}} \text{CH}_3^+ \text{CH}_3\text{CHCH}_2\text{CH}_3 (\text{Ia})
\]

A second decomposition mode involves the loss of the methyl group with the formation of the isobutyl radical.

\[
\text{CH}_3-\text{CH-CH}_2\text{-CH}_3 \xrightarrow{\text{CH}_3^+ \text{CH}_3\text{CHCH}_2\text{CH}_3 (\text{Ib})}
\]

The difference in $E_A$ for these two processes is about 4 KCal/Mole and thus (Ia) will be approximately 12 times faster than reaction (Ib).

A third possibility would involve decomposition into ethyl and isopropyl radicals; the endothermicity of this reaction can be calculated as follows:

\[
\Delta H_f (\text{CH}_3) = 31.5 \text{ KCal/Mole while } \Delta H_f (\text{C}_2\text{H}_5) = 26 \text{ KCal/Mole.}
\]

So examining the following process

\[
\text{iso-C}_5\text{H}_{12} \xrightarrow{\text{C}_2\text{H}_5^+ \text{CH}_3\text{CHCH}_3 (\text{Ic})}
\]

and comparing it with (Ia) we get the following:

\[
D(\text{CH}_3-\text{CH-CH}_2\text{-CH}_3) = \Delta H_f (\text{CH}_3) + \Delta H_f (\text{CH}_3\text{CHCH}_2\text{CH}_3) - \Delta H_f (\text{i-C}_5\text{H}_{12})
\]

and \[
D((\text{CH}_3)_2\text{CH-CH}_2\text{-CH}_3) = \Delta H_f (\text{C}_2\text{H}_5) + \Delta H_f (\text{CH}_3\text{CHCH}_3) - \Delta H_f (\text{i-C}_5\text{H}_{12})
\]
So \[ \text{D}(i-C_4H_9-CH_3) - \text{D}((CH_3)_2CH-C_2H_5) = \]
\[ \Delta H_f(CH_3) - \Delta H_f(C_2H_5) + \Delta H_f(CH_3CHCH_2CH_3) - \]
\[ \Delta H_f(CH_3CHCH_3) = 31.5 - 26 + 8 - 12.2 \approx 21 \text{ Kcal/Mole} \]
So \[ \text{D}(i-C_4H_9-CH_3) - \text{D}((CH_3)_2CH-C_2H_5) = 1 \text{ Kcal/Mole} \]

Average of \( \Delta H_f \) for t-butyl and n-butyl radicals 4.5 and 12 Kcal/Mole respectively were taken, following the empirical formula of Voervodskii, for the calculation of bond dissociation energies.

\[ D(C-H) \text{ (prim.)} = D(C-H)\text{ (second.)} + B = D(C-H)\text{ (tertiary)} + B \]
So \[ D(C-H) \text{ second.} = D(C-H)\text{ primary} + D(C-H)\text{ tert.}/2 \]

The above calculation indicates that reaction (Ic) can make a significant contribution to the initiation process. Error in calculation is due to approximation of \( \Delta H_f \) (isobutyl).

Initiation can be attributed to these three decompositions. Of course the contribution of these reactions to the overall process would be negligible if the chains are long, but will be very important if the chains are short. The distribution of the products, in the present study shows that reactions (Ia) and (Ib) make a greater contribution than reaction (Ic).

If these three reaction mechanisms have nearly the same energy of activation, then reaction (IC) must have a lower steric factor. The ratio of amounts of \( CH_4 \) and \( C_2H_6 \) which must be at least proportional to the concentrations of \( CH_3 \), and \( C_2H_5 \) respectively, varies markedly with pressure. The ratio \( CH_4/ C_2H_6 \) is nearly 9 for 50(mm) initial pressure, but falls to 7 for 70(mm) and to 4 for 100(mm) initial pressure.
These differences do not require that the steric factors vary with pressures but merely that \( \text{C}_2\text{H}_5 \) is converted more to \( \text{C}_2\text{H}_6 \) at higher pressures than at lower pressures.

The difference of 9-10 KCal/Mole for \( \text{D}(\text{C}-\text{H})_{\text{prim.}} \) and \( \text{D}(\text{C}-\text{H})_{\text{tert.}} \) will favor the abstraction of hydrogen by \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) radicals from the tertiary carbon. The fact that the increase in \( \text{C}_2\text{H}_6 \) is accompanied by decrease of \( \text{CH}_4 \) indicates the competition between \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) radicals for the propagation of the reaction.

The propagation will take place as follows:

\[
\begin{align*}
\text{CH}_3\text{-CH-CH}_2\text{CH}_2\text{-CH}_3 & \rightarrow \text{CH}_4\text{+ CH}_3\text{O-CH}_2\text{CH}_3, \quad (2) \\
\text{CH}_3\text{-CH-CH}_2\text{-CH}_3 & \rightarrow \text{C}_2\text{H}_6\text{+ CH}_3\text{O-CH}_2\text{CH}_3, \quad (3)
\end{align*}
\]

The activation energies for the reaction of \( \text{CH}_3 \) radical with paraffins is approximately (67) \( 6 - 8 \) KCal/Mole. Trotman-Dickenson and Steacie calculated that the abstraction of a secondary hydrogen by \( \text{CH}_3 \) requires \( 2 \) KCal/Mole. less than a primary hydrogen. Extending this calculation to tertiary hydrogen, and provided that for the reaction

\[
\text{CH}_3\text{-CH-CH}_2\text{CH}_2\text{-CH}_3 \rightarrow \text{CH}_4\text{CH}_3\text{-CH-CH}_2\text{CH}_3
\]

(68)

\( E_A = 8.1 \) KCal/Mole. and the steric factor \( P = 3 \times 10^{-4} \) we obtain for reaction (2) that \( E_A \) will be different, approximately by \( 5 \) KCal/Mole. with the same steric factor \( P = 3 \times 10^{-4} \).

For reaction (3) if

\[
\text{D}(\text{CH}_3\text{-H}) = 101 \text{ KCal/Mole. and D}(\text{C}_2\text{H}_5\text{-H}) = 98 \text{ KCal/Mole.}
\]

this difference of \( 3 \) KCal/Mole. would be encountered in reactions like
-123-

\[ \text{RH} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{R}. \]
\[ \text{RH} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{R}. \]

So \( E_A \) for reaction (3) is expected to be around 8-9 KCal/Mole., but the steric factor is unknown. So from the point of view of activation energies the following relative reaction constants for reaction (2) and (3) should be found

\[ \frac{k_2}{k_3} = e^{\frac{3.000}{RT}} = e^{\frac{3.000}{2} \times 800} \approx e^2 \]

Thus \( k_2 \approx 7.4 \times k_3 \); for \( T = 529^\circ \text{C} \) unless the steric factors are greatly different and counterbalance the difference in activation energy. Reaction (2) is expected to proceed at least 7 times faster than reaction (3).

The free radical produced \( \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3 \) is very unstable and \( \text{CH}_3\text{C} \) can decompose by two different mechanisms

\[ \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3 \]
\[ \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \quad (4a) \]

The relative probabilities of (4a) and (4b) were found to be \( 1/4 \) (69), but the present results indicate that the value is closer to \( 1/2 \). The ratio \( \text{i-C}_4\text{H}_8/\text{C}_3\text{H}_6 \) seems to be largely unaffected by pressure. Higher temperature appears to favor reaction (4b). The ratio \( \text{CH}_4/\text{C}_2\text{H}_6 \) on the other hand indicates the competitive reaction with isopentane of \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) radicals.
The radicals which were formed in the initiation process, also take part in the propagation.

\[
\text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \rightarrow \text{CH}_3\text{CH} - \text{CH}_2\text{-CH}_3 \quad (5)
\]

\[
\text{CH}_3\text{-CH-CH}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{+CH}_3 \quad (6)
\]

\[
\text{CH}_3\text{-CHCH}_3 \rightarrow \text{C}_2\text{H}_4\text{+CH}_3 \quad (7)
\]

Isomerization can change isobutyl into \text{n-butyl}. This radical decomposes as follows

\[
\text{C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6\text{+CH}_3 \quad E_A = 23 \text{ KCal/Mole.} \quad (5a)
\]

\[
\text{C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_4\text{+C}_2\text{H}_5 \quad E_A = 23 \text{ KCal/Mole.} \quad (5b)
\]

For the reaction (7) the activation energy is 26±4 KCal/Mole.\(^{(71)}\).

\[
\text{The absence of any } \text{i-C}_4\text{H}_8 \text{ of } \text{C}_3\text{H}_6 \text{ over } \text{i-C}_4\text{H}_8 \text{ gives indirect support for the reactions (5) and (6). The termination process takes place in both homogeneous and heterogeneous phases. The following might be included:}
\]

\[
\text{CH}_3\text{+CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad (8)
\]

\[
\text{CH}_3\text{+C}_2\text{H}_5 \rightarrow \text{CH}_4\text{+C}_2\text{H}_4 \quad (9)
\]

\[
\text{CH}_3\text{+C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_8 \quad (10)
\]

\[
2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4\text{+C}_2\text{H}_6 \quad (11a)
\]

\[
2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10} \quad (11b)
\]

\[
\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 \text{+ H}^- \quad (12)
\]

\[
2\text{H} \rightarrow \text{H}_2 \quad (13)
\]

Since \text{CH}_3\text{ can react very easily with other molecules its concentration on the system will always be very low and hence,
it is rather improbable to have reaction of CH$_3$ with CH$_3$

in homogeneous phase. Reaction (8) will probably take place

more easily on the wall, where adsorbed CH$_3$ can collide with

CH$_3$ striking the wall. The recombination has zero energy of

activation. Reaction (10) seems to be much more favored than

since (9) since its energy of activation would be zero, but it will

take place in homogeneous phase, and for this reason, it is

rather rare due to the small number of collisions. In con-

trast reaction (9), for which some $E_A$ is required, probably

takes place on the wall. The photolysis of mercury diethyl

(72) gives

$$E_A(11a) = E_A(11b) = 0.8 \pm 0.2 \text{ KCal/mole.}$$

A different investigation (73) reports that

$$E_A(11a) - E_A(11b) = 4.8 \text{ KCal/mole.}$$

and that the variation of $k_{11a}/k_{11b}$ with temperature is as

follows

<table>
<thead>
<tr>
<th>T °C</th>
<th>75</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{11a}/k_{11b}$</td>
<td>0.36</td>
<td>0.38</td>
<td>0.40</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Extrapolating these values to 500° we expect that reaction

(11a) would be half as fast as reaction (11b). However,

results of the present study show that C$_4$H$_{10}$ is not formed

and thus reaction (11b) does not appear to take place in the

temperature range used. Propane is formed in small amounts and

hence the probability of collision between CH$_3$ and C$_2$H$_5$ is

higher than between C$_2$H$_5$ and C$_2$H$_5$.

For reaction (12) a high activation energy is required.
By using mercury-photosensitized decomposition of ethane at high temperatures (74) the energy of activation was found to be 39.5 KCal/Mole. Hence reaction (12) takes place on the wall. The increase of \( \text{C}_2\text{H}_6 \) over \( \text{C}_2\text{H}_4 \) for higher pressures is a consequence of competition between reaction (11a) and (9) on the one hand, and (3) on the other. The production of \( \text{C}_3\text{H}_8 \) cannot be explained only by reaction (10) so that participation of \( \text{CH}_3\text{CHCH}_3 \) in another reaction besides (7) is expected at high pressures.

\[
i-\text{C}_5\text{H}_{12} + \text{CH}_3\text{CHCH}_3 \rightarrow \text{C}_3\text{H}_8 + i-\text{C}_5\text{H}_{11} \quad (7a)
\]

Finally the production of cis-butene-2 can be explained as follows at high pressures.

\[
\text{CH}_3\text{CHCH}_2\text{CH}_3 + \text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCH}_3 + \text{H} + \text{M} \quad (5c)
\]

The simultaneous appearance of cis-butene-2 and \( \text{H}_2 \) at high temperature and pressure can be explained by reaction (5c) or by an alternative

\[
\text{CH}_3\text{CHCH}_2\text{CH}_3 + \text{H} \rightarrow \text{cis-CH}_3\text{CH} = \text{CHCH}_3 + \text{H}_2
\]

**OVERALL MECHANISM**

The overall mechanism can be summarized as follows:

\[
\begin{align*}
\text{CH}_3\text{CH} \rightarrow \text{CH}_3\dot{\text{CHCH}}_2\text{CH}_3 & \quad \text{EA} = \text{D(C-C)}_{\text{sec.}} \quad (\text{Ia}) \\
\text{CH}_3 & \\
\text{CH}_3\text{CHCH}_2\text{CH}_3 - \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3 \quad \text{EA} = \text{D(C-C)}_{\text{prim.}} \quad (\text{ Ib}) \\
\text{CH}_3 & \\
\text{CH}_3\text{CHCH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3 \quad \text{EA} = \text{D(C-C)}_{\text{sec.}} \quad (\text{ Ic})
\end{align*}
\]
\[
\begin{align*}
\text{CH}_3\text{-CH-CH}_2\text{-CH}_3 + \text{CH}_3 & \rightarrow \text{CH}_4 + \text{CH}_3\text{C-CH}_2\text{CH}_3 \quad E_A = 5 \text{ KCal/Mole.} \quad (2) \\
\text{CH}_3\text{CH-CH}_2\text{-CH}_3 + \text{C}_2\text{H}_5 & \rightarrow \text{CH}_3\text{C-CH}_2\text{CH}_3 + \text{C}_2\text{H}_6 \quad E_A = 8-9 \text{ KCal/Mole.} \quad (3)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{-C-CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3 \quad (4a) \\
\text{CH}_3\text{-C-CH}_2\text{CH}_3 & \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \quad (4b)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{-C-CH}_2\text{CH}_3 + \text{M} & \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3\text{M} \\
\text{m-CH}_4\text{H}_9 & \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3 \quad E_A = 23 \text{ KCal/Mole.} \quad (5a) \\
\text{m-CH}_4\text{H}_9 & \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5 \quad E_A = 23 \text{ KCal/Mole.} \quad (5b)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{-C-CH}_2 & \rightarrow \text{CH}_3 + \text{CH}_3\text{CHCH}_2 \quad (6) \\
\text{CH}_3\text{CH-CH}_3 & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 \quad E_A = 26^{+} \text{ 4 KCal/mole.} \quad (7a) \\
\text{CH}_3\text{-CH-CH}_3 + \text{i-C}_5\text{H}_12 & \rightarrow \text{C}_3\text{H}_8 + \text{i-C}_5\text{H}_11 \quad (7b)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{+CH}_3 & \rightarrow \text{C}_2\text{H}_6 \quad E_A = 0 \quad (8) \\
\text{CH}_3\text{+C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4+\text{C}_2\text{H}_6 \quad E_A > 0 \quad (9) \\
\text{CH}_3\text{+C}_2\text{H}_5 & \rightarrow \text{C}_3\text{H}_8 \quad E_A = 0 \quad (10) \\
\text{2C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_5\text{+C}_2\text{H}_4 \quad E_A = 4.8 \text{ KCal/Mole.} \quad (11a) \\
\text{2C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10} \quad E_A = 0 \quad (11b) \\
\text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + \text{H} \quad E_A = 39.5 \text{ KCal/Mole.} \quad (12)
\end{align*}
\]
II N - Pentane

N - Pentane resembles isopentane in many respects as far as the mechanism is concerned. The differences in products are small. As has been shown previously the decomposition proceeds through a free radical mechanism. The molecules of N - pentane show preference for breaking at the 1 - 2 position than at the 2 - 3 position. Hinshelwood and Stubbs (36) had calculated the relative probabilities to be 1/0.78. They suggest that N - pentane is less stable than the more branched isomers, because of an inductive effect. They claim that the C-C bond in a branched isomer is strengthened because of the weakness of the adjacent C-H bond. Thus normal pentane, with four secondary hydrogens adjacent to the 2 - 3 position will tend to decompose relatively less than the 1 - 2 position, with two secondary hydrogens adjacent. Hence, decomposition will start as follows.

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

Reactions (2a) and (2b) have the same activation energy

\[ E_A = 23 \text{ KCal/Mole. (75)} \]

while the reaction
with $E_A = 40 \text{ KCal/Mole.}$ (75)

is of minor importance.

At 500°C, the medium is highly energetic so that reaction (3) can participate. Actually Frey and Hepp (76) found that the $\bullet - \text{C}_4\text{H}_9$ radical decomposes three quarters by mode (2b).

The relatively small amounts of $\bullet - \text{C}_4\text{H}_8$ in the present study, indicate that equation (3) is still important. The decomposition is propagated as follows:

$$\text{CH}_3. + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_4. \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$$ (4a)

$$\text{CH}_3. + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_4. \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3.$$ (4b)

Equation (4a) participates more than (4b) because of the stability of the primary hydrogens.

At higher $\text{C}_2\text{H}_5$ would compete with $\text{CH}_3.$ in the propagation.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$ (5a)

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2.$$ (5b)

The variation of $\text{CH}_4/\text{C}_2\text{H}_6$ with pressure is a justification of the above equations. The fact, no $\bullet - \text{C}_5\text{H}_{10}$ was detected excludes the reaction

$$2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \bullet - \text{C}_5\text{H}_{12} + \bullet - \text{C}_5\text{H}_{10}$$

for the experimental conditions of the present study, perhaps because $\text{n - pentyl radicals are very unstable and are unlikely to react with themselves without decomposition to smaller fragments. The relatively high amounts of } \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_6 \text{ that were found in comparison with } \bullet - \text{C}_4\text{H}_8 + \text{CH}_4 \text{ shows a preference for the decomposition of } \bullet - \text{C}_5\text{H}_{11} \text{ into } \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6$.
This point is in agreement with analytical results of other previous workers (77). The reaction thus could be propagated as follows:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \]  \hspace{1cm} (6a)

\[ \text{CH}_3 + \text{I-C}_4\text{H}_8 \]  \hspace{1cm} (6b)

For the isopentyl radical three possibilities exist:

\[ 2\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}==\text{CHCH}_2\text{CH}_3 + \text{n-C}_5\text{H}_{12} \]  \hspace{1cm} (7a)

\[ \text{n-C}_5\text{H}_{12} + \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{n-C}_5\text{H}_{12} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \]  \hspace{1cm} (7b)

\[ 2\text{CH}_3\text{CHCH}_2\text{CH}_3 \rightarrow \text{C}_{10}\text{H}_{22} \]  \hspace{1cm} (7c).

No indication of reaction (7a) was found. Reaction (7c) was not checked, since if some \( \text{C}_{10}\text{H}_{22} \) was formed would probably remain in the chromatography column. Reaction (7b) seems to be the more reasonable. In addition it is in agreement with isomerization theory (78) which suggests that iso-radicals can isomerize to a normal radical by collisions with other molecules.

\( \text{N-pentyl radicals can also react with methyl radicals leading to the termination of chains.} \)

\[ \text{CH}_3 + \text{n-C}_5\text{H}_{11} \rightarrow \text{CH}_4 + \text{I-C}_5\text{H}_{10} \]

This reaction can be detected at temperatures below 110° C. (79). At temperatures above 500° C, it must be highly improbable due to the high instability of \( \text{n-C}_5\text{H}_{11} \) radical. Methyl radicals of course react with the products of primary decomposition such as \( \text{I-butene} \) (80) but this investigation has been done largely at temperatures below 220° C.
Termination can take place as follows:

\[ \text{wall} \quad \text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6 \quad (8a) \]

\[ \text{homog.} \quad \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_8 \quad (8b) \]

Reaction (8a) seems to predominate since insignificant amounts of C\(_3\)H\(_8\) were detected. Another termination step would be

\[ 2 \text{C}_2\text{H}_5 \rightarrow \text{homog.} \quad \text{C}_4\text{H}_{10} \quad (9a) \]

\[ \text{wall} \quad \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (9b) \]

Reaction (9a) has a zero activation energy, but is ruled out by the fact that no C\(_4\)H\(_{10}\) was found. Reaction (9b) has an activation energy approximately 5 KCal/Mole. The reaction

\[ \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H} \quad (10) \]

although it has high activation energy, approximately 40 KCal/Mole, cannot be excluded, since it provides a source of H atoms for the production of H\(_2\). The reaction should take place more readily under heterogeneous conditions where lower energy is required. The low concentration of C\(_2\)H\(_5\) makes reaction (9b) less probable. Hence decomposition of C\(_2\)H\(_5\) by reaction (10) will be favored. If this reaction takes place on the walls it needs less energy. Methyl can disappear by recombination on the wall

\[ \text{CH}_3^+ + \text{CH}_3 \rightarrow \text{wall} \quad \text{C}_2\text{H}_6 \quad (11) \]

In spite of the fact that (11) has zero activation energy, it probably takes place on the wall due to the low concentration of CH\(_3\) and the low frequency of collisions. Reactions (9b), (10) and (11) will probably take place almost exclusively on the walls, because in the gas phase, they will be displaced.
by (4a), (4b), (5a) and (5b). Finally another termination takes place in homogeneous phase.

\[ \text{CH}_3+ \text{n-C}_4\text{H}_9 \rightarrow \text{CH}_4+\text{T} - \text{C}_4\text{H}_8 \quad (12) \]
\[ \text{C}_5\text{H}_{12} \quad (13) \]

The relative rate constants for these reactions are given as

\[ \frac{k_{12}}{k_{13}} = 0.15 \quad (81) \]

These reactions would be of minor importance at higher temperatures but they cannot be excluded.

The products do not follow first order kinetics with time, which suggests some complexity in their mechanism of formation. The main mode is rather (6a) and (6b), especially if the chains are long. The competition in the production of \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \) and the variation of \( \text{CH}_4/\text{C}_2\text{H}_6 \) is explained by reactions (4a) and (4b) on the one hand and (5a*) and (5b) on the other. The variation of \( \text{C}_3\text{H}_6 \) with pressure can be explained by the reaction

\[ \text{M}+\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{M}+\text{CH}_2=\text{CH}=\text{CHCH}_3 \quad (3a) \]

which will take place in homogeneous phase, and of course is favored by increased pressure.

OVERALL MECHANISM

The total mechanism can be summarized as follows:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3+\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \cdot \quad E_A = D(\text{C-C}) \quad (1) \]
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_3^+\text{CH}_3\text{CH} = \text{CH}_2 \quad E_A = 23 \text{ KCal/Mole.} \quad (2a) \]
\[ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \quad E_A = 23 \text{ KCal/Mole.} \quad (2b) \]
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \text{ wall } \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{H} \quad E_A = 40 \text{ KCal/Mole.} \quad (3) \]
\[ \text{M}+\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \cdot \text{homog.} \quad \text{M}+\text{CH}_3. + \text{CH}_3\text{CH} = \text{CH}_2 \quad (3a) \]
The decomposition of neo-pentane was investigated insufficiently. Its energy of activation 53.5 KCal/Mole.
which was found only from two temperatures, appears to be rather low. If the more branched isomer has higher thermal stability and the order of activation energies is reversed, that is

\[ E_A(\text{n-pentane}) \geq E_A(\text{isop.}) \geq E_A(\text{neo-pentane}) \]

the stability order must be governed by the steric factor. The following order must be valid to explain the relative stability in spite of the reversal of activation energies.

\[ P_{\text{neo-pent.}} \ll P_{\text{isopent.}} \ll P_{\text{n-pent.}} \]

It is well known that frequency factors are directly related to the entropy of activation

\[ P = e^{\Delta S^*} / R \]

while the collision number, \( z \), is a function of pressure and temperature.

The entropy for the localized (constant volume) gas, can be given by

\[ \bar{S} = R \left\{ \ln Q^T + T \frac{d \ln Q}{dT} \right\} \]

If we consider that, molecules of saturated hydrocarbons behave like ideal gases with negligible interaction energy, the total partition function should be the product of the partition functions for translation, rotation etc. so

\[ Q_{\text{tot.}} = q_{\text{trans.}} q_{\text{vibr.}} q_{\text{rot.}} q_{\text{el.}} q_{\text{mucl.}} \]

Experimental data show small difference in reactivity between isopentane and n-pentane, but much greater difference between
them and neo-pentane. This point is in agreement with experimental energies of activation. One important point in the treatment of paraffin molecules is that they appear more coiled than straight. Raman spectra of liquid C₄⁻C₇ hydrocarbons show more lines than those corresponding to straight configuration (82,83,84).

In the gas phase less coiling is expected than in liquid, but coiling still exists. Coiling has an important influence on the collision cross section, and thus on the reactivity of the molecule. Coiled molecules interact less than linear molecules to form free radicals, and these steric effects favor attack at the end of the molecule rather than in other parts, in spite of the fact that tertiary or secondary C-H are more vulnerable (85). McCUBREY et al (86) gave values for the collisional area according to Sutherland's equation. The small difference between n- and isopentane 19.6 and 18.9 Å² respectively, gives an account for the similar reactivity. Effective collision diameters given by DARWENT (87) show relative result for n- and isopentane but lower for neo-pentane. These values are 2.94, 3.52 and 1.22 x 10⁻⁸ cm respectively; collisions are much more favored in the case of n- and iso-pentane than in neo-pentane. A third point which relates to the coiling of molecules is the restriction in energy transfer in rotational and vibrational modes. These restrictions can be examined from thermal conductivity data (88). Defining the gas partition function, for no transfer restrictions, we have the following expressions
for partition function:

\[ q = q_{\text{transl.}} + q_{\text{rot.}} + q_{\text{vibr.}} \]

According to the Chapman-Enskog

\[ q_{\text{transl.}} = 2.5\eta \]

and according to the Eucuen's hypothesis

\[ q_{\text{rot.}} = \eta C \quad q_{\text{vib.}} = \eta C \]

where \( \eta \) is the viscosity and \( C \) is the heat capacity. The observed data lie between two extremes

\[ q (\text{no - restriction}) = \eta (2.5C_{\text{transl.}} + C_{\text{rot.}}) \]

\[ q (\text{vibration restriction}) = \eta (2.5C_{\text{transl.}} + C_{\text{rot.}}) \]

For the lower paraffins, there is no evidence for restrictions but for higher, there appear to be a restriction, connected with the coiling of the molecules. So the partition function due to vibrational transference appears to be reduced for more branched hydrocarbons and specifically for neo-pentane. Consequently the total partition function, and entropy in relation with it, will follow the same relationship. Since the \( P \) factor is an exponential function of \( S \), a small change in \( S \), results in a large change in \( P \). Thus

\[ P (\text{neo-pentane}) \ll P n-C_5H_{12} - C_5H_{12} \]

Thus the reduced reactivity can be accounted for.

The main products of neo-pentane decomposition are \( i-C_4H_8 \) and \( CH_4 \). For this reason its decomposition seems to be rather different from that of the other isomers.

The lack of inhibition at least for the first stages
indicates the possible occurrence of two mechanisms. The main process, a molecular rearrangement

\[
\begin{align*}
\text{CH}_3 - \text{C}-\text{CH}_3 & \rightarrow \text{CH}_4 + \text{CH}_2=\text{C}^< \text{CH}_3^> \quad \text{which dominates}
\end{align*}
\]

at least in the initial reaction, and a secondary reaction, a free radical process, indicated by the slight inhibition in overall rates. Lack of data do not allow confirmation of these mechanisms. A free radical mechanism such as

\[
\begin{align*}
\text{CH}_3 - \text{C}-\text{CH}_3 & \rightarrow \text{CH}_3^+ \quad + \quad \text{CH}_3
\end{align*}
\]

(1)

\[
\begin{align*}
\text{CH}_3 - \text{C}-\text{CH}_3 & + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2=\text{C}-\text{CH}_3
\end{align*}
\]

(2)

\[
\begin{align*}
\cdot \text{CH}_2=\text{C}-\text{CH}_3 & \rightarrow \text{CH}_3^+ \quad + \quad \text{CH}_2=\text{C}^< \text{CH}_3^>
\end{align*}
\]

(3)

does not explain the traces of C_3H_6 detected. Nitric oxide could react very easily with the stable radical

\[
\begin{align*}
\text{CH}_3 - \text{C}-\text{CH}_3
\end{align*}
\]

leading to the formation of \((\text{CH}_3)_3\text{C}-\text{NO}\), but this compound was not detected, although it should be reasonably stable. C_3H_6 may come from the pyrolysis of \(\text{CH}_2=\text{C}^< \text{CH}_3^>\).
Nitric oxide was used as the inhibitor in all cases. It was preferred to \( C_2H_6 \) for two reasons. First, because it is a much more potent inhibitor and secondly because, \( C_2H_6 \) is one of the decomposition products, so its consumption during reaction could not be checked. Previous workers found identical products for the normal and fully inhibited decomposition. In the present study, that has been shown to be not the case.

The limiting pressure of \( NO \) appears to be a function of the reaction vessel rather than of the hydrocarbon concentration. This fact can be related to the heterogeneous processes rather than to homogeneous processes. The limiting rate appears to be a function of hydrocarbon pressure for isopentane (Fig. 32.) The following variation of the ratio: rate of uninhibited \( V_0 \)/rate of fully inhibit. \( V_\infty \) with pressure was found

<table>
<thead>
<tr>
<th>P isop.</th>
<th>50 mm</th>
<th>80 mm</th>
<th>100 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_0/V_\infty )</td>
<td>5.3</td>
<td>4.8</td>
<td>3</td>
</tr>
</tbody>
</table>

This variation is contrary to Hinshelwood's ideas, that all chains are suppressed by \( NO \). The suppression is higher for lower pressures. If \( NO \) is related to the surface of the reaction vessel and consequently to heterogeneous processes, then only the heterogeneous ones are to be stopped by \( NO \). For lower pressures therefore, heterogeneous initiation is the predominant initiation reaction, so the rate falls very
sharply. For higher pressures, homogeneous initiation competes successfully with heterogeneous initiation and the reduction of ratio is not so sharp.

I. Isopentane

The required amount of NO, to attain full inhibition is 10 mm for the entire pressure range of 50 - 100 mm. Analysis of the products shows the difference between the normal and fully inhibited decompositions.

This is illustrated in results in Table XII.

**TABLE XII**

**ANALYTICAL RESULTS FOR ISOPENTANE**

<table>
<thead>
<tr>
<th>Products</th>
<th>( \text{Mole.} % )</th>
<th>( \text{NO estimated} )</th>
<th>( \text{NO excluded} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{i-C}<em>5\text{H}</em>{12} )</td>
<td>72</td>
<td>60</td>
<td>64.2</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6 )</td>
<td>10</td>
<td>10.65</td>
<td>11.25</td>
</tr>
<tr>
<td>( \text{i-C}<em>4\text{H}</em>{8} )</td>
<td>6.85</td>
<td>6.1</td>
<td>6.53</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>6.95</td>
<td>12.15</td>
<td>13.0</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>2.16</td>
<td>2.50</td>
<td>2.68</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>1.74</td>
<td>0.95</td>
<td>1.02</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>6.50</td>
<td>---</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>99.70</strong></td>
<td><strong>98.70</strong></td>
<td><strong>98.68</strong></td>
</tr>
</tbody>
</table>

From these results it is obvious that products such as \( \text{CH}_4 \),
$C_2H_4$, $C_2H_6$ are sharply influenced by the NO concentration. The total in the case of fully inhibited decomposition is 98.70 which means that either some NO is lost in the form of $NO_2$ which is kept in the column or in the form of nitroso-compounds, other than $C_2H_5NO$, which were not detected.

The energy of activation was calculated for the fully inhibited reaction and was found to be approximately $5 \, \text{KCal/Mole}$ with an $A$ factor of $1.4 \times 10^{12} \, \text{Sec}^{-1}$.

The estimated values for the rate constants were:

$$k_{519^o} = 1.65 \times 10^2 \, \text{mm min}^{-1}$$
$$k_{502^o} = 7.4 \times 10^2 \, \text{mm min}^{-1}$$

Those values are more or less in agreement with the corresponding ones found for higher pressures in uninhibited reaction; this seems to be reasonable from the point that in the fully inhibited decomposition all heterogeneous processes are stopped and only homogeneous decomposition takes place. This idea is supported by the variation of products with time. From those curves, presented in Chapter III it is concluded that for the later stages of the reaction

$$\frac{d(C_2H_4)}{dt} = k_1 \quad \frac{d(CH_4)}{dt} = k_2 \quad \frac{d(C_3H_6)}{dt} = k_3$$
and $$\frac{d(i-C_4H_8)}{dt} = k_4$$ where $k_1$, $k_2$, $k_3$, and $k_4$ are constants for constant initial pressure of hydrocarbon. Ethane shows a higher order dependence for reasons discussed in Chapter III.

When NO pressures exceed the limiting point, small amounts of a nitroso-compound were detected, which was believed to be $C_2H_5NO$ and whose concentration increased with increasing NO.
The reaction of NO with alkyl radicals has been discussed in the literature for lower temperatures (90,91,92,121). Nitroso-compounds, RNO, were eliminated from the pyrolyses of Hg(R)₂ with NO. Their stability around 350°C. varies as follows:

\[
\text{CH}_3\text{NO} < \text{C}_2\text{H}_5\text{NO} < \text{isopropyl-NO} < \text{tert. butyl-NO}
\]

The temperature used in the present work is very unfavorable for CH₃NO which does not appear at all, while C₂H₅NO is not completely decomposed. The fact that for PNO = 15 mm, there was no detectable C₂H₅NO although this amount is much more than the limiting value in PNO, shows that its decomposition is counterbalanced by its formation, which if favored by an increase in PNO up to 75 mm. The competition between NO and other molecules for C₂H₅ radicals is indicated by the variation of the ratio C₂H₆/C₂H₅NO with PNO, as well as, by the variation of C₂H₄/C₂H₅NO. The PNO used up was higher than the limiting value. The variation of the later ratio is not regular. Some values with PNO are given in Table XIII.
TABLE XIII

VARIATION OF C₂H₄/C₂H₅NO WITH P(NO)

<table>
<thead>
<tr>
<th>P(NO)</th>
<th>$\Delta P/P = 0.15$</th>
<th>$\Delta P/P = 0.2$</th>
<th>$\Delta P/P = 0.3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.37</td>
<td>---</td>
<td>3.38</td>
</tr>
<tr>
<td>40</td>
<td>1.96</td>
<td>1.67</td>
<td>2.9</td>
</tr>
<tr>
<td>50</td>
<td>3.9</td>
<td>1.95</td>
<td>2.14</td>
</tr>
<tr>
<td>75</td>
<td>1.2 ?</td>
<td>4.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

In chapter I the more important ideas about inhibition were introduced. These involve mainly inhibition as a homogeneous phenomenon. The results of the present study are accounted for by different points of views of both heterogeneous and homogeneous reaction. Thus, we are led to a twofold effect of NO. A heterogeneous effect at low concentrations of inhibitor with complete coverage of the active centers, in agreement with Voevodskii's hypothesis. Secondly, at higher concentrations of the inhibitor both heterogeneous and homogeneous effects operate. This later hypothesis is supported by the detection of a nitroso-compound and by the consumption of NO. The adsorption of NO by the walls suppresses not only heterogeneous initiation but also heterogeneous terminations. This later postulate is supported by the observation that surface effects occur even at high pressures of isopentane. This is a contention in disagreement with Voevodskii's ideas. He predicts an influence of surface only for low pressures.
An effect of different S/V ratio in both low and high pressures was found. That NO is not fixed on the wall but it attains a dynamic equilibrium is shown from the fact that NO is consumed slightly even for partially inhibited decompositions. Thus, the distinction between the two roles of NO is not sharp. At low pressure heterogeneous effects predominate and provided that heterogeneous initiation is the main reaction for low pressures, the effect is profound. This has been shown in experiments with full inhibition for the whole pressure range. For pressures lower than 20 (mm) decomposition was hard to detect. At those pressures only heterogeneous processes appear to participate and since they are suppressed decomposition does not occur.

Nitric oxide, itself a radical, is chemisorbed on quartz. Collision between NO and alkyl radicals especially CH₃ and C₂H₅ are more probable on the wall than in the gas phase. A relatively stronger N-C bond causes the rupture of the NO-quartz pseudo-bond and leads to the production of C₂H₅NO and CH₃NO. Nitroso-methane is very unstable and its decomposition is accelerated by NO (93). Collision between C₂H₅, CH₃, C₂H₅NO and CH₃NO on the wall and in the gas phase can take place leading to the production of CH₄, C₂H₄, and C₂H₆.

\[
\begin{align*}
\text{CH₃NO} + \text{CH₃} & \rightarrow \text{C₂H₆+NO} & (a) \\
\text{CH₃NO} + \text{C₂H₅} & \rightarrow \text{C₂H₄+CH₄+NO} & (b) \\
\text{C₂H₅NO} + \text{CH₃} & \rightarrow \text{C₂H₄-CH₄-NO} & (c) \\
\text{C₂H₅NO} + \text{C₂H₅} & \rightarrow \text{C₂H₄+CH₄+NO} & (d)
\end{align*}
\]
In the above set of reactions (a) and (b) are predominant because of the different stability of CH$_3$NO and C$_2$H$_5$NO.

The effect of NO remains largely as a function of the surface as long as we are below the limiting pressure of NO, but for higher amounts, another reaction takes place, the homogeneous reaction between the hydrocarbon and NO. In order to explain the fact that the rate is no longer suppressed, but actually there is some slight acceleration, NO is considered to participate in both homogeneous initiation and termination of chains as has been proposed by a number of previous workers. As far as the first point is concerned, the fact that the limiting amount of NO was independent of the partial pressures of hydrocarbon but is a function of the surface area provides enough support. By increasing the surface the limiting point was shifted to higher NO values. A linear relationship between this shift and the S/V ratio was not expected, since the important factor is not the whole surface but the number of active centers.

The effect of surface has been examined by other workers also for various hydrocarbons with both negative and positive results. PEARDS et al (94) reported some effect of surface which stopped at the early stages. However, they used pressures in the range 50 mm and up in which homogeneous reactions predominates. POLTORAK and VOEVODSKII (95) examining the decomposition of propane found the inhibited rate approximately of second order for an untreated quartz vessel. Treatment of the vessel with HF increased the rates
in the pressure range 30 - 60 (mm). PURNELL and QUINN (32) using different surfaces in the pyrolysis of n-butane report no change in product with the surface. In the present study variation in the product distribution with the surface area was found, particularly in the inhibited reaction. The fact that there is no real effect of surface on C₃H₆ or i-C₄H₈ suggests that the main mode of reaction is not affected by heterogeneous processes. Since heterogeneous initiation is completely suppressed, homogeneous initiation appears to be independent of surface processes. The decomposition can thus start as follows

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]  

(1)

\[ \text{CH}_3^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_4^+ + \text{CH}_3\text{CH}_2\text{C}^-\text{CH}_3 \]  

(2)

\[ \text{CH}_3\text{CO}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]  

(3)

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\]  

(4)

Extending the isomerization hypothesis proposed for isopropyl radicals to isobutyl radicals we get:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{i-C}_5\text{H}_{12} \rightarrow \text{i-C}_5\text{H}_{12} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ \]  

(6)

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\rightarrow \text{CH}_3^+, \text{C}_3\text{H}_6 \]  

(7)

The mechanism is now identical with that for the uninhibited reaction and no effect of NO is involved for higher pressures.
of NO, some homogeneous initiation takes place through collisions as:

\[ i-C_5H_{12} + NO \leftrightarrow i-C_5H_{11} + HNO \]  
\[ i-C_5H_{11} \rightarrow CH_3 + i-C_4H_8 \]  
\[ i-C_5H_{11} \rightarrow C_2H_5 + C_3H_6 \]  

An increase in rate of decomposition is thus expected for higher P(NO). This increase should partially be counterbalanced by homogeneous termination.

The formation of C\(_3\)H\(_6\) is unaffected by both NO and S/V ratio, which means that reaction (4) is unaffected by both P(NO) and S/V ratio. Accordingly reaction (3) must be similarly independent, because the probability in the decomposition of a radical remains unaltered. Actually the concentration of i-C\(_4\)H\(_8\) decreases slowly with NO. Thus there must exist another source of i-C\(_4\)H\(_8\), heterogeneous in nature, and of minor importance.

Ethylene and methane increase with P(NO), while C\(_2\)H\(_6\) decreases. All of them are favored by increased surface. This fact requires that termination is more affected by the surface than propagation. The CH\(_3\) and C\(_2\)H\(_5\) radicals can enter both homogeneous and heterogeneous processes.

\[ C_2H_5 + CH_3 \rightarrow CH_4 + C_2H_4 \quad E_A > 0 \]  

This reaction must predominate in the homogeneous reaction because of the higher probability of C\(_2\)H\(_5\) reacting with CH\(_3\) than of CH\(_3\) reacting with CH\(_3\) or of C\(_2\)H\(_5\) reacting with C\(_2\)H\(_5\). In the same time C\(_2\)H\(_5\) and CH\(_3\) collide with NO on the walls.
giving rise to the formation of \( \text{C}_2\text{H}_5\text{NO} \) and \( \text{CH}_3\text{NO} \).

\[
\begin{align*}
\text{CH}_3 + \text{NO} &\rightarrow \text{CH}_3\text{NO} \quad (9) \\
\text{C}_2\text{H}_5 + \text{NO} &\rightarrow \text{C}_2\text{H}_5\text{NO} \quad (10) \\
\text{CH}_3\text{NO} + \text{CH}_3 &\rightarrow \text{C}_2\text{H}_6 + \text{NO} \quad (11) \\
\text{CH}_3\text{NO} + \text{C}_2\text{H}_5 &\rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 + \text{NO} \quad (11a)
\end{align*}
\]

Reaction (11a) provides an explanation for the increasing of both \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \) as NO increases. At the same time \( \text{C}_2\text{H}_5 \) is retained by NO, and reaction (5) is suppressed, leading to decrease of \( \text{C}_2\text{H}_6 \) with increasing NO.

Nitrosoethane partially reacts with both \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) radicals.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{NO} + \text{CH}_3 &\rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 + \text{NO} \quad (12) \\
\text{C}_2\text{H}_5\text{NO} + \text{C}_2\text{H}_5 &\rightarrow \text{C}_4\text{H}_{10} + \text{NO} \quad (13) \\
\text{C}_2\text{H}_5\text{NO} + \text{C}_2\text{H}_5 &\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{NO} \quad (14)
\end{align*}
\]

Thus NO competes with \( \text{i-C}_5\text{H}_{12} \) in reacting with \( \text{C}_2\text{H}_5 \) causing a reduction in \( \text{C}_2\text{H}_6 \) and consequently an increase in \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \). Increasing the surface means that more molecules of adsorbed NO are available, so higher amounts of \( \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \) are produced. But reaction (11) is not sufficient to predict the increase of \( \text{C}_2\text{H}_6 \) that is observed for the increased surface unless it is assumed that NO also reacts with \( \text{C}_2\text{H}_5 \) homogeneously as follows:

\[
\text{C}_2\text{H}_5 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{NO} \quad (15)
\]
Thus the increased surface reduces the amount of NO available for the homogeneous reaction (15). The formation of C\textsubscript{2}H\textsubscript{5}NO whose stability is enough to allow it to remain as a final product for higher NO concentration, shows a slight increase with NO. Its formation competes with reaction (12), (13), and (14). It is not so stable as (CH\textsubscript{3})\textsubscript{2}CHNO or (CH\textsubscript{3})\textsubscript{3}CNO and at high temperatures its concentration appears constant with the time.

Nitric oxide is consumed in the reaction, but the amount is rather high in comparison with the concentration of C\textsubscript{2}H\textsubscript{5}NO. This raises the question: Is NO consumed only in that way? Actually no indication of other compounds was found in the infra-red, but small amounts of nitroso compound, undetected at the sensitivity used, could be responsible for the NO consumption. The relationship between C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{5}NO gives an indication that NO is consumed in competition with the formation of C\textsubscript{2}H\textsubscript{6}, which means a reaction between CH\textsubscript{3} and C\textsubscript{2}H\textsubscript{5}. This is not proof however that this is the only way.

All products, but C\textsubscript{2}H\textsubscript{6} increase linearly with time; this means, their formation follows a first order reaction for fully inhibited decompositions. Ethane competes with CH\textsubscript{3}NO and C\textsubscript{2}H\textsubscript{5}NO formation. In the first stages it appears very low in concentration, but increases very rapidly while CH\textsubscript{3}NO decomposes completely and C\textsubscript{2}H\textsubscript{5}NO partially.

Abstraction of hydrogen by NO has been proposed in reaction (1a). This is based on the observation that NO, catalyzes acetone decomposition at higher NO concentration. The
mechanism suggested is (53)

\[
\text{CH}_3\text{COCH}_3\text{+NO} \rightarrow \text{CH}_2\text{COCH}_3 + \text{NOH}
\]

The H - atom adjacent to the B - carbonyl are activated. HNO is believed to enter the equilibrium

\[
\text{HNO} \leftrightarrow \text{H} + \text{NO}
\]
or transfer H to another radical. This decomposition reaction can be considered of minor importance, if it will take place at all, in the case of isopentane, since H$_2$ was detected at most in traces.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_3 + \text{NO} \leftrightarrow \text{CH}_3\text{-CH}_2\text{CH}_3 + \text{HNO} \quad (1\alpha)
\]

\[
\text{HNO} \leftrightarrow \text{NO} + \text{H} \quad (16)
\]

\[
\text{CH}_3\text{+NOH} \rightarrow \text{CH}_4\text{+NO} \quad (17)
\]

Another cause of the decrease in C$_2$H$_6$ comes from the reaction

\[
\text{C}_2\text{H}_6\text{+NO} \rightarrow \text{C}_2\text{H}_5\text{+HNO} \quad E_A = 56 \text{ KCal/Mole.} \quad (53) \quad (18)
\]

The last reaction can take place more easily on the wall, where the required energy will be less than 56 KCal/Mole.

II n-pentane

In spite of the fact that inhibition in n-pentane decomposition has been exhaustively examined, relatively little is known so far, as the mechanism is concerned. The inhibition in n-pentane decomposition by NO was discovered by Hinshelwood and many investigations have been done by Hinshelwood and his collaborators (96,97,98,55,99,100). Unfortunately most of the work based on pressure change
results; i.e. for estimation of rates etc. The kinetics of the reaction and certain analytical results have been reported by Partington et al but no variation of the products with P\textsubscript{NO} has been examined. The idea that the products were identical for both inhibited and uninhibited decomposition was accepted in all these works. The apparent chain length given by the ratio of the uninhibited to the inhibited reaction rate, was considered to be very important in accordance with the idea that the inhibited reaction was not a free radical process but a molecular rearrangement. This contention is now believed to be invalid (Chapter I). From the reported values of apparent chain length (71) for isopentane and neo-pentane, it is quite obvious that inhibition falls in the order

\[ n\text{-pentane} > \text{iso-pentane} > \text{neo-pentane} \]

which conforms to the order of their reactivity. The apparent chain lengths decrease for increasing pressure for neo-pentane. This last observation is enough to cause doubt about the idea of complete suppression of chains.

In the present study of n-pentane, no nitroso-compound was detected, yet NO was found to be consumed. The last point raises a question about the fate of NO. The effect in many cases is the same as in the case of iso-pentane but not so marked. n-pentane itself is much more reactive than isopentane and the products which vary highly with NO concentration come from primary processes also. Their changes are of lesser importance.

Nitric oxide also appears to be involved in
heterogeneous processes, but no evidence was found for homogeneous reaction with NO. The relatively high yield of \( \text{C}_2\text{H}_5 \) and \( \text{CH}_3 \) radicals, may cause the decomposition of any nitroso-compound by reaction with these radicals. Finally the main features of the isopentane reactions would take place for \( \text{n-pentane} \) too.

III Neo-pentane

The effect of NO on neo-pentane, if any, is to cause a slight acceleration of rate in the first stages of the reaction, but the overall rate is slightly reduced by NO. Previous workers have calculated an apparent chain length nearly unity, which means that the decomposition is lightly suppressed by NO. This phenomenon does not conform to a free radical process, so radical reaction must participate to a very slight extent. The marked influence of NO on \( \text{i-C}_4\text{H}_8 \), on the one hand and the slight effect on \( \text{CH}_4 \), on the other, suggests that \( \text{CH}_4 \), is the main product with \( \text{i-C}_4\text{H}_8 \), of a molecular rearrangement, while \( \text{i-C}_4\text{H}_8 \) appears also to be main product of a free radical mechanism. The slight effect of NO can be explained by an initiation caused by it.

\[
\text{CH}_3^\cdot + \text{NO} \rightarrow \text{CH}_2^\cdot + \text{HNO}
\]

The activation energy for such a process appear to be around 50 KCal/Mole.

This is followed by:
In such a mechanism an influence of NO on i-C₄H₈ and CH₄ is expected but it does not explain the production of i-C₄H₁₀ found by other workers (94). The present investigation of neo-pentane suffers from a lack of experimental results and no real attempt to explain the mechanism can be made.
CHAPTER V

KINETIC LAWS IN THE THERMAL DECOMPOSITION OF ISOPENTANE

I. Uninhibited reaction

The mechanism for isopentane decomposition has been proposed in chapter IV. Its complexity makes quantitative treatment difficult. In order to find kinetic laws connecting the products with concentration of reactants etc., certain assumptions and facts are used. These are summarized as follows:

Equations (6), (7) and (8) in chapter IV are considered negligible for \( CH_3 \) production and consumption in comparison with (1a), (1b), (2), (4a), (9) and (10). Provided that the chain length is long enough, the main production of \( CH_3 \) comes from (4a), (1a) and (1b) and the main consumption from (2), (9) and (10). Bimolecular reactions like (8) contribute slightly. The same considerations hold for the \( C_2H_5 \) radical; reactions (1c), (3), (4b), (9) and (10) in which it is involved, are considered as the more important. For \( CH_3CHCH_3 \) reaction (1c) and (7a) are important provided that the pressure is high. For \( CH_3-C-CH_2-CH_3 \), reactions (2), (3), (4a) and (4b) are the only important reactions. Isobutene is considered to be produced only by (4a) while \( C_3H_6 \) is formed by (4b) and to a small extent by (6) for low pressures. The ratio \( k_2/k_3 \) is found to be approximately 7.4 (chapter IV).
and the ratio \( \frac{\text{CH}_2}{\text{CH}_3} = C \left( \frac{\text{CH}_3}{\text{CH}_3} / \text{C}_3\text{H}_6 \right) \)

is shown to be \(1/2\). Also \(k_{11a}/k_{11b}\) is approximately 0.5. The ratio \(\text{C}_2\text{H}_4/\text{C}_2\text{H}_6\) attains a nearly constant value approximately 0.85 at high pressures. The ratio \(\text{CH}_4/\text{C}_2\text{H}_6\) attains a nearly constant value of approximately 3. From these two ratios the ratio of \(\text{CH}_4/\text{C}_2\text{H}_4\) has an approximate value at high pressures of 3.2. Other results or assumption are employed as follows.

\[
2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_10 \quad \text{(11b)} \\
\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \quad \text{(11a)}
\]

for the reaction of \(\text{C}_2\text{H}_5\). Recent work (101) from photolysis data gave

\[k_{11a} = 4.2 \times 10^{-1} \text{ sec}^{-1} \]

The value \(k_{11a}/k_{11b}\) appears to take values between 0.12 to 0.40 (101,102,103). Under these conditions a value of approximately 0.20 is assumed to be probable. The homogeneous reaction

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad \text{(8)}
\]
certainly occurs but its steric factor is low

\[P = 8.10^{-6} \quad \text{(104)} \]

so its contribution to the disappearance of \(\text{CH}_3\) is neglected.

The last assumption is concerned with \(\text{CH}_3\text{CHCH}_2\) radical. Both \(\text{i-C}_3\text{H}_7\) and \(\text{n-C}_3\text{H}_7\) have been easily detected at room temperatures (105,106,107,108,109) but the effort to detect them at higher \(T\), failed absolutely (107,110,111,112,113). Thus it is assumed that \(\text{n-}\) and \(\text{iso C}_3\text{H}_7\) decompose very easily at high temperatures so the contribution of reaction (7b) is considered to be unimportant. For the decomposition
the A factor has been given as $3 \times 10^{-9}$ but this seems rather low. Under these assumptions a stationary state calculation for CH$_3$, C$_2$H$_5$, C$_3$H$_7$ and C$_5$H$_{11}$ can be made.

$$
\frac{d[CH_3]}{dt} = k_{la}[i-C_5H_{12}] + k_{lb}[i-C_5H_{12}] - k_2[i-C_5H_{12}CH_3] + \\
+ k_{4a}[iC_5H_{12}] - k_9[CH_3]C_2H_5 - k_{10}[CH_3][C_3H_2] = 0 
$$

(1)

$$
\frac{d[C_2H_5]}{dt} = k_{lc}[i-C_5H_{12}] - k_2[i-C_5H_{12}][C_2H_5] + k_{4b}[i-C_5H_{11}] - k_9[CH_3]C_2H_5 - k_{10}[CH_3][C_2H_5] = 0 
$$

(2)

$$
\frac{d[C_3H_7]}{dt} = k_{lc}[i-C_5H_{12}] - k_7b[C_3H_7][i-C_5H_{12}] - \\
- k_{7a}[C_3H_7] = 0 
$$

(3)

$$
\frac{d[i-C_5H_{11}]}{dt} = k_2[i-C_5H_{12}][CH_3] + k_3[i-C_5H_{12}][C_2H_5] - \\
-(k_{4a}+k_{4b})[i-C_5H_{12}] = 0 
$$

(4)

From (3)

$$
[C_3H_7] = \frac{k_{lc}[i-C_5H_{12}]}{k_{7b}[i-C_5H_{12}] + k_{7a}K_7} \approx \frac{k_{lc}}{k_{7b}} 
$$

(5)

For high-pressure

$$
[C_3H_7] \text{ reaches a limit } \sim \frac{k_{lc}}{k_{7b}} 
$$

By substracting (1) and (2) we get
\[ k_{1a} [i-C_5H_{12}] + k_{1b} [i-C_5H_{12}] - k_2 [i-C_5H_{12}] [CH_3] + k_{4a} [i-C_5H_{12}] - k_{1c} [i-C_5H_{12}] + k_3 [i-C_5H_{12}] [C_2H_5] - k_{4b} [i-C_5H_{12}] = 0 \]  

(6)

From (4) we get

\[ \left[ i-C_5H_{12} \right] = \frac{k_2 [CH_3] + k_3 [C_2H_5] [i-C_5H_{12}]}{k_{4a} + k_{4b}} \]  

(7)

By substituting (7) into (6) and we get

\[ \left\{ k_{1a} + k_{1b} - k_2 [CH_3] \right\} + \left( \frac{k_4 a - k_4 b}{k_{4a} + k_{4b}} \right) \frac{k_2 [CH_3] + k_3 [C_2H_5]}{k_{4a} + k_{4b}} - k_{1c} + k_3 [C_2H_5] [i-C_5H_{12}] = 0 \]

or

\[ k_{1a} + k_{1b} - k_2 [CH_3] + \left( \frac{k_4 a}{k_{4b}} - 1 \right) \left( \frac{k_2 [CH_3] + k_3 [C_2H_5]}{k_{4a} + k_{4b}} \right) - \frac{k_{1c} - k_3 [C_2H_5]}{k_{4b}} = 0 \]  

(8)

Provided that \( CH_2 = C < CH_3 \) and \( C_3H_6 \) are produced almost exclusively by \((4a),(4b)\) we have set

\[ \frac{d [CH_2= C < CH_3]}{dt} = k_4 [i-C_5H_{12}] \]

\[ \frac{d [C_3H_6]}{dt} = k_{4b} [i-C_5H_{12}] \]

Thus:

\[ \frac{i C_4H_8}{C_3H_6} = \frac{k_{4a}}{k_{4b}} = 0.5 \]  

(in accordance with the observed product distribution. No effect of pressure also is predicted, in accordance with the analytical results)
Thus equation (8) becomes

\[
\frac{k_2[CH_3] + k_3[C_2H_5]}{0.5+1} - k_{1c} - k_3[C_2H_5] = 0
\]

or rearranging the above formula

\[
1.5k_{1a} + 1.5k_{1b} - 1.5k_2[CH_3] - 0.5k_2[CH_3] - 0.5k_3[C_2H_5] - 1.5k_{1c} - 1.5k_3[C_2H_5] = 0
\]

Finally

\[-2k_2[CH_3] - 2k_3[C_2H_5] = 1.5k_{1c} - 1.5k_{1b} + 1.5k_{1a}\]

and

\[
\frac{k_2[CH_3] - k_2[C_2H_5]}{k_3} = 0.75 \left( \frac{k_{1a} + k_{1b} - k_{1c}}{k_3} \right)
\]

but

\[
\frac{k_2}{k_3} \approx 7.4 \quad \text{so}
\]

\[
7.4[CH_3] - [C_2H_5] = 0.57 \left( \frac{k_{1a} + k_{1b} - k_{1c}}{k_3} \right)
\]

and

\[
[C_2H_5] = 7.4[CH_3] - 0.57 \left( \frac{k_{1a} + k_{1b} - k_{1c}}{k_3} \right)
\]

The main source of production of \(C_2H_6\) and \(C_2H_4\) are equations (2) and (3) especially at high pressures where the long chain length makes (2) and (3) overwhelmingly predominant over (8) and (9). Thus we can write

\[
\frac{d[C_2H_6]}{dt} = k_3[i-C_5H_{12}][C_2H_5]
\]

\[
\frac{d[CH_4]}{dt} = k_2[i-C_5H_{12}][CH_3]
\]

and after integrating and using the limit in \(\frac{CH_4}{C_2H_6}\) for high
pressures we get

$$\frac{\text{CH}_4}{\text{C}_2\text{H}_6} = \frac{k_2[\text{CH}_3]}{k_3[\text{C}_2\text{H}_5]} \approx 2.7$$  \hspace{1cm} (12)

So $$[\text{CH}_3] = 2.7 \frac{k_3}{k_2} [\text{C}_2\text{H}_5]$$  \hspace{1cm} (13)

and by substituting (13) into (9) we get

$$[\text{C}_2\text{H}_5] = 7.4 \times 2.7 \frac{k_3}{k_2} [\text{C}_2\text{H}_5] - 0.57 \left( \frac{k_{1a}+k_{1b}-k_{1c}}{k_3} \right)$$

or

$$[\text{C}_2\text{H}_5] = \frac{0.57k_2(k_{1a}+k_{1b}-k_{1c})}{20k_3-k_3k_2}$$  \hspace{1cm} (13)

accordingly

$$[\text{CH}_3] = \frac{2.7 \times 0.57(k_{1a}+k_{1b}-k_{1c})}{20k_3-k_2}$$  \hspace{1cm} (14)

The variation of CH$_4$ and C$_2$H$_6$ with the pressure. It is shown that they follow approximately first order kinetics with respect to the pressure. Of course in reality the mechanism is first order only for high pressures where termination reactions are relatively reduced.

Ethylene comes from (5b), (7a), (9) and (11a) and thus

$$\frac{d\text{C}_2\text{H}_4}{dt} = k_5 [n-\text{C}_4\text{H}_9] + k_{7a}[\text{CH}_3\text{CHCH}_2] + k_9[\text{CH}_2\text{C}_2\text{H}_5] + k_{11a}[\text{C}_2\text{H}_5]^2$$

Isopropyl radical is constant for high pressures but slightly dependent on pressure at low pressures, n-butyl
radical depends on \(i-C_5H_{12}\) but at high pressures the contribution of reaction (5) seems to be rather small, because for long chains the abstraction of \(H\) atom from isopentane would be favored. Under these circumstances \(\frac{dC_2H_4}{dt}\) seems to be approximately independent of isopentane concentration for high pressures and slightly dependent on it for low pressures. This behavior approximately agrees with experimental results.

As far as the total rate is concerned we can write

\[
\frac{d[i-C_5H_{12}]}{dt} = (k_{la}+k_{lb}+k_{lc})[i-C_5H_{12}] + k_2[i-C_5H_{12}][CH_3] + k_3[i-C_5H_{12}][C_2H_5] + k_7b[i-C_5H_{12}][C_3H_7]
\]

Substituting (13), (14) and (5) into (15) we get

\[
\frac{d[i-C_5H_{12}]}{dt} = \left(k_{la}+k_{lb}+k_{lc}\right)[i-C_5H_{12}] + \frac{1.53k_2(k_{la}+k_{lb}-k_{lc})}{20k_3-k_2}[i-C_5H_{12}] + 0.57\left(k_{la}+k_{lb}+k_{lc}\right) + k_7b \left(\frac{k_{lb}}{k_{7b}+k_{7a}}\right)[i-C_5H_{12}]
\]

\[
[i-C_5H_{12}] = \frac{k_{la}+k_{lb}}{20k_3-k_2}(20k_3-k_2+1.53k_2+0.57k_2)[i-C_5H_{12}]
\]

\[
+ k_{lc}\left(\frac{20k_3-k_2-1.53k_2-0.57}{20k_3-k_2}\right)[i-C_5H_{12}]
\]

\[
+ k_7b \left(\frac{k_{lc}}{k_{7b}+k_{7a}}[i-C_5H_{12}]\right)[i-C_5H_{12}]
\]
\[
= \left(\frac{k_{1a} + k_{1b}}{20k_3 - k_2}\right)[i-C_5H_{12}] + k_{1c}\left(\frac{20k_3 - 3.1k_2}{20k_3 - k_2}\right)[i-C_5H_{12}]
\]

\[k_{7b}\left(\frac{k_{1c}}{k_{7b} + k_{7a}/[i-C_5H_{12}]}ight)[i-C_5H_{12}]=\]

\[= \left(\frac{k_{1a} + k_{1b}}{20k_3 - k_2}\right)(20k_3 + 1.1k_2) + \frac{k_{1c}(20k_3 - 3.1k_2)}{20k_3 - k_2}[i-C_5H_{12}]
\]

\[+ k_{7b}\left(\frac{k_{1c}}{k_{7b} + k_{7a}/[i-C_5H_{12}]}ight)[i-C_5H_{12}]
\]

\[k_{7b}\] is negligible while reaction (7a) is the only route for \(C_3H_7\) reaction, and thus the last term vanishes, and first ordered kinetics is established. For higher pressures the last term makes some contribution, reaction (7b) is no longer negligible and a slightly higher order results.

Reactions (1a), (1b) and (1c) do not differ by more than \(2-3\) KCal/Mole in activation energy. Reaction (3) is much more slower than reaction (2) especially at low pressures, so the overall rate constant can take the form

\[k_{\text{over}} = k_{\text{1a}}(k_{1a}/20k_3 - k_2)\]

since \(k_{1a}, k_{1b}, k_{1c}\) are approximately the same, for the high temperature of \(500^\circ\text{C}\).

where \(k = 3(20k_3 - 2k_2)\). and provided that reaction (2) and (3) differ by only \(2-3\) K Cal/Mole. it is assumed that

\[20k_3 - k_2 \approx 20k_3 - 2k_2\]

so

\[k_{\text{over}} = k_{1a}/3 \approx k_{1a}.
\]
Thus $K_{over}$ corresponds to the slower initiation process and consequently

$$E_{A(over)} = E_A$$ \hspace{1cm} (1a)$$

but $E_A$ (1a) is the $D(C-C)$. To calculate the bond energy the following data are used.

$$\begin{align*}
\text{CH}_3-\text{CH}-\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CH} \text{CH}_2\text{CH}_3^+ \text{CH}_3 \\
\end{align*}$$

$D(C-C) = \Delta H_f(\text{CH}_3\text{CHCH}_2\text{CH}_3) + \Delta H_f(\text{CH}_3) - \Delta H_f(i-C_5H_{12})$ \hspace{1cm} (71)

$$\begin{align*}
\Delta H_f(\text{CH}_3) &= 31.5 \text{ KCal/Mole.} \\
\Delta H_f(\text{isopentane}) &= -36.92 \text{ KCal/Mole.}
\end{align*}$$

For $\Delta H_f(\text{CH}_3\text{CHCH}_2\text{CH}_2)$: Voedvskii's empirical rule

$$A_{\text{tert.}} = A_{\text{sec.}} - B = A_{\text{prim.}} - 2B$$

So

$$A_{\text{sec.}} = \frac{A_{\text{prim.}} + A_{\text{tert.}}}{2}$$

for the $D(C-H)$ values.

Using the value $D(t-C_4H_9 \rightarrow H) = 89.6 \text{ KCal/Moles}$

and $D(n-C_4H_9 \rightarrow H) = 94 \text{ KCal/Mole.}$

Thus we find $D(\text{sec. C}_4\text{H}_9 \rightarrow H) = 91.8 \text{ KCal/Mole.}$

and using this value in the reaction

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3^+ \text{H}^-$$

we get

$$\Delta H_f(\text{CH}_3\text{CHCH}_2\text{CH}_3) = D(C-H) - \Delta H_f(\text{H}) - \Delta H_f(\text{CH}_3\text{CHCH}_2\text{CH}_3)$$

So

$$\Delta H_f(\text{CH}_3\text{CHCH}_2\text{CH}_3) = D(C-H) - \Delta H_f(\text{H}) - \Delta H_f(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3)$$
\[
162 \quad (116) \quad (117) \\
= 91.8 - 52 - 30.15 = 9.60
\]

Substituting this value into the previous formula for \(D(C-C)\) we get

\[
D(C-C) = 9.6 + 31.5 + 28.70 = 69.8 \text{ KCal/Mole.}
\]

\(E_A^{(exp)} = 64.1 \text{ KCal/Mole.} \) which appears in reasonable agreement with \(E_A^{(calc)}\) value, considering the inevitable error introduced by using thermochemical data. The value of 69.8 KCal/Mole, which calculated for homogeneous processes, must be lower at lower pressures due to heterogeneity, so the calculated value approaches still more the experimental.

II Inhibited decomposition

At low pressures the main effect of NO is the suppression of heterogeneous initiation so \(k_{overall}\) would correspond to \(k_{initial}^{(homog)}\). The activation energy is expected to be a little higher because surface is deactivated by NO. At higher pressures of NO, nitric oxide starts to participate in certain reactions as suggested in Chapter III. The rate must remain unchanged because NO does not interfere in the primary processes which are rate determining. For very high amounts of NO some homogeneous initiation by NO will take place, so slight acceleration is expected, as indicated in reaction (1a) Chapt. IV. \)
The rate can be expressed by
\[-\frac{d}{dt}(i-C_5H_{12}) = \frac{(k_{1a}+k_{1b}+k_{1c})}{20k_3-k_2} (20k_3+1.1k_2)[i-C_5H_{12}] + k_{7b} \left( \frac{k_{1b}}{k_{7b} + \frac{k_{7a}}{[i-C_5H_{12}]}[i-C_5H_{12}]} \right) + k_{1a} [i-C_5H_{12}] [NO] \]
but \(k_{1a}\) is very small.
Isobutene and \(C_3H_6\) appear unaffected by NO, because reactions (4a) and (4b) are not affected by it.
The rate of production of \(C_2H_4\) is given by
\[\frac{d}{dt}[C_2H_4] = k_5 [n-C_4H_9] + k_{7a} [CH_3CHCH_3] + k_9 [CH_3][C_2H_5] + k_{11a} [C_2H_5]^2 + k_6 [CH_3 NO][C_2H_5] + k_c [C_2H_5NO][CH_3] + k_d [C_2H_5 NO][C_2H_5] \]
Normal butyl and \(CH_3CHCH_3\) are not affected by NO concentration but the concentrations of \(CH_3\), and \(C_2H_5\) are constant only for constant NO, because they react with it. Thus the rate appears to depend on a NO concentration to a power greater than unity.
Methane has a similar dependence on NO concentration (Fig. 47).

For \(C_2H_6\) reaction (a) and (b) predict an increase but remembering that the main source of \(C_2H_6\) is reaction (3), reactions (a) and (b) simply compete with (3). At low NO concentration ethyl radical disappears almost completely through reaction (3) but at higher NO concentration the
irreversible process

\[ \text{C}_2\text{H}_5 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{NO} \]

also uses up \( \text{C}_2\text{H}_5 \) rapidly. Thus the yield of \( \text{C}_2\text{H}_6 \) is
reduced by increasing \( P_{\text{NO}} \).
REFERENCES

2. Rice, O.F. and Doley, M.O., J.A.C.S. 55-4245 (1933).
65. Rice, F.O., Johnston, W.R. and Evering, B.L., J.A.C.S. 54-3529 (1932)


111. Paneth, F.H. and Lautsch, W., Ber. 64-B-2708 (1931).
118. C.N. Hinshelwood, Disc. Farad Soc. 2-111 (1947).
APPENDIX I

CALCULATION OF ACTIVATION ENERGIES
AND FREQUENCY FACTORS

1. Isopentane

TABLE XIV

RATE CONSTANTS FOR VARIOUS PRESSURES
AND TEMPERATURES

( $\times 10^3$ ) mm$^{-1}$

<table>
<thead>
<tr>
<th>Pressure (mm)</th>
<th>775$^\circ$K</th>
<th>783$^\circ$K</th>
<th>792$^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5</td>
<td>2.0</td>
<td>3.2</td>
<td>4.9</td>
</tr>
<tr>
<td>70</td>
<td>2.3</td>
<td>3.7</td>
<td>5.4</td>
</tr>
<tr>
<td>100</td>
<td>2.7</td>
<td>4.6</td>
<td>6.4</td>
</tr>
<tr>
<td>150</td>
<td>3.6</td>
<td>5.4</td>
<td>7.5</td>
</tr>
<tr>
<td>200</td>
<td>4.2</td>
<td>7.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The $E_A$ were calculated from Arrhenius equation

$$E_A = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) 2.3 \log \left( \frac{k_2}{k_1} \right)$$

Substituting the values reported above we get table XV.

TABLE XV

Energies of activation with pressure

<table>
<thead>
<tr>
<th>Pressure (mm)</th>
<th>$E_1$ KCal/Mole.</th>
<th>$E_2$ KCal/Mole.</th>
<th>$E_3$ KCal/Mole.</th>
<th>$E$ KCal/Mole.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-50</td>
<td>63.8</td>
<td>61.4</td>
<td>67.3</td>
<td>64.1±2.7</td>
</tr>
<tr>
<td>70</td>
<td>59.2</td>
<td>62.3</td>
<td>55.7</td>
<td>59.1±3.4</td>
</tr>
<tr>
<td>100</td>
<td>62.8</td>
<td>56.5</td>
<td>46.5</td>
<td>55.6</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td>analogous</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

analogous
Frequency factors

substituting $E_A$ values in one of the equations of the system

$$\log k_1 = \log A - \frac{E}{RT_1} \log e$$

$$\log k_2 = \log A - \frac{E}{RT_2} \log e$$

$$\log A = \log k_1 + \frac{E}{RT_1} \log e$$

we get

$$\log A = \log 2\times10^{-3} + \frac{6.4\times10^3}{1.98 \times 775} = 0.434 = -2.7 + 18 = 15.3$$

so

$$A = 1.98 \times 10^{15} \text{ min}^{-1} = 3.3 \times 10^{13} \text{ sec}^{-1}$$

0-50 mm

$$\log A = 14.075$$

so

$$A = 1.19 \times 10^{14} \text{ min}^{-1} = 1.98 \times 10^{12} \text{ sec}^{-1}$$

70 mm

$$\log A = 13.126$$

so

$$A = 1.34 \times 10^{13} \text{ mm}^{-1} = 2.23 \times 10^{11} \text{ sec}^{-1}$$

100 mm

$$\log A = 13.36$$

or

$$A = 2.29 \times 10^{13} \text{ min}^{-1} = 3.8 \times 10^{11} \text{ sec}^{-1}$$

150 mm

$$\log A = 13.92$$

or

$$A = 2.9 \times 10^{13} \text{ min}^{-1} = 4.83 \times 10^{11} \text{ sec}^{-1}$$

II n-pentane

**TABLE XVI**

Rate constants for various pressures and temperatures (x10^2) min^{-1}

<table>
<thead>
<tr>
<th>Pressure (mm)</th>
<th>793(^0)K</th>
<th>802(^0)K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 - 30</td>
<td>1.75</td>
<td>2.9</td>
</tr>
<tr>
<td>50</td>
<td>1.85</td>
<td>2.95</td>
</tr>
<tr>
<td>100</td>
<td>2.7</td>
<td>4.2</td>
</tr>
<tr>
<td>120</td>
<td>3.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>
TABLE XVII

Energy of activation with pressure

<table>
<thead>
<tr>
<th>pressure (mm)</th>
<th>$E_A$ KCal/Mole.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 - 30</td>
<td>66.5</td>
</tr>
<tr>
<td>50</td>
<td>61.5</td>
</tr>
<tr>
<td>100</td>
<td>56.5</td>
</tr>
<tr>
<td>120</td>
<td>55.5</td>
</tr>
</tbody>
</table>

Frequency factor are treated similarly as above.

III Neo-Pentane

TABLE XVIII

Rate constants for various pressures and temperatures ($\times 10^3$) min$^{-1}$

<table>
<thead>
<tr>
<th>pressure (mm)</th>
<th>$T = 793^\circ K$</th>
<th>$T = 813^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-50</td>
<td>7.0</td>
<td>17</td>
</tr>
<tr>
<td>70</td>
<td>9.0</td>
<td>20.0</td>
</tr>
<tr>
<td>100</td>
<td>13.7</td>
<td>30.0</td>
</tr>
</tbody>
</table>

TABLE XIX

Activation energies with pressure

<table>
<thead>
<tr>
<th>pressure (mm)</th>
<th>$E_A$ kCal/Mole.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 - 50</td>
<td>57</td>
</tr>
<tr>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>100</td>
<td>47.5</td>
</tr>
</tbody>
</table>
APPENDIX II

Analytical results for n-pentane

TABLE XX

Analytical results for n-pentane

Mole. %

\( \Delta P/P_0 = 0.4 \quad T = 519^\circ C \quad P_{n-pent.} = 75 \text{ (mm)} \)

<table>
<thead>
<tr>
<th>Products</th>
<th>Mole. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_6)</td>
<td>38</td>
</tr>
<tr>
<td>n-C(<em>5)H(</em>{12})</td>
<td>25</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>11</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>10</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>9.4</td>
</tr>
<tr>
<td>l-C(_4)H(_8)</td>
<td>3.6</td>
</tr>
<tr>
<td>TOTAL</td>
<td>97.0</td>
</tr>
</tbody>
</table>