MERCURY-SENSITIZED PHOTOCHEMICAL REACTIONS
OF ISOPROPYL ALCOHOL

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OF ISOPROPYL ALCOHOL

THESIS

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CHAPTER I

INTRODUCTION

Photochemistry deals with the chemical processes that occur when a material system is illuminated by radiation from an external source. The particle of radiation is called the photon. In some photochemical reactions the photons of radiant energy are absorbed directly by substances engaging in the reaction. In others the activating photon is absorbed by a molecule or ion which is instrumental in initiating the reactions, but remains unchanged when the reaction is complete. The light absorbing substance, which functions as a catalyst for the reaction, is called a sensitizer. In this research the sensitized reaction is the one involved and mercury in the vapor state was employed as a sensitizer.

The sensitizer is usually characterized by a metastable state. A metastable state is an activated energy level which cannot go to a lower state with the emission of radiation. There are two ways in which an atom in a metastable state can get back to ground state. First, it has the

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2Edwin C. Markham and Sherman E. Smith, General Chemistry (Boston, 1954), p. 534.
opportunity to collide with another molecule and thus to lose its excitation energy without radiating. Second, it can gain enough energy to ionize, then pick up an electron and go to either ground state, depending on electron spin, or maybe back to metastable state. In this and preceding work, the first route is seen to be prevalent.\textsuperscript{3}

The energy of the photon is given by the Einstein equation where the quantititized energy is seen to be:

\[ E = N h \nu \]

where \( N \) is Avogadro's number, \( h \) is Planck's constant, and \( \nu \) is the frequency of vibration of the light particles. The units of \( E \) involved have been designated as the einstein.\textsuperscript{4}

The value of the einstein varies with the wavelength due to the fact that the relationship between frequency and wavelength is seen to be:

\[ \nu = \frac{c}{\lambda} \]

where \( c \) is the velocity of light in centimeters seconds\textsuperscript{-1}, and \( \lambda \) is the wavelength of vibration in centimeters.\textsuperscript{5}

The wavelength of the radiation employed was 2537 A, which is the mercury resonance line. Replacing frequency in the Einstein equation by \( \frac{c}{\lambda} \) and solving the expression, it is readily seen that for 2537 A radiation, \( E = 112.8 \) Kcal, per mole. This is seen to be sufficient energy to disrupt


\textsuperscript{4}Moore, \textit{op. cit.}, p. 597.

\textsuperscript{5}Herzberg, \textit{op. cit.}, p. 14.
the C-H (98.2 Kcal mole\(^{-1}\)), the C-O (88 Kcal mole\(^{-1}\)), the O-H (109.4 Kcal mole\(^{-1}\)), and also the C-C (80 Kcal mole\(^{-1}\)) bonds. 6

In a study on the mercury-sensitized photo-chemical reactions of hydrocarbons, Sutton, 7 Walker, 8 and Stallings 9 report that the reaction may be one of a C-C bond rupture or that of a C-H bond rupture, but that of the C-H bond rupture is supported by evidence. In view of this fact, it would be expected that the cleavage in the isopropyl alcohol molecule would occur between the C-H bond. It has also been noted that among tertiary, secondary, and primary hydrogen atoms that the tertiary C-H bond is the weakest; hence, it is the easiest broken. 10 Since isopropyl alcohol has a tertiary C-H bond, this would probably be the one broken preferentially.


In the previous work with mercury-sensitized photochemical reactions of isopropyl alcohol, Brown\textsuperscript{11} concluded that a reaction actually did occur. He was unable to identify the products produced due to small amounts actually obtained. Brown did not perform an analysis on the gaseous product.

In other studies at North Texas State College several relatively low molecular weight hydrocarbons have been subjected to ultraviolet radiation. Gary\textsuperscript{12} and Oliver\textsuperscript{13} irradiated mixtures of isobutane and isobutene and found that higher molecular weight hydrocarbons were produced. Layne\textsuperscript{14} irradiated cyclohexane and concluded that dicyclohexyl was produced. Consequently, on the basis of these findings, it is expected that isopropyl alcohol might undergo a similar reaction producing a higher molecular weight dihydroxy compound, through the cleavage of a tertiary C-H bond and

\begin{itemize}
\item \textsuperscript{12} Felice Gary, "Mercury-Sensitized Photochemical Action on a Mixture of Isobutane and Isobutene," unpublished master's thesis, Department of Chemistry, North Texas State Teachers College, Denton, Texas, June, 1939.
\item \textsuperscript{13} Bob M. Oliver, "The Photo-Alkylation of C\textsubscript{4} Hydrocarbons," unpublished master's thesis, Department of Chemistry, North Texas State Teachers College, Denton, Texas, August, 1942.
\end{itemize}
recombination of the 2-hydroxypropyl free radicals thus formed. The principal product of this reaction is expected to be 2,3-dimethyl-2,3-butanediol. Another possible reaction may be a rupture of the O-H bond on the 2-hydroxpropyl free radical giving rise to acetone. In addition, if any C-C bond scission does occur, a possible product formed might be acetaldehyde or some higher molecular weight aldehyde.

The nature and scope of this problem is to determine from the irradiation of isopropyl alcohol with 2537 Å, the behavior and mechanism of the reaction, since it is known that a reaction does occur. The biggest problem is seen to be the identification of the products. This is due to the very small amounts that are produced. Consequently, this paper will be primarily concerned with how the products were identified.
CHAPTER II

PROCEDURE

The apparatus used in the thermal run was the same as that used by Brown\textsuperscript{1} with the ultraviolet source removed. In photochemical runs, the apparatus consisted of an all glass system with no stopcocks present in the reaction system as shown in Figure 1. Table I gives the legend for Figure 1.

\textbf{TABLE I}

1. Separatory Funnel
2. Condenser-1
3. Condenser-2
4. Mercury Boiler-1
5. Mercury Boiler-2
6. Shield Surrounding Ultraviolet Lamps
7. "Ballast" Tank
8. To Vacuum Pump
9. Manometer-1
10. Manometer-2
11. Condenser-3
12. Main Boiler

\textsuperscript{1}Brown, \textit{op. cit.}
13. Fractionating Column
14. Magnetic Hammer
15. Trap
16. Gas Sample
X - Stopcock
→ - Copper Leads

The apparatus was checked for leaks in advance of each run by evacuating to approximately 2 mm pressure and noting pressure increases over a period of approximately five hours. If a pressure increase was not observed it was concluded that the system was free from leaks. The reaction system was then sealed off at the magnetic hammer (14).

A known volume of isopropyl alcohol was charged into the evacuated system through the separatory funnel (1). The separatory funnel was then sealed off and condenser water and heaters were turned on. The mercury boilers and fractionating column were brought up to operating temperatures. These temperatures were adjusted in such a way so as to produce a steady flow of material throughout the reaction system. The main boiler (12) vaporized the alcohol and it passed up into the fractionating column (13) where a reflux ratio was maintained. Condensers (2) and (3) condensed the vapors and controlled their rate of flow. As the liquid passed to mercury boiler (4) it was again vaporized as it passed up the glass tubing wrapped with a heating coil. The
vapor then passed through radiation zone which consisted of eight fifteen-watt General Electric Germicidal Lamps connected in series and was irradiated with 2537 A. The alcohol vapor was mixed with mercury vapors at boilers (4) and (5). As vapors passed out of radiation chamber they were condensed by condenser-3 (11) and passed on back to main boiler where they were re-cycled.

The radiation chamber consisted of a quartz cylinder, 20 centimeters by 2 centimeters diameter, surrounded by eight General Electric Hygeaire lamps which were all encased in a shield to prevent harmful radiation to workers. A thermometer was encased in radiation chamber so that temperature could be read at all times through a window in the shield.

The "ballast" tank acted to supply an increased volume to the system so pressure increases by gases produced would be more gradual, and to permit a larger yield of products before shutdown forced by pressure increases.

The pressure of the system was read periodically from the open end manometer (9).

When the irradiation period was completed, the seal was broken by the magnetic hammer (14) and the gas was allowed to flow to the "freeze" out trap (15) which was maintained at an acetone-dry ice temperature to freeze out any isopropyl alcohol or other high boiling components. This liquid was removed for identification. From the trap the gas was
allowed to flow to the stopcock (16), where a gas sample could be removed for a molecular weight determination. An infrared spectrum was run on this gas sample on the Perkin-Elmer Model 21 split-beam spectrophotometer.

The liquid remaining in the system was removed for fractionation and identification. The liquid products were fractionated on a Podbielniak Series 3300 Semi-Automatic Micro High Temperature Distillation Analyzer.
CHAPTER III

RESULTS

In the thermal run 185 ml. of isopropyl alcohol was charged into the evacuated system. The properties of charge stock can be observed in Table II and Figure 2. This experiment was allowed to run for 144 hours. There was no pressure increase noticed other than small deviations with temperature. The temperature of system was carried out over a range of 28.5°C to 36°C except for a short period of time when the temperature rose to 133°C.

Upon analysis of recovered liquid, it was seen that it had identical properties with that of charge stock. Table II gives a comparison of some of the physical properties of the charged liquid and the recovered liquid.

TABLE II

PHYSICAL PROPERTIES OF CHARGED LIQUID AND THE RECOVERED LIQUID FROM THERMAL RUN

<table>
<thead>
<tr>
<th></th>
<th>Charge Stock</th>
<th>Recovered Liquid</th>
</tr>
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<tbody>
<tr>
<td>Specific Gravity</td>
<td>.778</td>
<td>.778</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.3735</td>
<td>1.3735</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>82.5°C</td>
<td>81.0°C</td>
</tr>
</tbody>
</table>
Fig. 2—Podbielniak Distillation of Raw Charge Stock.
At the end of the run, the recovered liquid was run on Podbielniak Distillation Column and came over between 80° and 81°C with no deviations. The distillation curves of product and charge stock were identical.

This is seen to be sufficient evidence that a thermal reaction did not occur.

The photochemical run consisted of charging 125 milliliters of doubly-distilled isopropyl alcohol in the evacuated system. The vapor pressure was 77.5 millimeters at 48°C. The time of radiation was 58 hours. The pressure in the system rose steadily throughout the entire run. This is illustrated in Figure 3. The temperature of the experimental range fluctuated between 59°C and 75°C. When the pressure of the system increased above the atmospheric pressure, the run was terminated. The system was allowed to cool to room temperature or 28°C. At this temperature the pressure was 737 millimeters.

An analysis of the gas was made by Perry¹ and it was concluded that it was hydrogen gas.

The liquid sample from boiler was run against charge stock on Perkin-Elmer Model 21 split-beam spectrophotometer and an absorption peak occurred at 5.85 microns showing a carbonyl group to be present. Another moderate absorption peak occurred at 11.37 microns characteristic of acetone.

Fig. 3—Pressure Curve of Photochemical Experiment.
Approximately forty drops of liquid sample was removed from "freeze" out trap and combined with liquid sample removed from boiler. This liquid sample was fractionated by Perry and analyses were made of the fractions. Since a carbonyl group was detected by the spectrophotometer a 2,4-dinitrophenylhydrazine test for aldehydes and ketones was run on one of the fractions. The result was a very positive test and the precipitate was purified to be used as a derivative. A 2,4-dinitrophenylhydrazine derivative of acetone was prepared and purified and melting point determination was made. A mixed melting point was run on the two. These melting points were seen to check close enough to warrant further investigation of likelihood of acetone being present in sample. A semicarbazone derivative of this same fraction was prepared but due to low yield was not purified. However, a melting point was made of this derivative. Table III shows a comparison of observed melting points and theoretical melting points of acetone derivatives.

**TABLE III**

**OBSERVED AND THEORETICAL MELTING POINTS OF ACETONE DERIVATIVES**

<table>
<thead>
<tr>
<th></th>
<th>2,4-dinitrophenylhydrazine</th>
<th>Semicarbazone</th>
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<tbody>
<tr>
<td>Recorded</td>
<td>128</td>
<td>190</td>
</tr>
<tr>
<td>Observed</td>
<td>124</td>
<td>179-180</td>
</tr>
<tr>
<td>Mixed Melting Point</td>
<td>125</td>
<td>179-180</td>
</tr>
</tbody>
</table>
The melting point of semicarbazone derivative varied somewhat from recorded value but no other compound seems to be in this range. Consequently, based on the evidence available, it was concluded acetone was produced as one of the products. Due to small quantity of this material obtained further identification was prevented.

Another analysis was made on a very viscous fraction. Slightly below room temperature the fraction was a solid which melted at 27\(^{\circ}\)C and boiled at 125\(^{\circ}\)C at 747.7 millimeters. The fraction was soluble in both ether and water, placing it in Solubility Class E which contains low molecular weight compounds. A positive ceric nitrate test was observed indicating the presence of a hydroxyl group.\(^2\)

A periodic acid test was also run on this fraction and the result was a very positive test.\(^3\) This positive test indicates two hydroxyl groups present on adjacent carbon atoms. A molecular weight determination was then made using the freezing point depression method. The molecular weight was determined to be 91. However, due to experimental difficulties, this was considered merely an approximation.


Previous work and actual evidence determined from this experiment indicate the formation of 2,3-dimethyl-2,3-butanediol, frequently referred to as pinacol.

Perry\textsuperscript{4} also detected traces of an aldehyde from some of the fractions. However, due to extremely low quantities, he was unable to identify any aldehyde.

Since acetone has been definitely identified, a probable reaction for its formation is as follows:

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

A combination of the two hydrogen atoms would also account for the formation of hydrogen gas that was observed.

The pinacol that was tentatively identified is probably formed in the following manner:

\[
\begin{align*}
\text{H}^+ & \quad \text{OH}^- \\
\text{H} - \text{C} - \text{C} - \text{C} - \text{H} & \quad + \quad \text{H}^+ \quad \text{OH}^- \\
\text{H} - \text{C} - \text{C} - \text{C} - \text{H} & \quad \rightarrow \quad \text{H}^+ \quad \text{O} \quad \text{H}^- \\
\end{align*}
\]

In further work along this line, increasing the volume of the system would be helpful as it would increase the quantity of products produced. The small quantity obtained in this experiment prevented the desired analyses.

It is believed at this time that the liquid material that was frozen out in the "Treeze" out trap was a concentrated

\textsuperscript{4}Perry, \textit{op.-cit.}
solution of one of the products. Isolating it from the other recovered liquid and performing an analysis on it would probably be rewarding. In this experiment the recovered liquid was all added together and fractionated. Since the products were so very dilute, fractionation was very difficult.
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Books


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Unpublished Materials


