# Mechanism of the Gas Phase, Thermal Decomposition of Ozone*†

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The pyrolysis of ozone has been reinvestigated experimentally, and it is now shown that most of the known data are quantitatively explained on the basis of the simple mechanism,

$$M+O_3 \overset{1}{\underset{2}{\rightleftharpoons}} M+O_2+O$$

$$O+O_3 \overset{3}{\rightarrow} 2\,O_2,$$

where M may be $O_2$, $O_3$, $CO_2$, $N_2$, He, etc. There is no evidence for a direct bimolecular reaction of ozone to produce $O_2$ nor is there any evidence for important surface effects or energy chains. On the other hand, the results at very fast rates of decomposition indicate an acceleration which can be accounted for in terms of temperature gradients in the system. This region is usually very close to the thermal explosion limit.

The values found for the rate constants are (for M equal to $O_3$),

$k_1=4.61\pm0.25\times10^{12}\exp(-24\,000/RT)$ liter/mole-sec,
$k_2=6.00\pm0.33\times10^{7}\exp(+600/RT)$ liter²/mole²-sec,
$k_3=2.96\pm0.21\times10^{10}\exp(-6000/RT)$ liter/mole-sec.

The relative efficiencies of $O_2$, $N_2$, $CO_2$, and He in activating $O_3$ (compared to $O_3$ itself) are, respectively, 0.44, 0.41, 1.06, and 0.34.

As expected for energy transfer processes, $k_1$ has an abnormally high pre-exponential factor, and $k_2$ has correspondingly a negative energy of activation. It is further inferred that Reaction 3 which produces two $O_2$ molecules with 99 kcal of excess energy between them does not produce more than one excited electronic state of $O_2$ and that these hot $O_2$ molecules are not very efficient in exciting $O_3$ to decomposition. Calculations of the entropy of activation of Reaction 1 can be made and are shown to be in good agreement with this conclusion. From these findings it appears that the high quantum yields found in the photolysis of $O_3$ at short wavelengths, if real, probably are attributable to metastable O atoms [$^1D$] produced in the primary process which can generate chains in $O_3$.

It can be shown that the homogeneous production of O atoms from $O_2$ at high temperatures proceeds through two different paths having different activation energies, the lower energy path involving $O_3$ as an intermediate.

Finally, possible mechanisms are considered for the chemical sensitization of the thermal explosion of $O_3$ and its catalytic decomposition by H donors.

## INTRODUCTION

THE gas phase, thermal decomposition of ozone has been the object of many extensive investigations, yet no satisfactory mechanism has ever been proposed.

The early workers[1] studied the decomposition of dilute ozone directly from the ozonizer. In general, they attempted to explain their results in terms of an atomic mechanism,

$$O_3 \overset{1}{\underset{2}{\rightleftharpoons}} O_2+O, \qquad (1,2)$$

$$O+O_3 \overset{3}{\rightarrow} 2\,O_2, \qquad (3)$$

in which Reaction (2) is much faster than Reaction (3); i.e., under their conditions, the oxygen atoms are assumed to be at their equilibrium[2] concentration with respect to Reactions (1,2). The reproducibility of these dilute ozone experiments was very poor and no conclusive evidence was ever presented that the rate is exactly inversely proportional to the oxygen concentration as this mechanism would require.[3(a)]

Garvin,[3(b)] however, recently has reinvestigated the thermal decomposition of dilute ozone employing a flow technique. He found the rate to be nearly inversely proportional to the oxygen concentration and independent of the concentration of added nitrogen as the Jahn mechanism would predict.

Several investigations[4–8] have been carried out using concentrated ozone obtained by the fractional distillation of dilute ozone. The reliability of these studies is difficult to evaluate since possible important errors such as errors in the analyses for the final ozone concentration or in the dead space corrections cannot be determined from the published data. In some cases,[1,6] however, it is possible to show that a significant amount of ozone was

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[1] For references to this early work, see O. R. Wulf and R. C. Tolman, J. Am. Chem. Soc. **49**, 1183, 1202 (1927).

[2] This atomic mechanism in which the oxygen atoms are at their equilibrium concentration has become known as the "Jahn mechanism."

[3] (a) Although Wulf and Tolman[1] are quite critical of their own results and do not claim to have proven the Jahn mechanism, there appears to be a popular misconception that their results did verify the rate law proposed by Jahn. That this is not the case may be seen by referring to Table XII of reference 1 and Table III of reference 1. The lack of reproducibility of their second-order rate constants obtained with their "best" ozone is shown in Table V of reference 1. The earlier results of Jahn are similarly inconclusive in proving the Jahn mechanism. (b) D. Garvin, J. Am. Chem. Soc. **76**, 1523 (1954).

[4] E. H. Riesenfeld and W. Bohnholtzer, Z. physik. Chem. **130**, 241 (1927).

[5] E. H. Riesenfeld and H. J. Schumaker, Z. physik. Chem. **A138**, 268 (1928).

[6] E. H. Riesenfeld and E. Wassmuth, Z. physik. Chem. **A143**, 397 (1929).

[7] H. J. Schumaker and G. Sprenger, Z. physik. Chem. **6B**, 446 (1930).

[8] A. Glissman and H. J. Schumaker, Z. physik. Chem. **21B**, 323 (1933).



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present at the "infinite" time reading because the reaction vessel was not heated to a high enough temperature. Most of these investigators represented their results empirically in terms of simultaneous first- and second-order reactions.

The most satisfactory investigation, with respect to both the experimental methods employed and the wide range of conditions covered, appears to be that of Glissman and Schumaker.[8] They studied the reaction between 70 and 110°C in vessels varying in size from one-half to twelve liters and in the presence of added oxygen, nitrogen, helium, and carbon dioxide. They proposed the following mechanism involving simultaneous bimolecular and atomic reactions:

$$O_3+O_3 \xrightarrow{4} 3\,O_2, \tag{4}$$

$$O_2+O_3 \xrightarrow{5} O_2+O_2+O, \tag{5}$$

$$M+O+O_2 \xrightarrow{2} M+O_3, \tag{2a}$$

$$O+O_3 \xrightarrow{3} 2\,O_2. \tag{3b}$$

They also included activated oxygen molecule reactions in their mechanism.

In terms of this mechanism, Glissman and Schumaker were able to explain their results obtained with ozone-oxygen mixtures quite well. There is, however, an error in this scheme since it may be shown[9] that Reaction (5) must have the same form of pressure dependence as Reaction (2). This error does not show up too markedly in their experiments on ozone-oxygen mixtures since, according to their mechanism, the atomic reaction is only important under conditions where the ozone concentration is small. This mechanism, however, does not account for the marked acceleration which is observed when inert gases, especially carbon dioxide, are added. Schumaker[10] points out that this must be due to the effect of the inert gases on the rate of Reaction (5) but he is at a loss to explain why the acceleration is the greatest under conditions where Reaction (4) should predominate. Another difficulty with this mechanism is, as discussed by Geib,[11] that the value assigned[10] to the rate constant of Reaction (4) yields a steric factor of close to $10^{+2}$ which is abnormally high for this type of bimolecular reaction.

A reinvestigation of the thermal decomposition was undertaken in this laboratory in an effort to discover the mechanism of this interesting reaction. Our experimental procedure is similar to that employed by Glissman and Schumaker.[8]

[9] S. W. Benson and A. E. Axworthy, Jr., J. Chem. Phys. **21**, 428 (1953).

[10] H. J. Schumaker, *Chemische Gasreaktion* (Theodor Steinkopff Verlag, Dresden, Germany, 1938), p. 433.

[11] K. H. Geib, Z. Electrochem. **47**, 761 (1941).

## EXPERIMENTAL

Following several preliminary experiments which had to be discarded since the amount of ozone decomposing at an unknown rate in the dead space was quite large, four experiments have been carried out at 99.8±0.1°C in two different reaction vessels.[12] Two of the experiments, one with about 500 mm Hg of oxygen added initially, were carried out in a 537-cc Pyrex sphere and the other two in an irregularly shaped, 461-cc Pyrex vessel with about 45% greater surface.

The pressure was measured using a Pyrex Bourdon gauge sensitive to 0.1 mm Hg as a null instrument to a Hg manometer. The final pressure was measured after heating the reaction vessel above 200°C for eight hours or longer. The maximum dead space was 14 cc, and this was quite efficiently flushed with oxygen at the start of each experiment. The ozone pressure at any time, $t$, was calculated from the total pressure at that time and the total pressure at infinite time by means of the following equation which corrects for the dead space (assuming the small amount of ozone present in the dead space is stable during the entire experiment):

$$P_{O_3}{}^t = 2P_T{}^t \cdot \left[\left(\frac{P_T{}^\infty}{P_T{}^t}\right)^K - 1\right], \quad K \equiv 1+\frac{T_R V_D}{T_D V_R}, \tag{I}$$

where the subscripts $R$ and $D$ refer to the reaction vessel and the dead space.

Tank oxygen was passed over hot CuO, through an anhydrous $CaSO_4$ tube, a glass wool trap at −80°C, and a Pyrex ozonizer.[13] The ozone-oxygen mixture was partially condensed at the temperature of liquid oxygen, cooled in liquid nitrogen, and then opened to the pumps until nearly all of the oxygen was removed. The ozone was then twice trap-to-trap vacuum distilled, the final portion of the second distillation being discarded. After the evacuated reaction vessel had reached reaction temperature, the ozone was allowed to evaporate into it.[14] Oxygen was then added in some of the experiments, the dead space was flushed with oxygen, and the pressure readings begun. In the experiments cited, the ozone pressure was followed from an initial pressure of about 100 mm Hg to a final pressure of about 10 mm Hg.

The hollow-bore, vacuum stopcocks used in the sys-

[12] Vessel *I*, $v/s = 537/376 = 1.43$ cm; Vessel *II*, $v/s = 461/547 = 0.84$ cm.

[13] This source of oxygen was abandoned for future experiments as it probably contains nitrogen which would lead to the formation of nitrogen oxides in the ozonizer.

[14] At this point the danger of explosion is quite high (especially if sufficient ozone is present so that its initial concentration in the reaction vessel is much above 100 mm Hg). During the course of our investigation, we have encountered a total of eight explosions, three of which were quite damaging and none of which occurred at room temperature or below. One occurred upon immersing a 1-liter vessel containing 250 mm of ozone in a liquid bath at 99°C; four occurred during the evaporation of the ozone into the hot reaction vessel; and three occurred after this evaporation when large amounts of oxygen were bled into the reaction vessel. Approximately one hundred rapid distillations and evaporations have been made at room temperature and below without difficulty.

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TABLE I. Comparison of results with those of Glissman and Schumaker.

$T$=99.8°C. $k_3$ is second-order rate constant in l/M-sec. Pressures are in mm Hg. Values in parentheses are predicted from the mechanism proposed in this paper.

| | (Benson and Axworthy) | | | | (Glissman-Schumaker) | | |
|---|---|---|---|---|---|---|---|
| Experiment number | 1 | 2 | 3 | 4 | 45 | 43 | 66[b] |
| Vessel | *I* | *I* | *II* | *II* | *II*[a] | *II* | *II* |
| Final oxygen pressure at total decomposition | 620.2 | 301.3 | 207.2 | 208.1 | 408.8 | 254.6 | 125.9 |
| $k_3\times10^3$ at an ozone pressure of 95 mm | ··· | 128 (119) | 103 (99) | 97 (99) | 131 (131) | 113 (110) | ··· ··· |
| $k_3\times10^3$ at an ozone pressure of 70 mm | 157 (142) | 141 (140) | 118 (119) | 117 (119) | 145 (149) | 126 (131) | ··· ··· |
| $k_3\times10^3$ at an ozone pressure of 55 mm | 163 (151) | 149 (160) | 138 (138) | 141 (139) | 160 (165) | 144 (151) | 415 (406) |
| $k_3\times10^3$ at an ozone pressure of 40 mm | 170 (161) | 178 (187) | 161 (168) | 163 (169) | 178 (188) | 166 (181) | 475 (478) |
| $k_3\times10^3$ at an ozone pressure of 20 mm | 188 (179) | 225 (254) | 241 (253) | 259 (253) | ··· ··· | ··· ··· | 605 (641) |

[a] One liter spherical vessel.
[b] 610 mm of nitrogen present in this experiment.

tem were lubricated with Halocarbon (high-temperature grade) stopcock lubricant. The usual precautions were taken to minimize the amount of Hg vapor in the system.

## RESULTS

The results of our investigation are tabulated in Table I along with two similar experiments of Glissman and Schumaker. Our data is in qualitative agreement with theirs but the results cannot be compared exactly, except in terms of a specific mechanism, since the total pressures were not the same. Our experiments 3 and 4 represent nearly identical conditions and, therefore, indicate the order of reproducibility of our results.

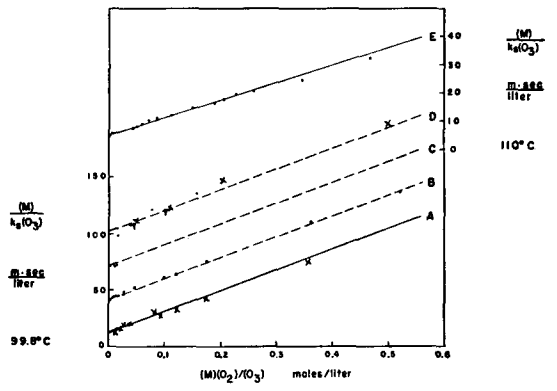



FIG. 1. Comparison of the results of this investigation at 99.8°C and the results of Glissman and Schumaker at 99.8°C and 110°C with the proposed mechanism. Solid lines correspond to values predicted from the mechanism and rate constants given in this paper. The dotted lines have been shifted from the solid line (A) for the sake of clarity.

(A)-4[a] B. and A. 99.8°C. No inert gases. (×) Vessel *I*. (•) Vessel *II*.
(B)-5 G. and S. 99.8°C. No inert gases. Vessel *II*. $P_{O_3}$=15 to 95 mm Hg.
(C)-2 G. and S. 99.8°C. No inert gases. Vessel *II*. $P_{O_3}$=100 to 160 mm Hg.
(D)-3[b] G. and S. 99.8°C. Added $N_2$. Vessel *II*. (•) 200 mm Hg. (♂) 410 mm Hg. (×) 610 mm Hg.
(E)-3 G. and S. 110°C. No inert gases. Vessel *II*. $P_{O_3}$=16 to 50 mm Hg.

[a] Numbers following hyphens denote the number of experiments which are represented.
[b] The coordinates have been expanded on graph D for convenience. The correct ordinates and abscissas may be obtained from the apparent values (read off the corresponding point on graph A) as follows: Abscissas: correct =apparent ÷5. Ordinates: correct = (apparent −12.5) ÷5+12.5.

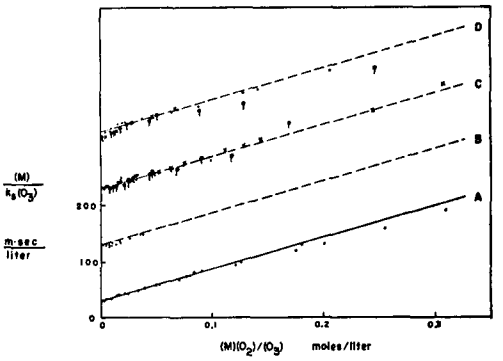



FIG. 2. Comparison of the results of Glissman and Schumaker at 90°C with the proposed mechanism. Solid line corresponds to values predicted from the mechanism and rate constants given in this paper. The dotted lines have been shifted from the solid line (A) for the sake of clarity.

(A)-10 G. and S. 90.0°C. No inert gases. Vessel *II*. $P_{O_3}$=21 to 100 mm Hg.
(B)-6 G. and S. 90.0°C. No inert gases. Vessel *II*. $P_{O_3}$=130 to 280 mm Hg.
(C)-10[a] G. and S. 90.0°C. Vessel *II*. (•) Added He. (♂) Added $N_2$. (×) Added $CO_2$.
(D)-10[b] G. and S. 90.0°C. No inert gases. (•) Vessel *I*. (♂) Vessel *III*. (×) Vessel *IV*.

[a] The coordinates have been expanded on graph C. The correct values may be obtained from the apparent values as follows: Abscissas: correct =apparent ÷2. Ordinates: correct = (apparent −30.1) ÷2+30.1.
[b] The coordinates have been expanded on graph D. Abscissas: correct =apparent ÷3. Ordinates: correct = (apparent −30.1) ÷3+30.1.

The same general trends occur in our data as were observed by Glissman and Schumaker. The second-order rate constants[15] increase markedly during a given run, the magnitude of this effect decreasing with increasing oxygen pressure. At a given ozone pressure, the addition of oxygen accelerates the rate at high ozone pressures and inhibits it at lower ozone pressures.

## DISCUSSION OF RESULTS

The simple atomic mechanism,

$$M+O_3\underset{2}{\overset{1}{\rightleftharpoons}}M+O_2+O, \qquad (1,2)$$

$$O+O_3\overset{3}{\longrightarrow}2\,O_2 \qquad (3)$$

appears to be compatible with the quantitative features

[15] These second-order rate constants were obtained by taking tangents at various points on a $1/(O_3)$ *vs* time plot. All of the data of Glissman and Schumaker were plotted in this manner in order to obtain the most reliable rate constants their results would yield. Unfortunately, they allowed rather long time intervals to pass between readings and the accuracy of their results is greatly decreased because of this. Actually, a dead space correction should enter here also since the ozone is disappearing by two paths (reaction and flow into the dead space). The correction, however, is less than experimental error.

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of this reaction. Although the rate law derived from this mechanism is completely integrable, it was found to be simpler to test the data in terms of the differential rate expression. The rate expression obtained, assuming Reaction (1,2) to be at its low-pressure limit, may be put in the following form:

$$(M)/k_s(O_3)=(k_2/2k_1k_3)(M)(O_2)/(O_3)+1/2k_1, \quad \text{(II)}$$

where

$$(M)=(O_3)+a_{O_2}(O_2)+a_{N_2}(N_2)+a_{CO_2}(CO_2)+a_{He}(He) \quad \text{(III)}$$

and[15]

$$k_s=-[d(O_3)/dt]/(O_3)^2. \quad \text{(IV)}$$

In order to test this proposed mechanism, $(M)/k_s(O_3)$ was plotted against $(M)(O_2)/(O_3)$ for our results as well as those of Glissman and Schumaker.[16] The best fit was obtained using

$$(M)=(O_3)+0.44(O_2)+0.41(N_2)+1.06(CO_2)+0.34(He).$$

The agreement between these data and this atomic mechanism may be seen in Figs. 1(ABDE), 2(ACD), and 3(ABD). This is excellent agreement considering that $k_s$ may vary by a factor of more than six at a given temperature depending upon the conditions (see Table I).

The values of $k_1$ and $k_1k_3/k_2$ obtained from the intercepts and slopes of these graphs[17] are plotted in the Arrhenius form in Fig. 4. From this are obtained the values (for M equal to $O_3$),

$$k_1=4.61\pm0.25\times10^{12}\exp(-24\,000/RT) \text{ liter/mole-sec},$$

$$k_1k_3/k_2=2.28\pm0.16\times10^{15}\exp(-30\,600/RT) \text{ sec}^{-1}.$$

The values obtained by Garvin[3(b)] for the quantity $k_1k_3/k_2$ at higher temperatures are nearly identical with those obtained from the preceding expression. This may be seen by comparing our Fig. 4 with his Fig. 1. From known thermal data,[18]

$$K_{eq}=k_1/k_2=7.7\times10^4\exp(-24\,600/RT) \text{ moles/liter},$$

$$k_2=6.00\pm0.33\times10^7\exp(+600/RT) \text{ liter}^2/\text{mole}^2\text{-sec},$$

$$k_3=2.96\pm0.21\times10^{10}\exp(-6000/RT) \text{ liter/mole-sec}.$$

The rates observed by Glissman and Schumaker are appreciably higher than those predicted by the preceding mechanism when the absolute rate of the reaction is greater than about $1\times10^{-6}$ mole/liter-sec. These effects are shown in Figs. 1(C), 2(B), and 3(C). Three possible explanations of these abnormally high rates have been considered: first, secondary activation of ozone by the activated oxygen molecules formed in Reaction (3); secondly, a direct bimolecular reaction as proposed by Glissman and Schumaker; and, finally, the possible existence of temperature gradients in the system.

The importance of secondary activation (energy chains) would depend on the ratio of the ozone concentration to the rate of deactivation of the activated

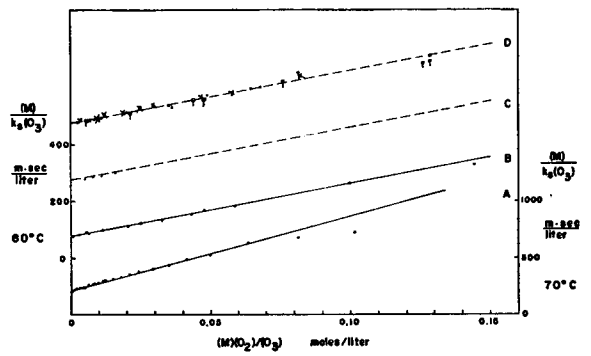



FIG. 3. Comparison of the results of Glissman and Schumaker at 70°C and 80°C with the proposed mechanism. Solid lines correspond to values predicted from the mechanism and rate constants given in this paper. The dotted lines have been shifted from the solid line (B) for the sake of clarity.

(A)-3 G. and S. 70.0°C. No inert gases. Vessel *II*. $P_{O_3}=34$ to 270 mm Hg.
(B)-3 G. and S. 80.0°C. No inert gases. Vessel *II*. $P_{O_3}=30$ to 200 mm Hg.
(C)-1 G. and S. 80.0°C. No inert gases. Vessel *II*. $P_{O_3}=250$ to 350 mm Hg.
(D)-7[a] G. and S. 80.0°C. Vessel *II*. (•) Added $N_2$. (×) Added He. (♂) Added $CO_2$.

[a] The coordinates have been expanded on graph D. The correct values may be obtained from the apparent values as follows: Abscissas: correct = apparent ÷2. Ordinates: correct = (apparent −76.5) ÷2 +76.5.

[16] All 47 experiments of Glissman and Schumaker were plotted in this manner except Experiments 31, 37, and 94 which had numerical or typographical errors in the tabulated data.

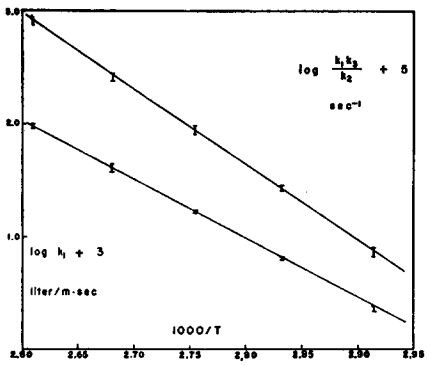



FIG. 4. Arrhenius plots of values obtained from the slopes and intercepts in Figs. 1–3.

[17] Since our results at 99.8°C without added inert gases agree well with the results of Glissman and Schumaker under the same conditions in terms of the proposed mechanism, it would appear that the large body of data presented by them is probably quite reliable. The values of the rate constants, activation energies, and *a*'s presented in this paper were obtained by the reinterpretation of the results of Glissman and Schumaker.

[18] Natl. Bur. Standards Tables, Circular 500. Using the heat capacities given, the values have been corrected to the mean temperature of 90°C to make the equilibrium constant fit the form of the Arrhenius equation in this region. For Reactions (1,2), $\Delta H^0=25.2$ kcal/mole; $\Delta E^0=24.6$ kcal $=E_1-E_2$.

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oxygen molecules. Since this rate of deactivation should be nearly temperature independent, the effect of energy chains should be equally important at 70° and 90°C for the same ozone and oxygen concentrations. That this is not the case may be seen by comparing Figs. 3(A) and 2(B). In order for a direct bimolecular reaction to compete with Reaction (1), it must have an activation energy of less than 24 kcal since, as will be discussed later, the frequency factor of $k_1$ is higher than would be expected for an ordinary bimolecular reaction. On the other hand, unless this possible direct bimolecular reaction to form oxygen has an activation energy appreciably greater than has Reaction (1), it should compete equally as well at 70 as at 90°C again contrary to the observed results.

The possible existence of temperature gradients in reacting systems has been treated theoretically,[19] and it is predicted that their magnitude should be proportional to the absolute rate of the reaction, i.e., to the rate of heat evolution in this case. Harteck and Dondes[20] have observed a temperature rise of a few degrees in the center of a vessel of rapidly decomposing ozone, and it would seem likely that temperature gradients also should exist under some of the conditions studied by Glissman and Schumaker.[21] Since the magnitude of this rate increase over the predicted rate is apparently only dependent on the absolute rate of the reaction (although these increases are, in general, not large compared with the average experimental error, making them difficult to treat quantitatively), it would seem that these abnormalities in the data can be explained best in terms of the existence of small temperature gradients. The observed rates are about 25% high [Fig. 2(B)], corresponding to an average temperature increase of 2.3°C when the rate is $6.8\times10^{-6}$ mole/liter-sec.

The value of $a_{O_2}$ [efficiency of oxygen compared with ozone at the same concentration[22] in transferring energy in Reaction (1,2)] is known only within ±20%. When sufficient oxygen is present to contribute appreciably to M, the reverse reaction, Reaction (4.2), is fast enough that the effect of M on the over-all rate is limited. For this reason $a_{O_2}$ cannot be determined more accurately with the data available. The values obtained for $k_1$ and, therefore, $k_2$ are nearly independent of the value chosen for $a_{O_2}$. The value for $k_3$ varies by ±10% when $a_{O_2}$ is varied by ±20%. If accurate data were available in the low ozone region where the "Jahn mechanism" prevails, $k_3$ could be obtained independently of $a_{O_2}$.

The rate constants listed were obtained[17] from the data in which no inert gases were added. Equation (II) was then solved for the individual $a$'s and their values determined directly from the data. The values of $a$ listed for the inert gases are accurate to about ±10% since they may be measured under conditions where Reaction (1) is nearly rate determining.

The uncertainty in the activation energies of $k_1$ and $k_2$ is 0.5 kcal and of $k_3$ it is approximately 0.7 kcal.

No trend is observed in the data which can be attributed to surface effects even though the surface to volume ratio was varied by a factor of nearly six[23] [see Figs. 2(A) and 2(D)]. This indicates that surface reactions, if present at all, must contribute to less than 10% of the rate. Harteck and Dondes[20] found that increasing the surface by a factor of 100 increased the rate by a factor of only four to six. This also seems to indicate that surface effects are small in an unpacked vessel.

## DISCUSSION OF MECHANISM

Reaction (4.1) is a unimolecular decomposition apparently at its low-pressure limit as would be expected[24] for a nonlinear triatomic molecule. The experimentally measured activation energy of 24.0 kcal will be compared later with the critical energy (bond dissociation) of 23.9 kcal known from thermal data.[25]

The frequency factor for $k_1$ is higher than the value of about $10^{11}$ liter/mole-sec usually expected as a maximum for bimolecular reactions but is considerably smaller than the values of $2\times10^{14}$, $2\times10^{16}$, and $6\times10^{13}$ found previously for similar energy transfer processes in the decompositions of $N_2O_4$,[26(a)] $N_2O_5$,[26(b)] and $NO_2Cl$.[26(c)] From the data of Russell and Simon[27] on the rate of recombination of I atoms, a value of $3.5\times10^{13}$ liter/mole-sec is obtained for the frequency factor of the reaction:

$$O_2+I_2\underset{6'}{\overset{6}{\rightleftharpoons}}O_2+I+I. \qquad (6,6')$$

This can be compared with our value of $2.0\times10^{12}$

[19] S. W. Benson, J. Chem. Phys. **22**, 46 (1954).

[20] P. Harteck and S. Dondes, J. Chem. Phys. **21**, 2240, 2241 (1953).

[21] A similar effect has been observed by Allen and Rice in the decomposition of azomethane near the explosion limit [A. O. Allen and O. K. Rice, J. Am. Chem. Soc. **57**, 310 (1935)].

[22] The efficiency of oxygen compared with ozone per collision in activating ozone is about $a_{O_2}$ since the ratio of $O_2-O_3$ collisions to $O_3-O_3$ collisions in a mixture containing ozone and oxygen is twice the ratio of oxygen to ozone. $a_{O_2}=k_1(O_2)/k_1(O_3)=\beta Z_{O_2}/Z_{O_3}$, where $Z_{O_2}$ and $Z_{O_3}$ are the collision frequencies of oxygen and ozone with ozone and $\beta$ is the relative efficiency of oxygen compared with ozone per collision in Reaction (1). Kinetic theory gives $Z_{O_3}\sim1/2Z_{O_2}$ (if we neglect the small differences in collision diameters). However, in a collision of two $O_3$ molecules, there are twice as many chances of activation as in a collision $O_2+O_3$, so $\beta\sim1$.

[23] The vessels used by Glissman and Schumaker had the following volume/surface ratios in cm: $I=0.85$, $II=2.1$, $III=2.25$, and $IV=4.74$.

[24] S. W. Benson, J. Chem. Phys. **20**, 1064 (1952). Assuming deactivation at every collision, the method presented in this reference predicts that, at 200 mm total pressure, 1% of the activated ozone molecules formed would be deactivated before decomposing. As discussed later, ozone is deactivated by oxygen (for example) not at every collision but at one in 140. This method predicts, therefore, that ozone should be within 1% of its low-pressure limit at a total pressure of 30 atmos.

[25] Estimated from Natl. Bur. Standards data (reference 18) as the $\Delta E_0^0$.

[26] (a) T. Carrington and N. Davidson, J. Chem. Phys. **57**, 418 (1953); (b) H. S. Johnston, J. Am. Chem. Soc. **75**, 1567 (1953); (c) H. F. Cordes and H. S. Johnston, *ibid.* **76**, 4264 (1954).

[27] K. E. Russell and J. Simon, Proc. Roy. Soc. (London) **A217**, 271 (1953).

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liter-mole-sec (for M equal to $O_2$). Rice[28(a)] has suggested an explanation for these "high"-frequency factors essentially in terms of a large entropy of activation.

Recently the relative effects of various inert gases on the rate of unimolecular reactions in the intermediate pressure region have been studied.[28(b),28(c)] Although these results are of considerable interest, only measurements made at the low-pressure limit yield directly values for the actual rate of energy transfer without dependence on the validity of any specific theory of unimolecular reaction rates. Apparently, the only reactions which have been studied previously at or near the low-pressure limit are those previously mentioned ($N_2O_4$, $N_2O_5$, and $NO_2Cl$) and, of course, the recombinations of atoms.[29,30] The relative efficiencies of He, $O_2$, and $CO_2$ in Reaction (6), compared with $N_2$ equal to 0.41 for convenience, are 0.15, 0.60, and 1.20, respectively.[27]

Although the relative efficiencies of these various inert gases on the rates of activation of $I_2$ and $O_3$ are somewhat similar, each gas is much less efficient in activating $O_3$ per collision than in activating $I_2$ as can be seen from the following. If we consider Reaction (2) and Reaction (6′) from the point of view of a triple collision and compare the values of $k_2(300°K)=7.2\times10^7$ (for M equal to $O_2$) and $k_{6'}(300°K)=13.9\times10^9$ liter$^2$/mole$^2$-sec, we see that $O_2$ is only about 1/200 as efficient in stabilizing $O_3$* as it is in stabilizing $I_2$*.

If we compare these rates with that of a hypothetical triple collision frequency of about $1\times10^{10}$ liter$^2$/mole$^2$-sec, we see that $O_2$ deactivates $I_2$* at almost every collision while only about 1 in 140 collisions is effective in deactivating $O_3$*. From the principle of microscopic reversibility, one concludes that the reverse process, Reaction (4.1), has a similar inefficiency despite the rather large frequency factor. In fact, if these calculations of the inefficiency of energy transfer are used to correct the frequency factor of $k_1$, then one gets values closer to $10^{15}$ liter/mole-sec which reflects much more properly the real entropy increase occurring in Reaction (1).[31]

An uncertainty is introduced in the foregoing estimation of the efficiencies of various gases in activating and deactivating ozone since the frequency of triple collisions cannot be calculated exactly from kinetic theory. The duration of a bimolecular collision enters into the calculation, and, since this quantity is not known, the triple collision frequency used previously is only a minimum value so that the foregoing calculated efficiencies for Reactions (2) and (6′) are upper limits.

In terms of the Lindemann mechanism for unimolecular reactions,

$$M+O_3 \underset{b}{\overset{a}{\rightleftharpoons}} M+O_3^*, \qquad (a,b)$$

$$O_3^* \underset{d}{\overset{c}{\rightleftharpoons}} O_2+O, \qquad (c,d)$$

$k_1$ may be identified with $k_a$ if the decomposition of ozone is truly at its low pressure limit. If the entropy change in Reaction (a), the entropy of activation, can be estimated, then the frequency factor of Reaction (b) can be calculated from it and $k_1$[32] and can be compared directly with the collision frequency of M and ozone. The entropy change in Reaction (a) must be equal to the difference in entropies of $O_3$* and $O_3$ since the equilibrium between $O_3$* and $O_3$ is independent of M at the high-pressure limit and, of course, cannot change in going from the high-pressure to the low-pressure limit.[33]

Using the fundamental vibrational frequencies of 705, 1043, and 1110 cm$^{-1}$ assigned by Wilson and Badger,[34] it may be calculated that heating ozone from 363°K to about 3250°K will increase its internal energy (vibrational plus rotational) by 24 kcal/mole which is equal to the activation energy of Reaction (1). If we now assume that an activated ozone molecule has the same internal thermodynamic properties as would an average ozone molecule at 3250°K, we obtain an entropy change for Reaction (a) of 17.0 eu. This would imply that Reaction (b) has a frequency factor (for M equal to oxygen) $\leqslant 3.9\times10^8$ liter/mole-sec which, when compared with a bimolecular collision frequency of about $2\times10^{11}$ liter/mole-sec, leads to the conclusion that oxygen deactivates $O_3$* once in about every 500 collisions.[35] This figure is in

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[28] (a) O. K. Rice, J. Chem. Phys. **9**, 258 (1941); (b) Pritchard, Sowden, and Trotman-Dickenson, Proc. Roy. Soc. (London) **A217**, 563 (1953); (c) *ibid.* **A218**, 416 (1953).

[29] Christie, Norrish, and Porter, Proc. Roy. Soc. (London) **A216**, 152 (1953). See also Christie *et al.*, *ibid.* **A231**, 466 (1955).

[30] R. Marshal and N. Davidson, J. Chem. Phys. **21**, 659 (1953).

[31] Thus if we write the bimolecular rate constant in the collisional form, $sZ'P(e)$ (where $Z'$ is the familiar Collision frequency, $s$ is the steric factor, and $P(e)$ is the Boltzman probability factor for having energy "$e$" distributed between the internal degrees of freedom and the relative kinetic energy along the line of centers of the colliding pair), then, although $s$ may be of the order of $10^{-2}$ (representing the probability that at least $e^*$ of the energy wind up in the internal degrees of freedom of $O_3$ after the collision), $P(e)$ has the form, $10^3\exp(e/RT)$ where the factor $10^3$ represents the probability increment arising from the number of different ways there are of having such a prescribed collision (i.e., an entropy term). The net result of these two compensating effects is to give an over-all increase in the frequency factor above the apparent collision frequency. Such high-frequency factors are quite common in energy transfer reactions and never occur (to our knowledge) in any other kind of bimolecular reaction. We believe that this arises from the fact that in the usual metathetical reaction like atom transfer, the requirements on energy localization are much more severe than in the energy transfer reaction where the energy may be distributed over many degrees of freedom of the activated molecule. Or, in other words, the large entropy increases usually accompany activation, not *reaction*.

[32] i.e., $k_b=k_a/K_{eq(a,b)}=A_1\exp(-\Delta S_{(a,b)}/R)$ by setting $E_1=\Delta E_{(a,b)}$.

[33] The average energy of $O_3$* reacting does differ at the two limits, but, if we restrict our discussion to the equilibrium with $O_3$* having energies equal to the average energy of $O_3$* reacting at the low-pressure limit, this will not affect our argument.

[34] M. K. Wilson and R. M. Badger, J. Chem. Phys. **16**, 741 (1948).

[35] Use of the vibrational frequencies favored by Herzberg of 710, 1043, and 1740 cm$^{-1}$, leads to an entropy of activation of 16.4 eu yielding a collisional deactivation efficiency of 1/330 [G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945)].

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reasonable agreement with the efficiency of 1/140 estimated on the basis of triple collisions.[36]

In terms of this model, the activation energy may be compared now with the bond dissociation energy. The average ozone molecule at 90°C has 1.3 kcal of internal energy (mostly rotational), and, if we add to this the energy of activation, we find that the average $O_3$* which reacts has 25.3 kcal of internal energy. This may be compared with $E_c+RT=23.9+0.7=24.6$ kcal predicted by classical theory for the average energy of $O_3$* at the low-pressure limit.[37]

Reaction (3) has a steric factor of about 0.1 which is typical for atom abstraction reactions of this type. The reaction is exothermic by 93.2 kcal, and, if we add to this the activation energy of 6.0 kcal, we see that the oxygen molecules produced will carry away 99.2 kcal of excess energy which may be present as electronic, vibrational, rotational, or translational energy. Of the available electronic states, only the lowest electronic states $^1\Delta_g$, $^1\Sigma_g^+$, and the ground state $^3\Sigma_g^-$ can participate.[38] The first two are metastable with lowest levels at 22.5 kcal and 37.5 kcal above the ground state. If spin selection rules are to be preserved in the collision of [$^3$P]O atom with the singlet ozone molecule, then we must expect at least one triplet oxygen molecule, and this then implies a maximum of one electronically excited oxygen molecule so that at least 61.7 kcal of energy must be distributed between the two oxygen molecules as vibrational, rotational, and translational energy.

From the absence of hot molecule effects in the kinetics, particularly at high ozone concentrations, one is forced to conclude that the efficiency of transfer of this energy to ozone in amounts large enough to break the $O_2-O$ bond is very low compared to the rate at which this energy is dissipated by successive collisions of the hot oxygen molecules.[39] This conclusion is compatible with our previous conclusion that oxygen (as well as other gases) is rather inefficient in activating ozone to decomposition.

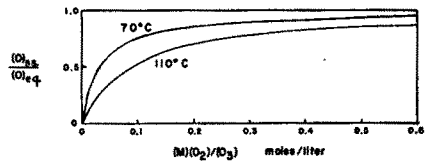



FIG. 5. Ratio of steady-state O atom concentration to the equilibrium value predicted from the proposed mechanism. The quantity plotted as the abscissa is proportional to the rate of Reaction (2) divided by the rate of Reaction (3). The ordinate values also represent the fraction of the O atoms formed which react by way of Reaction (2).

This atomic mechanism requires, of course, that the O atom concentration be less than that which would be present if equilibrium prevailed with respect to Reactions (1,2). The ratio of this steady-state O atom concentration to that calculated from the equilibrium of Reaction (1,2) depends on the relative rates of Reactions (2) and (3) and, therefore, on the ratio $(M)(O_2)/(O_3)$. The predicted values for the ratio of O atom concentrations are plotted in Fig. 5.

The homogeneous recombination O atoms can never compete with Reaction (2) since Reaction (2) goes at about once in every 140 three-body collisions and the ratio of $O_2$ to O atoms is, of course, much greater than this. The diffusion of O atoms to the wall might become important at low total pressures or in very small vessels since it is a first-order process which, therefore, could compete with Reactions (2) and (3). As discussed previously, no serious trends appear in the data which could be attributed to this heterogeneous recombination of O atoms. It is interesting to note that under conditions where $R_3 \gg R_2$, the diffusion of O atoms to the wall to form oxygen would inhibit the rate whereas, if $R_2 \gg R_3$, this same surface reaction would accelerate the over-all rate.

## MECHANISM OF HOMOGENEOUS PRODUCTION OF OXYGEN ATOMS FROM OXYGEN

We are able to evaluate one other rate constant in this atomic mechanism, namely that for Reaction (3′),

$$O_2+O_2 \xrightarrow{3'} O_3+O. \qquad (3')$$

From known thermal data[18] and the value of $k_3$ we obtain,

$$k_{3'}=6.7\times10^9 \exp(-99\,200/RT) \text{ liter/mole-sec.}$$

This reaction will not be important in the thermal decomposition of ozone because of its high activation energy. However, it may give rise to some interesting effects in high-temperature kinetic studies where the rate is dependent on the rate of formation of oxygen atoms in the system.

At high temperatures, O atoms may be formed homogeneously by Reaction (3′) or by Reaction (7).

$$O_2+O_2 \text{ (or M)} \xrightarrow{7} 2\,O+O_2 \text{ (or M)}. \qquad (7)$$

[36] The foregoing computation of the entropy of activation may be low since it does not include the contributions of anharmonicity or centrifugal distortion, both of which would tend to increase the internal entropy at the high average internal temperatures of the activated ozone complex. On the other hand, it is probably high by about $R\ln(3250/363)=4.4$ eu because of the difference in average spread of energy states available in the flask *vs* the hypothetical 3250°K.

[37] The average lifetime of $O_3$*, $\tau$, may be calculated by $\tau=1/k_{(6)}=(K_{eq(a,d)}k_{(d)})^{-1}$. But $K_{eq(a,d)}=K_{eq(1,2)}/K_{eq(a,b)}=\exp[(\Delta S_{1,2}-\Delta S_{(a,b)})/R]$ on setting $\Delta E_{(1,2)}=\Delta E_{(a,b)}$. And if we set $k_{(d)}=Z_{(d)}'$ (the collision frequency of $O+O_2\approx2\times10^{11}$ liter/mole-sec, then $\tau\geq10^{-13}$ sec which seems very short and is probably much smaller than the real value. This arises from our neglect of the nonequilibrium situation prevailing in the reaction which is producing "cold" (i.e., low entropy) $O_2+O$.

[38] The lowest lying known excited state, $^3\Sigma_u^+$, lies at 103 kcal above the ground state and so is just barely too high for the energy balance. See G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), second edition.

[39] This seems quite reasonable if the excess energy is mainly translational since the bulk of present evidence points to the rather inefficient transfer between vibration and translation in collisions and for these processes transfer of more than one vibrational quantum at a time is not indicated.

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Since ozone is unstable at these high temperatures, both of these reactions lead to the formation of two O atoms. Reaction (7) should have an activation energy close to 117 kcal and a frequency factor (for M equal to $O_2$) about the same[40] as that of Reaction (6) yielding a probable rate constant of

$$k_7 = 3.5\times10^{13}\exp(-117\,000)\ \text{liter/mole-sec.}$$

Using these rate constants, it is found that the rates of Reactions (3′) and (7) would be equal at about 1100°K.

## PHOTOLYSIS OF OZONE

Although results on the photolysis of ozone are not nearly as complete or quantitative as on the pyrolysis, there does seem to be considerable evidence[41,42] for the fact that at wavelengths below 2500 A and high $O_3/O_2$ ratios, the quantum yield for dry ozone can rise well above two with a maximum value of about six at 2100 A.

The results of Kistiakowsky[43,44] on the decomposition by red light agree within experimental error with the values of $k_2$ and $k_3$ presented in this paper except at very high $O_3/O_2$ values where the quantum yield rises slightly above the value of two which would be expected in this region. On the other hand, the results at wavelengths less that 3100 A give values of around two for the quantum yield[41,42] under conditions where the pyrolytic results and the results in red light would both predict a value of 0.2 or less.

These high quantum yields in the ultraviolet have been attributed to energy chains carried by hot oxygen molecules produced in the strongly exothermic Reaction (4.3). However, as we have just seen, this explanation is not consistant with the pyrolytic results. An alternative explanation may be found in the primary process

$$O_3+h\nu \xrightarrow{I_a} O_2+O, \qquad (8)$$

which at 2537 A produces $O_2$+O with excess energy amounting to about 88 kcal. A maximum of 32 kcal of this can be used in electronic excitation of $O_2$. However, there are two metastable states of O, $[^1D]$, and $[^1S]$ lying at 45 kcal and 96.5 kcal, respectively, above the ground state $[^3P]$. The first of these, $[^1D]$ is compatible with the energies involved, and we see that, even if the $O_2$ produced is the $[^1\Sigma_g^+]O_2$ molecule, there is still about 11 kcal of energy left over for translational and vibrational excitation. It seems quite reasonable that the high quantum yields in the ultraviolet are compatible with the reaction chain,

$$\text{Chain}\begin{cases} [^1D]O+O_3 \xrightarrow{9} [^3\Sigma_u^-]O_2^*+O_2 & (9)\\ [^3\Sigma_u^-]O_2^*+M \xrightarrow{10} [^1D]O+[^3P]O+M & (10)\end{cases}$$

$$\text{Termination } [^1D]O+M \xrightarrow{11} [^3P]O+M^*. \qquad (11)$$

The bond dissociation energy of $[^3\Sigma_u^-]O_2^*$ is less than 20 kcal and so the above sequence may constitute a reasonably fast chain cycle at room temperature.

TABLE II. Thermal explosion limits of ozone.

The maximum and minimum explosion limits in mm Hg have been calculated from Eq. (V) for values of $\delta$ of 3.3 and 12. The values in the parentheses are the highest pressures studied by Glissman and Schumaker. The value in brackets is the highest value attained without explosion in the present study.

| Temperature | ½ liter vessel | 1 liter vessel | 2 liter vessel |
|---|---|---|---|
| 70°C | 535–1020 | 424–810 | 336–640 |
| 80°C | 348–665 | 275–525 (376) | 218–416 |
| 90°C | 222–424 | 174–332 (298) | 138–264 |
| 100°C | 149–285 | 118–225 (181) [220] | 94–180 |
| 110°C | 101–193 | 80–153 | 64–122 |

## THERMAL EXPLOSIONS

In order to determine if any of the explosions encountered in this work[14] could have been caused by exceeding the explosion limit, these limits have been estimated using the equation for spherical vessels presented by Rice[45] (modified to a second-order form),

$$\delta = Qn^2r_0^2k_0/\lambda T^*, \qquad (V)$$

where $T^*$, the critical temperature increase, is equal to $RT_0^2/E$. The theoretical value of $\delta$ is 3.3 while the experimentally determined values for the reactions discussed by Rice vary between 5 and 12. The values found from Eq. (V) for the thermal explosion limits of pure ozone for $\delta$ values of 3.3 and 12 are tabulated in Table II (assuming a thermal conductivity of ozone of $3.5\times10^{-5}$ cal/deg cm sec). Also tabulated are the maximum pressures studied by Glissman and Schumaker which, of course, must be less than the actual explosion limits. The highest pressure obtained in one of our earlier crude experiments is also listed and would indicate a minimum value of $\delta$ of 12. This pressure may be in error by 10–15% but supported by the pressure values attained by Glissman and Schumaker it would appear to place a lower limit of 10 on the value of $\delta$ for ozone.

From these results, it appears quite possible that, in one or two of the explosions which occurred without the

[40] The $O_2-O_2$ collision frequency is ½ that of $I_2-O_2$, but either $O_2$ may be activated so that the net rate of activation should be about the same.

[41] L. J. Heidt and G. S. Forbes, J. Am. Chem. Soc. **56**, 2365 (1934).

[42] L. J. Heidt, J. Am. Chem. Soc. **57**, 1710 (1935).

[43] G. Kistiakowsky, Z. physik. Chem. **117**, 337 (1925).

[44] H. J. Schumaker, J. Am. Chem. Soc. **52**, 2377 (1930).

[45] O. K. Rice, J. Chem. Phys. **8**, 727 (1940).

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addition of oxygen, the ozone concentration may have been above the explosion limit. The three explosions which occurred on the rapid addition of oxygen to hot ozone were probably caused by adiabatic compression of the ozone above the explosion limit in the lower portion of the cylindrical vessel. A similar experiment in a spherical vessel where mixing would be more rapid did not explode.

## CHEMICAL SENSITIZATION

Although the thermal decomposition of ozone has been described in terms of an atomic mechanism, it is by no means a chain decomposition. However, the known sensitivity of ozone to explosions sensitized by small amounts of impurities such as hydrocarbons, $N_2O_5$, $Cl_2$, etc.,[46] and the sensitivity of the normal decomposition to catalysis by traces of organic matter,[4] indicate that fast chains may be established in ozone and that under these conditions thermal explosions may be initiated.

In the case of $Cl_2$ the chain carriers are probably ClO and Cl, while in the $N_2O_5$ case they are undoubtedly $NO_2$ and $NO_3$. It appears plausible to suppose that in the case of hydrocarbons and other H donors, the chain carriers are HO and $HO_2$. If we represent by RH any H donor present in ozone, then we can write for the chain,

Initiation $$O+RH\xrightarrow{12}OH+R \qquad (12)$$

Chain $$\begin{cases} HO+O_3\xrightarrow{13}HO_2+O_2 & (13) \\ HO_2+O_3\xrightarrow{14}HO+2\,O_2 & (14) \end{cases}$$

Termination $$2\,HO_2\xrightarrow{k_T}\text{Stable Products} \qquad (15)$$

and for the stationary rate of chain decomposition (neglecting contribution for R):

$$-d(O_3)_{ch}/dt=2k_{14}(O_3)(HO_2)$$
$$=2k_{14}[k_{12}(RH)(O)/k_T]^{\frac{1}{2}}(O_3). \qquad (VI)$$

The ratio of this to the rate at near equilibrium concentration of O atoms is given by (note this is lower limit for $\theta$):

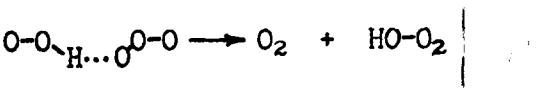
$$\theta=\text{rate}_{ch}/\text{rate}_{eq}=[k_{14}/k_3][k_2(O_2)/k_T]^{\frac{1}{2}}$$
$$\times[k_{12}(RH)/k_1(O_3)]^{\frac{1}{2}}. \qquad (VII)$$

Since the activation energy of $k_{12}$ is very likely not in excess of about 10 kcal, very small ratios of RH to ozone can still lead to appreciable values of $\theta$ if the activation energy of (14) is not in excess of 6 kcal.[47] When the pressure of ozone is 70% of that required for the thermal explosion a value of $\theta=1$ would be sufficient to bring the system to the limit so that this appears to be a reasonable pathway to explain the chemical sensitization.

Wulf and Tolman[1] have observed that ozone obtained from oxygen produced by the electrolysis of NaOH solutions decomposes faster than ozone produced from other sources and also that the oxygen produced by the electrolysis of NaOH contains a catalyst which accelerates ozone decomposition. It is very likely that the catalyst in these cases is $H_2O_2$ which is also produced at the anodes. $H_2O_2$ is expected to be an excellent H donor in reactions such as (12) since the H bond energy in $HO_2-H$ is about 90 kcal.[48]

[46] C. E. Thorp, *Bibliography of Ozone Technology* (Armour Research Foundation, Chicago), Vol. 2, p. 30.

[47] It may at first be considered unlikely that this is the case since the similar reaction $2\,O_3\rightarrow 3\,O_2$ probably has an activation energy in excess of 20 kcal. However, the two reactions are not precisely comparable because of the presence of H in $HO_2$ and moreover Reaction (14) may take place via *H* transfer through a structure,




whereas the reaction of $2\,O_3$ can only take place via O atom transfer.

[48] S. N. Foner and R. L. Hudson, J. Chem. Phys. **23**, 1364 (1955), have estimated the bond energy from appearance potential measurements of $HO_2$ from $H_2O_2$ together with the ionization potentials of $HO_2$ produced in electric discharges or thermally from $H+H_2O_2$.

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