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Short Communication

The mechanism of the H_2O-catalyzed chain photodecomposition of O_3 and the reaction of HO with O_3

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Ozone was photolyzed at 2537 Å and 25°C in the presence of H_2O, both in the absence and presence of excess O_2. The presence of O_2 did not completely quench the chain decomposition of O_3, thus establishing the chain propagating steps as

$$HO + O_3 \rightarrow HO_2 + O_2 \quad (1)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \quad (2)$$

From the data of Lissi and Heicklen the rate constant ratio k_1k_2/k_{11} was found to be 8.1×10^{-20} cm^3 s^{-1}, where reaction (11) is

$$HO + HO_2 \rightarrow H_2O + O_2 \quad (11)$$

With the most recent values of $k_2 = 1.1 \times 10^{-15}$ cm^3 s^{-1} and $k_{11} = 2.0 \times 10^{-10}$ cm^3 s^{-1}, k_1 is computed to be 1.5×10^{-14} cm^3 s^{-1}. This value is a lower limit since wall termination steps were omitted in the analysis, and including them would raise the value of k_1. When the result from the Lissi and Heicklen data is compared with two other recent measurements for k_1, the three determinations are consistent with $k_1 = (5 \pm 3) \times 10^{-14}$ cm^3 s^{-1}.

Introduction

For a long time it has been known[1,2] that the photodecomposition of O_3 with radiation between 2100 and 2800 Å in the presence of H_2O leads to a long chain decomposition of O_3. Norrish and his coworkers[3-5] suggested that the chain decomposition could proceed via the reactions

$$HO + O_3 \rightarrow HO_2 + O_2 \quad (1)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \quad (2)$$

For a time it was believed that this sequence was an important mechanism for O_3 destruction in the stratosphere.

De More[6] raised objections to reactions (1) and (2), based on a comparison with Kaufman's results[7]. De More proposed that the chain steps were

$$HO^{\neq} + O_3 \rightarrow H + 2O_2 \qquad (3)$$

$$H + O_3 \rightarrow HO^{\neq} + O_2 \qquad (4)$$

where $HO^{\neq}$ is vibrationally excited HO. Support for this hypothesis was obtained from the liquid phase photolysis of O_3 at −186°C. In that system, the addition of O_2 suppressed the chain indicating that O_2 scavenged the H atoms and that HO_2 did not react with O_3, at least at low temperatures in the liquid phase. The failure of the Norrish mechanism appeared to confirm the flash-photolysis results of Langley and McGrath[8] who reported that low lying levels of HO ($v = 0, 1$) did not react with O_3, *i.e.* $k_1 < 10^{-16}$ cm^3 s^{-1}. Furthermore, Potter *et al.*[9] found that $HO^{\neq}$ ($v = 9$) reacted readily with O_3, thus substantiating reaction (3). The reaction scheme of De More was adopted by Lissi and Heicklen[10] in their studies of the photolysis of wet ozone, even though this scheme required that H_2O be extremely inefficient in quenching $HO^{\neq}$. Also, the Norrish mechanism has been discarded in recent aeronomical models of the stratosphere[11].

Recently, however, evidence has appeared which indicates that reaction (1) may be important. Coltharp *et al.*[12] have now measured the reactivity of $HO^{\neq}$ with O_3 for each vibrational level between 2 and 9, and find rate coefficients varying from 2×10^{-12} cm^3 s^{-1} for $v = 2$ to 8×10^{-12} cm^3 s^{-1} for $v = 9$. Extrapolation of their data suggests that for $v = 0$, the rate coefficient will be orders of magnitude greater than 10^{-16} cm^3 s^{-1}. Kaufman and Anderson[13] have preliminary results indicating that $k_1 = (5.5 \pm 1.5) \times 10^{-14}$ cm^3 s^{-1}. De More[14] has made a very recent study and reports that $k_1 = 8 \times 10^{-14}$ cm^3 s^{-1}. Also, we have recently found[15] that $k_2 = 3.3 \times 10^{-14} \exp(-2000/RT)$ cm^3 s^{-1}.

It appears that the report of Langley and McGrath may be incorrect. If so, the conclusion of De More[6] may also be in error, and the Norrish mechanism may be operative. In this communication, we report experiments which in fact do show that the Norrish, and not the De More, mechanism is operative.

The two mechanisms for the H_2O-catalyzed chain photodecomposition of O_3 can be tested by considering the mechanism

$$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D) \qquad (5)$$

$$O_2(^1\Delta) + O_3 \rightarrow 2O_2 + O(^3P) \qquad (6)$$

$$O(^1D) + O_3 \rightarrow O_2 + O_2^* \qquad (7a)$$

$$\rightarrow 2O_2 \qquad (7b)$$

$$O(^3P) + O_3 \rightarrow 2O_2 \qquad (8)$$

$$O_2^* + O_3 \rightarrow 2O_2 + O(^3P) \qquad (9)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (10a)$$

In the Norrish mechanism the chain steps are

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (1)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \qquad (2)$$

and the terminating steps are

$$HO_2 + HO \rightarrow H_2O + O_2 \qquad (11)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (12)$$

$$2HO \rightarrow H_2O + O(^3P) \qquad (13)$$

In the De More mechanism, as developed by Lissi and Heicklen[10], the steps are

$$O(^1D) + H_2O \rightarrow HO + HO^{\neq} \qquad (10b)$$

$$HO^{\neq} + O_3 \rightarrow H + 2O_2 \qquad (3)$$

$$H + O_3 \rightarrow HO^{\neq} + O_2 \qquad (4)$$

$$2HO \rightarrow H_2O + O(^3P) \qquad (13)$$

$$HO^{\neq} + HO \rightarrow H_2O + O(^3P) \qquad (14)$$

$$HO^{\neq} + H_2O \rightarrow HO + H_2O \qquad (15)$$

The Norrish mechanism leads to the rate law

$$-\Phi\{O_3\} = 3 + (3k_{7a} + k_{7b})(1-\beta)/k_7 + \frac{2k_2[O_3](\beta/I_a)^{1/2}}{(k_{12} + k_{11}k_2/k_1)^{1/2}} \qquad (I)$$

where $\beta \equiv k_{10}[H_2O]/(k_7[O_3] + k_{10}[H_2O])$.

In the above expression, termination by reaction (13) has been neglected, since all the experiments have been done under conditions in which it would be unimportant. The De More mechanism leads to the rate law

$$-\Phi\{O_3\} = 3 + \beta + (3k_{7a} + k_{7b})(1-\beta)/k_7 + 2(k_{10b}/k_{10}k_{14})k_3[O_3](k_{13}\beta/I_a)^{1/2} \qquad (II)$$

In this expression, reaction (15) has been neglected, because for the conditions under which experiments have been performed it was not important. Since, when the water chain is applicable, $-\Phi\{O_3\}$ is large (*i.e.* > 6), and since $\beta < 1$, the two rate equations are essentially indistinguishable.

However, if excess O_2 is added to the system, the following reactions also ocur.

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (16)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (17)$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \qquad (18)$$

The rate laws from the two mechanisms are then changed in very different ways. The Norrish mechanism gives

$$-\Phi\{O_3\} = 1 + (k_7[O_3]-k_{18}[O_2])/(k_7[O_3] + k_{10}[H_2O] + k_{18}[O_2]) + \\ + \frac{2k_2[O_3](\beta'/I_a)^{1/2}}{(k_{12} + k_{11}k_2/k_1)^{1/2}} \qquad (III)$$

where $\beta' \equiv k_{10}[H_2O]/(k_7[O_3] + k_{10}[H_2O] + k_{18}[O_2])$.

Since $k_{7a}/k_7 = 0.75$[10], the addition of excess O_2 will reduce $-\Phi\{O_3\}$ only slightly if the Norrish mechanism is applicable.

However, if the De More mechanism is applicable, then the rate expression on the presence of O_2 becomes

$$-\Phi\{O_3\} = 1 + \frac{(k_7[O_3]-k_{18}[O_2])}{(k_7[O_3] + k_{10}[H_2O] + k_{18}[O_2])} + \\ + \frac{k_{10b}\beta'\,(2k_4[O_3] + k_{17}[O_2][M])}{k_{10}\,k_{17}[O_2][M]} \tag{IV}$$

Lissi and Heicklen[10] found $(k_{10b}/k_{10})\,(k_3/{}_{14}) = 3 \times 10^{-4}$. From the results of Coltharp *et al.*[12], we now know that $k_3 > 2 \times 10^{-12}$ cm^3 s^{-1}. Also the upper limit for k_{14} is 2×10^{-10} cm^3 s^{-1}. Thus, $k_{10b}/k_{10} < 0.03$. Also, $k_4 = 2.6 \times 10^{-11}$ cm^3 s^{-1} (ref. 16). The coefficient $k_{17} = 1.6 \times 10^{-32}$ cm^6 s^{-1} with Ar as a chaperone[17], but the rate is between 18 and 25 times larger with H_2O as a chaperone[18]. Consequently $-\Phi\{O_3\}$ should fall to < 2.5 for experiments with $[O_2]/[O_3] > 30$ and H_2O pressures in excess of 15 Torr.

Experiments were performed in which O_3 was photolyzed at 2537 Å in the presence of H_2O vapor both in the absence and presence of excess O_2. The experimental procedure has been described in detail previously[10,15]. For these experiments, the quartz reaction cell was 2 cm long to permit the use of sufficiently high O_3 pressures and yet have uniform light absorption in the reaction cell.

The results are in Table 1 for a cell conditioned by several experiments (the initial experiments gave slightly higher quantum yields). In the absence of O_2, the H_2O-catalyzed chain decomposition is apparent and $-\Phi\{O_3\}$ as high as 10 were reached. With excess O_2 added, $-\Phi\{O_3\}$ dropped slightly to ~ 7, thus establishing that the Norrish, and not the De More, mechanism is operative.

TABLE 1

H_2O-INITIATED PHOTODECOMPOSITION OF O_3 AT 2537 Å AND 24 °C

$[O_3]$ (mTorr)	I_a (mTorr/min)	$-\Phi\{O_3\}$
$[H_2O] = 17.5 + 1.5$ Torr, $[O_2] = 0$		
460	0.45	10.0
510	0.45	10.0
560	0.40	8.7
560	0.40	10.0
$[H_2O] = 17.5 \pm 0.5$ Torr, $[O_2] = 17 \pm 1$ Torr		
460	0.45	6.3
630	0.58	7.3
730	0.68	9.0

Three previous studies gave extensive results on the H_2O-catalyzed chain photodecomposition of O_3. Forbes and Heidt[2] studied the reaction at very high $[O_3]$ and found a rate law that went as $I_a^{0.37}$ with incident radiation at 2100 Å and as $I_a^{0.24}$ with incident radiation at 2537 and 2800 Å. The failure of the rate law to go as $I_a^{1/2}$ is probably due to the high O_3 pressures which led to non-uniform light absorption in the reaction vessel. The studies of Norrish and Wayne[5] showed even less of a dependence on I_a than those of Forbes and Heidt. It is not clear why this should be.

The most recent results are those of Lissi and Heicklen[10], and the chain-part of the decomposition could be fitted to a dependence on $[O_3]$ and $I_a^{1/2}$ as expected. They interpreted their data according to the De More mechanism. In terms of the Norrish mechanism, the intercept of their log–log plot (their Fig. 8) of 5.2×10^{-10} $cm^{3/2}$ $s^{-1/2}$ corresponds to $2k_2/(k_{12} + k_2k_{11}/k_1)^{1/2}$. The value of $k_2/k_{12}^{1/2}$ has been found to be[14,15] $6.4 \times 10^{-10} cm^{3/2} s^{-1/2}$ at 25° C. Thus $k_1k_2/k_{11} = 8.1 \times 10^{-20}$ cm^3 s^{-1}. The most recent values of k_2[15] and k_{11}[19] are, respectively, 1.1×10^{-15} and 2.0×10^{-10} cm^3 s^{-1}. Thus $k_1 = 1.5 \times 10^{-14}$ cm^3 s^{-1}. Our limited data give $-\Phi\{O_3\}$ somewhat lower than those of Lissi and Heicklen for corresponding conditions, and lead to a value for the rate constant of $\sim 3 \times 10^{-15}$ cm^3 s^{-1}.

The values for k_1 found from the H_2O-catalyzed decomposition of O_3 are very sensitive to the chain length, which in turn is sensitive to the termination steps. In the analysis, wall termination was neglected, though it should occur to some extent. In the Lissi and Heicklen experiments, wall termination can be estimated to be about 20% of the termination; thus k_1 rises to between 2 and 3×10^{-14} cm^3 s^{-1}. In the experiments performed here, the reaction cell was much smaller than the one used by Lissi and Heicklen and wall termination could have accounted for $\sim$ 50% of the termination. If so, k_1 would be 4 times larger than the estimate of $\sim 3 \times 10^{-15}$ cm^3 s^{-1} or $\sim 1.2 \times 10^{-14}$ cm^3 s^{-1}.

The other recent values reported for k_1 are $(5.5 \pm 1.5) \times 10^{-14}$ cm^3 s^{-1} found by Kaufman and Anderson[13] and 8×10^{-14} cm^3 s^{-1} found by De More[14]. All of the results are concordant with a value of $k_1 = (5 \pm 3) \times 10^{-14}$ cm^3 s^{-1}.

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