PHOTOLYSES OF KETENE AT 3130 Å AND 3340 Å

by

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B.Sc., University of Sydney, Australia, 1953

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ABSTRACT

Previous research on the photolyses of ketene at 2700 Å and 3650 Å has shown that considerably different mechanisms are necessary to explain the experimental results. Exactly how the process of deactivation of the excited ketene molecule was affected by change in wavelength was not fully understood.

It was felt that investigations of the primary quantum yields at intermediate wavelengths would be fruitful in obtaining a better understanding of the variation of reaction mechanism with wavelength.

At 2700 Å, using pure ketene, the only primary process is dissociation and therefore the primary quantum yield is unity, while at 3650 Å dissociation occurs by way of an excited state which has a finite lifetime during which the excited ketene molecule may undergo collisional deactivation and internal conversion. At 3650 Å therefore the primary quantum yield is much less than unity even at low pressure, and decreases with increasing pressure.

This research has shown that in the case of ketene at 3130 Å the primary quantum yield is approximately unity at low pressures, 20 mm., and decreases to 0.6 at one atmosphere. At 3340 Å the primary quantum yield is approximately 0.7 at 26 mm. and 0.2 at 400 mm. and increases with increasing temperature.
The dependence of primary quantum yield on pressure at 3130 A and 3340 A was anticipated and can be explained by almost the same mechanism as that proposed for 3650 A radiation. The amount of radiation absorbed during each run was very accurately measured and it was therefore possible to determine quantum yields to within ± 2% at 3130 A, and within ± 10% at 3340 A.

For the photolysis at 3650 A the ratios of the rate constants of collisional deactivation and product formation and of internal conversion and product formation at 26°C are $4.6 \times 10^4$ litres/mole and 28 respectively. At 3130 A and 37°C this research has shown these ratios to be 16.8 litres/mole and zero respectively, while at 3340 A the ratios are $1.64 \times 10^2$ litres/mole and 0.25 at 37°C and $0.99 \times 10^2$ and 0.1 at 100°C.
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Date April 16th, 1958
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My appreciation is due to the British Columbia Sugar Refining Company for a 1957/1958 Scholarship.

I am grateful to Dr. J. Ferguson for performing the transmission determinations on the filter solutions used.

My sincerest thanks go to my wife Margery R. Connelly for the encouragement and assistance given throughout this research and for typing and proofreading this thesis.
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</tbody>
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INTRODUCTION

Previous experiments have shown that the primary quantum yield of ketene decomposition is a function of the wavelength of the absorbed radiation.

At 2700 A Strachan and Noyes \(^1\) found the primary quantum yield to be unity within experimental error, independent of pressure and temperature. At 3650 A \(^1\) the primary quantum yield, extrapolated to zero pressure of ketene, is much less than unity, decreases as pressure is increased and increases with increase in temperature.

Following the absorption of 2700 A radiation and the formation of an excited ketene molecule, dissociation occurs in less time than that required for collision with another molecule, to give a methylene radical and a molecule of carbon monoxide. The methylene radical then attacks another ketene molecule to form ethylene and another carbon monoxide molecule, according to the following mechanism:

\[
\begin{align*}
K + h\nu (2700 \text{ A}) &= K^m \\
K^m &= \text{CH}_2 + \text{CO} \tag{Im} \\
\text{CH}_2 + K &= \text{C}_2\text{H}_4 + \text{CO} \tag{2m}
\end{align*}
\]

where K is a ketene molecule and \(K^m\) is a ketene molecule excited by 2700 A radiation. For each photon absorbed, one molecule of ketene is dissociated, two molecules of carbon monoxide and one molecule of ethylene are formed.
Strachan and Noyes \(^1\) found the quantum yield of carbon monoxide formation to be \(2.12 \pm 0.15\). They also found the ratio of the quantum yield of carbon monoxide formation to the quantum yield of ethylene to be 2.2 instead of the 2.0 expected from reactions (1m) and (2m). It is evident therefore that some methylene radicals are involved in another reaction such as:

\[
\text{CH}_2 + y \text{CH}_2\text{CO} = \text{polymer} + \text{CO}
\]

At 3650 Å, the low quantum yields can be attributed to collisional deactivation and internal conversion of the excited ketene molecules \(^2\), according to the following mechanism:

\[
\begin{align*}
K + h\nu (3650 \text{ Å}) &= K^q \quad (1q) \\
K^q &= \text{products} \quad (2q) \\
K^q &= K \quad (3q) \\
K^q + K &= 2K \quad (4q)
\end{align*}
\]

The energy is dissipated in processes (3q) and (4q) as heat, since no fluorescence has ever been observed.

It is evident from the low quantum yield that reaction (3q) is more rapid than reaction (2q). As the pressure is increased the rate of reaction (4q) increases from zero to become the dominant process. Extrapolation to zero pressure at 26°C gives a carbon monoxide quantum yield of approximately 0.07. At 3650 Å therefore dissociation occurs only after a finite time interval
during which the excited ketene molecule may be deactivated.

Kistiakowsky and Mahan 3 found that the primary quantum yield at 3130 A was independent of pressure and suggested a value of unity. However, they apparently investigated the photolysis over a narrow range of pressures and their results are therefore of minor importance. Investigation of the quantum yield at a number of wavelengths provides the means of determining the relation between the rate of dissociation and the energy of the dissociating molecule.

It was therefore decided to investigate the photolysis of ketene at 3130 A more carefully over a wide range of pressures using a technique whereby quantum yields could be determined to within 1 or 2%. This technique would reveal any small effect of pressure on the primary quantum yield that may have escaped detection in previous work.3

It was felt that since another mercury-arc line, namely 3340 A, occurs between 2700 A and 3650 A, precise quantum yield determinations at this wavelength would substantially increase our understanding of the process of deactivation.
EXPERIMENTAL

A medium pressure 100 watt Hanovia mercury-arc lamp was used as the light source for runs at 3130 A. The lamp was encased in aluminium tubing with a ½" diameter hole opposite the arc. It was found best not to air or water cool the lamp housing. The lamp was run from a constant voltage regulator (115 volts).

For runs at 3340 A a B.T.H. medium pressure mercury-arc lamp was used.

The divergent light beam passed through a combination of two quartz convex lenses of effective focal length 1.5 cm. A filter cell block consisting of two compartments each 2.5 cm. long and with quartz windows, together with a 2 mm. Corning 9863 filter to exclude visible radiation, were placed between the lenses and the cell. The quartz reaction cell of length 14.8 cm. and diameter 3.6 cm. was housed in an aluminium block. Fourteen turns of fine gauge wire, insulated with asbestos sheet from the aluminium, constituted the heating power of the oven.

The entire block was well insulated with asbestos, glass wool, and Alundum cement. A 0-110°C thermometer was mounted in the oven. A thermo-regulator in the aluminium block gave accurate temperature control to within ± 0.1°C. The emergent beam was passed through
another convex lens and focused on the cathode of an RCA 935 photocell.

The filter solutions used at 3130 A were similar to those of Hunt and Davis \(^4\) although the nickel chloride was omitted. Solutions used were:

- Potassium biphthalate \(0.08 \text{ gm/100 ml}\)
- Potassium chromate \(0.008 \text{ gm/100 ml}\)

These solutions in 2.5 cm. cells gave transmissions of:

- 0 at 2700 A
- 36.4% at 3130 A (Filter A)
- 24.0% at 3340 A
- 3.5% at 3650 A

A 2 mm. Corning 9863 filter was used to absorb visible radiation.

The relative intensities of the 3130, 3340 and 3650 A lines of the mercury-arc and the absorption coefficients of ketene at each wavelength indicated that the results obtained with these filter solutions might be appreciably different from results using monochromatic 3130 A radiation.

A second filter was prepared which contained:

- Potassium biphthalate... \(0.08 \text{ gm/100ml}\)
- Potassium chromate... \(0.019 \text{ gm/100 ml}\)
These solutions in 2.5 cm. cells gave transmissions of:

<table>
<thead>
<tr>
<th>Transmission</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2700 A</td>
</tr>
<tr>
<td>16.0%</td>
<td>3130 A</td>
</tr>
<tr>
<td>0.4%</td>
<td>3340 A</td>
</tr>
<tr>
<td>less than 0.1%</td>
<td>3650 A</td>
</tr>
</tbody>
</table>

The Corning 9863 filter was again used.

The filter solutions used at 3340 A consisted of:

- Nickel sulphate hexahydrate... saturated solution
- Naphthalene... 0.44 gm/50 ml. methyl alcohol

Each solution contained in a 1 cm. cell. These solutions were similar to those of Kasha and gave transmissions of:

<table>
<thead>
<tr>
<th>Transmission</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2700 A</td>
</tr>
<tr>
<td>0</td>
<td>3130 A</td>
</tr>
<tr>
<td>26.0%</td>
<td>3340 A</td>
</tr>
<tr>
<td>0.03%</td>
<td>3650 A</td>
</tr>
</tbody>
</table>

A Corning 9863 filter was used as for 3130 A.

**Gas Analyses** were carried out in an all-glass high vacuum system evacuated by a standard type oil pump and a single stage mercury diffusion pump. In this system mercury cut-offs replaced the conventional stopcocks, in order to eliminate the use of stopcock grease wherever possible because of the absorption of ketene and products in the grease.

The carbon monoxide analysis was performed by allowing
the products to flow through successive baths cooled to
-78°C, -196°C, -210°C (dry ice-acetone, liquid nitrogen
and solid nitrogen respectively). The solid nitrogen
trap was prepared by pumping on fresh liquid nitrogen for
about fifteen minutes.

Ketene was condensed in the first two baths and the
ethylene was collected in the solid nitrogen trap.
Carbon monoxide was the only product not condensed at
-210°C and was measured with a McLeod-Toepler gauge ¹.
If, after the carbon monoxide had been collected, the
solid nitrogen trap was removed, a quantity of ethylene
equal to $1/2.14$ of the carbon monoxide yield was
obtained.

**Purification of Diethyl ketone and Ketene**

Diethyl ketone, used as the internal actinometer for runs
at 3130 Å, was the distillation fraction boiling at 101°C.
Once on the line the diethyl ketone was distilled under
vacuum, the middle third being retained.

Prior to each run, a quantity of diethyl ketone was
transferred from a blackened storage bulb to a dry ice-
acetone cooled trap and outgassed three times until all
non-condensables and low boiling gases were removed.
Ketene was prepared in the vacuum system by pyrolyzing
acetic anhydride ⁶. A slow stream of acetic anhydride
vapour flowed through an oven heated to 504°C.
The unused acetic anhydride and acetic acid produced were collected in a dry ice-acetone bath on the low pressure side of the oven and the ketene was collected in liquid nitrogen; approximately 10 ml. was obtained in one hour.

Trap to trap distillation was performed on the freshly prepared ketene and the middle third retained. Prior to each run, a quantity of ketene was thoroughly outgassed by three distillations similar to those for diethyl ketone. The ketene was stored in a trap immersed in liquid nitrogen to prevent slow polymerization.

Actinometry

Diethyl ketone was selected for experiments at 3130 A where the quantum yield of carbon monoxide formation is 1.0 at 100°C. The use of an internal actinometer was found to be very convenient because it is devoid of the errors usually associated with external actinometers. These errors arise because the amount of radiation incident to the external cell is considerably less than that incident to the reaction cell.

The measurement of the intensity absorbed during a run was performed by the conversion of the current from the photocell into a voltage which was continuously recorded on a 10 millivolt recorder. The following scale readings were taken;
The recorder scale was calibrated using diethyl ketone as an internal actinometer. Scale readings were taken before and after each run to determine the average $R_i$. This was necessary because of the fluctuation and decay of the lamp, and polymer formation. $R_t$ was measured continuously during each run.

The difference $R_i - R_t = R_a$ was calibrated in terms of absolute intensity by the measurement of carbon monoxide yields from the photolysis of diethyl ketone at 100°C. It was possible to measure $R_a$ to within ± 0.5% and, on averaging the results of a number of diethyl ketone runs, quantum yields of carbon monoxide formation from ketene were obtained within ± 3%.

At 3130 Å, a second actinometer was used, but because of the large amount of reflection from the glass-air interfaces and because of the suspected polymer on the exit wall of the reaction cell, the values for the absolute intensity of the light were considerably lower than those obtained using diethyl ketone. Twelve runs were performed using potassium ferrioxalate actinometer; consistent results indicated the need for a conversion factor to be applied when the external liquid actinometer was used to estimate the energy absorbed during runs.
The intensity found from a ferrioxalate run when multiplied by this conversion factor gave the intensity incident to the cell, reproducible to within ± 10%.

The potassium ferrioxalate actinometer was used for runs at 3340 Å since no internal actinometer is available for this wavelength. The intensities obtained by this actinometry, when multiplied by the conversion factor found previously, were used to calibrate the recorder scale. Absorbed intensities were obtained from measurements of $R_i$, $R_t$, and $R_a$ as described previously.
RESULTS

3130 A

Using filter solution combination A, at low pressures of ketene, a carbon monoxide quantum yield of 1.82 was obtained whereas at high pressures around one atmosphere, the carbon monoxide quantum yield decreased to 1.08 as shown in Table I. A decrease in the carbon monoxide quantum yield at high pressures was expected.

The results of five diethyl ketone actinometer runs, at pressures ranging from 60 to 155 mm. of diethyl ketone, and interspersed between the ketene runs, gave a light intensity of approximately $5.4 \times 10^{14}$ quanta per second.

Using filter solution combination B, a new series of diethyl ketone actinometer runs gave intensities of approximately $1.6 \times 10^{14}$ quanta per second. The carbon monoxide quantum yield at low pressures of ketene was 2.0 within experimental error, and at one atmosphere a value of 1.18 was obtained as shown in Table II.

Absorbed intensities varied from $0.442 \times 10^{14}$ quanta per second at 17 mm. to $1.911 \times 10^{14}$ quanta per second at 751 mm. All ketene runs were conducted at 37°.0 C.

It was found that the transmissions at 3130 A of filters A and B were appreciably lower after two weeks constant use.
### TABLE I

**PHOTOLYSIS OF KETENE AT 3130 A**

Cell Temperature 37°.0 C

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure of Ketene mm.</th>
<th>Length of Run secs.</th>
<th>Intensity Absorbed x 10⁻¹⁴</th>
<th>( \phi = \frac{1}{2} \phi_{co} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.8</td>
<td>3600</td>
<td>2.305</td>
<td>0.91 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>56.5</td>
<td>1800</td>
<td>2.855</td>
<td>0.93 ± 0.02</td>
</tr>
<tr>
<td>4</td>
<td>201.6</td>
<td>2700</td>
<td>4.360</td>
<td>0.74 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>402.7</td>
<td>900</td>
<td>4.790</td>
<td>0.59 ± 0.01</td>
</tr>
<tr>
<td>3</td>
<td>444.5</td>
<td>914</td>
<td>4.580</td>
<td>0.57 ± 0.01</td>
</tr>
<tr>
<td>7</td>
<td>726.8</td>
<td>1800</td>
<td>4.290</td>
<td>0.54 ± 0.01</td>
</tr>
</tbody>
</table>
**TABLE II**

PHOTOLYSIS OF KETENE AT 3130 Å

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure of Ketene (mm)</th>
<th>Length of Run (secs)</th>
<th>Intensity Absorbed (quanta/sec)</th>
<th>$\phi = \frac{1}{2} \Phi_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>17.0</td>
<td>3600</td>
<td>0.442</td>
<td>$1.03 \pm 0.04$</td>
</tr>
<tr>
<td>13</td>
<td>40.8</td>
<td>2460</td>
<td>0.846</td>
<td>$1.00 \pm 0.03$</td>
</tr>
<tr>
<td>12</td>
<td>57.1</td>
<td>1800</td>
<td>1.029</td>
<td>$1.00 \pm 0.03$</td>
</tr>
<tr>
<td>11</td>
<td>135.8</td>
<td>2407</td>
<td>1.428</td>
<td>$0.94 \pm 0.02$</td>
</tr>
<tr>
<td>9</td>
<td>230.3</td>
<td>2400</td>
<td>1.710</td>
<td>$0.83 \pm 0.02$</td>
</tr>
<tr>
<td>10</td>
<td>679.1</td>
<td>1920</td>
<td>1.584</td>
<td>$0.63 \pm 0.02$</td>
</tr>
<tr>
<td>8</td>
<td>750.7</td>
<td>2400</td>
<td>1.911</td>
<td>$0.59 \pm 0.01$</td>
</tr>
</tbody>
</table>
The naphthalene in methyl alcohol solution darkened after only a few hours exposure to the lamp and its transmission at 3340 A decreased noticeably. Even when a pyrex window, which absorbs 50% of the light at 3130 A and 100% of light of shorter wave lengths was placed in front of the naphthalene solution, darkening continued. This effect may have been caused by the attack of methyl alcohol on the adhesive used to bond the quartz windows to the pyrex cell.

The intensity of the beam as measured using the ferrioxalate actinometer, when multiplied by the conversion factor of 2.72 gave an incident intensity of approximately $2.1 \times 10^{15}$ quanta/second. When related to the recorder this became $0.87 \times 10^{14}$ quanta/second/scale division.

The intense B.T.H. lamp necessitated short runs of between 3 and 10 minutes whereas 30 to 60 minute runs were needed with the Hanovia lamp at 3130 A.

The carbon monoxide quantum yields were determined at both 37°C and 100°C and the results are summarized in Table III.
## TABLE III

PHOTOLYSIS OF KETENE AT 3340 A

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure of Ketene (mm.)</th>
<th>Length of Run (secs.)</th>
<th>Intensity Absorbed quanta/sec.</th>
<th>$\Phi = \frac{1}{2} \Phi_{e0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>26.0</td>
<td>180</td>
<td>1.221</td>
<td>0.72</td>
</tr>
<tr>
<td>15</td>
<td>39.7</td>
<td>4200</td>
<td>0.771</td>
<td>0.72</td>
</tr>
<tr>
<td>16</td>
<td>47.0</td>
<td>1800</td>
<td>2.545</td>
<td>0.51</td>
</tr>
<tr>
<td>17</td>
<td>105.3</td>
<td>600</td>
<td>2.825</td>
<td>0.41</td>
</tr>
<tr>
<td>20</td>
<td>177.8</td>
<td>390</td>
<td>1.841</td>
<td>0.37</td>
</tr>
<tr>
<td>19</td>
<td>384.6</td>
<td>900</td>
<td>2.023</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Cell Temperature 37°.0 C

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure of Ketene (mm.)</th>
<th>Length of Run (secs.)</th>
<th>Intensity Absorbed quanta/sec.</th>
<th>$\Phi = \frac{1}{2} \Phi_{e0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>26.1</td>
<td>180</td>
<td>0.811</td>
<td>0.80</td>
</tr>
<tr>
<td>23</td>
<td>56.7</td>
<td>240</td>
<td>1.239</td>
<td>0.74</td>
</tr>
<tr>
<td>22</td>
<td>121.8</td>
<td>255</td>
<td>1.579</td>
<td>0.58</td>
</tr>
<tr>
<td>21</td>
<td>299.5</td>
<td>600</td>
<td>1.920</td>
<td>0.37</td>
</tr>
</tbody>
</table>
DISCUSSION

The photolysis of ketene at 2700, 3130, 3340 and 3650 Å can be explained by the following processes:

\[
\begin{align*}
K + h\nu(2700 \text{ Å}) &= K^m \\
K + h\nu(3130 \text{ Å}) &= K^n \\
K + h\nu(3340 \text{ Å}) &= K^p \\
K + h\nu(3650 \text{ Å}) &= K^q \\
K^m &= \text{Products} \\
K^n &= \text{Products} \\
K^p &= \text{Products} \\
K^q &= \text{Products} \\
K^m + K &= 2K \\
K^n + K &= 2K \\
K^p + K &= 2K \\
K^q + K &= 2K
\end{align*}
\]

where \( K \) is a molecule of ketene
and \( K^m, K^n, K^p \) and \( K^q \) are excited ketene molecules in order of decreasing vibrational energy.

Reactions 1 represent activation.
Reactions 2 represent product formation.
Reactions 3 represent internal conversion.
Reactions 4 represent collisional deactivation.
It is not implied that the above mechanism which represents the activation and deactivation of excited molecules $K^m, K^n, K^p,$ and $K^q,$ formed at wavelengths 2700 A, 3130 A, 3340 A, and 3650 A is complete. It is obvious that a ketene molecule in vibronic state $m$ can lose its excess energy by a series of vibrational cascades to states $n, p, q$ etc. until it eventually reaches the equilibrium vibrational state. The number of vibronic states may be 100 or more for a molecule initially in state $m$. The kinetics of such a process are very complicated.

For simplicity the present discussion will consider only reactions 1, 2, 3, and 4 to represent the activation, deactivation and dissociation of excited ketene molecules in states $m, n, p$ and $q$.

For the photolysis at 3650 A the relevant processes are 1q, 2q, 3q and 4q. The rates of these reactions are $I_a, k_{2q}[K^q], k_{3q}[K^q]$, $k_{4q}[K][K^q]$ respectively, and rate of formation of:

$$K^q = I_a - k_{2q}[K^q] - k_{3q}[K^q] - k_{4q}[K][K^q]$$

If steady state conditions are applied, the right hand side of the above expression equals zero, therefore:

$$k_{2q}[K^q] + k_{3q}[K^q] + k_{4q}[K][K^q] = I_a$$

$$\left(K^q\right)_{ss} = \frac{I_a}{k_{2q} + k_{3q} + k_{4q}[K]}$$
Rate of product formation  =  \( k_2q \frac{[K]}{k_2q + k_3q + k_4q[K]} \)

Rate of product formation  =  quantum yield

and:

\[
\phi = \frac{k_2q}{k_2q + k_3q + k_4q[K]}
\]

therefore

\[
\frac{1}{\phi} = 1 + \frac{k_3q}{k_2q} + \frac{k_4q[K]}{k_2q}
\]

Equations of the same form can be derived for each of the other wavelengths.

In general

\[
\frac{1}{\phi} = 1 + \frac{k_3}{k_2} + \frac{k_4[K]}{k_2}
\]

where  \([K]\) = concentration of ketene in moles/litre

\(\phi\) = primary quantum yield

\(k_3/k_2\) = intercept on \(1/\phi\) axis in the plot \(1/\phi\) against pressure.

\(k_4/k_2\) = slope of plot in litres/mole.
Strachan and Noyes\(^1\) found that the quantum yield of carbon monoxide formation was approximately two. According to the proposed mechanism the primary quantum yield is thus unity. It is evident therefore that over the range of pressures and temperatures used, there is neither internal conversion nor collisional deactivation of the excited ketene molecules. The only way in which these molecules can lose their excess energy is by dissociation. The observed quantum yields can be explained by the mechanism:

\[(1m), \ (2m)\]

That internal conversion and collisional deactivation are absent may be seen from the intercept of unity and the zero slope of the plot of \(\sqrt{\phi}\) against pressure.

The primary quantum yield of ketene decomposition at this wavelength appears as an isolated number in several papers devoted to ketene photolyses at other wavelengths.\(^3\), 9, 10, 11 However only the recent work of Kistiakowsky and Mahan\(^3\) gives experimental data. From the limited amount of information given it appears that photolyses were only performed at low pressures, in the region of 20 mm. It was found\(^3\) that the primary quantum yield was independent of
pressure and possibly equal to unity.

This research has shown that when light which was not monochromatic but which contained quantities of both 3340 and 3650 Å radiation was used, primary quantum yields of 0.91 at 35.8 mm. and 0.54 at 726.8 mm. were obtained as shown in Table I.

The plot of $\frac{1}{\phi}$ against pressure intercepts the $\frac{1}{\phi}$ axis at approximately 1.1 and has a positive slope. It is likely therefore that internal conversion and collisional deactivation of the excited ketene molecule contribute slightly to the deactivation process.

Because of the known low quantum yields at 3650 Å and the suspected low yields at 3340 Å, a new series of experiments was performed using monochromatic 3130 Å radiation. The results of these experiments are shown in Table II. The primary quantum yield is 1.0 at pressures between 17 and 60 mm., and 0.59 at 750.7 mm.

The plot of $\frac{1}{\phi}$ against pressure is shown in Figure 1; although the extrapolation to zero pressure is unity, because of experimental error the presence of internal conversion is not entirely excluded from the mechanism. The positive slope of the plot in Figure 1 indicates the presence of collisional deactivation, and hence the mechanism:

$$(1n), (2n), (3n), (4n)$$
FIGURE 1. DEPENDENCE OF PRIMARY QUANTUM YIELD ON PRESSURE AT 3130 A.
may be postulated in which the extent of reaction (3n)
is very small. $k_3/k_2$ is approximately zero while
$k_4/k_2 = 16.8$ litres/mole.

The mechanism of ketene decomposition at 3130 A is
intermediate between those postulated for 2700 A and
3650 A. From Table II it appears that at low pressures
of ketene, each excited ketene molecule dissociates to
form products whereas at pressures greater than
approximately 60 mm., a large fraction of the excited
molecules lose their energy by collision with unexcited
molecules of ketene.

The photolysis at 3130 A was not extended to higher
temperatures because it was thought that little or no
significant information would be obtained.

In three experiments the ethylene quantum yield was
found to be $1/2.14$ of the carbon monoxide quantum yield.
This is approximately the same as that found at 2700 A\(^1\)
and 3650 A\(^1, 12\)

3340 A
This research has indicated that for photolyses at 37°C
the primary quantum yield is 0.72 at 26 mm. and 0.21 at
384 mm. The zero pressure intercept in Figure 2 is 1.25.
The slope of the plot is much steeper than for 3130 A and
is $1.64 \times 10^2$ litres/mole. This indicates that
considerable collisional deactivation of $K^p$ occurs.
FIGURE 2. DEPENDENCE OF PRIMARY QUANTUM YIELD ON PRESSURE AT 3340 A.
Four runs were performed at 100°C and as expected, both the slope and the intercept were smaller than for runs at 37°C. At 26.1 mm. the primary quantum yield is 0.80 and at 300 mm. equals 0.37. The zero pressure intercept at 100°C is 1.1 and the slope of the straight line is $0.99 \times 10^2$ litres/mole, both obtained from Figure 2. The ratio of the rates of internal conversion to product formation at 100°C is 0.1.

The mechanism for the activation and deactivation of $K^P$ is:

$$(1p), (2p), (3p), (4p),$$

at both 37°C and 100°C.

From the information in Table III and Figure 2, it was possible to estimate approximately the activation energy of reaction (2p) from the slope of the plot of $\log_e(k_4/k_2)$ against $1/T$ where $T$ is the absolute temperature. The slope is $(E_2 - E_4) / R$, where $R$ is the gas constant in calories degree$^{-1}$ mole$^{-1}$. If $E_4$ is assumed to be zero, then $E_2$ is approximately 2 Kcal./mole. This value is subject to a large error.

3650 Å

Strachan and Noyes found a zero pressure intercept of 28 in the plot of reciprocal primary quantum yield against pressure. This corresponds to a primary quantum yield of approximately 0.036 at 26°C. The slope of the linear
plot is \(4.65 \times 10^4\) litres/mole. Both the intercept and the slope decrease with increasing temperature.

4.5 Kcal./mole is the activation energy of reaction \((2q)^1\).

\(k_3/k_4\) as a function of wavelength

At 2700 A this ratio is indeterminant. Values of approximately \(3 \times 10^{-3}\), \(1.2 \times 10^{-3}\) and \(6 \times 10^{-4}\), all expressed in moles/litre, are found for 3130 A, 3340 A and 3650 A respectively. It must be emphasized that the values found for 3340 A and particularly 3130 A are subject to possible large errors. The value given for 3130 A may be in error by as much as 100%.

\(k_2/k_4\) as a function of wavelength

The slope of the plot of reciprocal quantum yield against pressure shows a marked dependence on wavelength, increasing from zero at 2700 A to \(4.65 \times 10^4\) litres/mole at 3650 A. The intermediate values are 16.8 litres/mole at 3130 A and \(1.64 \times 10^2\) litres/mole at 3340 A. It should again be pointed out that the result at 3650 A was found at 26°C whereas the other values were obtained at 37°C.

\(k_2/k_4\) is thus infinity, 0.06, \(0.61 \times 10^{-2}\) and \(0.22 \times 10^{-4}\) moles/litre at 2700, 3130, 3340 and 3650 A respectively.

In Figure 3 these values are plotted against the energy of the exciting radiation. The slope increases rapidly as the energy of excitation increases.
FIGURE 3. VARIATION OF $k_2/k_4$ WITH ENERGY OF EXCITATION
If it is assumed that $k_4$, related to collisional deactivation, is virtually independent of the energy of the radiation, Figure 3 represents the variation of $k_2$ with energy of the exciting radiation. It is evident therefore that the dissociation rate constant increases rapidly with increasing energy.

A further assumption that $k_4$ is the collision rate constant, $1.29 \times 10^{11}$ moles$^{-1}$ litres sec.$^{-1}$ calculated for a collision diameter of 3.5 Å, gives absolute values for $k_2$ of infinity, $7.74 \times 10^9$, $7.87 \times 10^8$ and $2.84 \times 10^6$ sec$^{-1}$ at 2700, 3130, 3340 and 3650 Å respectively.

A more plausible value of $k_2$ at 2700 Å appears to be approximately $10^{10}$ sec$^{-1}$.

Energy of Activation of Reaction 2 as a function of wavelength $E_A$, the energy of activation, may be assumed to be zero at 2700 Å, and has been found to be approximately 2 Kcal/mole at 3340 Å and 4.6 Kcal/mole at 3650 Å$^1$. These values have very large errors.

The energy difference of 2.6 Kcal/mole calculated from above is much smaller than the 8 Kcal/mole energy difference between 3340 Å and 3650 Å radiation.

This indicates a mechanism involving more vibronic states than shown in reactions 1, 2, 3 and 4.
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