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A STUDY OF CRACKED GASOLINE (CONTINUED)

AND

THE REACTION OF BROMINE WITH PRIMARY ALIPHATIC ALCOHOLS

A THESIS BY
NAT HUYLER MARSH
PRESENTED TO THE FACULTY OF
THE RICE INSTITUTE
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

HOUSTON, TEXAS

MAY, 1942
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PART I

A STUDY OF CRACKED GASOLINE (CONTINUED)
INTRODUCTION

During the month of September, 1938, a systematic investigation of the chemical constitution of a fraction (27 – 70°) of a typical cracked gasoline was begun. In May, 1940, a thesis (1) for the degree of Master of Arts was prepared which outlined in detail the problem, method of solution, and results obtained up to that date. For purposes of continuity a brief summary of the thesis will now be given.

The material used for analysis was a fraction cut from a cracked gasoline produced from East and West Texas pressure distillate plus reformed naphtha. The fraction was furnished by the Shell Oil Company, Houston Refinery. Before delivery to us, the sample was refluxed first with solid caustic to remove acidic sulfur compounds, then with maleic anhydride to remove conjugated olefins. Following this chemical treatment, the gasoline was distilled through a large chain packed distilling column stated to have sixty theoretical plates. The distillate was collected in sixty-one one-gallon fractions, each of which was sealed in an atmosphere of nitrogen after having been inhibited with 0.005% alpha naphthol added as an isopropyl alcoholic solution.

After delivery to us, the boiling point, density, and refractive index of each fraction were taken. A consideration of the physical properties likely to be found indicated that for pur-
poses of analysis the fractions should be grouped as follows:

<table>
<thead>
<tr>
<th>Group</th>
<th>Fraction Number</th>
<th>Boiling Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-28</td>
<td>27-35</td>
</tr>
<tr>
<td>II</td>
<td>29-44</td>
<td>35-38</td>
</tr>
<tr>
<td>III</td>
<td>45-59</td>
<td>38-70</td>
</tr>
</tbody>
</table>

Equal portions (by volume) from each fraction in the group were combined and treated with bromine (see page ) at low temperatures (−5°C ≤ 0°C). In this way the olefins present were converted into dibromides.

\[
R - \ce{C} \Rightarrow \frac{R}{\ce{C}} - \ce{Br}_2 \rightarrow R - \frac{\ce{C}}{\ce{Br}} - \frac{\ce{C}}{\ce{Br}}
\]

By simple distillation the unreacted saturated hydrocarbons were removed from the less volatile dibromides. The unsaturated hydrocarbons were regenerated from the dibromides by the use of the Gladstone-Tribe (see page 11) copper-zinc couple in the presence of 95% alcohol.

\[
R - \frac{\ce{C}}{\ce{Br}} - \frac{\ce{C}}{\ce{Br}} + \ce{Cu} \xrightarrow{\text{95% alcohol}} \frac{R}{\ce{C}} \Rightarrow R - \frac{\ce{C}}{\ce{Br}} - \frac{\ce{C}}{\ce{Br}} + \ce{Cu} + \frac{\ce{Br}_2}{\text{alcohol}}
\]

Thus a separation of the olefins from the paraffins was obtained.

The saturated and unsaturated portions of each group were separately distilled through a one hundred plate bubble cap column designed by Brunn (3). During the course of these distillations, the reflux ratio was maintained within the range 40/1 to 60/1. Table I gives the data obtained from these analysis distillations.

* — In general, a horizontal interval on the plot of the boiling point versus the volume distilled obtained by distilling a mixture through an efficient fractionating column indicates the presence of either a compound, an asestropic mixture, or two or more compounds each of which boils at the same temperature.
TABLE I

Temperatures at which horizontal intervals occur on the plot of the boiling point versus the volume distilled.

<table>
<thead>
<tr>
<th></th>
<th>Group I</th>
<th></th>
<th>Group II</th>
<th></th>
<th>Group III</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>paraffins</td>
<td>olefins</td>
<td>paraffins</td>
<td>olefins</td>
<td>paraffins</td>
<td>olefins</td>
</tr>
<tr>
<td>28°</td>
<td>30°</td>
<td>36°</td>
<td>36°</td>
<td>36°</td>
<td>36°</td>
<td>36°</td>
</tr>
<tr>
<td>36°</td>
<td></td>
<td>36°</td>
<td>36°</td>
<td>49°</td>
<td>36°</td>
<td>36°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60°</td>
<td>44°</td>
<td>60°</td>
<td>36°</td>
<td>44°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>63°</td>
<td>54°</td>
<td>63°</td>
<td>63°</td>
<td>54°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>68°</td>
<td>63°</td>
<td></td>
<td>67°</td>
<td></td>
</tr>
</tbody>
</table>

In order to determine the nature of the materials represented by the horizontal intervals (see Table I), it was necessary to select from the original sample a fraction boiling in the neighborhood of the interval in question and distill from it a narrow cut, the boiling range of which included the boiling point of the interval. Each narrow cut thus obtained was separated into saturated and unsaturated parts by the bromination-debromination method already described.

The materials from the narrow cuts, after being separated into saturated and unsaturated portions, were again distilled in the hundred plate column using a reflux ratio 50/1 to 100/1. As a result of the careful distillation of the narrow cuts, the compounds isopentane, n-pentane, isohexane, 3-methylpentane, n-hexane, and pentene-1 were obtained pure, while the compounds cyclopentane, benzene, and pentene-2 were isolated but could not be obtained in a high state of purity.
The pure saturated hydrocarbons were identified by comparing their physical properties with those of known compounds, a method which is justified only if the physical data on the unknown and known materials are trustworthy. Fortunately, the physical constants of the paraffin hydrocarbons boiling within the range 27-70 are well known.

The olefins were identified jointly by the method of comparison of physical properties and by the method of ozonolysis.
DISCUSSION OF RESULTS

Thus the work up to May, 1940, accounted for all of the saturated hydrocarbons in the mixture which fall within the boiling range 27-70°, as well as for the unsaturated hydrocarbons boiling up to 36°. The following discussion concerns itself with the unsaturated hydrocarbons boiling within the range 36-70°. The results of the analytical distillations given in Table I indicate that at least six olefins would be encountered in the range mentioned.

The nature of the compounds represented by the 36° and 39° intervals was clarified by the careful distillation of 1,300 ml of olefins whose simple boiling range was 35-39°. Using a reflux ratio of 150/1 two compounds were isolated, one boiling at 36.7° and the other at 33.5°. These compounds were found to be pentene-2 and 2-methylbutene-2. Pentene-2 was identified by ozonolysis

\[
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 + \text{O}_3 \quad \xrightarrow{\text{cold pentane solution}} \quad \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 + \text{O}_2
\]

\[
\text{H}_2\text{O} \quad \xrightarrow{\Delta} \quad \text{CH}_3 - \text{CH} = \text{CH} + \text{H}_2 + \text{CH}_3 + \text{H}_2\text{O}_2,
\]

while 2-methylbutene-2 was identified through its solid nitrososchloride (4).

\[
\text{CH}_3\]
\[
\text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 + \text{Cl} - \text{N}=\text{O} \quad \xrightarrow{\text{ethyl nitrite}} \quad \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3
\]

The 44° interval represented a mixture of two compounds, pentadiene-1,3, and cyclopentene. A separation of these two compounds as such cannot be obtained by distillation through the one hundred plate column because of the closeness of their boiling points (43°
for pentadiene-1,3 and 44.2° for cyclopentene). Advantage was taken of the fact that the addition of bromine to the mixture converted the cyclopentene into a dibromide and the pentadiene-1,3 into a tetrabromide.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

and

\[
\begin{align*}
\text{CH}_3 - \text{CH} & = \text{CH} - \text{CH} = \text{CH}_2 + 2 \text{Br}_2 & \rightarrow & \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 \\
& \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br}
\end{align*}
\]

The resulting di and tetrabromides were readily separated by distillation at reduced pressure. The elimination of bromine from the dibromocyclopentane gave crude cyclopentene, which on distillation (reflux ratio 200/1) gave pure cyclopentene. Cyclopentene was identified by converting it into cyclopentyl alcohol, characteristic derivatives of which were prepared (5), (6).

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{O} & \quad \text{SO}_2 & \quad \text{OH} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

Pentadiene-1,3 was identified through its tetrabromide (7).

The 54° interval was found to contain 4-methylpentene-1.

This compound was easily obtained pure by carefully distilling 925 ml of narrow boiling range olefins. A reflux ratio of 140/1 was used. The pure compound was identified by ozonolysis.

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

(6)
The chief constituent of the 67° interval was found to be hexene-1. Although the distillation for this compound was carried out on a large sample and at a high reflux ratio (100/1), an absolutely pure compound could not be obtained. The high refractive index and high density (see Table II) indicated the presence of a small amount of some compound whose boiling point is very near that of hexene-1. Whatever the impurity, it did not interfere with the identification of hexene-1 by ozonolysis - since both formaldehyde and valeraldehyde were readily obtained.

\[ \text{CH}_3-\text{CH}-\text{CH} = \text{CH} + \text{O}_3 \rightarrow \text{CH}_2-\text{CH} = \text{CH} \]

\[ \text{H}_2 \text{O}_2 \]

The 67° interval represented a mixture inseparable by distillation. The physical properties of the mixture indicated that the constituents were hexene-3 and 2-methylpentene-2. 2-Methylpentene-2 was found to be present in the mixture. The identity of the compound was established with the aid of nitrosyl chloride.

\[ \text{CH}_3 \]

\[ \text{CH} = \text{CH} = \text{CH} + \text{Cl-N}=0 \rightarrow \text{C} = \text{C} = \text{C} \]

\[ \text{H} = \text{C} = \text{C} = \text{C} \]

It is convenient to remember that compounds which have side chains next to a double bond usually give solid nitrosoclorides. Hexene-3 was not positively identified in the mixture for two reasons. First, because no solid derivative for hexene-3 is known. Second, because the ozonolysis of a mixture of 2-methylpentene-2 and hexene-3 would give only propionaldehyde and acetone, both of which could be accounted.
TABLE II

Comparison of physical properties obtained in this and in other laboratories

<table>
<thead>
<tr>
<th>Compound</th>
<th>Investigator</th>
<th>B.P. (760 mm) in °C ± 0.02</th>
<th>d 20/4</th>
<th>n 20/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentene-2</td>
<td>Author (9)</td>
<td>36.6-36.7</td>
<td>0.6506</td>
<td>1.3801</td>
</tr>
<tr>
<td>cis-pentene-2</td>
<td></td>
<td>37.0</td>
<td>0.6562</td>
<td>1.3822</td>
</tr>
<tr>
<td>trans-pentene-2</td>
<td>(10)</td>
<td>36.25</td>
<td>0.6486</td>
<td>1.3790</td>
</tr>
<tr>
<td>2-methylbutene-2</td>
<td>Author (11)</td>
<td>38.54</td>
<td>0.6624</td>
<td>1.3879</td>
</tr>
<tr>
<td>&quot;</td>
<td>(12)</td>
<td>38.4</td>
<td>0.6620</td>
<td>1.3878</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>38.2-38.4</td>
<td>0.6625</td>
<td>1.3877</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>Author (13)</td>
<td>44.25</td>
<td>0.7713</td>
<td>1.42267</td>
</tr>
<tr>
<td>&quot;</td>
<td>(14)</td>
<td>44.3</td>
<td>0.7735</td>
<td>1.42246</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>44.02</td>
<td>0.7716</td>
<td>1.42207</td>
</tr>
<tr>
<td>4-methylpentene-1</td>
<td>Author (15)</td>
<td>54.00</td>
<td>0.6648</td>
<td>1.38332</td>
</tr>
<tr>
<td>&quot;</td>
<td>(16)</td>
<td>53.6-53.9</td>
<td>0.6646</td>
<td>1.3825</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>53.8-54.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexene-1</td>
<td>Author (15)</td>
<td>63.5</td>
<td>0.679</td>
<td>1.390</td>
</tr>
<tr>
<td>&quot;</td>
<td>(17)</td>
<td>63.4-63.7</td>
<td>0.675</td>
<td>1.388</td>
</tr>
<tr>
<td>2-methylpentene-2</td>
<td>Author (15)</td>
<td>67.6-67.7</td>
<td>0.681</td>
<td>1.394</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>67.2-67.5</td>
<td>0.690</td>
<td>1.401</td>
</tr>
</tbody>
</table>

(8)
for if only 2-methylpentene-2 were present.

\[
\begin{align*}
\text{Ozoneysis} & : \text{C}_8 \text{H}_8 \rightarrow \text{C}_8 \text{H}_6 + \text{H}_2 + \text{C}_2 \text{H}_4 + \text{H}_2 \text{O}_2 \\
\text{Ozoneysis} & : \text{C}_8 \text{H}_8 \rightarrow \text{C}_8 \text{H}_6 + \text{H}_2 + \text{C}_2 \text{H}_4 + \text{H}_2 \text{O}_2
\end{align*}
\]

Table II gives the physical properties of the olefins obtained in this laboratory. Comparison data obtained in other laboratories are also given.

A note on the purity of some of the hydrocarbons obtained in this investigation. The compounds given in Table III have been isolated in a high state of purity. The physical properties listed are thought to be good for either or both of the following reasons: first, because each compound has a boiling point that is widely separated from that of its nearest possible neighbor, and/or second, because clean cut methods of chemical separation are available. Details concerning the paraffins listed in the table may be found in reference (1).

Table III

Physical properties of pure hydrocarbons obtained in this laboratory

<table>
<thead>
<tr>
<th>Compound</th>
<th>B,P. (760 mm)</th>
<th>d 20/4</th>
<th>n 20/0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in °C</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>isopentane</td>
<td>27.95</td>
<td>0.6197</td>
<td>1.35392</td>
</tr>
<tr>
<td>n-pentane</td>
<td>36.04</td>
<td>0.6262</td>
<td>1.35768</td>
</tr>
<tr>
<td>isoHexane</td>
<td>60.32*</td>
<td>0.6532</td>
<td>1.37154</td>
</tr>
<tr>
<td>n-hexane</td>
<td>68.76*</td>
<td>0.6534</td>
<td>1.37501</td>
</tr>
<tr>
<td>pentene-1</td>
<td>30.11</td>
<td>0.6415</td>
<td>1.37233</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>44.25</td>
<td>0.7713</td>
<td>1.42267</td>
</tr>
<tr>
<td>4-methylpentene -1</td>
<td>54.00</td>
<td>0.6648</td>
<td>1.38332</td>
</tr>
</tbody>
</table>

* — See page 20
The M. A. thesis (1), page 27, contained a table showing the percentage composition of the 27-70°C fraction taken for analysis. The values of the percentage composition were calculated from distillation data. When the table was first prepared the identity of several of the fractions was unknown. The identity of these fractions has since been determined, hence Table IV may now be considered complete.

**TABLE IV**

Volume % composition of the 27-70°C fraction

<table>
<thead>
<tr>
<th>Boiling Point C</th>
<th>Paraffin</th>
<th>Olefin</th>
<th>Vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.9</td>
<td>isopentane</td>
<td>pentene-1</td>
<td>14.2</td>
</tr>
<tr>
<td>30.1</td>
<td></td>
<td>pentene-2</td>
<td>33.6</td>
</tr>
<tr>
<td>36.0</td>
<td>n-pentane</td>
<td>2-methylbutene-2</td>
<td>18.2</td>
</tr>
<tr>
<td>36.6</td>
<td></td>
<td>pentene-2</td>
<td>11.5</td>
</tr>
<tr>
<td>38.5</td>
<td></td>
<td>2-methylpentene-1</td>
<td>2.9</td>
</tr>
<tr>
<td>44.2</td>
<td></td>
<td>cyclopentene</td>
<td>1.6</td>
</tr>
<tr>
<td>49.0</td>
<td>cyclopentane</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.0</td>
<td></td>
<td>4-methylpentene-1</td>
<td>1.6</td>
</tr>
<tr>
<td>60.3</td>
<td>2-methylpentane</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>63.2</td>
<td>3-methylpentane</td>
<td></td>
<td>3.9</td>
</tr>
<tr>
<td>63.5</td>
<td></td>
<td>hexene-1</td>
<td>1.5</td>
</tr>
<tr>
<td>67.6</td>
<td></td>
<td>2-methylpentene-2</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68.7</td>
<td>n-hexane</td>
<td></td>
<td>0.1</td>
</tr>
</tbody>
</table>

(10)
EXPERIMENTAL

A. CHEMICAL AND PHYSICAL METHODS OF SEPARATION

In order to decrease the complexity of the mixtures to be separated in the search for pure hydrocarbons, it was considered desirable to combine chemical and physical methods of purification. Preliminary distillation divided the 27-70° sample into three fractions. Chemical separations involving the use of bromine (see section 1 below) divided each fraction into olefin and paraffin subfractions. Finally, careful fractional distillation (see section 2 below) of each olefin and paraffin subfraction was carried with the view of obtaining pure hydrocarbons – a goal not reached in every instance.

1. CHEMICAL SEPARATION. - Samples composed of mixtures of olefin and paraffin hydrocarbons were cooled to -5° and bromine was added with stirring until a slight coloration persisted for 10 minutes. In this way the olefins present were converted into high boiling dibromides.

\[
\begin{align*}
R - C = C - R + Br_n & \xrightarrow{\text{cold}} R - C = C - R + Br \cr
\text{at} & \Rightarrow \ R - C = C - R + Br
\end{align*}
\]

Simple distillation served to remove the unreacted paraffins from the dibromides. The last traces of saturates were flashed from the dibromides by reducing the pressure to 45 mm and warming.

The olefins were regenerated from the dibromides by the use of the Gladstone-Tribe copper-zinc couple (2)

\[
\begin{align*}
R - C = C - R + Cu + H_2 + Br_n & \xrightarrow{\text{alcohol}} R - C = C - R + Cu + H_2 + Br_n \\
(11)
\end{align*}
\]
The following adaptation of the Gladstone–Tribe technique was found to be satisfactory.

Fine grained zinc (2 moles, 20 mesh) was agitated with three 150 ml portions of 1.5% cupric sulfate solution. The copper–zinc couple thus prepared was placed in a large three neck flask equipped with stirrer, dropping funnel, thermometer, and an exit tube leading to an efficient condenser. The couple was covered with 150 ml of 95% alcohol and the whole warmed to 70°. The dibromides (1 mole) were added at a rate sufficient to maintain the temperature within the range 70-6°-75°. The olefins distilled from the hot reaction mixture as soon as they were formed.

The olefins resulting from the above reaction were washed with water and dried over anhydrous sodium sulfate. A distillation of the dry olefins through a 20” Widmer removed any dibromides which may have come over during the regeneration reaction. The olefins were inhibited with hydroquinone to prevent oxidation.

2. PHYSICAL SEPARATION—DISTILLATION. — The distillation apparatus used in this investigation was a one hundred plate bubble cap column designed by Bruun (3). Bruun and Faulconer (3) determined the number of theoretical plates (each theoretical plate accomplishes the equivalent of a single simple distillation) in a column of this design using a mixture of n-heptane (b.p. 98.4°) and methylcyclohexane (b.p. 100.8°). The results of their efficiency runs were:

<table>
<thead>
<tr>
<th>Mol % n-heptane</th>
<th>Number of theoretical plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>still pot</td>
<td>top of column</td>
</tr>
<tr>
<td>2.5</td>
<td>76.7</td>
</tr>
<tr>
<td>5.8</td>
<td>87.2</td>
</tr>
</tbody>
</table>

mean 72
The number of theoretical plates was calculated with the aid of an equation proposed by Fenske (28).

\[ \frac{x_{c_i}}{x_{c_k}} = \alpha^{n+1} \frac{x_{f_i}}{x_{f_k}} \]

where

- \( x_{c_i} \) — mol fraction of more volatile compound in the condensate
- \( x_{c_k} \) — " " less " " " " "
- \( x_{f_i} \) — " " more " " " still pot
- \( x_{f_k} \) — " " less " " " " "

\( \alpha \) — ratio of the vapor pressures of the more and less volatile compounds at the temperature of distillation

\( n \) — number of theoretical plates

The Fenske equation holds only for total reflux (no product removed).

The question now arises: What can be done with a fractionating column of 72 theoretical plates? The answer to the above question will be equivalent to answering several less general questions such as: (i) how far apart must two compounds boil before the 72 theoretical plate still will be able to give a product of at least 95% purity with respect to the desired component? (ii) what is the effect of still pot concentration on product purity? (iii) what is the importance of reflux ratio (ratio of the condensate returned to the still to that removed as product? (iv) and finally, how are problems (i), (ii), and (iii) related to each other?

Answers to the questions just proposed may be had by employing equations derived by Smoker (29) and Dodge and Huffman (30). The equations developed by these men adequately relate the variables mentioned. However, these same equations suffer one
serious disadvantage when applied to batch fractionation. The source of the trouble is that the compositions of the still pot and product materials are changing continually through the distillation.

Rose (31) and Rose and Long (32) suggest that the best way to deal with the problem of changing compositions is to use the shape of the actual curve of product composition versus percentage distilled as the measure of effectiveness of separation and thus relate the conditions (\(\alpha\), \(n\), and the reflux ratio, \(R\)) of the distillation directly to the result. As a standard separation, Rose and Long have settled on an average purity of at least 95% for the first 40% distilled. This standard is based on an assumed initial concentration of 50 mol percent. Equivalent results would obtain for all initial concentrations between 10 and 90 mol percent since changes in the initial composition merely displace the distillation curves in a horizontal direction.

After having calculated a large number of batch fractionations, Rose (32) concluded that it is not necessary to fix absolutely the number of plates required to achieve the standard separation. The limits within which \(n\) may vary were found to be:

\[
\begin{align*}
n(\text{maximum}) &= \frac{3.6}{\log \alpha} ; \\
n(\text{optimum}) &= \frac{2.85}{\log \alpha} ; \\
n(\text{minimum}) &= \frac{2.7}{\log \alpha} .
\end{align*}
\]

Once \(n\) has been chosen, the reflux ratio, \(R\), is fixed by the equations:

\[
\begin{align*}
R(\text{min.}) &= \frac{2}{3}n(\text{max.}) ; \\
R(\text{opt.}) &= \frac{1}{3}n(\text{opt.}) ; \\
R(\text{max.}) &= \frac{3}{2}n(\text{min.}).
\end{align*}
\]

The relative volatility, \(\alpha\), (see page 13) may be obtained in several ways: (i) from vapor pressure data, (ii) from
liquid-vapor equilibria, or (iii) from boiling points. Method (iii) is usually used only in the absence of data for methods (i) or (ii).

The calculation of $\alpha$ from boiling points is possible by combining Trouton's rule with the Clausius-Clapeyron equation (31). Using the value of Trouton's constant given in (1) page 32, the expression is

$$\log \alpha = 9.436 \left( \frac{T_B - T_A}{T_A + T_B} \right)$$

Where $T_A$ and $T_B$ are the boiling points (°K) of the compounds A and B. The equation emphasises the dependence of $\alpha$ on the temperature of boiling as well as on the difference in boiling points.

A table may now be prepared as a guide for the use of the 72 theoretical plate still. Combining the equation relating $n$ to $\alpha$ with the equation of $\alpha$ from boiling points, the equation

$$n = \frac{k}{9.436 \left( \frac{T_B - T_A}{T_A + T_B} \right)} = \frac{k}{9.436 \left( \frac{\Delta t}{T_A + T_B} \right)}$$

results, where $n = 72$ and $k$ has the values 3.6, 2.85, or 2.3, depending on the reflux ratio used. The values of $T_A - T_B = \Delta t$ represents the minimum difference in boiling points of compounds A and B which may undergo a standard separation in a still of 72 theoretical plates.
TABLE V

Minimum difference in boiling points of two compounds which may undergo a standard separation in a still of 72 theoretical plates.

<table>
<thead>
<tr>
<th>Average temperature of boiling °C</th>
<th>$\Delta t$ = minimum difference in boiling points</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R = 108/1$</td>
</tr>
<tr>
<td>30°</td>
<td>2.05°</td>
</tr>
<tr>
<td>40°</td>
<td>2.12°</td>
</tr>
<tr>
<td>50°</td>
<td>2.18°</td>
</tr>
<tr>
<td>60°</td>
<td>2.26°</td>
</tr>
<tr>
<td>70°</td>
<td>2.32°</td>
</tr>
</tbody>
</table>

The standard separation was defined as one in which the first 40% of material distilled possessed an average purity of at least 95%. Of this first 40% distilled, the first few percent will exceed and the last few percent will fall short of the required 95% purity — as a consequence of the changing still pot concentration. The same thing may be said, in reverse order, of the last 40% distilled. Thus during the distillation of a two component mixture, the best times at which to collect pure compounds will be at the beginning and at the end of the distillation.

It is to be understood that difference in boiling points greater or less than those shown in Table V will give (under the same conditions of $n$ and $R$) products, the purity of which will be correspondingly greater or less than 95%.

B. PHYSICAL MEASUREMENTS

The methods of measuring density, refractive index, pressure, and temperature were fully described in (1).

(16)
For the present work an improved thermocouple for the measurement of temperature was constructed. The thermocouple, prepared according to the suggestions of W. P. White and others (18), (19), was of the copper-constantan variety, consisting of four junctions (two hot, two cold). Since White found that a cubic equation of the form

\[ e.m.f. = a + bt + ct^2 + dt^3 \]

was quite satisfactory for relating the e.m.f. to the temperature within the range 0 to 100°, then four primary reference points were necessary for the calibration of the couple. The reference points selected were:

<table>
<thead>
<tr>
<th>Reference point</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>0.000</td>
</tr>
<tr>
<td>Sodium sulfate decahydrate transition point (20)</td>
<td>32.384</td>
</tr>
<tr>
<td>Chloroform boiling point (21)</td>
<td>61.204</td>
</tr>
<tr>
<td></td>
<td>(dt/dP = 0.04037)</td>
</tr>
<tr>
<td>Water boiling point (22)</td>
<td>100.000 + 0.0368 (P - 760) + 0.000022 (P - 760)^2</td>
</tr>
</tbody>
</table>

Sodium sulfate decahydrate was purified by the method recommended by the National Bureau of Standards (20); that is, by recrystallizing three times a C.P. grade. Chloroform was purified by distilling a C.P. grade through the one hundred plate still.

Pure water was used for the steam point, and distilled water ice for the ice point.

Temperature-e.m.f. measurements of the liquid standards were made in the distillation apparatus, whereas those of the sodium sulfate decahydrate and ice were carried out in a large test tube.
surrounded by a thermos flask. The cold junction was maintained at 0° in an ice filled one quart thermos flask. E.m.f. measurements were determined with a Leeds and Northrup type K potentiometer. The following data were collected:

<table>
<thead>
<tr>
<th>Standard</th>
<th>t °C</th>
<th>e.m.f. (volts x 10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>0.00</td>
<td>-0.25</td>
</tr>
<tr>
<td>Sodium sulfate decahydrate</td>
<td>32.38</td>
<td>255.9</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61.14</td>
<td>498.2</td>
</tr>
<tr>
<td>Water</td>
<td>100.02</td>
<td>848.8</td>
</tr>
</tbody>
</table>

Equation (i) then becomes

(ii) \( e.m.f. = -0.25 + 7.6298 \; t + 8.7593 \times 10^3 \; t^2 - 3.5236 \times 10^6 \; t^3 \).

According to White (18), the limit of reproducibility of temperature measurements from a correctly calibrated copper-constantan thermocouple is determined by the instrument with which the e.m.f. is measured. The potentiometer-galvanometer apparatus used in this investigation was sensitive to ±0.1 e.m.f. unit (±0.00001 volt). Hence, by equation (ii), the temperature may be read to ±0.02°; but, since a factor of safety must be allowed for, temperatures will be reported to ±0.02°.

It may be noted that equation (ii) gives the e.m.f. as a function of \( t \). During the operation of the still, temperature measurements were made for each 10 ml of distillate collected. In order to avoid the time consuming procedure of solving the third degree equation for each e.m.f. measurement, a table of \( t \), e.m.f. values was prepared. The tabulated values of \( t \) and e.m.f. must cover intervals so small that linear interpolation will introduce no signi-
significant error. As a means of determining the maximum temperature interval for which linear interpolation will introduce no significant error, let

\[ t_1 \] - one tabulated value of temperature
\[ t_2 \] - the next higher tabulated value of temperature
\[ t_i \] - temperature calculated by linear interpolation \( (t_1 < t_i < t_2) \)
\[ t_c \] - temperature calculated from \( E \) using equation (ii)
\[ E_1 \] - e.m.f. corresponding to \( t_1 \)
\[ E_2 \] - e.m.f. corresponding to \( t_2 \)
\[ E_o \] - observed e.m.f. corresponding to \( t_c \), with

\[ E_o = \frac{E_2 - E_1}{2} \quad \text{for maximum effect} \]

then

(iii) \[ E_o = a + bt_c + ct_c^2 + dt_c^3 \]

and

(iv) \[ t_i = t_1 + E_o - E_i \left( \frac{t_1 - t_i}{E_2 - E_1} \right) \]

The solution of equations (iii) and (iv) in the neighborhood of \( 40^\circ \) gave:

<table>
<thead>
<tr>
<th>( t_i - t_1 )</th>
<th>( t_c - t_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.001</td>
</tr>
<tr>
<td>4</td>
<td>0.004</td>
</tr>
<tr>
<td>8</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Therefore, linear interpolation for \( t \) will introduce no significant error if the difference between any two tabulated values of \( t \) is no greater than \( 4^\circ \).
### Table V

Solution to equation (11)

<table>
<thead>
<tr>
<th>t</th>
<th>m.m.f.</th>
<th>Δt/m.m.f.</th>
<th>t</th>
<th>m.m.f.</th>
<th>Δt/m.m.f.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>236.43</td>
<td>0.1223</td>
<td>70</td>
<td>575.55</td>
<td>0.1132</td>
</tr>
<tr>
<td>34</td>
<td>269.15</td>
<td>0.1213</td>
<td>74</td>
<td>610.89</td>
<td>0.1124</td>
</tr>
<tr>
<td>38</td>
<td>302.14</td>
<td>0.1203</td>
<td>78</td>
<td>646.49</td>
<td>0.1116</td>
</tr>
<tr>
<td>42</td>
<td>335.39</td>
<td>0.1193</td>
<td>82</td>
<td>682.35</td>
<td>0.1108</td>
</tr>
<tr>
<td>46</td>
<td>368.91</td>
<td>0.1184</td>
<td>86</td>
<td>718.46</td>
<td>0.1100</td>
</tr>
<tr>
<td>50</td>
<td>402.70</td>
<td>0.1175</td>
<td>90</td>
<td>754.81</td>
<td>0.1093</td>
</tr>
<tr>
<td>54</td>
<td>436.75</td>
<td>0.1166</td>
<td>94</td>
<td>791.42</td>
<td>0.1085</td>
</tr>
<tr>
<td>58</td>
<td>471.06</td>
<td>0.1157</td>
<td>98</td>
<td>828.28</td>
<td>0.1078</td>
</tr>
<tr>
<td>62</td>
<td>505.63</td>
<td>0.1148</td>
<td>102</td>
<td>865.38</td>
<td>0.1071</td>
</tr>
<tr>
<td>66</td>
<td>557.97</td>
<td>0.1140</td>
<td>106</td>
<td>902.73</td>
<td></td>
</tr>
</tbody>
</table>

### C. Boiling Points of 2-Methylpentane and n-Hexane

Using the thermocouple calibrated above, the boiling points of the pure compounds 2-methylpentane and n-hexane (1), page 20 were determined. The boiling point apparatus used was essentially a small distillation column operated under total reflux. The data obtained are given below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.P. (760 mm) in °C ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylpentane</td>
<td>60.32</td>
</tr>
<tr>
<td>n-hexane</td>
<td>68.76</td>
</tr>
</tbody>
</table>

### D. Preparation of Ozone

The ozone generator was constructed from a 45 cm condenser (see diagram). One electrode was made by wrapping the
outside of the condenser's inner tube with tin foil. The other electrode consisted of a brass rod covered with a closely fitting glass tube. Thus a gas passing through the inner tube of the condenser would pass between the electrodes. Connections exposed to ozone may be made of cork. A coating of rosin-beeswax cement was found adequate for preventing leaks at the cork joints. The source of power was a 15,000 volt Neon transformer. During operation the ozone generator was kept cool by running ice water through the condenser jacket.

Commercial oxygen was found to be suitable for use in the ozonizer. Before entering the ozonizer, the oxygen was passed through concentrated sulfuric acid in order to remove any water vapor that might be present. After leaving the ozonizer, the ozonized oxygen was washed with 5% sodium hydroxide and concentrated sulfuric acid (27). When the apparatus was operated at a rate of 9.6 l. 0/hour, the ozone concentration in the oxygen averaged 3.2 volume 5.

E. COMPOUNDS ISOLATED AND/OR IDENTIFIED

1. Pentene-2 and 2-Methylbutene-2. - The source of materials for the isolation of pentene-2 and 2-methylbutene-2 was the fractions 44, 45, and 46. See (1), page 33. A sample boiling within the range 76 - 40°C was distilled from charges from each of these fractions.

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Charge to still (l)</th>
<th>Volume of 76 - 40°C material collected (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>2.0</td>
<td>1.38</td>
</tr>
<tr>
<td>45</td>
<td>3.2</td>
<td>1.43</td>
</tr>
<tr>
<td>46</td>
<td>1.0</td>
<td>0.35</td>
</tr>
</tbody>
</table>

(21)
The olefins present in 3.0 l. of the 36 - 40° sample were converted into dibromides by the addition (see page 11) of 21 moles (3,35 kg) of bromine. The major part of the unreacted paraffins was removed from the dibromides by warming on the steam bath; the last traces were flashed off by reducing the pressure to 45 mm and warming. The regeneration of the olefins from the dibromides using the Gladstone-Tribe copper-zinc couple (see page 11) was carried out with a yield of 70%.

The olefins thus obtained were washed with water and dried with anhydrous sodium sulfate. A distillation of the dry olefins through a 20° Widmer removed any dibromides which may have come over during the regeneration reaction. Hydroquinone was added to the purified olefins to prevent oxidation.

A charge of 1,300 ml of the above olefins was distilled with a reflux ratio of 150/1 to give two flats, a and b.

a. **PENTENE-2.** - The flat a contained 30 ml of material boiling over the range 36.6 - 36.7°, having d20/4 = 0.6506 and n20/D = 1.3801. Ozonolysis revealed this material to be pentene-2 (1), page 24.

Although numerous attempts have been made to separate the isomers of pentene-2, no satisfactory results have yet been published. For further details, see (23) and references given there.

b. **2-METHYL-2-BUTENE-2.** - The flat b contained 40 ml of material boiling at 38.5°, and having d20/4 = 0.6624 and n20/D = 1.3879. This material was identified through its solid nitrosocloride (4).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} - \text{CH} \quad \text{Cl - NO} \\
\text{CH}_3 & \quad \text{CH} - \text{CH}_3
\end{align*}
\]

(22)
A small quantity (about 2 ml) of olefin was mixed with an equal volume of freshly prepared iso-amyl nitrite and cooled in an ice bath. On the addition of 2 ml of cold concentrated hydrochloric acid (added stepwise) a white solid separated. This solid melted at 73.5 - 74° after two recrystallizations from alcohol: mixed melting point with synthetic product 73.5 - 74°.

2. CYCLOPENTENE AND PIPERYLENES. - The source of materials for the isolation of cyclopentene was the fractions 45 and 46. See (1), page 33. A sample boiling within the range 42 - 45° was collected from charges from each of these fractions.

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Charge to still (l.)</th>
<th>Volume of 42 - 45° material collected (l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>3.2</td>
<td>0.89</td>
</tr>
<tr>
<td>46</td>
<td>1.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The olefins present in 1.25 l. of the 42 - 45° sample were converted into dibromides by the addition (see page 11) of 13.5 moles (2.16 kg) of bromine. The major part of the unreacted paraffins was removed from the reaction mixture by warming on the steam bath: the last traces were flashed off by reducing the pressure to 45 mm and warming.

A sample of the dibromides obtained above was cooled in an ice-hydrochloric acid mixture. On standing in the cold for some time, a small amount of crystals settled from the liquid. This solid was found to melt at 114° after two recrystallizations alcohol. Piperylene tetrabromide (1, 2, 3, 4 tetrabromopentane) melts at 114.7° (7).

1, 2 dibromocyclopentane was effectively separated from
piperylene tetrabromide by distillation at reduced pressure. As the result of a vacuum distillation, a 1.94 kg sample of dibromides of the following properties was collected: boiling point 91.5 – 92 at 28 mm, d20/4 = 1.963, and n20/D = 1.548.

The regeneration of the olefin from the purified dibromide using the Gladstone-Tribe copper-zinc couple (see page 11) was carried out with a yield of 89%.

A charge of 590 ml of the above olefin was distilled with a reflux ratio of 200/1 to give only one flat. A portion of this flat (170 ml) was collected and found to have the following properties: boiling point 42.25°, d20/4 = 0.7713, and n20/D = 1.42267.

The olefin was identified as cyclopentene by the series of reactions outlined below. To a cooled mixture of 40 ml of concentrated sulfuric acid and 20 ml of water there was slowly added with shaking 24 ml (18 g) of olefin. Shaking was continued for 10 minutes after all of the olefin had been added. The reaction mixture was diluted with 150 ml of cool water and slowly distilled until a 50 ml distillate was collected. The distillate was saturated with potassium carbonate and the top layer removed. This top layer was dried with anhydrous potassium carbonate and distilled. As a result of the distillation 9 g of an alcohol, boiling point 140 – 141° and n20/D = 1.452 was collected. Noller and Adams (5) give 139° and 1.453 as the boiling point and refractive index of cyclopentanol. The derivatives given below were prepared from the alcohol. Cyclopentyl N-phenylcarbamate, recrystallized from 95% alcohol or ligroin, melting point = 136.0 – 136.4°; mixed melting point with synthetic = 136.0 – 136.4°. Cyclopentyl N- naphthylcarbamate, recrystallized
from ligroin, melting point = 121.0 - 121.5°; mixed melting point with synthetic = 121.0 - 121.5°. Cyclopentyl p-nitrobenzoate, recrystallized from 50% alcohol, melting point = 58.8 - 59.1°; mixed melting point with synthetic = 58.8 - 59.1°. It may be noted that W. Meiser (6) gives 135° as the melting point of cyclopentyl N-phenylcarbamate.

3. **4-METHYLPENTENE-1.** — The source of material for the isolation of 4-methylpentene-1 was the fraction 47. See (1) page 33. The olefins present in 2.1 l. of this fraction were converted into dibromides by the addition of 11.6 moles (1.86 kg) of bromine. The major part of the unreacted paraffins was removed from the dibromides by warming on the steam bath: the last traces were flashed off by reducing the pressure to 45 mm and warming. The regeneration of the olefins from the dibromides using the Gladstone-Tribe copper-zinc couple (see page 11) was carried out with a yield of 76%.

A charge of 925 of the above olefins was distilled with a reflux ratio of 140/1 to give only one flat. A portion of this flat (120 ml) was collected and found to have the following properties: boiling point = 54.00°, d20/4 = 0.6648, and n20/D = 1.38332. The olefin was identified as 4-methylpentene-1 by ozonolysis. A solution of 3.5 ml of the olefin in 28 ml of n-hexane was placed in a large test tube and cooled to -17° by a mixture of ice and hydrochloric acid contained in a quart thermos bottle. Ozonized oxygen was passed through the cold solution until the exit gas gave a positive test for ozone.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C}=\text{CH}_2 + \text{O}_3 \rightarrow & \quad \text{CH}_3 - \text{CH} - \text{CH} = \text{CH}_2 - \text{CH} - \text{O} \\
& \rightarrow \quad \text{CH}_3 - \text{CH} - \text{CH} = \text{CH}_2 - \text{H} + \text{HCO}_2
\end{align*}
\]
The ozonide in the n-hexane was hydrolysed by refluxing with an excess of 20 mesh zinc (10 g) covered with water (20 ml) containing a trace each of silver nitrate and hydroquinone (24). Advantage was taken of the fact that if a mixture of formaldehyde and any other aldehyde of higher molecular weight is allowed to distribute itself between two immiscible liquids such as water and n-hexane, then the formaldehyde will go largely into the water phase and the higher aldehyde will go largely into the hydrocarbon phase. Accordingly, after the ozonide was hydrolysed (about 30 minutes are required), the hydrolysis mixture was distilled until 15 ml of water in addition to the ozonide hydrolysis products and the n-hexane had been collected.

The formaldehyde present in the aqueous layer of the distillate was converted into methylene-di-beta-napthol (25) by the following method.

First, the aqueous layer was brought to a boil to expell any higher aldehydes which may have been present. Then to 2 ml of this water layer there was added 1 ml of alcohol, 0.04 g of beta-napthol, and 4 drops of concentrated hydrochloric acid. This mixture was boiled until a white solid developed. The solid was filtered from the hot reaction mixture and washed with 1 ml of 50% alcohol. After two re-crystallizations from 50% alcohol, the melting point was found to be
198 - 199°; mixed melting point with the synthetic product 199 - 200°.

The iso-valeraldehyde present in the hydrocarbon layer of the distillate was converted into the p-nitrophenylhydrazone by the method of Dakin (26). Dakin demonstrated that p-nitrophenylhydrazones may be conveniently made by the addition of the aldehyde or ketone to a freshly prepared solution of p-nitrophenylhydrazine in 40% acetic acid.

\[
\begin{align*}
\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}^+ + \text{H}_2\text{N}-\text{NH}-\text{N}=\text{N}=\text{O}_2 & \rightarrow \text{H}_2\text{N}-\text{NH}-\text{N}=\text{N}=\text{O}_2 \\
\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}^+ + \text{H}_2\text{N}-\text{NH}-\text{N}=\text{N}=\text{O}_2 & \rightarrow \text{H}_2\text{N}-\text{NH}-\text{N}=\text{N}=\text{O}_2
\end{align*}
\]

After two recrystallizations from 50% alcohol, the derivative was found to melt at 108 - 109°; mixed melting point with the synthetic product 108 - 109°.

4. HEXENE-1. - The source of materials for the isolation of hexene-1 was the fractions 50, 53, 57, and 59. See (1), page 33. A sample boiling within the range 58 - 66° was collected from each of the above fractions.

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Charge to still (l.)</th>
<th>Volume of 58 - 66° material collected (l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.0</td>
<td>1.27</td>
</tr>
<tr>
<td>53</td>
<td>1.5</td>
<td>0.85</td>
</tr>
<tr>
<td>57</td>
<td>2.5</td>
<td>1.00</td>
</tr>
<tr>
<td>59</td>
<td>2.5</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The olefins present in 3.5 l. of the 58 - 66° sample were converted into dibromides by the addition (see page 11) of 12 moles (1.91 kg) of bromine. The major part of the unreacted paraffins
was removed from the dibromides by warming on the steam bath: the last traces were flashed off by reducing the pressure to 45 mm and warming. The regeneration of the olefins from the dibromides using the Gladstone–Tribe copper–zinc couple (see page 11) was carried out with a yield of 67%.

A charge of 970 ml of the above olefins was distilled with a reflux ratio of 100/1 to give only one flat. It may be noted that the "flat" was not exactly horizontal. A volume of 280 ml was observed to boil within the range 63° - 63.5°; this interval was followed by an additional 40 ml of material boiling at 63.5°. The 40 ml of material boiling at 63.5° had d20/4 = 0.679 and n20/D = 1.390.

The olefin was identified as hexene-1 by ozonolysis.

\[
\text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}_2 + \text{O}_3 \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}\text{-CH}_2\text{-OH}
\]

\[
\text{H}_2\text{O} \xrightarrow{\Delta} \text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}_2 + \text{H}_2\text{O}
\]

The method used was that described for 2-methylpentene-1 (see page 26). Formaldehyde and n-valeraldehyde were the products of the ozonolysis.

Formaldehyde was again identified via the methylene-di-beta-naphthol derivative (25). The derivative, after two recrystallisations from 50% alcohol, melted at 198 - 199°; mixed melting point with synthetic product, 199 - 200°.

n-Valeraldehyde was converted into the 2,4-dinitrophenyl-hydrasone. After two recrystallizations from 95% alcohol the derivative melted at 108 - 109°; mixed melting point with the synthetic
product, 107 - 108°.

5. 2-METHYLPENTENE-2. - The source of materials for the identification of 2-methylpentene-2 was the fractions 57 and 59. See (1), page 33. A sample boiling within the range 66 - 69° was collected from each of these fractions.

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Charge to still (L)</th>
<th>Volume of 66 - 69° material collected (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>2.5</td>
<td>1.1</td>
</tr>
<tr>
<td>59</td>
<td>2.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The olefins present in 2.3 L of the 66 - 69° sample were converted into dibromides by the addition of 4.2 moles (0.76 kg) of bromine (see page 11). The major part of the unreacted paraffins was removed from the dibromides by warming on the steam bath: the last traces were flashed off by reducing the pressure to 45 mm and warming. The regeneration of the olefins from the dibromides using the Gladstone-Tribe copper-zinc couple (see page 12) was carried out with a yield of 68%.

A charge of 400 ml of the above olefins plus 300 ml of residue from the hexene-1 run was distilled with a reflux ratio of 100/1 to give only one short flat. The 30 ml flat boiled within the range 67.6 - 67.7° and had d20/4 = 0.681 and n20/D = 1.393.

2-methylpentene-2, one of the constituents of this flat, was identified through its solid nitrosochloride.
The method of preparation of the solid nitrosochloride (8) was the same as that described for 2-methylbutene-2 (see page 22). After two recrystallizations from 95% alcohol, the derivative melted at 74 - 75°; mixed melting point with the synthetic product, 74 - 75°.

**SUMMARY**

The compounds 2-methylbutene-2, cyclopentene, and 4-methylpentene-1 were isolated in pure form from the 27 - 70° fraction of a typical cracked gasoline. The compounds pentene-2, hexene-1, 2-methylpentene-2, and piperylene were identified in the same sample.

The chemical individuals listed above, together with those reported in the M. A. Thesis, (1) page 28, are the chief constituents of the 27 - 70° fraction of a typical cracked gasoline. Thus the systematic investigation originally proposed, (1) page 4, has been brought to a close.
PART II

THE REACTION OF BROMINE WITH PRIMARY ALIPHATIC ALCOHOLS
INTRODUCTION

The action of halogens on aliphatic alcohols has been the subject of more than a hundred investigations.

A large number of researchers, starting with Liebig (33) in 1832, have studied the action of chlorine (or some salt capable of yielding chlorine) on alcohols, the principle object being the preparation of chloroform or chloral.

On the other hand, relatively few attempts have been made to examine the action of bromine on alcohols. S. Bugarszky (34) and E. nona (35) studied the reaction of bromine with dilute aqueous solutions of alcohols. Their work seemed to justify the assumption that the main reaction in dilute solution may be formulated:

\[
\begin{align*}
R-C{H}_{2}-C{H}_{2}-C{H}_{2}-H + Br_2 & \xrightarrow{H_2O} R-C{H}_{2} + 2 HBr \\
R-C{H}_{2}-C{H}_{2}-C{H}_{2}-H + 2 Br_2 & \xrightarrow{H_2O} R-C{H}_{2}-C{H}_{2}-C{H}_{2}-H + HBr
\end{align*}
\]

Louis Henry (36) used bromine to distinguish between 2° and 3° alcohols. Henry noticed that 2° alcohols reacted violently with bromine. The HBr formed during the reaction

\[
\begin{align*}
R & \xrightarrow{H_2O} \xrightarrow{Br_2} R
\end{align*}
\]

was absorbed at first, i.e., as long as any alcohol remained. The further addition of bromine to the ketone gave halogenated ketones and HBr.

K. N. Malaviya and N. R. Dhar (37) investigated the photo-chemical reaction between bromine and alcohols with the object of
determining quantum yields, effective frequencies, etc. No mention was made of the nature of the reaction products.

L. A. Nikolaev (38) saturated freshly activated samples of charcoal with chlorine, bromine, and iodine. The charcoal samples containing chlorine and iodine were not very active, whereas the sample containing adsorbed bromine was found to react with benzene and ethyl alcohol. The products of the reaction were bromobenzene and ethylbromide.

E. Hardy (39) and J. Traube and O. Neuberg (40) studied the action of bromine on ethyl alcohol. Both reported that the reaction products contained ethyl bromide, HBr, and organic compounds containing various amounts of bromine. Important data, as for example, temperature, reaction time, yields, etc., were not reported.

Etard (41), M. C. Friedel (42), and J. P. J. Dippy, H. B. Watson, and E. D. Yates (43) have investigated the action of bromine on isopropyl alcohol. Quantitative data was given only by Dippy, Watson, and Yates (43). The reaction products obtained from 935 g of bromine and 500 ml of isopropyl alcohol showed the ultimate fate of the bromine to be: 39.6% as isopropylbromide, 28.8% as bromine substitution products of acetone, and 8.5% as HBr.

After having completed his work on the photobromination of paraffin hydrocarbons, Schiller (44) started a study of the bromination of aliphatic alcohols. This investigation involved the addition of bromine to aliphatic alcohols under three distinctively different sets of conditions.

(1). The addition of a small amount of bromine to a primary alcohol. - A small quantity (1 ml) of bromine was placed in 25 ml of pentanol-1 at room temperature. At the end of two weeks, the
color of bromine remained, altho a little HBr could be detected by blowing the breath across the mouth of the containing vessel. Illumination to the bromine-alcohol mixture with a Photoflood lamp did not hasten the reaction.

(2). The addition of a large amount of bromine to a primary alcohol in the presence of copper powder. - The fact that copper powder caused ethyl hypochlorite to explode (45), together with the fact that copper and copper salts are used as elimination catalysts in the Gattermann and Sandmeyer reactions prompted the experiment of pouring bromine into alcohol in the presence of copper powder. During a period of 15 minutes, 37 g (0.23 M) of bromine was added to a mixture of 20.4 g (0.23 M) pentanol-1 and 14.7 g (0.23 M) copper powder. A vigorous reaction took place, accompanied by the production of a large amount of heat. No HBr was observed to escape during the course of the reaction. The main products of the reaction were Cu₂Br₂ and n-amyl bromide. The weight of the n-amyl bromide recovered was 17 g, representing 24.5% of the bromine used; the weight of the Cu₂Br₂ was 32.5 g, accounting for another 49% of the bromine. By subtraction, 26.5% of the bromine remained unaccounted for.

(3). The addition of a large amount of bromine to a primary alcohol in the presence of cupric bromide. - During a period of 10 minutes, 69 g (0.43 M) bromine was added to a mixture of 80 g (1.07 M) butanol-1 and 240 g (1.07 M) cupric bromide. Large quantities of heat were generated during the somewhat rapid addition of the bromine. After all of the bromine had been added, the reaction mixture was refluxed for 10 minutes. An analysis of the reaction products revealed 240 g cupric bromide (i.e., all put in was recov-
ered), 102 g butyl bromide, representing 86.5% of the bromine used, and 13 g n-butyl-alpha-bromo-n-butyrate, representing 8.6% of the bromine used. The conversion of 86% of the initial bromine into alkyl halide seems not to be typical since the average conversion in eight similar reactions was 65%. 
DISCUSSION AND RESULTS

A consideration of some of the details of the reaction of bromine with primary aliphatic alcohols in the presence of copper or cupric bromide (44) gives rise to two important questions:
(i) What role does copper or cupric bromide play in the reaction?
(ii) What is the probable origin of the alkyl bromide found among the reaction products?

In an attempt to answer the questions raised above, the following reactions were carried out.

Bromine (1 M) was added with stirring and cooling to a mixture of copper (1 M) and butanol-1 (1 M) at 15°. When one-half of the bromine had been added, only gray-white Cu₂Br₂ could be seen. (Cu and CuBr₂ cannot exist in the same mixture since the reaction Cu + CuBr₂ → Cu₂Br₂ goes with great ease.) As soon as the addition of the second half of the bromine had been started, black CuBr₂ made its appearance. Analysis of the reaction products revealed that all of the bromine used appeared as cupric bromide; no butyl bromide was formed.

It will be remembered that an experiment using similar molar quantities of primary alcohol, bromine, and copper (44) resulted in 50% of the bromine appearing as cuprous bromide, 25% as alkyl bromide, and 25% unaccounted for. The point of distinction is that the experiment which gave no alkyl bromide was carried out in the cold, that is, at 15°, whereas the reaction which gave the alkyl bromide was run at an elevated temperature—the elevated temperature arising from the heat developed when bromine was added rapidly to the alcohol-copper mixture.
The fact that the reaction carried out in the cold gave CuBr₂ and no alkyl bromide, while the reaction run in the hot gave Cu₂Br₂ and alkyl bromide suggested that there may be some reaction between CuBr₂ and the alcohol. However, when CuBr₂ was refluxed with butanol-1 for several hours, very little, if any, butyl bromide was formed.

At this point the following conclusions may be drawn: (1) The normal, unhindered reaction of bromine with copper, even in the presence of an alcohol, occurs in the steps shown:

\[ \text{Br}_2 + 2 \text{Cu} \rightarrow \text{Cu}_2\text{Br}_2 \]
\[ \text{Cu}_2\text{Br}_2 + \text{Br}_2 \rightarrow 2 \text{CuBr}_2 \]

(ii) If the addition of bromine (1 M) to copper (1 M) in the presence of alcohol does not result in the formation of CuBr₂ according to the equation

\[ \text{Cu} + \text{Br}_2 \rightarrow \text{CuBr}_2 \]

then there is some reaction which is in competition with the copper for the bromine. This competing reaction is aided by heat and is associated with the formation of alkyl bromide.

Additional information was gained by studying the reaction of bromine with butanol-1 in the presence of cupric bromide. The reaction was carried out at two different temperatures.

The low temperature reaction consisted in the slow addition of bromine to butanol-1 in the presence of cupric bromide at 15 – 20°. After all of the bromine had been added, the reaction was allowed to continue at 20° for 10 hours. Among the reaction products were aldehydes, esters, HBr, free bromine, butyl alcohol, but no butyl bromide. The presence of aldehydes, esters, and HBr, together with
the absence of butyl bromide indicate two things: (i) The bromine had slowly oxidized some of the alcohol, and during the oxidation had itself been reduced to HBr. (ii) The HBr did not react with available alcohol to form butyl bromide at the temperature employed.

The high temperature reaction consisted in the addition of bromine to butanol-1 in the presence of cupric bromide at 100°C. The bromine reacted rapidly and completely with the alcohol. No HBr was observed to escape from the reaction mixture. Butyl alcohol, esters, and butyl bromide were among the reaction products. The amount of butyl bromide obtained represented 59% of the bromine used in the reaction. The reaction just described was repeated with all conditions remaining the same except one; that is, no cupric bromide was used. Again the bromine was rapidly and completely absorbed. Again no HBr was seen to escape from the reaction mixture. This time the butyl bromide obtained from the reaction mixture accounted for 55% of the bromine used. Thus the presence of cupric bromide seems to be of no consequence. The rapid absorption of the bromine by the hot alcohol, the absence of free HBr at the end of the reaction, and the presence of butyl bromide suggest two things: (i) The previously observed slow oxidation of the alcohol by the bromine (and the simultaneous production of HBr) has become much more rapid because of the higher temperature used. (ii) The HBr formed during the oxidation process reacts quickly with the alcohol to give alkyl bromide.

Thus the following may be said about the reaction of bromine with primary alcohols. (1) The reaction at 15 - 20°C. (a) If cupric bromide is or is not present, then the main reaction is the very slow oxidation of the alcohol and the simultaneous production of HBr; the HBr does not react with the alcohol. (b) If copper is present, only
a copper halide is formed. (2) The reaction at or near 100°. (a) If cupric bromide is or is not present, then the main reactions are the rapid oxidation of the alcohol, followed by the equally rapid reaction to the HBr with the alcohol to produce alkyl bromide. (b) If copper is present, then there are competing reactions. (i) Oxidation of the alcohol as in (2)(a) directly above, and (ii) Reaction with copper to give a copper bromide.

Hence it seems that neither copper nor cupric bromide takes part in the reaction of bromine with primary aliphatic alcohols, although in some of the early experiments the reaction of bromine with copper (Cu + \( \frac{1}{2} \) Br = CuBr + 24, 980 cal) did serve to warm up the reaction mixture to the point at which the oxidation reaction could carry on with reasonable speed.

If the technique of reasoning by analogy is permitted, then the mechanism of the reaction of bromine with primary aliphatic alcohols may be something like the following. (Most of the work cited in the reference below was carried out with chlorine and various alcohols.)

1. \( R\text{-}CH\text{-}CH\text{-}OH + Br_2 \rightarrow R\text{-}CH\text{-}CH\text{-}Br + HBr \)
2. \( R\text{-}CH\text{-}CH\text{-}Br \rightarrow R\text{-}CH\text{-}CH\text{-}Br + HBr \)
3. \( R\text{-}CH\text{-}CH\text{-}OH + HBr \rightarrow R\text{-}CH\text{-}CH\text{-}Br + H_2O \)
4. \( R\text{-}CH\text{-}CH\text{-}H + Br_2 \rightarrow R\text{-}CH\text{-}CH\text{-}Br + H_2O \)
5. \( R\text{-}CH \rightarrow R\text{-}CH\text{-}Br + H_2O \)
6. \( R\text{-}CH\text{-}CH\text{-}CH\text{-}R + HBr \rightarrow R\text{-}CH\text{-}CH\text{-}CH\text{-}R + H_2O \)

\( (38) \)
Equation 3. accounts for the alkyl bromide, while equations 4. and 5. account for the bromo ester, the two main compounds found among the reaction products resulting from the action of bromine on primary aliphatic alcohols. Were it not for the formation of the bromo ester, all of the bromine could be utilized to give alkyl bromide.
A. THE REACTION OF BROMINE WITH COPPER IN THE PRESENCE OF n-BUTYL ALCOHOL AT 15°.

To a well stirred mixture of 20 ml (0.22 M) n-butyl alcohol and 12.7 (0.2 M) finely powdered copper maintained at 15°, there was slowly added 32 g (0.2 M) bromine. At the half way point of the bromine addition, only gray-white cuprous bromide could be seen. As soon as the addition of the second half of the bromine was started, black cupric bromide made its appearance. The addition of the rest of the bromine resulted in a thick paste of cupric bromide. Steam distillation of the mixture gave a two layer distillate, the organic portion of which was completely soluble in cold concentrated sulfuric acid. Therefore, no alkyl bromide resulted from the above described reaction.

B. THE REACTION OF CUPRIC BROMIDE WITH COPPER IN THE PRESENCE OF n-BUTYL ALCOHOL.

Cupric bromide, 4.7 g (0.02 M), was slowly added to copper powder, 1.3 g (0.02 M), in the presence of 5 ml n-butyl alcohol.

The cupric bromide reacted immediately with the copper to give gray-white cuprous bromide. Therefore, copper and cupric bromide cannot exist together under the conditions described.

C. THE REACTION OF CUPRIC BROMIDE WITH n-BUTYL ALCOHOL.

Cupric bromide, 7.0 g (0.03 M), was placed in 4 ml n-butyl alcohol and the whole refluxed for five hours. Steam distillation of the mixture gave a two layer distillate, the organic portion of which was completely soluble in cold concentrated sulfuric acid. Therefore, cupric bromide will not react with primary aliphatic
alcohols to yield alkyl bromides.

D. THE REACTION OF BROMINE WITH n-BUTYL ALCOHOL IN THE PRESENCE OF CUPRIC BROMIDE AT 15°.

To a well stirred mixture of 20 ml (0.22 M) n-butyl alcohol and 44.6 g (0.2 M) cupric bromide maintained at 15°, there was slowly added 32 g (0.2 M) bromine. The addition of the bromine required 20 minutes. The reaction mixture was maintained at 15° for 1.5 hours and then at 20° for 10 hours. At the end of the reaction time some free bromine remained. On opening the flask to the atmosphere, dense white fumes of HBr could be observed. The free bromine was destroyed with bisulfite and the volatile contents of the flask steam distilled. During the steam distillation, the ester and aldehyde odor was pronounced. Although the organic portion of the steam distillate was heavier than water, nevertheless it dissolved completely in cold concentrated sulfuric acid. The conclusions drawn from this experiment may be found on page 36.

E. THE REACTION OF BROMINE WITH n-BUTYL ALCOHOL IN THE PRESENCE OF CUPRIC BROMIDE NEAR 100°.

To a boiling mixture of 70 g (0.3 M) cupric bromide in 30 ml (0.33 M) n-butyl alcohol add 16.7 g (0.104 M) bromine over a period of 20 minutes. The bromine reacted rapidly with the hot mixture. No HBr was observed to escape during the reaction. The mixture was refluxed for 1.3 hours after all of the bromine had been added, then steam distilled. The organic layer of the steam distillate was washed with two 25 ml portions of cold concentrated sulfuric acid. The acid insoluble material (butyl bromides) weighed 17 g, representing 59% of the bromine used in the reaction.
F. THE REACTION OF BROMINE WITH n-BUTYL ALCOHOL NEAR 100°.

This reaction was carried out with all conditions, amounts, etc., similar to those given for reaction E. above except that no cupric bromide was used. Again the bromine was rapidly and completely absorbed. Again no HBr was observed to escape from the reaction mixture. The butyl bromide isolated from the steam distillate weighed 16 g, representing 55% of the bromine used in the reaction. The conclusions drawn from experiments E and F may be found on page 37.
SUMMARY

The main product resulting from the reaction of bromine with a primary aliphatic alcohol in an alkyl bromide. The reaction is believed to take place in two steps. The first step is the reduction of the bromine to HBr by the alcohol. The second step is the reaction of the HBr with the alcohol to give an alkyl bromide. Neither step is influenced by copper or cupric bromide. Both steps of the reaction are speeded up by an increase in temperature.

ACKNOWLEDGMENT

See (1), page 28.
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