MERCURY-SENSITIZED PHOTOCHEMICAL REACTIONS
OF ISOPROPYL ALCOHOL

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OF ISOPROPYL ALCOHOL

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CHAPTER I

INTRODUCTION

The chief concern of the subject of photochemistry is with the chemical reactions resulting from the exposure of a system to radiation. The term radiation, strictly speaking, includes electromagnetic vibrations ranging from electric waves of low frequency, through the infrared, visible and ultraviolet portions of the spectrum on to the high frequency x-rays and γ-rays; the most used range for photochemical reactions, however, is in the visible and ultraviolet regions. In recent years much work has been done with the lower energy portion of the spectrum, radio, and microwave frequencies.

The field of photochemistry has had a slow development since its modern beginning in 1925, when Franck presented a qualitative picture of the variation of potential energy with intermolecular distance for a diatomic molecule (7). The study of photochemistry is beset with such problems as kinetic studies of thermal reactions and the need for monochromatic light.

Light incident upon a system can either be transmitted, refracted and scattered, or absorbed. The light absorbed and the chemical change occurring in a photochemical
reaction are obviously related. The connection can be made by the generalization first presented on theoretical grounds by T. Van Grotthuss (1817) and later by experimental methods by J. W. Draper (1841). The relation is generally known as the Grotthuss-Draper Law, and may be stated as follows: Only radiations which are absorbed by the reacting system are effective in producing a chemical change. It does not follow, however, that all light absorbed produces a chemical change (5).

"A photon of radiation is a unit of radiation which possesses one quantum of radiation. Frequently, however, the term quantum is used interchangeably with the term photon" (4). Several things may happen when a photon interacts with a molecule or an atom. There will be no chemical or physical change if it is not possible for the atom or molecule to use the exact amount of energy which the photon possesses in some manner such as atomic or molecular excitation. If there is some change within the molecule or atom which corresponds to the energy of the photon and is not forbidden by quantum restrictions, there may occur the absorption of energy by the molecule. The molecule may give up the energy by collision with other molecules giving rise to an increase in the thermal or kinetic energy of the latter; thus the transformation from electromagnetic energy to thermal motion. This is the most common effect which occurs in the absorption of radiant energy.
To summarize the types of transformations which may occur, the following list is given.

1. Heat - The temperature of the absorbing medium is increased.

2. Excited molecule - The molecule retains the energy until it is (a) transferred to another molecule by collision or (b) it is combined chemically to another atom or molecule.

3. Dissociation - The excited molecule undergoes a chemical breakdown.

4. Dissociation and excitation - The dissociated fragments are excited and may undergo any reaction which the original excited molecules could have undergone.

5. Ionization - An electron is ejected leaving a positively charged ion.

6. Fluorescence - The excited molecule re-emits at the same wavelength (resonance fluorescence) or at a different wavelength. If there is a time lag, the phenomenon is referred to as phosphorescence.

7. Physical interaction - Electrons give rise to the Compton effect or interaction to give atomic molecular action as in the Raman effect.

Along with the Grotthuss-Draper Law, Einstein's Law of photochemical equivalence must be considered. Einstein's Law in its simplest form may be stated as follows: In a primary photochemical reaction each molecule undergoing reaction is activated by the absorption of one quantum (5).
Using Einstein's Law it is seen that for each gram mole of material reacting, \( N \times (6.023 \times 10^{23}) \) quanta must be absorbed. This number of quanta has been called the "einstein".

The energy \( (E) \) of one quantum is given by the product of Planck's constant \( (h) \) and the frequency \( (\nu) \).

\[
E = h\nu
\]

The energy \( (E) \) per einstein is the product of the energy per quantum and Avogadro's number \( (N) \).

\[
E = Nh\nu
\]

\( E = 6.023 \times 10^{23} \times 6.52 \times 10^{-27} \times \text{ergs/mole} \)

The frequency \( (\nu) \) and wavelength \( (\lambda) \) are related by the following, where \( c \) is the speed of light.

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

\[
E = \frac{2.859 \times 10^5}{\lambda} \text{ Kcal/mole}
\]

where \( \lambda \) is in Angstrom units.

Some reactions, in fact most, do not obey the photochemical equivalent law due to side and chain reactions. To determine if a reaction obeys the law it is necessary to measure the absorbed radiation and the number of molecules decomposed. The quantum yield \( (\phi) \) of efficiency is given by

\[
\phi = \frac{\text{number of molecules decomposed}}{\text{number of quanta absorbed}}
\]

The quantum yield should be one if the Einstein Law of Photochemical Equivalence is to hold exactly. However, this was only for primary reactions.
When the molecules which absorb the light take part in the photochemical reaction only in an indirect manner and act as carriers of the energy, they are referred to as photosensitizers. A photosensitizer is defined as a material which, when present in the system, absorbs the activating radiation without itself being permanently changed and permits the absorbed radiation to be used in starting chemical reactions between other molecules (6).

Mercury has been used as a photosensitizer in various photochemical systems. Mercury vapor is activated by the absorption of 2537 Å radiation. This activation is due to an electronic shift from the $^1S^o$ state (normal) to the $^3P^1$ state. If an excited mercury atom does not collide with other atoms and release the energy in that manner, it will give off 2537 Å radiation and return to the normal state. The life of the activated state is in the order of $10^{-7}$ to $10^{-8}$ seconds (8). The energy of one einstein at 2537 Å is 112.8 Kcal/mole.

The following is a brief resume of the photochemistry of isopropyl alcohol using mercury sensitized reactions with 2537 Å radiation.

Brown (2) ran an experiment with isopropyl alcohol, mercury vapor and 2537 Å radiation for 550 hours. A gas product having a molecular weight of twenty-three was obtained along with a liquid which had a higher boiling point than pure isopropyl alcohol. The liquid from the run contained some solid product but of an insufficient amount to analyze.
Perry (9), with a run of fifty-eight hours, obtained a gas with a molecular weight of four, and the presence of acetone in the residue was proven. An infrared spectrogram of the gas gave only a small carbon dioxide peak and the gas was assumed to be hydrogen.

Brady (1), with the products of this same run, reported a liquid infrared spectrogram which indicated acetone. The identification of 2,3-dimethyl-2,3-dihydroxybutane was reported. This is often called pinacol.

From the following table of bond energies it is seen that the tertiary C-H bond is the weakest of the C-H bonds, while the O-H bond is strong by comparison. However, 2537 Å radiation (112.8 Kcal/mole) has sufficient energy to disrupt any bond in isopropyl alcohol.

**TABLE I**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O</td>
<td>81.8</td>
</tr>
<tr>
<td>C-C</td>
<td>83.9</td>
</tr>
<tr>
<td>C-H primary</td>
<td>97.7</td>
</tr>
<tr>
<td>C-H secondary</td>
<td>95.2</td>
</tr>
<tr>
<td>C-H tertiary</td>
<td>91.2</td>
</tr>
<tr>
<td>O-H</td>
<td>109.9</td>
</tr>
</tbody>
</table>

By noting the following possible reactions, the most probable products can be shown.
1. \[ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{Hg}^* \rightarrow \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{H}^* + \text{Hg} \]

2. \[ 2\text{H}^* + \text{wall} \rightarrow \text{H}_2 \]

3. \[ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{H}^* \rightarrow \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{H}^* \]

4. \[ \text{Hg}^* + \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \rightarrow \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{Hg} + \text{HO}^* \]

5. \[ \text{H}^* + \cdot \text{OH} \rightarrow \text{H} \cdot \text{O} \cdot \text{H} \]

6. \[ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{Hg}^* \rightarrow \text{H} - \text{C} - \text{C} - \text{C} - \text{H} + \text{H}^* + \text{Hg} \]

The probability of free radicals combining should be rather low. In previous works (1,3,9) the production of acetone and pinacol has been proven. It is noted that propylene and water are excellent possibilities. These products will be discussed in greater detail later.

A discussion of the rate of production of gas and the dependence of gas production rate on the intensity of the radiation will be presented. A quantum yield (moles gas produced/einstein) will be calculated.
BIBLIOGRAPHY

CHAPTER I


CHAPTER II

APPARATUS

The apparatus used consisted of an all glass system similar to that used by Perry (2) and Brady (1). Experimental conditions were held as near constant as possible for each of the runs except as noted about the source. Figure I shows the apparatus used in the experiments. Table II gives the legend for this drawing.

TABLE II

LEGEND

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Entry tube</td>
</tr>
<tr>
<td>2</td>
<td>Reaction zone</td>
</tr>
<tr>
<td>3</td>
<td>&quot;Ballast&quot; tank</td>
</tr>
<tr>
<td>4</td>
<td>Sampling point 1</td>
</tr>
<tr>
<td>5</td>
<td>Sampling point 2</td>
</tr>
<tr>
<td>6</td>
<td>Boiler no. 1</td>
</tr>
<tr>
<td>7</td>
<td>Column no. 1</td>
</tr>
<tr>
<td>8</td>
<td>Condenser system no. 1</td>
</tr>
<tr>
<td>9</td>
<td>Sampling point 3</td>
</tr>
<tr>
<td>10</td>
<td>Boiler no. 2</td>
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<tr>
<td>11</td>
<td>Tap column no. 2</td>
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</table>
TABLE II - Continued

<table>
<thead>
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<th>Symbol</th>
<th>Name</th>
</tr>
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<tbody>
<tr>
<td>12</td>
<td>Sampling point 5</td>
</tr>
<tr>
<td>13</td>
<td>Voltage Column no. 2</td>
</tr>
<tr>
<td>14</td>
<td>Sampling point 4</td>
</tr>
<tr>
<td>15</td>
<td>Mercury boiler 1</td>
</tr>
<tr>
<td>16</td>
<td>Magnetic hammer</td>
</tr>
<tr>
<td>17</td>
<td>Manometer</td>
</tr>
<tr>
<td>18</td>
<td>Thermostatic box</td>
</tr>
<tr>
<td>19</td>
<td>Blower</td>
</tr>
<tr>
<td>20</td>
<td>Condenser no. 2</td>
</tr>
<tr>
<td>21</td>
<td>Mercury boiler 2 and thermometer</td>
</tr>
<tr>
<td>22</td>
<td>Cold condenser</td>
</tr>
<tr>
<td></td>
<td>Copper leads</td>
</tr>
</tbody>
</table>

The system was evacuated and the isopropyl alcohol charged at one; it was then sealed off to prevent leaks through the stopcocks. The system was allowed to attain an equilibrium pressure which was checked for agreement with the recorded vapor pressure of isopropyl alcohol at the temperature of the system.

The temperature of the thermostatic box was raised to seventy degrees centigrade. The blower was started to circulate the air within the box. The voltages on the various boilers and fractionation columns were controlled.
to achieve the desired reflux ratio and flow of alcohol through the system. The voltage on the number two mercury boiler was increased until the temperature was such that the mercury boiled to saturate the vapor passing through the reaction zone with mercury vapor. The ultraviolet source was then energized. This source was a battery of eight General Electric "Hygeaire" fifteen watt lamps. In some runs four alternate lamps were covered with aluminum foil to reduce the intensity of the source. The reaction zone was a section of twenty-five millimeter "Vycor" tubing thirty-five centimeters in length. This was narrowed or necked down at both ends and connected to the pyrex system through thirteen millimeter graded seals.

Alcohol passing through the reaction zone was condensed at condenser twenty-two; the condenser operated at water-ice temperature. The condensate was fractionated in the number one fractionation column and products heavier than isopropyl alcohol were concentrated at sampling point two. From the number one column, the sample moves to the middle of the number two column where products lighter than isopropyl alcohol are sent to the top of the number two column (sampling point five) and are concentrated; pure alcohol is returned to the reaction zone via mercury boilers one and two. The "ballast" tanks (three) served to increase the volume of the system to minimize any pressure increase permitting runs of satisfactory duration.
At the completion of a run, the gas sampling system was evacuated and the magnetic hammer used to break an inclosed seal. The gaseous product was passed through a dry ice-acetone trap very slowly to remove any alcohol at that temperature and pressure. The gas was then compressed into a ten-centimeter infrared sample cell and the spectrogram was obtained on a Perkin-Elmer Model 21 Spectrophotometer. In some runs liquid samples were removed at positions one, two, three, four, and five for identification and concentration checks.
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CHAPTER II


CHAPTER III

RESULTS

Figure 2 is a graph of milligram-moles $\times 10^{-1}$ of gas produced versus time. The heavy line designates runs made with all eight lamps exposed while the dotted line designates runs made with four alternate lamps encased in aluminum foil to prevent their irradiation of the reaction vessel. The slope of the line for full radiation from eight lamps is 1.67 times the slope of the line for radiation from four lamps.

The products are discussed under three headings: gaseous products, liquids lighter than isopropyl alcohol, and liquids heavier than isopropyl alcohol. The last section of this chapter is a general discussion of the analytical methods.

Gaseous Products

The products from the run made by Brady (1) and Perry (3) using a quartz reaction vessel passed through a dry ice-acetone freeze-out trap. These products had a molecular weight of 4.3 and the infrared spectrogram of the gas in a ten centimeter cell at 26.4 centimeters (mercury absolute) pressure was void of absorption peaks. The
Fig. 2--Milligram moles gas vs time
absence of these peaks and the low molecular weight indicated hydrogen (3, p. 19).

The quartz reaction vessel was lost in an explosion and was replaced by a "Vycor" vessel thirty-five centimeters long and two and one-half centimeters in diameter. In experiments employing the Vycor vessel, propylene was found in all of the gaseous products.

A spectrogram of the gas product with 36.2 as a molecular weight is given in Figure 3. There are strong absorption peaks at 3.4μ, 7.5μ, 10.4μ, and 10.9μ. Conversely, in Figure 4 the infrared spectrogram of pure propylene has absorption peaks at 3.4μ, 5.5μ, 6.2μ, 6.9μ, and 10.9μ. Thus the products of the reaction had two absorption peaks which propylene did not have and the propylene had three peaks which the gaseous product did not show.

The comparison of the infrared spectrograms of the gas products of still other runs and propylene are given in Figure 5. Curve one (dotted) is propylene. Curve two (solid) is the gaseous product. The agreement of the curves is complete except for the products which have an absorption peak at 7.6μ. This peak could be due to an isopropyl group.

\[
\text{CH}_3\text{CH}_2\text{CH}_3
\]
Fig. 3—Gas spectrum
Fig. 5--Pure propylene and product
Liquids - Lighter Than Isopropyl Alcohol

In fractions separated by Brady (1, p. 13) and Perry (3, p. 23), the presence of acetone was proven both by wet laboratory methods and by infrared analysis.

Liquids - Heavier Than Isopropyl Alcohol

In the heavier, bottom liquids the presence of a glycol, pinacol, was substantiated by Carrico (2).

General Analytical Methods

After five minute intervals of irradiation, one milliliter samples were withdrawn at the five sampling points (See Figure 1) by injection of hypodermic needles through the rubber injection caps covered with mercury. It was anticipated that an analysis for the concentration of acetone, pinacol, and water could be achieved. Samples of pinacol in isopropyl alcohol, known milligrams of pinacol per milliliter of alcohol, were prepared and diluted five milliliters of mix to ten milliliters of 2,2,4-trimethylpentane. The absorbency of the known samples with a one to two isopropyl alcohol:2,2,4-trimethylpentane mix in the reference beam of a Beckman DK-1 were made at 235 millimicrons (high absorbency), and at 275 millimicrons (low absorbency). These were plotted as shown in Figure 6. Similar series of absorption versus milligrams acetone per milliliter of isopropyl alcohol were made at 235
millimicrons (low absorbency) and at 275 millimicrons (high absorbency), as is shown in Figure 6. The absorbency of water in isopropyl alcohol at 1935 millimicrons was measured and is illustrated in Figure 6. From this graph, equations for calculating concentrations from the measured absorption in one centimeter quartz cells may be written as follows:

\[
\begin{align*}
A_{275} &= 0.283 c_{\text{acetone}} + 0.025 c_{\text{pinacol}}. \\
A_{235} &= 0.025 c_{\text{acetone}} + 0.120 c_{\text{pinacol}}. \\
A_{1935} &= 0.0590 c_{\text{water}}.
\end{align*}
\]

Samples withdrawn at five-minute intervals were analyzed and the results for the concentration of pinacol, acetone, and water were found to be erratic. The injection caps used for removal of the samples leaked after repeated perforations by the hypodermic needles as was expected. After a fourteen-hour run with four lamps enclosed in aluminum foil, samples were withdrawn at the five sampling points and the results are shown in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Product</th>
<th>Millimoles Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>12.5</td>
</tr>
<tr>
<td>Pinacol</td>
<td>13.5</td>
</tr>
<tr>
<td>Water</td>
<td>5.0</td>
</tr>
<tr>
<td>Gas</td>
<td>12.0</td>
</tr>
</tbody>
</table>
The molecular weight of the gas was approximately ten. The pinacol-acetone ratio was calculated and found to be approximately 1.1:1.0. The gas production, 12.0 milligram moles, was lower than the expected 30.8 milligram moles.

For an actinometer 0.50 molar monochloroacetic acid at seventy degrees centigrade was used. A quantum yield of 0.68 chloride ion per quantum was used (4, p. 2300). The Vycor reaction vessel was filled with monochloroacetic acid and irradiated with the unfiltered radiation from the eight bare lamps. The chloride ion formed was titrated with 0.1N silver nitrate after the solution was neutralized with solid potassium carbonate. The thermal decomposition was taken into account. The Vycor vessels showed $6.3 \times 10^{20}$ quanta absorbed per hour. The same intensity ($I$) absorbed was assumed for the system when mercury vapor at seventy degrees centigrade was the absorbent for 2537 Å radiation. Using eight lamps, the heavy line in Figure 6 shows a quantum yield of 1.39 molecules of gas produced per quantum absorbed. The ratio of absorbed radiation with eight lamps ($I_{\text{abs}8}$) to absorbed radiation with four lamps ($I_{\text{abs}4}$) was found to be 1.32:1.00. From Figure 2, it is seen the ratio of the two rates (eight lamps to four lamps) is 1.67:1.00.

$$\frac{\text{Rate eight lamps}}{\text{Rate four lamps}} = \left( \frac{I_{\text{abs}8}}{I_{\text{abs}4}} \right)^n \Rightarrow 1.67 \approx (1.32)^2$$

The rate of production of products is approximately proportional to $(I_{\text{abs}})^2$. 
The mechanisms for the reactions can not be further elaborated until additional work has been done on the composition of the products as well as concentration time studies.
BIBLIOGRAPHY

CHAPTER III


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Books


Articles


Unpublished Materials

