

METASTABLE INTERMEDIATE IN THE FORMATION OF OZONE BY RECOMBINATION

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(Received April 28, 1986)

Summary

New measurements were made of the rate constant for recombination of $O(^3P)$ plus O_2 to examine a systematic discrepancy between the accepted rate constant, based on the rate of disappearance of $O(^3P)$, and the rate constant based on the rate of appearance of $O_3(^1A_1)$. The results are consistent with a previous suggestion that a major part of the ozone is first formed in an excited electronic state, probably $O_3(^3B_2)$. The value $\alpha = 0.42 \pm 0.08$ obtained for the fraction which forms ground state ozone directly is consistent with the previous estimate. The interpretation of the quenching data is revised to give $k_2^0 = (2.9 \pm 0.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the quenching rate constant in pure O_2 , and the relative rates $[M_2] = [O_2] + (0.37 \pm 0.10)[N_2] + (0.47 \pm 0.12)[Ar]$ for the effect of other gases.

1. Introduction

The addition reaction in which ozone is formed from oxygen atoms and molecular oxygen is obviously a significant reaction of atmospheric photochemistry [1, 2]. Measurements of its rate constant fall into two classes, those of the rate of disappearance of $O(^3P)$ and those of the rate of formation of O_3 . Measurements of the rate of disappearance of $O(^3P)$ generally agree with each other [3 - 13]. Recent measurements [11 - 13] yield the recombination rate constant accepted by critical reviewers [14]. Measurements of the rate of formation of ozone give results that are more scattered [15 - 17]. This is due partly to changes in the spectral absorption coefficient of ozone with the vibrational excitation that accompanies recombination [18 - 26]. Even allowing for this difficulty, the apparent rate of formation of ground state O_3 is consistently smaller than the rate of disappearance of $O(^3P)$ [27 - 30].

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A previous paper from this laboratory [29] pointed out that this discrepancy would result if part of the recombination led to the formation of ozone in a metastable state that is not immediately observed. Theoretical calculations indicate that $O_3(^3B_2)$ is stable and correlates with $O(^3P)$ and ground state O_2 [31, 32]. Spectroscopic features observed in a number of different experiments have been attributed to metastable states of ozone [27, 28, 33, 34].

The purpose of this paper is to describe the results of more extensive measurements of the rate of formation of ozone following flash photolysis of O_3 and/or O_2 .

2. Functional form of the reaction rate

The processes and corresponding rate parameters for a mechanism involving the formation and disappearance of a metastable O_3^* intermediate are defined as follows.



The accepted rate constant for the disappearance of $O(^3P)$ is k_1 (s^{-1}) = $k_1^0 [O_2] [M_1]$, where the coefficients of $[M_1] = [O_2] + 0.9[N_2] + 0.6[Ar]$ are reasonably well established [11 - 14]. The rate constant for deactivation of the intermediate, k_2 (s^{-1}) = $k_2^0 [M_2]$, contains a weighted total concentration $[M_2]$ whose coefficients are not known. This mechanism is applicable when the rates of reactions (1) and (2) are large in comparison with competing reactions. In this case, all odd oxygen ($O(^3P)$ plus O_3^*) eventually forms ground state O_3 , and the relative ozone concentration at time t is related to the ozone absorbances of a time-resolved experiment by the equation

$$\frac{[O_3]_t - [O_3]_0}{[O_3]_\infty - [O_3]_0} = \frac{A_t - A_0}{A_\infty - A_0} \quad (3)$$

The subscripts define values at times $t = 0$, $0 < t < 180 \mu s$ and $t = \infty$. The initial oxygen atom concentration is $[O(^3P)]_0 = [O_3]_\infty - [O_3]_0$.

The mathematical form of the rate of formation of ground state O_3 from an initial concentration of $O(^3P)$ by this mechanism is closely related to a textbook case [35].

$$\frac{A_t - A_0}{A_\infty - A_0} = 1 - \exp(-k_1 t) - \frac{(1-a)k_1}{k_1 - k_2} \{ \exp(-k_2 t) - \exp(-k_1 t) \} \quad (4)$$

The two terms on the right hand side are related to $[O(^3P)]$ and $[O_3^*]$ respectively. It will be shown that time-resolved absorbance data following a

photolysis flash of short but finite duration can be corrected to conform to this mechanism. Writing the rate constant ratio $f = k_2/k_1$, eqn. (4) can be rearranged to describe the relaxation as the sum of two exponential terms:

$$Z = \frac{A_\infty - A_t}{A_\infty - A_0} = \frac{1-a}{1-f} \exp(-k_2 t) + \frac{a-f}{1-f} \exp(-k_1 t) \quad (5)$$

where Z is the relative concentration of odd oxygen. Characteristic features of the reaction can be verified from plots of calculated values of $-\ln Z$ in Fig. 1. For $f = \infty$, the relation reduces to $-\ln Z = k_1 t$, a linear upper limit corresponding to the rate of disappearance of $O(^3P)$. At the other limit, $f = 0$ and $Z(t)$ relaxes to $Z = 1 - a$, the relative concentration of ozone formed as O_3^* . For $f = a$, the relaxation rate, $-\ln Z = k_2 t$, is linear with slope $k_2 = a k_1$. In general, the slope of $-\ln Z$ increases with increasing f . The curvature is positive for $f < a$, negative for $f > a$, zero for $f = a$ and also zero at $f \gg a$. The apparent singularity at $f = 1$ disappears when l'Hôpital's rule is applied to this limiting case of eqn. (5).

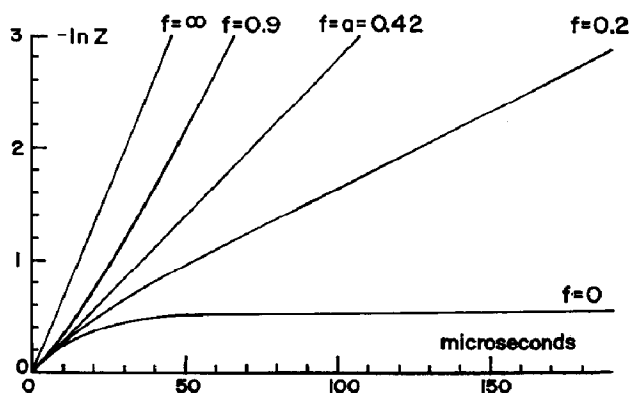


Fig. 1. Time dependence of Z for different values of $f = k_1/k_2$, the ratio of the rate of disappearance of $O(^3P)$ to the rate of quenching O_3^* using $k_1 = 0.0672 \mu s^{-1}$.

If O_3^* is a triplet state, the theory of unimolecular reactions [36 - 38] requires a fraction of the ozone initially formed in the ground state to be in the range $0.25 < a < 1$, depending on the stability of the metastable state. The apparent discrepancy in the rates is consistent with a value in this range. The purpose of the present experiment is to measure the recombination rate over a range of oxygen and inert gas concentrations to determine whether the following additional factors are consistent with this interpretation.

According to eqn. (5), observed values for $Z(t)$ depend only on a , k and f , that is on the mixture of O_2 and added inert gas but not on the ozone concentration, the origin of the $O(^3P)$, or the initial $O(^3P)$ concentration. This invariance of $Z(t)$ is tested for each O_2 -inert gas mixture by photolyzing oxygen in mixtures with no initial ozone, photolyzing both ozone and oxygen in mixtures with initial ozone present, photolyzing only the ozone in ozone-oxygen mixtures and changing the flash energy.

The values of $Z(t)$ depend systematically on the concentration of O_2 . Measurements in pure O_2 test whether f is inversely proportional to P_{O_2} , as required by the mechanism.

The values of $Z(t)$ also depend systematically on concentrations of other gases. Measurements in different mixtures containing added nitrogen or argon test whether $(fk_1/k_2^0) - P_{O_2}$ is proportional to the pressure of added gas, as required by the mechanism.

3. Experimental details

3.1. Materials

The sample mixtures contained research grade cylinder gases O_2 , N_2 and argon which were used without further purification. In many systems the initial ozone concentration is the product of the first shot of a two-shot sequence. The first shot measures recombination of the $O(^3P)$ produced by the photolysis of oxygen alone. The second shot measures recombination of $O(^3P)$ produced by photolysis of both oxygen and the ozone formed by the first shot. For experiments where photolysis is limited to ozone by placing filters around the flash lamps, the ozone was produced by complete conversion of oxygen in a discharge.

3.2. Measurement procedure

The absorbance by the gas sample is measured in four traversals of a 10 l cell following flash photolysis using a capacitor energy of 2000 or 4000 J. The absorption background, a xenon square flash of duration about 200 μs , is split into sample and reference channels using the upper and lower halves of the slit of a monochromator with a resolution of approximately 1 Å. The resulting photomultiplier signals are converted to parallel sets of 32 data points by boxcar integration over 2.5 μs at 3 μs intervals or over 5.5 μs at 6 μs intervals. Timing is initiated by the rise of the photolysis flash intensity, as detected through a fiber optic link. In addition to the signal during the photolysis flash, data are taken for various concentrations which are applied using an on-line computer. Each condition represents six to ten replicate shots (separate cell fillings) plus the associated correction data.

3.3. Measurements

The results in pure O_2 include data from previous recombination studies from this laboratory [20, 22, 29] in which the time-resolved ozone concentrations were obtained from integrated band strengths determined from absorbances at a sequence of frequencies throughout the Hartley band. This avoids problems due to the vibrational excitation of ozone. Most of the measurements in gas mixtures are carried out at higher pressures at the single wavelength least susceptible to the influence of vibrational excitation.

The duration of the absorption background source limits the experiment to about 200 μs . The new experiments use as much of this range as

possible. In a few cases, the time range was extended by a second experiment in which a digital delay was introduced in the absorption background and the measurement.

4. Analysis of the results

The experimental data are analyzed by first reducing the observed absorbances to values of $Z(t)$ and then examining the results for the characteristics that have been described. The approximations used in deriving eqn. (5) are tested by numerical integration of the rate equations for more detailed mechanisms which include the effects of the finite duration of the flash and the effect of neglected reactions, particularly the reactions of singlet molecular oxygen.

4.1. Initial conditions, A_0 and t_0

The solid curve in Fig. 2(a) was calculated by numerical integration of the rate equations for known reactions in a typical system with no initial ozone. The rate of photolysis is obtained from the observed intensity of scattered light from the flash. The values of a and f are adjusted for agreement with experiment. The broken curve was calculated using the same extent of photolysis and assuming that the $O(^3P)$ is formed by a pulse at a specified time. Agreement between the two curves is obtained by setting $t = 0$ of the pulse model equal to $t = 12 \mu s$ of the real flash model. This is also the time obtained by extrapolating the observed absorbances to zero.

For a system containing an initial ozone concentration, as shown in Fig. 2(b), there is a minimum in the plot of the ozone concentration vs. time. Extrapolating the observed absorbances to A_0 at $t = 12 \mu s$ gives the initial condition which brings the pulse model into agreement with the real

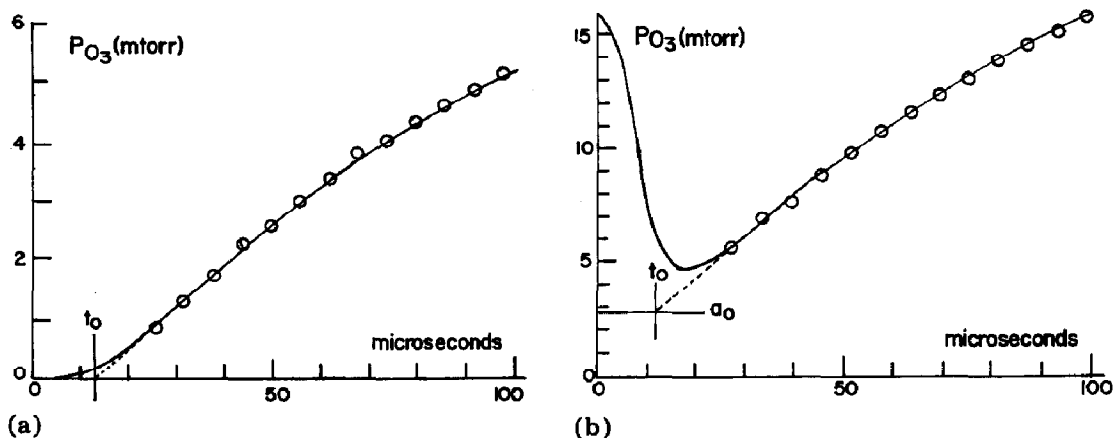


Fig. 2. Comparison of the real flash model with a model giving a photolysis pulse at time $t_0 = 12 \mu s$ (broken curve) and with data points for a typical experiment: (a) with no initial ozone; (b) with ozone initially present.

flash model. There is no major uncertainty regarding the initial conditions with or without initial ozone.

4.2. Final ozone absorbance, A_∞

The final absorbance after many seconds is typically significantly greater than the last observed value, even when the observed data appear to approach completion in the range 0 - 180 μ s. A previous paper [29] attributed the apparent ozone formation in the time range 0 - 180 μ s to direct formation of O_3 by reaction (1a) and the slower formation to deactivation of metastable O_3^* by reaction (2).

A semiquantitative exploration of the longer time regime in Fig. 3 shows that this interpretation is incorrect. In O_2 , the slow reaction is not monotonically related to the fast reaction but changes irregularly over a period of several seconds starting only after nearly 0.5 s has elapsed. This is the expected time domain of diffusion processes. The conclusion from these and other similar data is that changes at longer times result from inhomogeneities in the gas mixture which are due largely to the fact that oxygen absorption by lines of the Schumann-Runge bands is not optically thin but is concentrated in the vicinity of the flash lamps. The observed absorption is confined to the central 2 in diameter of a cell of diameter 6 in. The slower changes occur when gas from higher and lower intensity regions diffuses through the observation region. The difference in final absorbance of the two oxygen systems is attributed to pressure broadening of the lines. The homogeneity of the central part of the system during the fast time period is an uncertainty to be examined further.

The discrepancy between the rate of formation of $O_3(^1A_1)$ and the accepted rate of disappearance of $O(^3P)$ remains when the final ozone concentration is taken to be that found at the end of the fast reaction period, typically a factor of 2 slower than that given by the accepted recombination rate constant, but dependent on the experimental conditions. In the

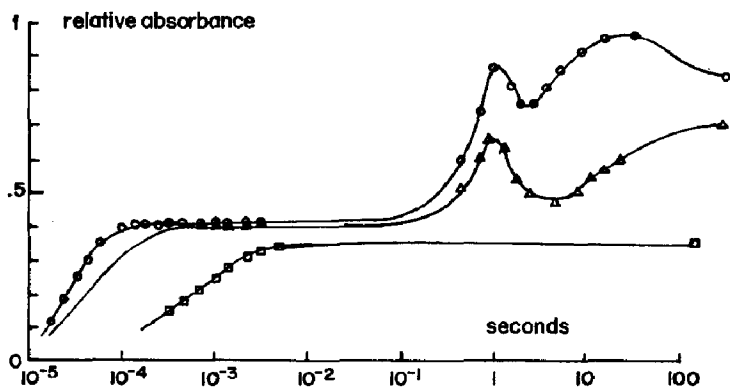


Fig. 3. Time dependence of the observed ozone absorbance over seven decades of time: \circ , 167 Torr O_2 , 533 Torr argon; Δ , 167 Torr O_2 ; \square , 5 Torr O_2 , 695 Torr argon, 15 mTorr O_3 .

revised interpretation, the reaction in which $O_3(^1A_1)$ is formed by quenching of the intermediate is partly concurrent with direct recombination. Except for a slight curvature in $-\ln Z(t)$, the two processes are distinguishable only by the discrepancy between the observed slope of $-\ln Z(t)$ and that predicted by the accepted rate of disappearance of $O(^3P)$.

4.3. Invariance of $Z(t)$

Figure 4 shows the experimental data for $-\ln Z(t)$ for the O_2-N_2 mixtures in the experiments described in Table 1. A similar systematic dependence on the composition of the major components is observed in each of the other gas mixtures. The extent of recombination ranges from about 6 to 24 mTorr O_3 . The set includes experiments in which the absorbance is obtained by integration over a series of wavelengths, experiments with no initial ozone, experiments in which both ozone and oxygen are photolyzed and experiments in which the photolysis is limited to ozone by flash lamp filters. The uncertainty in $Z(t)$ is primarily due to its sensitivity to the uncertainty in A_∞ .

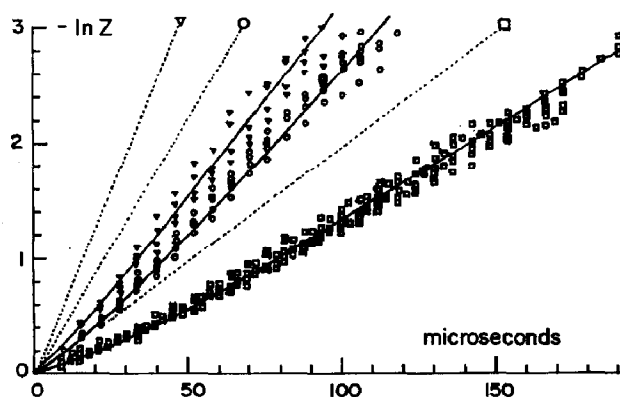


Fig. 4. Time dependence of $-\ln Z$ for the 17 O_2-N_2 mixtures in Table 1, illustrating the systematic dependence on quenching gases and relative invariance with respect to other conditions. The full lines correspond to $k_2 = 92.1(P_{O_2} + 0.37P_{N_2}) s^{-1}$. The broken lines are values for no intermediate formation. ∇ , 167 Torr O_2 plus 533 Torr N_2 ; \circ , 115 Torr O_2 plus 585 Torr N_2 ; \square , 50 Torr O_2 plus 650 Torr N_2 .

The invariance of $-\ln Z(t)$ with respect to these conditions shows that the uncertainties due to vibrational excitation, inhomogeneity of oxygen photolysis and reactions of singlet molecular oxygen lie largely within the uncertainty in A_∞ . This conclusion was confirmed by analyzing the data with a detailed kinetic model which includes all known reactions. The relative uncertainty in A_∞ has a lower limit of about 1% for measurements where $A_\infty - A_0$ is large and the recombination reaches completion. The average uncertainty is closer to 5%. Within this uncertainty, the invariance of $Z(t)$ was used as a criterion for determining the value of A_∞ . The value selected was close to an upper limit for measurements at a single wavelength, as opposed to measurements of the integrated absorbance, indicating that

TABLE 1

Summary of results from experiments to determine the quenching efficiency of nitrogen and argon relative to oxygen

<i>Experiment</i>	P_{O_2} (Torr)	P_M (Torr)	k_1 (μs^{-1})	A_0 (mTorr)	A_f (mTorr)	f	b_n^a
<i>M</i> \equiv N_2							
jrl-5	167	533	0.0672	0.0	12.5	0.45	0.30
jrl-8				5.56	36.6	0.48	0.34
jrl-11				0.0	8.5	0.57	0.47
jrl-14				9.83	29.4	0.55	0.44
jrl-4	115	585	0.0459	0.0	10.6	0.65	0.36
jrl-7				4.75	31.2	0.70	0.40
jrl-10				0.0	8.2	0.80	0.48
jrl-13				9.35	27.4	0.75	0.44
jrl-29				3.18	13.9	0.75	0.44
jrl-32				5.96	13.7	0.78	0.47
jrl-1	50	650	0.0198	0.0	11.9	1.10	0.29
jrl-2				4.24	29.4	1.15	0.30
jrl-3				0.0	7.7	1.12	0.29
jrl-6				3.31	21.8	1.20	0.32
jrl-9				0.0	6.0	1.15	0.30
jrl-12				7.80	20.8	1.20	0.32
jrl-28				3.26	13.3	1.20	0.32
<i>M</i> \equiv Ar							
jrl-17	167	533	0.0506	0.0	11.4	0.67	0.38
jrl-23				0.0	8.6	0.80	0.51
jrl-16	115	585	0.0333	0.0	9.9	0.90	0.36
jrl-22				0.0	7.6	1.25	0.57
jaj-3	115	230	0.0181	0.0	13.0	1.20	0.52
jaj-2	115	115	0.0132	0.0	14.0	1.20	0.49

^aFor $M \equiv N_2$, $\langle b_1 \rangle = 0.37 \pm 0.07$; for $M \equiv Ar$, $\langle b_2 \rangle = 0.45 \pm 0.08$.

vibrational excitation may have a small effect. Data for argon mixtures containing an initial ozone concentration were omitted from the analysis owing to the relatively large effect of $O_2(^1\Sigma)$.

4.4. Value of the branching ratio a

The values for a and f are inversely coupled. They are most distinguishable when they are comparable. For all of the conditions that were examined $f > a$. A comparison of typical calculated and observed values in Fig. 5 shows the range of values of a and f that agree with the data for a particular mixture under conditions which minimize the uncertainty in A_∞ . The relative uncertainties in a , f and A_∞ are comparable and agreement between the calculated and observed $Z(t)$ has about the same sensitivity to each. A value $a = 0.42 \pm 0.08$ satisfies all of the conditions that were studied.

The experimental data in Fig. 5 compare two experiments using 50 Torr O_2 plus 650 Torr N_2 with and without an initial ozone concentration.

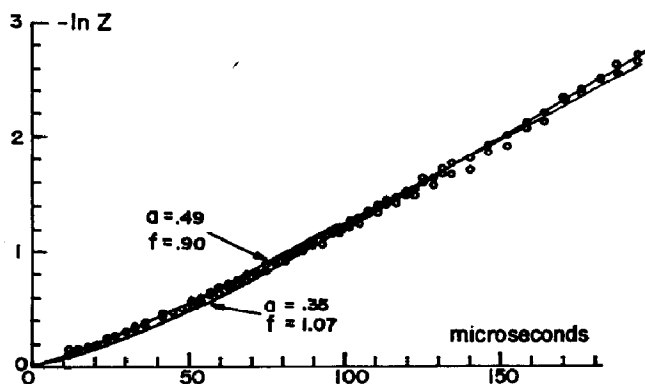


Fig. 5. Comparison of observed and calculated values of $-\ln Z$ showing the range of reasonable combinations of a and f .

Their agreement shows that homogeneity problems are not significant in this time range.

4.5. Rate of deactivation of the intermediate, k_2^0

The best data for determining the rate of deactivation in pure oxygen came from previous work in which the integrated absorbance by ozone was measured following flash photolysis of pure oxygen. The values of f obtained for the data in pure oxygen, given in Table 2, are proportional to $1/P_{O_2}$, as required by the mechanism. Using $k_1^0 = 6.0 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ the relationship gives $k_2^0 = (2.9 \pm 0.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as the rate constant for quenching by O_2 .

TABLE 2

Summary of experimental data for the value of the rate constant k_2^0 for deactivating metastable ozone by various gases

Experiment	P_{O_2} (Torr)	k_1 (μs^{-1})	A_0 (mTorr)	A_f (mTorr)	f	k_2^{0a} ($\text{Torr}^{-1} \text{ s}^{-1}$)
tek-3	230	0.0329	0.0	12.0	0.58	83.0
jaj-5	167	0.0173	0.0	12.5	0.95	98.7
tek-2	167	0.0173	0.0	10.2	0.92	95.6
tek-1	115	0.00823	2.35	20.0	1.30	93.0
jaj-1	115	0.00823	0.0	14.0	1.35	96.6
jaj-4	115	0.00823	0.0	12.5	1.20	85.8

These data are from refs. 29 and 30 and are based on measurements of the integrated absorbance at a series of at least 20 wavelengths.

^a $\langle k_2^0 \rangle$ ($\text{Torr}^{-1} \text{ s}^{-1}$) = 92.1 ± 6.3 .

4.6. Deactivation of the intermediate by inert gases

According to the definitions of the rate constants, $(fk_1/k_2^0) - P_{O_2}$ is proportional to the pressure of added inert gas, and their ratio is the

quenching efficiency relative to oxygen. Table 1 summarizes the data for recombination in mixtures containing nitrogen or argon. According to these data, the quenching rate constant is

$$k_2 = k_2^0 \{P_{O_2} + (0.37 \pm 0.10)P_{N_2} + (0.47 \pm 0.12)P_{Ar}\}$$

5. Conclusions

The experimental results meet the following tests for consistency with a mechanism in which a major fraction of the ozone is formed in a metastable electronic state which is then quenched to the ground state.

(1) The rate of formation of the $O_3(^1A_1)$ ground state is slower than the rate of disappearance of $O(^3P)$. The discrepancy depends systematically on the gas composition and is characterized by $f = k_2/k_1$, the ratio of the rate of disappearance of $O(^3P)$ to the rate of quenching the intermediate.

(2) The variable $Z(t)$ depends systematically on the concentrations of the major gases but is essentially invariant with respect to the initial $O(^3P)$ concentration, the extent of photolysis, the origin of the $O(^3P)$ and the concentration of O_3 or other minor gases, in agreement with the mechanism.

(3) In pure O_2 , f is inversely proportional to P_{O_2} , as required by the mechanism. The ratio fk_1/P_{O_2} gives a realistic value for the rate constant for deactivation of the intermediate by O_2 .

(4) In mixtures of O_2 with other gases M , $\{(fk_1/k_2^0) - P_{O_2}\}$ is proportional to P_M as required by the mechanism, and the ratio is a realistic value for the quenching efficiency relative to O_2 .

(5) According to the theory of unimolecular reactions, a binding energy in the range 0.5 ± 0.2 eV is required for a metastable state giving the observed fraction of the reaction that first forms metastable ozone. This is within the range of uncertainty in current theoretical values for $O_3(^3B_2)$ [31, 32].

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