In (a), addition of foreign gas is accompanied by increase in the rate of reaction, the relative accelerations corresponding to those calculated on kinetic theory considerations and being expressed by the series

\[ \text{CCl}_4 > \text{CO}_2 > \text{N}_2 > \text{A} > \text{H}_2 \text{ and He.} \]

In (b), addition of foreign gas decreases the rate of reaction by facilitating the recombination of bromine atoms. The series representing the efficiencies of the triple collision process is given by

\[ \text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{A} > \text{He} > \text{H}_2. \]

Attention is drawn to the parallelism existing between this series and that of the corresponding accommodation coefficients as determined from thermal conductivity measurements.

---

**The Thermal Decomposition of Ozone**

By Mowbray Ritchie (B.Sc., Ph.D.), Department of Chemistry, University of Edinburgh

(Communicated by J. Kendall, F.R.S.—Received May 23, 1934.)

The thermal decomposition of ozone has been generally regarded as essentially a bimolecular reaction. The exact determination of the nature of the mechanism has, however, been attended by the discovery of several conflicting influences, the interpretations of which have been matters of no small difficulty and interest. It can scarcely be said that the mechanism of decomposition has been definitely established.

General discussion has centred round the calculation of the absolute rate of reaction from the experimentally determined energy of activation, from which it appears that the velocity coefficient, calculated in the usual way, is much less than the experimentally determined value when the decomposition is regarded as bimolecular. Thus Riesenfeld and Wassmuth* inclined to the idea of an energy chain reaction, the length of the chains being sufficient to explain the discrepancy, while Schumacher and Sprenger† considered that

The Thermal Decomposition of Ozone

the energy of activation cannot adequately be considered on the "two squared terms" basis, but that allowance must be made for the possible other degrees of freedom of the ozone molecule. This view is regarded as supported by recent work of Glissmann and Schümacher.*

Jahn† and Perman and Greaves‡ concluded that the rate of decomposition varied inversely as the pressure of oxygen present, and Jahn suggested that the course of the reaction was not the simple one

\[ 2O_3 \rightarrow 3O_2, \]

but consisted of the stages

\[ O_3 = O_2 + O \]
\[ O + O_3 = 2O_2. \]

The first stage was assumed rapid and reversible, and the observed rate determined by the second reaction. This mechanism, however, was rejected by Wulf and Tolman§ on the basis of a calculation showing the number of collisions between ozone molecules and oxygen atoms as too small to account for the observed rate of reaction.

In the previous paper on the photochemical formation of hydrogen bromide, the effects of foreign gases have been arranged in two series, one corresponding to an acceleration of the rate of reaction by virtue of the suppression of a wall reaction, and the other to a retarding action attributed to a triple collision process. In the thermal decomposition of ozone, a surface action and an accelerating influence of inert gases have been reported, while a retarding influence of oxygen has been observed in certain circumstances||; it therefore appeared possible that where no definite effect of oxygen could be observed, the explanation was the cancelling of the accelerating and inhibiting influences.

The thermal decomposition of ozone therefore has here been examined from this point of view. The results now to be reported are interpreted as indicating that the primary decomposition of ozone is the "unimolecular" process

\[ O_3 = O_2 + O. \] (1)

In the absence of oxygen, inert gases such as argon, helium, and nitrogen,

increase the rate of reaction by preventing the diffusion of the oxygen atoms to the wall and thereby facilitating the reaction

\[ O + O_3 = 2O_2. \]  
(2)

Addition of oxygen at first increases the rate of reaction by the above diffusion effect, but this is succeeded by a decrease in total reaction velocity by virtue of the triple collision

\[ O + O_2 + O_2 = O_3 + O_2. \]  
(3)

The addition of other gases to ozonized oxygen mixtures of sufficiently high oxygen content produces a similar decrease in rate of decomposition, by the reaction

\[ O + O_2 + M = O_3 + M. \]  
(4)

In the presence of large pressures of oxygen, the mechanism is then such as to render the total rate of decomposition apparently bimolecular with respect to the ozone; the apparent heat of activation obtained under these conditions involves the velocity coefficients of the reactions quoted above.

**Experimental**

The apparatus used has been described in detail in the preceding paper. The same quartz reaction vessel was employed, experiments being carried out at 80°, 90° and 100° C., the increase in pressure due to the decomposition being accurately measured by the calibrated telescope-Bourdon gauge system. Ten divisions of the eyepiece scale corresponded to 1.7 mm Hg, and since readings were accurate to 0.1 division, changes in pressure down to 0.015 mm could be recorded.

Ozone was prepared in a single ozonizer (Berthelot type, employing copper sulphate solution) by subjecting dry oxygen to the silent discharge provided by an induction coil. In the ozonizer itself the oxygen was kept at atmospheric pressure, while the liquid air trap in which the ozone was collected was evacuated by water filter-pump to approximately 10 mm pressure, the connecting tap thus controlling the rate of flow of oxygen through the ozonizer. The vapour pressure of ozone at the temperature of liquid air is very small (<0.05 mm): residual oxygen was removed finally by direct application of a Hyvac oil pump. Analysis of ozone samples prepared in such a manner and collected in an analysing bulb (200 cc volume) by manipulation similar to that involved in the introduction of ozone into the reaction vessel for any
The Thermal Decomposition of Ozone

thermal decomposition experiment, gave concordant values of 95–96% purity, as estimated by the neutral potassium iodide-thiosulphate method.* Complete decomposition, by a hot platinum wire, of similar samples gave values of 97%; the ozone as prepared above and as introduced into the reaction vessel contained, therefore, only a small proportion of oxygen.

Nitrogen, argon, helium and oxygen were obtained as described in the preceding paper.

Rates of reaction were recorded immediately the ozone had been introduced into the reaction vessel. The sensitivity of the glass spring gauge was such as to render possible accurate measurement of the rate of reaction in the initial stages where the amount of oxygen formed by the decomposition remained relatively small. Correspondingly the rate was measured over a small change in ozone concentration.

Results

Ozone-nitrogen Mixtures—Table I gives details of experiments showing the influence of nitrogen on the rate of decomposition. The initial pressure of ozone was calculated on the basis of the analyses already recorded, showing that 100 mm gas, as introduced into the reaction vessel, contained 5 mm oxygen. The average pressure of ozone was taken as the arithmetic mean of initial and final concentrations. The increase in pressure \( \Delta p \) is given in divisions of the telescope eyepiece scale for the time \( t \) (seconds), while the rate of decomposition \( r_{\text{exp}} \) is calculated in millimetres ozone decomposing per second over the range. Since an increase in pressure of \( \Delta p \) represents a decrease in ozone pressure of 2(\( \Delta p \)),

\[
r_{\text{exp}} = \frac{2(\Delta p)}{t} \times F,
\]

Table I—Temperature = 90·0° C

<table>
<thead>
<tr>
<th>[N₂] mm</th>
<th>Initial [O₃]</th>
<th>Av. [O₃]</th>
<th>Av. [O₃]</th>
<th>( \Delta p )</th>
<th>t secs</th>
<th>( r_{\text{exp}} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·0</td>
<td>19·5</td>
<td>18·3</td>
<td>2·7</td>
<td>6·8</td>
<td>570</td>
<td>4·06</td>
</tr>
<tr>
<td>0·0</td>
<td>19·5</td>
<td>18·3</td>
<td>2·8</td>
<td>6·95</td>
<td>600</td>
<td>3·94</td>
</tr>
<tr>
<td>0·0</td>
<td>20·0</td>
<td>18·8</td>
<td>4·8</td>
<td>7·3</td>
<td>450</td>
<td>5·50</td>
</tr>
<tr>
<td>241·1</td>
<td>19·5</td>
<td>18·1</td>
<td>8·1</td>
<td>8·1</td>
<td>480</td>
<td>5·75</td>
</tr>
<tr>
<td>43·0</td>
<td>19·8</td>
<td>18·6</td>
<td>3·8</td>
<td>7·2</td>
<td>510</td>
<td>4·80</td>
</tr>
<tr>
<td>65·8</td>
<td>19·3</td>
<td>17·7</td>
<td>4·3</td>
<td>8·95</td>
<td>600</td>
<td>5·07</td>
</tr>
<tr>
<td>0·0</td>
<td>19·8</td>
<td>18·7</td>
<td>2·6</td>
<td>6·4</td>
<td>540</td>
<td>4·03</td>
</tr>
<tr>
<td>285·4</td>
<td>19·2</td>
<td>17·7</td>
<td>8·2</td>
<td>8·7</td>
<td>510</td>
<td>5·80</td>
</tr>
<tr>
<td>88·9</td>
<td>19·5</td>
<td>18·2</td>
<td>5·0</td>
<td>7·4</td>
<td>510</td>
<td>5·00</td>
</tr>
<tr>
<td>134·2</td>
<td>19·6</td>
<td>18·3</td>
<td>6·5</td>
<td>7·8</td>
<td>480</td>
<td>5·52</td>
</tr>
<tr>
<td>0·0</td>
<td>19·4</td>
<td>18·2</td>
<td>2·8</td>
<td>7·0</td>
<td>600</td>
<td>3·90</td>
</tr>
</tbody>
</table>

where $F$ is the factor $0.17$ converting eyepiece divisions to millimetres of mercury. The results are given in the order in which they were obtained.

The nitrogen used in these experiments was found by analysis to contain approximately 1.5% oxygen; this correction has been included in the numbers of Table I. The differences in Av. $[O_a]$ and Av. $[O_2]$ for the various experiments are small, and for the present purpose it is sufficient to consider the results as applying to the values $[O_a] = 18.0$ mm and $[O_2] = 4.0$ mm for the different concentrations of nitrogen. The results are thus shown graphically in fig. 1; the increase in rate of decomposition on the addition of nitrogen is immediately apparent.

This increase on the addition of such a foreign gas suggests at once the gradual lessening of the wall effect reported by many observers for low pressure conditions. The reaction mechanism which is here put forward on the basis of the above and subsequent results is founded on the recognition of the oxygen atom as the reactive diffusing body; for the conditions of Table I the scheme is represented as follows:

1. $O_3 = O_2 + O$ $k_1$
2. $O + O_3 = 2O_2$ $k_2$
3. $O \rightarrow \frac{1}{2}O_2$ $S$

The coefficient $S$ represents the rate at which oxygen atoms reach the wall and are destroyed. The total rate of decomposition then depends on the relative effects of reactions 2 and 3; obviously the addition of an inert gas such as nitrogen will increase the rate of reaction by preventing the oxygen atoms from reaching the wall. On the basis of the above mechanism, then,

$$\frac{d(O)}{dt} = k_1 [O_3] - k_2 [O] [O_3] - S [O] = 0,$$

whence

$$[O] = \frac{k_1 [O_3]}{(k_2 [O_3] + S)}.$$

The rate of ozone decomposition is thus

$$-\frac{d(O_3)}{dt} = k_1 [O_3] \left[1 + \frac{k_2 [O_3]}{(k_2 [O_3] + S)}\right]. \quad (a)$$

The effect of the surface is hence most appreciable at low pressures of ozone; conversely, if sufficient inert gas be present to render the surface effect negligible, the rate of ozone decomposition is given by

$$-\frac{d(O_3)}{dt} = 2k_1 [O_3].$$
The Thermal Decomposition of Ozone

If now $D_{O_3}$ and $D_X$ are the diffusion coefficients of the oxygen atom with respect to ozone and to a foreign gas such as nitrogen respectively (neglecting the small amount of oxygen for the present),

$$S \propto \left( \frac{1}{D_{O_3}} + \frac{1}{D_X} \right)^{-1}.$$

For a binary mixture (atom A and foreign gas M)

$$D_M \propto \frac{1}{[M] \sigma_{AM}^2 \left( \frac{1}{M_A} + \frac{1}{M_M} \right)^{-\frac{1}{3}}},$$

where $\sigma_{AM}$ is the sum of the radii of atom and inert gas, and M is the molecular or atomic weight, and hence we can put

$$S = V \left( \frac{1}{D_{O_3}} + \frac{1}{D_{N_2}} \right)^{-1},$$

where V is a constant which will otherwise vary with the shape and material of the reaction vessel. For a given temperature, the ratio of rates of ozone decomposition with and without added inert gas X is then calculated as

$$R = \frac{\left[2 [O_3] \{P \{O_3\} + Q [X]\} + V/k_2 \right] \left[[O_3] \{P \{O_3\} + V/k_2\} \right]}{\left[[O_3] \{P \{O_3\} + Q [X]\} + V/k_2 \right] \left[2 [O_3] \{P \{O_3\} + V/k_2\} \right]}, \quad (b)$$

where

$$P = \sigma_{O_3-O_3}^2 \left( \frac{1}{M_{O_3}} + \frac{1}{M_{O_2}} \right)^{-\frac{1}{3}}$$

and

$$Q = \sigma_{O_3-X}^2 \left( \frac{1}{M_{O_3}} + \frac{1}{M_X} \right)^{-\frac{1}{3}}.$$

The nitrogen curve of fig. 1 was constructed on this basis; the standard rate of decomposition when $[N_2] = 0$ was taken from the results of Table I as $4.00 \times 10^{-3}$ mm ozone per second for the conditions $[O_3] = 18.0$ mm. The following values were employed in the calculations:

$$\sigma_{O_3} = 3.6 \times 10^{-8} \text{ cm}, \quad \sigma_{N_2} = 3.1 \times 10^{-8} \text{ cm}, \quad \sigma_{O_2} = 3.0 \times 10^{-8} \text{ cm}$$

$$\sigma_O = 1.5 \times 10^{-8} \text{ cm}, \quad V/k_2 = 30000 \times 10^{-16}.$$

The rates calculated by formula (b) above are compared in Table II with those obtained experimentally.

The figures of the last column show that experimental rates are well expressed by the above expression and, correspondingly, reliance is placed in the value obtained for $[N_2] = \infty$. This rate, as previously pointed out, represents the
rate of ozone decomposition when surface action is negligible, and is related to $k_1$ by the formula

$$\frac{-d (O_3)}{dt} = 2k_1 [O_3].$$

The velocity coefficient $k_1$ is thus calculated from these figures as

$$\frac{6.52 \times 10^{-3}}{2 \times 18.0} = 1.81 \times 10^{-4} \text{ sec}^{-1} \text{ at } 90^\circ \text{ C}.$$ 

**Ozone-argon and Ozone-helium Mixtures**—The value of $V/k_2$ having been determined as $30,000 \times 10^{-16}$ in the appropriate units, it is possible to calculate on the above basis rates of reaction in the presence of inert gases other than nitrogen, from a knowledge of the corresponding molecular weights and diameters. Experimentally, rates of decomposition were determined as before for ozone-argon and ozone-helium mixtures. In Table III these are given and compared with values calculated as above, $\sigma_A$ and $\sigma_{He}$ being taken, for purposes of calculation, as $2.85 \times 10^{-8}$ and $1.90 \times 10^{-8}$ cm respectively.

The ratios of the final column ($r_{exp.}/r_{calc.}$) show that experimental rates are again in good agreement with those calculated on the basis of the diffusion theory.

**Table III—Temperature = 90.0°C [O₃] = 18 mm**

<table>
<thead>
<tr>
<th>Added gas</th>
<th>Initial [O₃]</th>
<th>Av. [O₃]</th>
<th>Av. [O₃]</th>
<th>$\Delta P$</th>
<th>$t$</th>
<th>$r_{exp.} \times 10^3$</th>
<th>$r_{calc.} \times 10^3$</th>
<th>$r_{exp.}/r_{calc.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>32.8</td>
<td>19.0</td>
<td>17.6</td>
<td>2.0</td>
<td>8.0</td>
<td>600</td>
<td>4.53</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>79.3</td>
<td>19.4</td>
<td>18.1</td>
<td>2.0</td>
<td>7.7</td>
<td>540</td>
<td>4.85</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>151.0</td>
<td>19.7</td>
<td>18.4</td>
<td>1.9</td>
<td>7.6</td>
<td>480</td>
<td>5.38</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>221.9</td>
<td>19.2</td>
<td>17.9</td>
<td>1.9</td>
<td>7.5</td>
<td>450</td>
<td>5.66</td>
<td>5.68</td>
</tr>
<tr>
<td>Helium</td>
<td>0</td>
<td>19.1</td>
<td>17.9</td>
<td>1.8</td>
<td>6.86</td>
<td>570</td>
<td>4.98</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>59.0</td>
<td>19.1</td>
<td>17.8</td>
<td>1.9</td>
<td>7.5</td>
<td>600</td>
<td>4.25</td>
<td>4.31</td>
</tr>
<tr>
<td></td>
<td>75.0</td>
<td>19.3</td>
<td>18.0</td>
<td>1.9</td>
<td>7.4</td>
<td>570</td>
<td>4.42</td>
<td>4.39</td>
</tr>
<tr>
<td></td>
<td>103.5</td>
<td>19.4</td>
<td>18.1</td>
<td>2.0</td>
<td>7.7</td>
<td>600</td>
<td>4.36</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>196.0</td>
<td>19.5</td>
<td>18.4</td>
<td>1.7</td>
<td>6.5</td>
<td>480</td>
<td>4.60</td>
<td>4.85</td>
</tr>
</tbody>
</table>
The Thermal Decomposition of Ozone

Mixtures containing Oxygen—Further experiments were carried out in which oxygen was introduced as the foreign gas, the temperature and concentration of ozone being kept as in the preceding series. Results are given in Table IV.

Table IV—Temperature $= 90 \cdot 0^\circ C$ \([O_3] = 18 \text{ mm}\)

<table>
<thead>
<tr>
<th>Av. $[O_2]$</th>
<th>Initial $[O_3]$</th>
<th>Av. $[O_3]$</th>
<th>$\Delta p$ (divs)</th>
<th>$t$ (secs)</th>
<th>$r_{exp.} \times 10^2$</th>
<th>$r_{calc.} \times 10^2$</th>
<th>$r_{exp.}/r_{calc.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>10.1</td>
<td>17.8</td>
<td>8.1</td>
<td>660</td>
<td>4.17</td>
<td>4.03</td>
<td>1.03</td>
</tr>
<tr>
<td>28.5</td>
<td>10.4</td>
<td>18.0</td>
<td>8.2</td>
<td>660</td>
<td>4.22</td>
<td>4.48</td>
<td>0.94</td>
</tr>
<tr>
<td>60.6</td>
<td>10.2</td>
<td>17.8</td>
<td>8.2</td>
<td>600</td>
<td>4.64</td>
<td>4.63</td>
<td>1.00</td>
</tr>
<tr>
<td>90.6</td>
<td>10.6</td>
<td>17.8</td>
<td>8.2</td>
<td>600</td>
<td>4.64</td>
<td>4.60</td>
<td>1.01</td>
</tr>
<tr>
<td>104.3</td>
<td>10.5</td>
<td>18.2</td>
<td>8.1</td>
<td>630</td>
<td>4.37</td>
<td>4.97</td>
<td>0.88</td>
</tr>
<tr>
<td>2.1</td>
<td>10.3</td>
<td>17.9</td>
<td>8.2</td>
<td>690</td>
<td>4.04</td>
<td>4.03</td>
<td>1.00</td>
</tr>
<tr>
<td>203.8</td>
<td>10.4</td>
<td>17.9</td>
<td>8.8</td>
<td>960</td>
<td>3.12</td>
<td>3.21</td>
<td>0.97</td>
</tr>
<tr>
<td>250.1</td>
<td>10.4</td>
<td>18.1</td>
<td>8.05</td>
<td>1020</td>
<td>2.68</td>
<td>2.70</td>
<td>1.00</td>
</tr>
<tr>
<td>309.7</td>
<td>10.4</td>
<td>18.1</td>
<td>7.8</td>
<td>1200</td>
<td>2.21</td>
<td>2.10</td>
<td>1.05</td>
</tr>
<tr>
<td>373.5</td>
<td>10.0</td>
<td>17.7</td>
<td>7.9</td>
<td>1500</td>
<td>1.72</td>
<td>1.62</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Fig. 1

The average ozone concentrations being in each experiment approximately 18 mm as before, the results are also shown graphically in fig. 1. Addition of oxygen at first increases the rate of ozone decomposition by reason of the diffusion effect, but this is rapidly succeeded by a decrease in the rate of reaction, 350 mm oxygen reducing the rate to approximately half its original value. Before discussing these effects, it is of advantage to give another set of experimental results, Table V, when the rate of reaction was recorded for $[O_3] = 18 \text{ mm}$, as before, while the initial concentration of oxygen was approximately 100 mm, and nitrogen or argon were added to various pressures.
M. Ritchie

Table V—Temperature = 90·0° C

<table>
<thead>
<tr>
<th>Added gas</th>
<th>Av. [O₂]</th>
<th>Initial [O₂]</th>
<th>Av. [O₃]</th>
<th>Δp</th>
<th>t</th>
<th>r_exp, x 10³</th>
<th>r_calc, x 10³</th>
<th>r_exp/r_calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>50·1</td>
<td>109·8</td>
<td>19·3</td>
<td>17·8</td>
<td>8·6</td>
<td>750</td>
<td>3·90</td>
<td>4·14</td>
</tr>
<tr>
<td></td>
<td>83·6</td>
<td>103·1</td>
<td>19·7</td>
<td>18·3</td>
<td>8·1</td>
<td>690</td>
<td>4·00</td>
<td>4·03</td>
</tr>
<tr>
<td></td>
<td>130·1</td>
<td>103·3</td>
<td>19·2</td>
<td>17·9</td>
<td>7·5</td>
<td>660</td>
<td>3·86</td>
<td>3·74</td>
</tr>
<tr>
<td></td>
<td>154·7</td>
<td>103·3</td>
<td>19·6</td>
<td>18·2</td>
<td>8·2</td>
<td>780</td>
<td>3·58</td>
<td>3·58</td>
</tr>
<tr>
<td></td>
<td>200·2</td>
<td>102·4</td>
<td>19·4</td>
<td>18·0</td>
<td>8·0</td>
<td>840</td>
<td>3·41</td>
<td>3·36</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0</td>
<td>2·0</td>
<td>19·8</td>
<td>18·4</td>
<td>8·0</td>
<td>690</td>
<td>3·94</td>
<td>4·00</td>
</tr>
<tr>
<td></td>
<td>80·4</td>
<td>103·3</td>
<td>19·4</td>
<td>18·0</td>
<td>8·5</td>
<td>780</td>
<td>3·70</td>
<td>3·76</td>
</tr>
<tr>
<td></td>
<td>130·6</td>
<td>102·5</td>
<td>19·5</td>
<td>18·1</td>
<td>8·2</td>
<td>840</td>
<td>3·32</td>
<td>3·31</td>
</tr>
<tr>
<td></td>
<td>180·0</td>
<td>102·6</td>
<td>19·4</td>
<td>18·2</td>
<td>6·95</td>
<td>780</td>
<td>3·03</td>
<td>2·95</td>
</tr>
<tr>
<td></td>
<td>244·1</td>
<td>102·6</td>
<td>20·0</td>
<td>18·5</td>
<td>9·0</td>
<td>1320</td>
<td>2·32</td>
<td>2·56</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1·8</td>
<td>19·2</td>
<td>18·0</td>
<td>7·1</td>
<td>600</td>
<td>4·03</td>
<td>4·00</td>
</tr>
</tbody>
</table>

From the results of Table V, it is evident that the addition of "inert" gas to the oxygen ozone mixtures, more particularly when the "inert" gas is nitrogen, decreases the rate of ozone decomposition, in contradistinction to the increase in reaction velocity observed when no oxygen was present; the diffusion effect due to nitrogen must occur as before, but, under the conditions, is small and overshadowed by some reaction in which both oxygen and nitrogen are involved. This reaction is then most probably a triple collision involving the nitrogen molecule, the oxygen molecule and the oxygen atom, reformed ozone being stabilized by the triple collision,

$$O + O_2 + M = O_3 + M.$$  

Thus the retardation by oxygen alone is represented by

$$O + O_2 + O_2 = O_3 + O_2,$$

where oxygen molecules themselves play the part of the third colliding body.

On this basis we formulate the reaction mechanism as follows:

$$O_3 = O_2 + O$$

$$O + O_3 = 2O_2$$

$$O \rightarrow \frac{1}{2}O_2$$

$$O + O_2 + O_2 = O_3 + O_2$$

$$O + O_2 + M = O_3 + M$$

The rate of ozone decomposition is then obtained as before as

$$- \frac{d (O_3)}{dt} = \frac{k_1 [O_2] [2k_2 [O_3] + S]}{(k_2 [O_3] + k_3 [O_2]^2 + k_4 [O_2] [M] + S)}.$$  (6)

In this expression S represents the rate at which oxygen atoms are removed.
from the gas phase by wall action and can therefore be replaced as in the theory given previously by

\[ V ([O_3]P + [O_2]Q + [X]R)^{-1}, \]

where

\[ P = \sigma_{0-o_0}^2 \left( \frac{1}{M_o} + \frac{1}{M_{o_0}} \right)^{-\frac{1}{2}}, \]

\[ Q = \sigma_{0-o_1}^2 \left( \frac{1}{M_o} + \frac{1}{M_{o_1}} \right)^{-\frac{1}{2}}, \]

and

\[ R = \sigma_{0-x}^2 \left( \frac{1}{M_o} + \frac{1}{M_X} \right)^{-\frac{1}{2}}. \]

The value of \( V/k_2 \) at 90°C has already been determined as \( 30,000 \times 10^{-16} \) in the appropriate units. For oxygen-ozone mixtures, the ratios of rates with and without added oxygen are then given by

\[
\]

The values of \( r_{\text{calc}} \) in Table IV have been obtained by means of this expression by taking as standard the rate of \( 4 \cdot 00 \times 10^{-8} \) mm ozone per second for \([O_3] = 18 \cdot 0 \) mm, with \( \sigma_{0-o_0} = 2 \cdot 55 \times 10^{-8} \) cm, \( \sigma_{0-o_1} = 2 \cdot 25 \times 10^{-8} \) cm, and \( k_3/k_2 = 4 \cdot 5 \times 10^{-4} \). Again the ratios of the final column of Table IV show that the experimental rates are well reproduced by the above expression.

For oxygen-argon-ozone and oxygen-nitrogen-ozone mixtures, the ratios of rates with and without added oxygen and nitrogen or argon are given by

\[
\]

where \( X \) refers to nitrogen or argon. The values of \( r_{\text{calc}} \) in Table V have been obtained by taking \( k_4/k_2 = 6 \cdot 4 \times 10^{-4} \) for argon, and \( k_2/k_2 = 10 \cdot 2 \times 10^{-4} \) for nitrogen, in conjunction with the previously determined values of \( k_3/k_2 \) and \( V/k_2 \). Again satisfactory agreement is to be observed between experimental and calculated values, Table V.

**Velocity Coefficients and Energies of Activation**

Examination of formula (c) above indicates that in the presence of large pressures of oxygen, when \( S \) will be small, the total rate of decomposition will
be approximately proportional to the square of the ozone concentration, since under these circumstances the denominator remains approximately constant. The reaction under these conditions will appear bimolecular, as has been observed by many workers. The apparent heats of activation obtained from experiments in which mixtures of ozone and oxygen were used will in general depend on the relative concentrations of ozone and oxygen as well as on the velocity coefficients $k_1$, $k_2$ and $k_3$.

From Tables I and II, comprising the results for ozone-nitrogen mixtures, the value of $k_1$ has been found to be $1 \cdot 81 \times 10^{-4}$ sec$^{-1}$ at 90·0° C. Corresponding series of experiments were carried out with ozone-nitrogen mixtures at 80·0° C and 100·0° C with a view to obtaining by similar calculation the variation of $k_1$ for such a change in temperature, and from this the true energy of activation in this reaction. Results are given in Tables VI and VII.

<table>
<thead>
<tr>
<th>$N_2$</th>
<th>Initial</th>
<th>Av.</th>
<th>Av.</th>
<th>$\Delta p$</th>
<th>$t$</th>
<th>$r_{\text{exp}, \times 10^9}$</th>
<th>$r_{\text{cal}, \times 10^9}$</th>
<th>$r_{\text{exp}}/r_{\text{cal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>divs</td>
<td>secs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>19·4</td>
<td>18·1</td>
<td>1·9</td>
<td>7·1</td>
<td>300</td>
<td>8·05</td>
<td>7·8</td>
<td>1·03</td>
</tr>
<tr>
<td>78·5</td>
<td>19·5</td>
<td>18·3</td>
<td>3·2</td>
<td>6·9</td>
<td>240</td>
<td>9·75</td>
<td>9·8</td>
<td>1·00</td>
</tr>
<tr>
<td>125·0</td>
<td>19·5</td>
<td>18·1</td>
<td>5·0</td>
<td>8·0</td>
<td>270</td>
<td>10·1</td>
<td>10·45</td>
<td>1·03</td>
</tr>
<tr>
<td>175·0</td>
<td>19·7</td>
<td>18·2</td>
<td>5·2</td>
<td>8·7</td>
<td>270</td>
<td>11·0</td>
<td>10·9</td>
<td>1·01</td>
</tr>
<tr>
<td>237·0</td>
<td>19·3</td>
<td>18·0</td>
<td>6·8</td>
<td>7·6</td>
<td>240</td>
<td>10·9</td>
<td>11·2</td>
<td>0·97</td>
</tr>
<tr>
<td>292·3</td>
<td>19·0</td>
<td>17·6</td>
<td>7·0</td>
<td>8·0</td>
<td>240</td>
<td>11·3</td>
<td>11·5</td>
<td>0·98</td>
</tr>
<tr>
<td>∞</td>
<td>19·5</td>
<td>18·2</td>
<td>2·1</td>
<td>7·6</td>
<td>330</td>
<td>7·8</td>
<td>7·8</td>
<td>1·00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$N_2$</th>
<th>Initial</th>
<th>Av.</th>
<th>Av.</th>
<th>$\Delta p$</th>
<th>$t$</th>
<th>$r_{\text{exp}, \times 10^9}$</th>
<th>$r_{\text{cal}, \times 10^9}$</th>
<th>$r_{\text{exp}}/r_{\text{cal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>divs</td>
<td>secs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>19·2</td>
<td>17·9</td>
<td>1·9</td>
<td>7·6</td>
<td>1440</td>
<td>1·79</td>
<td>1·80</td>
<td>1·00</td>
</tr>
<tr>
<td>70·0</td>
<td>19·3</td>
<td>18·0</td>
<td>3·0</td>
<td>7·6</td>
<td>1140</td>
<td>2·27</td>
<td>2·23</td>
<td>1·02</td>
</tr>
<tr>
<td>113·4</td>
<td>19·7</td>
<td>18·4</td>
<td>4·0</td>
<td>7·4</td>
<td>1080</td>
<td>2·33</td>
<td>2·37</td>
<td>0·98</td>
</tr>
<tr>
<td>198·0</td>
<td>19·8</td>
<td>18·6</td>
<td>5·8</td>
<td>7·25</td>
<td>960</td>
<td>2·56</td>
<td>2·54</td>
<td>1·01</td>
</tr>
<tr>
<td>261·9</td>
<td>19·8</td>
<td>18·5</td>
<td>5·2</td>
<td>7·4</td>
<td>990</td>
<td>2·54</td>
<td>2·63</td>
<td>0·97</td>
</tr>
<tr>
<td>339·0</td>
<td>19·6</td>
<td>18·4</td>
<td>7·8</td>
<td>7·35</td>
<td>930</td>
<td>2·67</td>
<td>2·68</td>
<td>1·00</td>
</tr>
<tr>
<td>∞</td>
<td>19·3</td>
<td>18·0</td>
<td>2·0</td>
<td>7·7</td>
<td>1440</td>
<td>1·82</td>
<td>1·80</td>
<td>1·01</td>
</tr>
</tbody>
</table>

Again addition of inert gas raises the rate of reaction, 300 mm nitrogen increasing the rate by the factor 1·45 as at 90° C. The calculated rates of Tables VI and VII have been obtained by means of formula (b), the value of $V/k_2$ being taken as $30,000 \times 10^{-16}$ as before. This term $V/k_2$ must vary with temperature, but experimental results are satisfactorily represented by the constant value; both $V$ and $k_2$ apparently increase with rise in temperature in such a way as to render the quotient practically independent of the temperature over the range concerned. The standard rates ($N_2 = 0$) were $7·85 \times 10^{-3}$ mm per second at 100·0° C and $1·80 \times 10^{-3}$ mm per second at 80·0° C.
The Thermal Decomposition of Ozone

Calculating the appropriate value of \( k_1 \) from \( r_\infty \) at each temperature, we can summarize the numbers obtained as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( k_1 ) (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.0</td>
<td>0.835 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>90.0</td>
<td>1.81 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>100.0</td>
<td>3.61 ( \times 10^{-4} )</td>
</tr>
</tbody>
</table>

The energy of activation calculated in the usual way is found to be 19,600 cals, from results at 80° and 90° C, 18,600 from results at 90° and 100° C, and 19,000 from the results at 80° and 100° C. The value thus taken as representing the energy of activation of reaction 1

\[ \text{O}_3 = \text{O}_2 + \text{O}_1 \]

is 19,000 calories, from results at \([\text{O}_3] = 18 \text{ mm}\).

It has already been pointed out that the energy of activation calculated in the usual way for oxygen-ozone mixtures will vary with the composition of the mixtures. Clement* used ozonized oxygen in vessels where the surface factor would be small by reason of the temperatures employed (150–200° C), the apparent value of E being 26,000 calories. Wulf and Tolman† found for ozonized oxygen of 2% ozone \( E = 29,600 \), Belton, Griffith and McKeown‡ give \( E = 27,800 \) for roughly 10% ozone-oxygen mixtures. The values obtained by Glissmann and Schumacher (\( E > 23,000 \)) are considered later.

Details of three experiments on approximately 10% mixtures at 100° C are now given in Table VIII, these having been carried out in the manner already described.

Table VIII—Temperature = 100·0° C

<table>
<thead>
<tr>
<th>Av. ([\text{O}_3])</th>
<th>Initial ([\text{O}_3])</th>
<th>Av. ([\text{O}_2])</th>
<th>( \Delta p )</th>
<th>( t )</th>
<th>( r_{\exp} \times 10^3 )</th>
<th>( r_{\text{calc}} \times 10^3 )</th>
<th>( r_{\exp}/r_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. ([\text{O}_2])</td>
<td>mm</td>
<td>divs</td>
<td>secs</td>
<td>7.7</td>
<td>360</td>
<td>7.3</td>
<td>7.4</td>
</tr>
<tr>
<td>200.2</td>
<td>19.7</td>
<td>18.3</td>
<td>( \text{divs} )</td>
<td>7.7</td>
<td>360</td>
<td>7.3</td>
<td>7.4</td>
</tr>
<tr>
<td>231.1</td>
<td>19.9</td>
<td>18.5</td>
<td>( \text{divs} )</td>
<td>7.9</td>
<td>390</td>
<td>6.9</td>
<td>6.8</td>
</tr>
<tr>
<td>225.0</td>
<td>19.5</td>
<td>18.1</td>
<td>( \text{divs} )</td>
<td>7.8</td>
<td>390</td>
<td>6.8</td>
<td>6.85</td>
</tr>
<tr>
<td>400.0</td>
<td>18.0</td>
<td>( \text{divs} )</td>
<td>3.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values of \( r_{\text{calc}} \) were obtained by formula (d) by inserting the appropriate concentrations of oxygen with \( k_3/k_2 = 3 \cdot 2 \times 10^{-4} \), and \( V/k_2 = 30,000 \times 10^{-16} \). Ratios of total decomposition rates at oxygen concentrations of 0, 200, and

400 mm may then be examined for the two temperatures 100·0 and 90·0° C (cf. fig. 1).

<table>
<thead>
<tr>
<th>[O₃] mm</th>
<th>r x 10² 100°</th>
<th>r x 10² 90°</th>
<th>r₁₀₀/r₉₀</th>
<th>E'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.00</td>
<td>7.9</td>
<td>1.95</td>
<td>18100</td>
</tr>
<tr>
<td>200</td>
<td>3.30</td>
<td>7.4</td>
<td>2.24</td>
<td>22000</td>
</tr>
<tr>
<td>400</td>
<td>1.45</td>
<td>3.64</td>
<td>2.51</td>
<td>25000</td>
</tr>
</tbody>
</table>

E' is the apparent heat of activation calculated from these figures; it will be observed to increase as the percentage oxygen increases, becoming 25,000 for an ozone-oxygen mixture of approximately 5% ozone. It appears probable therefore that the high values obtained by the workers cited above are to be explained at least partly on this basis.

The results of Tables IV and VIII indicate that \( k_2/k_3 \) has the value 4·5 x 10⁻⁴ at 90·0° C, and the value 3·2 x 10⁻⁴ at 100° C. Thus \( (k_2^{100}/k_2^{90})/(k_3^{100}/k_3^{90}) = 1·4 \). Replacing in both instances \( (k^{100}/k^{90}) \) by \( e^{-E/2×373}/e^{-E/2×363} \), we calculate \( E_2 - E_3 \) as equal to 9000 cals. This figure may be checked by considering the collision efficiencies of reactions 2 and 3 (\( e'_2 \) and \( e'_3 \) respectively) in conjunction with the ratio \( R' \) of total binary collisions to total ternary collisions at, say, 100 mm pressure of ozone and of oxygen. Since \( k_3/k_2 = 4·5 \times 10^{-4} \) at 90° C,

\[
\frac{2·2 \times 10^{-1} \times e'_3}{e'_2} = R'.
\]

By taking \( e' = e^{-E/RT} \) for both reactions as before, with \( E_2 - E_3 = 9000 \) cals, \( R' \) is calculated as approximately 5 x 10⁴, a figure in good agreement with the accepted value for the pressures under consideration.

For very dilute ozone-oxygen mixtures, i.e., when the pressure of oxygen is very high and surface effects correspondingly negligible, the rate of reaction will be proportional to \( k_1k_2/k_3 \) (cf. formula (c)), and the apparent heat of activation would then be \( E_1 + E_2 - E_3 \); on the basis of the above results the maximum apparent heat of activation which could be observed would be in the neighbourhood of 19000 + 9000 = 28000 calories.

At 90° C, the maximum rate of decomposition obtained with [O₃] = 18·0 mm is 6·52 x 10⁻³ mm O₃ per second (= 2\( k_1[O_3] \)), no oxygen atoms being then removed by wall action. On the other hand, if all oxygen atoms were removed at the wall, the rate would be half this value, namely, 3·26 x 10⁻³ mm per second. For [O₃] = 18·0 mm, no inert gas being present, the actual recorded rate was 4·00 x 10⁻³; in other words the ratio of oxygen atoms removed by collision with ozone molecules to those removed by the wall in the particular
The Thermal Decomposition of Ozone

reaction vessel is \( \frac{4 \cdot 00 - 3 \cdot 26}{6 - 52 - 4 \cdot 00} = 0 \cdot 294 \). If now at any instant during the decomposition \( N_1 \) atoms of oxygen are produced per cc per sec by reaction (1) these \( N_1 \) atoms make \( \pi \sigma^2 \cdot 0 \cdot N_1 n_2 \sqrt{\bar{u}_1^2 + \bar{u}_2^2} \), collisions with ozone molecules where \( n_2 \) is the number of ozone molecules per cc and \( \bar{u}^2 \) represents the mean square velocity as calculated in the usual way. If \( E_2 \) be the energy of activation of reaction (2)

\[
O + O_3 = 2O_2,
\]

the fraction of impacts which are effective is \( e^{-E_2/RT} \) and the number of effective collisions per sec per cc is \( \pi \sigma^2 \cdot 0 \cdot N_1 n_2 \sqrt{\bar{u}_1^2 + \bar{u}_2^2} \cdot e^{-E_2/RT} \). For \([O_3] = 18 \cdot 0 \) mm, under the experimental conditions the number of atoms removed by such a process is \( 0 \cdot 294 \cdot N_1 \) and therefore

\[
0 \cdot 294 \cdot N_1 = \pi \sigma^2 \cdot 0 \cdot N_1 n_2 \sqrt{\bar{u}_1^2 + \bar{u}_2^2} \cdot e^{-E_2/RT}.
\]

The value of \( E_2 \) is then calculated as 14200 cals. Now \( E_2 - E_3 \) has been found experimentally to be 9100 calories, and hence the energy of activation \( E_3 \) of the triple collision

\[
O + O_2 + O_2 = O_3 + O_2,
\]

is approximately 5000 calories. This small value is in accordance with general considerations regarding the rates of reaction when three bodies are involved, in the sense that an appropriate ternary collision is an event of comparative rarity. At the temperature of the above experiments, for the above triple collision, the value of \( e^{-E_3/RT} \) is \( 1 \cdot 03 \times 10^{-3} \), i.e., roughly 1 collision in 1000 is efficient.

The Initial Stage

We may now proceed with a further discussion of the initial step in the scheme for the decomposition of ozone, namely,

\[
O_3 = O_2 + O.
\]

On the basis of the kinetics developed above, this reaction is "unimolecular," i.e., the rate of decomposition in this equation would be directly proportional to the number of molecules of ozone. In recent years, considerable attention has been directed to the probable mechanism of such a process, and in particular Lindemann* has shown that molecules may receive their energy of activation

by collision with other molecules, but nevertheless may be transformed chemically at a rate independent of the pressure over a very large range.

A knowledge of the energy of activation $E$ as obtained experimentally should give a calculated velocity constant much greater than the value recorded in the region where the reaction follows the unimolecular law; but this calculation leads to the result that unimolecular reactions in general proceed at a rate many times greater than the expression $Ze^{-E/kT}$ requires. It then appears that unimolecular reactions are characteristic of complex molecules possessing a necessary number of internal degrees of freedom. The decomposition of ozone, if unimolecular, should be of considerable interest in view of the comparatively simple nature of the molecule. The correction for the number of internal degrees of freedom would presumably be small, and hence the rate calculated on the ordinary basis might still be greater than that experimentally determined. At the same time, it is to be remembered that the existence of the unimolecular reaction depends on the time lag between activation and chemical transformation, and this time lag can reasonably be assumed to be connected with the complexity of the molecule; on this view, the less the complexity the more quickly would the unimolecular reaction tend to become bimolecular on reducing the pressure.

A series of experiments was therefore carried out with varying pressures of ozone. The removal of oxygen atoms by the surface of the reaction vessel was rendered small by the addition of a suitable quantity of nitrogen; under these circumstances the rate of the initial reaction is approximately half the experimentally recorded rate. The results are given in Table X, values of $k_1$ being calculated by means of the general expression previously derived:

$$\frac{-d(O_3)}{dt} = \frac{k_1 [O_3] (2k_2 [O_3] + S)}{(k_2 [O_3] + k_3 [O_3]^2 + k_4 [O_2] [N_2] + S)}.$$

Table X—Temperature $= 90 \cdot 0^\circ C$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial $[O_3]$</th>
<th>Av. $[O_3]$</th>
<th>Av. $[O_2]$</th>
<th>$[N_2]$</th>
<th>$\Delta t$</th>
<th>$t$</th>
<th>$r_{exp} \times 10^3$</th>
<th>$k_1 \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.5</td>
<td>7.9</td>
<td>6.9</td>
<td>294.0</td>
<td>6.4</td>
<td>1800</td>
<td>1.21</td>
<td>1.19</td>
</tr>
<tr>
<td>2</td>
<td>19.2</td>
<td>17.7</td>
<td>8.2</td>
<td>285.4</td>
<td>8.7</td>
<td>510</td>
<td>5.80</td>
<td>2.02</td>
</tr>
<tr>
<td>3</td>
<td>31.8</td>
<td>28.4</td>
<td>9.6</td>
<td>270.5</td>
<td>17.3</td>
<td>480</td>
<td>12.2</td>
<td>2.52</td>
</tr>
<tr>
<td>4</td>
<td>53.0</td>
<td>45.6</td>
<td>14.6</td>
<td>184.6</td>
<td>16.8</td>
<td>240</td>
<td>23.8</td>
<td>2.92</td>
</tr>
<tr>
<td>5</td>
<td>68.1</td>
<td>58.8</td>
<td>17.7</td>
<td>245.1</td>
<td>25.0</td>
<td>240</td>
<td>35.4</td>
<td>3.27</td>
</tr>
<tr>
<td>6</td>
<td>80.2</td>
<td>70.2</td>
<td>19.5</td>
<td>239.7</td>
<td>30.9</td>
<td>240</td>
<td>43.7</td>
<td>3.56</td>
</tr>
<tr>
<td>7</td>
<td>96.4</td>
<td>84.4</td>
<td>23.0</td>
<td>174.0</td>
<td>30.2</td>
<td>180</td>
<td>56.8</td>
<td>3.66</td>
</tr>
<tr>
<td>8</td>
<td>104.1</td>
<td>89.6</td>
<td>26.9</td>
<td>197.0</td>
<td>32.5</td>
<td>180</td>
<td>61.3</td>
<td>3.76</td>
</tr>
</tbody>
</table>
The Thermal Decomposition of Ozone

It will be observed that a five-fold variation in \([O_3]\) (from 18 to 90 mm) corresponds to an approximately ten-fold variation in the rate of the initial reaction; if this reaction were strictly bimolecular, the rate would, of course, have increased 25 times. At the same time the adoption of a bimolecular mechanism for the initial stage would mean, on the basis of the results already reported, that in oxygen-rich mixtures the total rate of decomposition would be proportional to \([O_3]^n\), where \(n > 2\); experiment gives little or no evidence in support of this point of view.

Of considerable interest in this connection are the results of Bowen, Moelwyn-Hughes, and Hinshelwood* on the decomposition of ozone in carbon tetrachloride solution. The decomposition is found to be strictly unimolecular, as would be expected from the above general ideas—oxygen content small and surface effect negligible. The rate of decomposition is given by the relation

\[
k = 5 \cdot 82 \times 10^{12} \times e^{-26169/RT} \text{ sec}^{-1},
\]

which becomes \(5 \cdot 2 \times 10^{-4} \text{ sec}^{-1}\) at 80° C. This figure corresponds to the total rate \(2k_1\) in the preceding mechanism; hence half this value will represent the rate of the initial stage, namely, \(2 \cdot 6 \times 10^{-4} \text{ sec}^{-1}\), and is to be compared with the \(k_1\) values of the gas phase experiments. In Table X the values of \(k_1\) range from \(2 \times 10^{-4}\) to \(4 \times 10^{-4} \text{ sec}^{-1}\) at 90° C; at 80° C, \(k_1\) will be approximately half these values. It can easily be shown from the above figures that the reciprocal of \(k_1\) varies linearly with the reciprocal of \([O_3]\); extrapolation gives a value of approximately \(2 \cdot 3 \times 10^{-4}\) for infinite pressure. The agreement between the two sets of experimental results thus affords strong support to the recognition of the first step in the thermal decomposition of ozone at ordinary pressures as predominantly unimolecular.

It may be mentioned that the ozone employed in experiments 7 and 8 of Table X was heated, before use in these experiments, in a large glass bulb at 100° C until approximately one-third had been decomposed. The residual ozone was condensed out by means of liquid air, oxygen removed by evacuation, and experiments 7 and 8 then carried out. The object of this procedure was to destroy any "impurities" which might increase the rate of reaction; the substance \(O_4\) for example, might conceivably have been formed initially in the ozonizer and might be responsible for the higher values of \(k_1\), obtained. The results of experiments 7 and 8 are, however, in reasonable agreement with the rates to be expected from examination of the general results of Table X.

M. Ritchie

It is possible also that this relative increase on the further addition of ozone is due to a chain reaction of short duration, this being perhaps formulated as follows:

\[ O_3 = O_2 + O \]
\[ O + O_3 = 2O^*_2 \]
\[ O^*_2 + O_3 = O + O_2 + O_2. \]

One might expect, however, that at low pressures of ozone and high pressures of nitrogen, this effect would be small, the nitrogen presumably acting as a deactivator of the \( O^*_2 \) molecules; at low pressures, however, the discrepancy does not disappear but appears to be accentuated (cf. Experiment 1, Table X).

Glissmann and Schumacher\(^\dagger\) have carried out an extensive series of experiments on the thermal decomposition of ozone with and without the addition of oxygen and other gases. The general results show a decided similarity to the results reported in this paper; surface action is recognized, which becomes relatively less as the total pressure becomes greater, together with the acceleration of the rate of reaction by inert gases such as carbon dioxide, nitrogen, and argon when little oxygen is present, the acceleration by oxygen when the oxygen concentration is not too high, and the increase in the apparent heat of activation as the oxygen content increases. In the reaction mechanism advanced by these workers, however, the initial step is regarded as strictly bimolecular, and the oxygen atom is not regarded as playing a dominant part in the total rate of decomposition. It is admitted by Glissmann and Schumacher that the increased rate of reaction in ozone-inert gas mixtures is not definitely accounted for.

The value of the energy of activation adopted by Glissmann and Schumacher for ozone containing little oxygen is larger (24500) than that obtained by the writer (19000). This latter value was obtained for a relatively low pressure of \([O_3]\), namely, 18 mm, while the experiments of Glissmann and Schumacher were carried out at higher pressures. The temperature ranges considered are the same. Examination of their results and comparison with the result for 18 mm obtained by the writer indicates that the higher the pressure of ozone, the higher the calculated heat of activation. Glissmann and Schumacher give a mean value of approximately 24000 cals. for the range 25–100 mm \( O_3 \), but values of 27300, 29700, 25100, and 27000 calories are recorded for pressures of 144, 172, 284 and 376 mm respectively. This increase might be explained

The Thermal Decomposition of Ozone

by reference to the possible chain reaction involving activated oxygen molecules as already mentioned; if this be so, the value of 19000 calories would be nearer to the correct value for the initial reaction. On the other hand, a decrease in apparent energy of activation as calculated in the ordinary way, has been recorded in reactions which are definitely regarded as of the unimolecular type, in that region where the decomposition is showing definite bimolecular characteristics.* Comparison may also be made by reason of the fact that the reciprocal of \( k_1 \) bears here a linear relationship to the reciprocal of the pressure. The value of 19000 calories obtained by the writer for ozone at 18 mm pressure is less than the usually recognized figure for the heat of the (endothermic) reaction, namely, 24000 calories; under such conditions the simple expression

\[
\frac{d (\log k)}{dt} = \frac{E}{RT^2}
\]

is not strictly applicable. A more reasonable value of the energy of activation would be the value recorded by Glissmann and Schumacher for the higher pressures of ozone (28000 cals.) or that obtained for the decomposition of ozone in carbon tetrachloride solution, where the reaction is strictly unimolecular; according to Bowen, Moelwyn-Hughes, and Hinselwood (loc. cit.), this is 26160 calories. The rate of decomposition then calculated in the ordinary way from this latter figure is approximately \( 4 \times 10^{-5} \) sec\(^{-1} \) at 90° and is thus one-tenth the experimental value; the adoption of Glissmann and Schumacher’s heat of activation increases the divergence; the difference between calculated and experimental values is then to be ascribed to the part played by the internal energy of the ozone molecule.

The author desires to acknowledge the interest and encouragement afforded to him by Dr. E. B. Ludlam and Professor James Kendall. His thanks are also due to the Earl of Moray Endowment Fund for the quartz reaction vessel used.

Summary and Conclusions

The thermal decomposition of ozone has been investigated manometrically for the temperature range 80–100° C, the pressure of ozone being varied from 10 to 100 mm. The initial stage is recognized as the pseudo-unimolecular reaction

\[
O_3 = O_2 + O
\]

The thermal decomposition of ozone

the oxygen atom thus formed leading to further ozone decomposition by the reaction

\[ O + O_2 = 2O_3. \]  

(2)

In the absence of appreciable amounts of oxygen, addition of inert gases increases the rate of total decomposition by preventing the diffusion of oxygen atoms to the wall. In the presence of oxygen, due allowance having been made for the diffusion effect, the rate of decomposition is retarded by the triple collision effect

\[ O + O_2 + M = O_3 + M, \]  

(3)

where M may be a molecule of oxygen or of other added gas. The apparent heat of activation depends then on the relative concentrations and the velocity coefficients of reactions (1), (2) and (3).

At the higher pressures of ozone employed, reaction 1 is regarded as predominantly unimolecular: \( k_1 \) is approximately \( 4 \times 10^{-4} \, \text{sec}^{-1} \) at \( 90^\circ \) C and agrees satisfactorily with the value of \( k_1 \), obtained by other workers, for the decomposition of ozone in carbon tetrachloride solution. At the lower pressures, bimolecular characteristics become increasingly evident.

The heat of activation of reaction 1, calculated in the usual way, is 19000 calories, from results at 18 mm pressure of ozone; comparison with results of other workers indicates that this activation energy when calculated in the usual way depends on the pressure of ozone in this transition region.

The energy of activation of reaction 2 is estimated as 14000 calories and that of the triple collision

\[ O + O_2 + O_2 = O_3 + O_2, \]

as 5000 calories.