METASTABLE INTERMEDIATES IN THE FORMATION OF OZONE BY RECOMBINATION

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Summary

The rate of formation of ozone by $O(^3P) + O_2(^3\Sigma_g^-)$ recombination following an energy pulse such as flash photolysis or pulse radiolysis is typically only about half the rate of disappearance of $O(^3P)$. Measurements of the growth of the Hartley band of ozone under several experimental conditions are shown to be consistent with reaction of 0.62 of the available $O(^3P)$ to form a metastable state of ozone. Deactivation of the metastable state by ground state O_2 is slow (approximately 10^{-16} cm^3 molecule^{-1} s^{-1}), but it is significant because of its large excess. Deactivation and decomposition of the metastable state by singlet molecular oxygen is rapid.

1. Introduction

The rate of formation of ozone by recombination has been measured in a number of different laboratories by several different methods [1 - 8] and the observed rate constants have been the subject of critical evaluations [9, 10]. The accepted value is based primarily on resonance fluorescence measurements of the rate of disappearance of $O(^3P)$ following flash photolysis of oxygen [1]. Measurements by several other methods lend support to this choice.

In principle the rate of growth of the Hartley band of ozone is also a measure of the rate of recombination. Several difficulties are associated with this method. In reactions initiated by an energy pulse, *e.g.* flash photolysis [11 - 15] or pulse radiolysis [16 - 18], there are obvious anomalies in the shape of the ozone spectrum and the apparent rate of formation of ozone is significantly slower than that predicted by the measurements of the rate of disappearance of $O(^3P)$. Recent work from this laboratory [14] has shown that the anomalies in the spectrum are almost completely attributable to vibrational excitation of the recombined ozone and that the proper measure of ozone concentration is the integrated absorbance over the entire Hartley band. Nevertheless the discrepancy in the rate constant remains.

Formation of an unobserved intermediate state of ozone could account for an apparent low value for the rate of recombination and could also account for a part of the infrared emission which accompanies recombination [19]. The existence of a metastable $^3B_2$ state of ozone has been predicted theoretically [20, 21] and may account for certain features of the energy loss spectrum following electron bombardment [22]. Since more than half of the ozone present may be in excited vibrational states under typical conditions of measurement, the possible effect of vibrational excitation on the observed reaction rates must also be considered. The purpose of the present experiments is to examine these aspects of the rate of formation of ozone following flash photolysis more quantitatively.

2. Experimental method and conditions

The experiments consisted of time-resolved measurements of the absorbance in the Hartley band of ozone as it was formed following flash photolysis of pure oxygen or of a mixture of ozone and oxygen. Ozone was made by passing dry oxygen through a discharge. The product was distilled from an isopentane slush bath and stored as a pure liquid under vacuum, pumping occasionally to remove traces of oxygen. A comparison of manometric and photometric measurements indicated that the ozone purity was typically greater than 97% before mixing with oxygen. Matheson "extra dry" oxygen was used without further purification.

The essential elements of the apparatus were (1) a square flash absorption background source, (2) a multiple reflection gas absorption cell containing a pair of flash lamps connected to a 4 kJ energy source, (3) a medium resolution grating monochromator with transfer optics to provide independent sample and reference beams through the upper and lower halves of the slits, and (4) an especially constructed digital transient analyzer.

The data were recorded as a sequence of photolysis and correction shots, as described in previous work from this laboratory [23]. Corrections were made for the baseline offset, beam balance, beam mixing and scattered light from the photolysis flash. In the mixture which initially contained ozone the absorbance was recorded before each flash in order to compare the photometric and the manometric measurements of the ozone concentration. The absorbance was measured 20 s after each photolysis flash to determine the ozone concentration at the end of all reactions. Artificially enhanced scattered light from the photolysis flash was recorded to determine the flash shape.

For each initial condition absorbances were measured at a series of 18 - 21 wavelengths covering the Hartley band. A series of 8 - 10 identical shots was made at each wavelength, giving averaged absorbances at 32 specified times before, during and after the flash. To maintain comparable photometric sensitivity at different wavelengths, the path was varied in the range 3 - 15 m.

The primary data were reduced to concentrations by reconstructing the absorption band at each time as a series of polynomials based on the observed data points. These were used to obtain integrated absorbances which were a measure of the ozone concentration not affected by variations in the band shape caused by vibrational excitation. After determining the concentration, the data at each time were normalized to the same integrated absorbance. The average vibrational energy was then determined as the change in the first moment of the absorption frequency, as explained in ref. 13.

In choosing the initial conditions, the principal consideration was to make the rate of recombination fast enough to exhibit the non-equilibrium anomalies to be studied. This required a relatively high concentration of molecular oxygen, but not high enough to cause high optical density at the photolysis wavelengths. Although the amount of ozone formed by photolysis of O_2 was not quite a linear function of the O_2 pressure, the deviation from linearity was not large enough to cause concern about the homogeneity of the system.

Even photolysis of pure oxygen produces some $O_2(^1\Delta)$ and some $O_2(^1\Sigma)$ because of photolysis of the ozone formed by recombination during the flash. To obtain an indication of the possible effects of singlet O_2, systems of pure O_2 were compared with a system containing enough added ozone to increase the singlet O_2 concentration by an order of magnitude.

Since the concentration of $O(^3P)$ was not observed directly, the extent of primary photolysis and the concentration of $O(^3P)$ were inferred from the concentration of ozone observed at the end of all reactions. This is possible if reactions removing odd oxygen (O or O_3) are either negligible or have known rates. The principal concern was whether the rate of reaction of O_3 with $O(^3P)$ was sufficiently enhanced by the vibrational excitation of ozone to compete with recombination. This possibility was checked by comparing the final ozone concentration in systems with added argon. The final ozone concentration was constant within experimental error indicating that recombination is the eventual fate of virtually all oxygen atoms. This conclusion is consistent with recent measurements of the rate of removal of laser-excited $O_3^\dagger$ by $O(^3P)$ [24], which indicate that the enhancement of the total rate is modest and is caused more by vibrational deactivation than by chemical reaction.

3. Analysis of the results

The experimental results were analyzed by comparing the data with numerically integrated rate expressions for various trial mechanisms. The rate expressions evaluated by Hampson and Garvin [9] were used as a core mechanism which was taken to be correct in the absence of anomalies produced by high concentrations of metastable intermediates, including vibrationally excited molecules. These reactions are summarized in Table 1.

TABLE 1

Reactions of the standard mechanism[a]

Reaction		Rate constant (cm^3 molecule^{-1} s^{-1})	
$O_2 + h\nu$	$\rightarrow 2O(^3P)$		(1)
$O_3 + h\nu$	$\rightarrow O(^1D) + O_2(^1\Delta)$		(2)
$O(^1D) + O_2$	$\rightarrow O_2(^1\Sigma) + O(^3P)$	2.9×10^{-11} exp(67/T)	(3)
$O_2(^1\Delta) + O_3$	$\rightarrow 2O_2 + O(^3P)$	4.5×10^{-11} exp($-2830/T$)	(4)
$O_2(^1\Sigma) + O_3$	$\rightarrow 2O_2 + O(^3P)$	2.3×10^{-11}	(5)
$O(^3P) + O_3$	$\rightarrow 2O_2$	1.9×10^{-11} exp($-2300/T$)	(6)
$O(^3P) + O_2 + M$	$\rightarrow O_3 + M$[b]	6.6×10^{-35} exp(510/T)	(7)

[a]The extent of primary photolysis was measured as described in the text. The rate constant for reaction (5) is that given in ref. 26. All other rate constants are given in ref. 9.
[b][M] = 1.7 [O_2].

The relative intensity of the flash was measured as a function of time and was used in the model as a polynomial. The flash had a full width at half maximum of 13.5 μs and decayed to less than 2% of the peak intensity 33.5 μs after the peak. The rate constant for the primary photolysis of oxygen was determined from the concentration of ozone measured 20 s after the flash. The rate constant for the primary photolysis of ozone was based on measurements of the ozone concentration 60 - 100 μs after the flash in an O_3–N_2 mixture containing the same amount of ozone as the O_3–O_2 mixture being modeled. Primary photolysis is the only significant reaction during the first 100 μs. Since the spectral radiant power of the flash decreases with spectral frequency in the region of the Hartley band, the extent of primary photolysis increases with vibrational excitation of ozone. A correction factor for this effect is the product of the change in spectral radiant power with frequency at 255 nm and the change in the first moment of the spectral absorbance due to vibrational excitation. Although the correction is approximate, the analysis is not highly sensitive to it. The rate constant used for reaction (5) is supported by measurements from several different laboratories [25 - 27]. The principal uncertainties in the mechanism are the extent to which reaction (3) produces $O_2(^1\Sigma)$, and the extent to which reaction (5) results in ozone decomposition as opposed to physical deactivation of $O_2(^1\Sigma)$. The major pathways are widely believed to be those represented in Table 1, although experiments have not been sufficiently direct to establish the extent conclusively. The effect of alternative pathways must be taken into account in any conclusions that are reached.

A reasonably exhaustive attempt was made to account for the discrepancy (see Fig. 1) by using enhanced rates of reaction of vibrationally excited ozone with intermediates such as $O(^3P)$, $O_2(^1\Delta)$, $O_2(^1\Sigma)$ and $O_3^{\dagger}$ itself. Reactions with singlet oxygen tend to be ruled out by the fact that the discrepancy is no larger in the O_3–O_2 mixture, where the concentrations of

singlet oxygen are an order of magnitude greater, than in systems of pure O_2. Reaction with $O(^3P)$ tends to be ruled out by the arguments used to verify the extent of primary photolysis in oxygen. Arguments to eliminate energy pooling mechanisms among $O_3^\dagger$ are not totally conclusive; however, when the small concentration of $O_3^\dagger$ (typically 2×10^{14} cm^{-3}) is taken into consideration, all of the foregoing reactions require cross sections equal to or greater than the gas kinetic cross section in order to be a principal cause of the discrepancy. There is no good reason to supsect that vibrational excitation of the ozone plays a significant role in causing the discrepancy in the apparent recombination rate.

4. Formation and relaxation of metastable ozone by recombination

It remains to examine whether the discrepancy in the rate of recombination is consistent with the formation and relaxation of a metastable intermediate, e.g. the predicted $O_3(^3B_2)$ state, which does not contribute to the observed absorbance. Accordingly the process

$$O(^3P) + O_2 + M \rightarrow O_3(^3B_2) + M \tag{8}$$

is added to the mechanism. It is assumed that the overall rate of recombination has the accepted value, measured as the disappearance of $O(^3P)$, and that this rate is distributed between reactions (7) and (8) according to some branching ratio to be determined from the data. With this inclusion, but excluding relaxation of the intermediate to $O_3(^1A_1)$, the calculated concentration of $O_3(^1A_1)$ must lie at or below the observed concentration. This criterion sets a lower limit to the branching ratio for the formation of the triplet. The solid curves in Fig. 2 were calculated using a branching ratio such that k_8 was equal to $0.62\,k_{total}$.

The discrepancy which remains in Fig. 2 is qualitatively that which is expected to result from neglecting deactivation and/or decomposition and recycling of the $O_3(^3B_2)$. The correlation of this discrepancy with the major constituent of the system, ground state molecular oxygen, is poor. The smallest discrepancy is in the system with the intermediate oxygen pressure. The correlation with the expected concentration of singlet molecular oxygen is qualitatively correct. Singlet molecular oxygen ($O_2(^1\Delta)$ and $O_2(^1\Sigma)$) occurs in the systems starting with pure oxygen only as a result of photolysis of the small fraction of the ozone which has recombined during the flash. This component of singlet oxygen increases with oxygen pressure, but the ozone initially present at the low oxygen pressure provides a much larger component. Hence the smallest discrepancy occurs at the intermediate oxygen pressure.

Since there are no features of the data which distinguish the two species of singlet oxygen, it is only possible to examine their effect using a schematic mechanism which cannot be taken literally. The curves in Fig. 3 were ob-
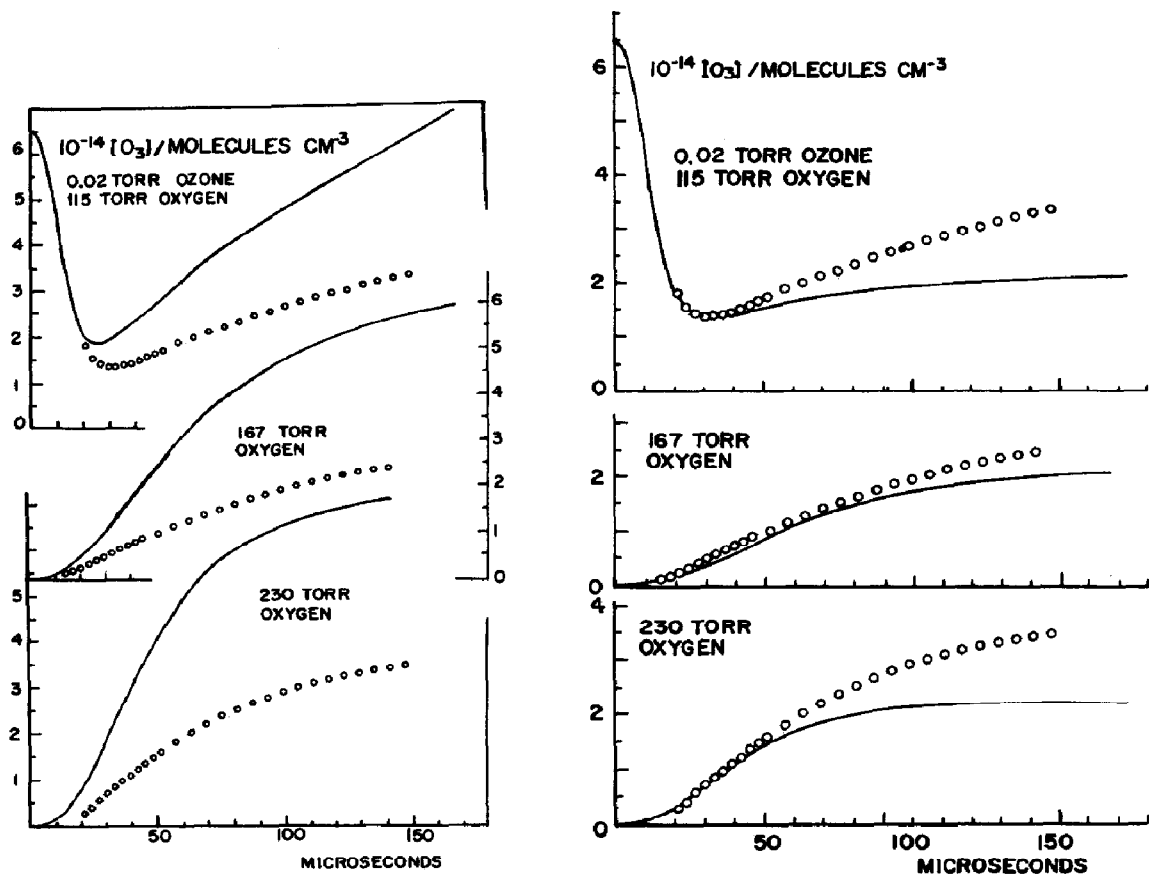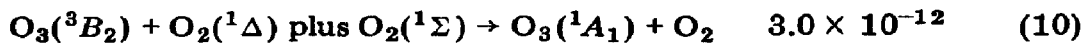
Fig. 1. Observed rate of formation of $O_3(^1A_1)$ (circles) following flash photolysis of pure O_2 and of O_3–O_2 mixtures. The solid curves represent the currently accepted model of known reactions associated with ozone photolysis.

Fig. 2. Observed rate of formation of $O_3(^1A_1)$ (circles) compared with a model (solid line) in which 0.62 of the recombination forms an unobserved metastable state of ozone such as $O_3(^3B_2)$.

tained by adding the following processes to the mechanism, using the rate constants shown with units of cm^3 molecule^{-1} s^{-1}:

$$O_3(^3B_2) + O_2 \rightarrow O_3(^1A_1) + O_2 \qquad\qquad 2.30 \times 10^{-16} \qquad (9)$$

$$O_3(^3B_2) + O_2(^1\Delta) \text{ plus } O_2(^1\Sigma) \rightarrow O_3(^1A_1) + O_2 \qquad 3.0 \times 10^{-12} \qquad (10)$$

$$O_3(^3B_2) + O_2(^1\Delta) \text{ plus } O_2(^1\Sigma) \rightarrow 2O_2 + O(^3P) \qquad 5.0 \times 10^{-11} \qquad (11)$$

Assuming the mechanism to be correct, the rate constants were obtained by minimizing the standard deviation between the calculated curves and the observed data points at six points, one at the center (about 60 μs) and one at the end (about 144 μs) of the data at each oxygen pressure. This is sufficient information to provide constants that are reasonably unique for the mechanism used.
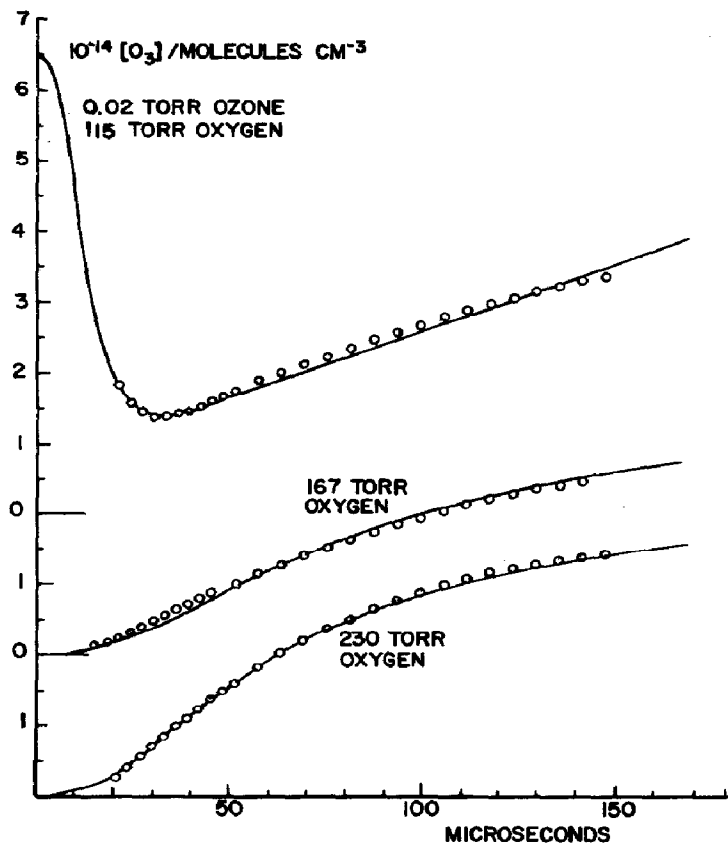
Fig. 3. Observed rate of formation of $O_3(^1A_1)$ (circles) compared with a model (solid line) which allows for the formation and relaxation of an unobserved intermediate such as $O_2(^3B_2)$.

The purpose of the last step in the analysis is not so much to establish the mechanism of deactivation as to determine whether reaction (8) is a quantitatively plausible source of the discrepancy indicated in Fig. 1. The branching ratio 0.62 is not greatly affected by uncertainties in the behavior of $O_2(^1\Sigma)$, since it is determined by the initial rate of formation of ozone before the effect of deactivation of $O_3(^3B_2)$ has become important. The principal effect of a significantly smaller concentration of $O_2(^1\Sigma)$ from reaction (3) [28, 29] would be to require larger values for k_9 and k_{10}. The slight systematic discrepancy remaining in Fig. 3 might well be removed by a more detailed differentiation between the effect of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ than is warranted by the current state of knowledge or by the available data.

The agreement between the calculated and observed data in Fig. 3 is taken as sufficient to establish reaction (8) as a plausible source of the discrepancies in the observed rate of recombination.

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