

The Reaction of $O(^3P)$ with H_2O_2

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Abstract

The rate constant for the reaction of $O(^3P)$ with H_2O_2 was measured as a function of temperature and the $[H_2O_2]_0/[O]_0$ ratio. The numerical solution of the appropriate rate equations was used to arrive at a mechanism which adequately describes our results and the rather divergent data in the literature. A recommended expression for the temperature dependence of the absolute rate constant is presented from consideration of the available experimental data.

Introduction

There have been four reports in the literature of kinetic studies of the reaction of $O(^3P)$ with H_2O_2 [1–4]. Two of these [1,2] report estimates of the rate constant at 300 K differing by three orders of magnitude. The other two [3,4] give Arrhenius expressions for the rate constant differing by about an order of magnitude in preexponential factor and by about 8 kJ/mol in activation energy. There are also significant differences in the mechanisms proposed in these reports to account for their results. It was therefore felt that a reinvestigation of the reaction was desirable.

We report here the results of kinetic experiments as a function of temperature covering a wide range of values of $[H_2O_2]_0/[O]_0$. The numerical solution of the appropriate rate equations was used to deduce a mechanism which provides a reasonable description both of our results and of those in the literature.

Experimental

The reaction was studied in a conventional fast-flow system similar to those used in previous work [5]. The $O(^3P)$ was produced by adding NO to $N(^4S)$ atoms formed in a microwave discharge through N_2 or a mixture of a few percent of N_2 in He. The $O(^3P)$ concentrations were measured by determining the intensity of emission from excited NO_2 produced by a small amount of NO in excess of that required to completely consume the $N(^4S)$. The purification procedures for NO, N_2 , and He are described in detail elsewhere [6,7]. The rate constants were independent of the amount of

excess NO used. The rate constants for the overall reaction were calculated from the pseudo-first-order loss of $O(^3P)$ in the presence of excess H_2O_2 as described elsewhere [7].

Hydrogen peroxide (50%) was concentrated by pumping off the water until the purity of the product was better than 99%, as determined by titration with $KMnO_4$. Flow rates of H_2O_2 were determined either by trapping the condensable gases with liquid nitrogen for a known time and titrating the product with $KMnO_4$, or by monitoring the ion signal at m/e 34 with a CEC model 21-104 mass spectrometer. In the latter case the instrument was first calibrated by the trapping and titration method described above.

The numerical solution of the rate equations appropriate to the various mechanisms tested was done on a DEC-10 and a CDC Cyber 170 computer using a Fortran program described by Stabler and Chesick [8].

Results and Discussion

As noted in earlier work [3], the pseudo-first-order plots of $O(^3P)$ decay were curved at long reaction times, even when the H_2O_2 concentration was sufficiently large that only a negligible proportion of it was consumed. Kinetic measurements were therefore restricted to relatively short reaction times over which no curvature was detectable. In all cases, consumption of H_2O_2 was insignificant over the range of reaction times employed. The experimental rate constants k_e were determined by dividing the pseudo-first-order decay coefficients by the H_2O_2 concentration.

Over a modest range of values of the ratio $[H_2O_2]_0/[O]_0$ (such as 10–40) at 300 K, the value of k_e was independent of this ratio within experimental error. However, with $[H_2O_2]_0/[O]_0$ in the vicinity of 100, the value of k_e decreased appreciably. This behavior was more pronounced at higher temperatures. The results obtained at 303 and 346 K are shown in Figure 1. This implies that the stoichiometric coefficient required to obtain absolute rate constants from the experimental ones varies with the ratio $[H_2O_2]_0/[O]_0$, even at quite large values of this ratio. Direct measurement of this stoichiometric coefficient was impossible with our apparatus because of the limited sensitivity of our mass spectrometer and also because of the extremely small proportion of H_2O_2 consumed, particularly when H_2O_2 was in very large excess of $O(^3P)$. Moreover, since secondary reactions of both H_2O_2 and $O(^3P)$ appear to be important, as will be discussed later, it is doubtful that the measured stoichiometric coefficient would be appropriate for use in calculating absolute rate constants. The limitations on the use of experimental stoichiometric coefficients for calculating absolute rate constants have been referred to elsewhere [5].

Because thermal decomposition of H_2O_2 became appreciable in our apparatus at temperatures above about 370 K, kinetic measurements were

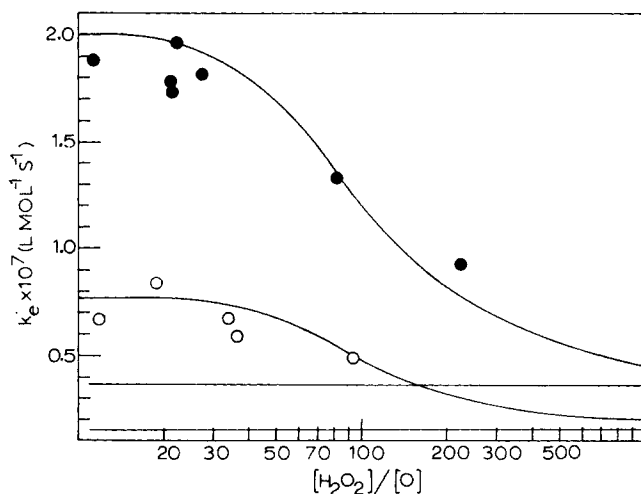


Figure 1. Computed and experimental dependence of k_e on $[H_2O_2]_0/[O]_0$. The solid curves represent the behavior predicted by the reaction mechanism, while the plotting symbols indicate experimental results. \circ —302 K \pm 1; \bullet —346 K \pm 3. The horizontal lines indicate the limiting value of k_e at large values of $[H_2O_2]_0/[O]_0$.

restricted to lower temperatures. Decomposition was measured by monitoring the ion signal at m/e 34 with a reaction time of about 150 ms. While decomposition of H_2O_2 at such low temperatures is presumably heterogeneous, it rendered the H_2O_2 concentration uncertain and precluded kinetic measurements at higher temperatures. While such decomposition was not detected in one earlier study [3], more recent work [4] did encounter this difficulty and was restricted to about the same upper temperature limit as the present work. Within this temperature range, the experimental rate constants gave a linear Arrhenius plot provided that the $[H_2O_2]_0/[O]_0$ ratio was kept moderately constant (Fig. 2, Table I). Experiments with widely different values of this ratio gave Arrhenius plots which were parallel (Fig. 2), suggesting that the preexponential factor but not the activation energy was sensitive to the value of this ratio. This supports our earlier suggestion that the value of the $[H_2O_2]_0/[O]_0$ ratio affects the overall reaction stoichiometry. With $[H_2O_2]_0/[O]_0$ in the range of 5–30, the experimental rate constants were considerably larger than those reported in earlier work [2–4]. When this ratio was increased to 80–100, the experimental rate constants were comparable to those of [3], as read from [3, Fig. 5] (see our Fig. 2), which were obtained with similar values of this ratio. The values of k_e were, however, substantially larger than those reported in [4] for experiments in which the value of this ratio is likely to have been one or two orders of magnitude greater. While our activation energy (19 ± 3 kJ/mol) agrees well with that of [4] (18 ± 2 kJ/mol), it is significantly smaller than that

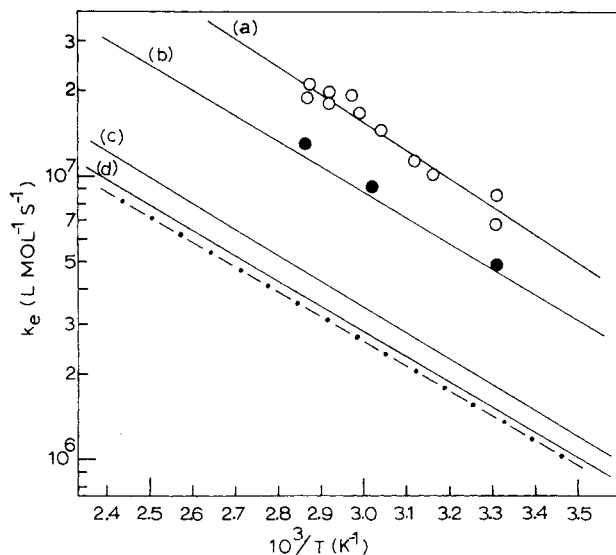
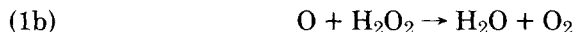
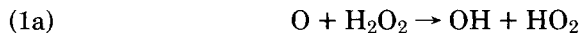


Figure 2. Computed and experimental Arrhenius plots of the reaction of $O(^3P)$ with H_2O_2 . Solid lines represent the behavior predicted by the postulated reaction mechanism. Line (a)— $[H_2O_2]_0/[O]_0 = 10$; line (b)— $[H_2O_2]_0/[O]_0 = 10^2$; line (c)— $[H_2O_2]_0/[O]_0 = 10^3$; line (d)— $[H_2O_2]_0/[O]_0 = 10^4$; \circ —this work, $[H_2O_2]_0/[O]_0 = 5$ –30; \bullet —this work, $[H_2O_2]_0/[O]_0 = 80$ –100; --- calculated from the low-temperature Arrhenius behavior of [3]; - - - calculated from the Arrhenius expression of [4].

reported in [3] (26 ± 3 kJ/mol). If, however, the data of [3] at temperatures above those used here and in [4] are discarded, the activation energy calculated from the remaining points is (14 ± 3 kJ/mol) which agrees fairly well with the other values. Careful examination of the data in [3, Fig. 5] shows that their Arrhenius plot curves upward at temperatures above about 400 K. Since the bulk of their rate constants were obtained above this temperature, this upward curvature is presumably responsible for their higher activation energy.

In the discussion of a reaction mechanism in [3], secondary reactions are neglected and about equal probability is assigned to the reactions



The basis for this was their direct measurement of $\Delta[O]/\Delta[H_2O_2]$ (2.5 ± 0.3 between 500 and 800 K) and their observation that rate constants based on H_2O_2 decay were 2.3 ± 0.2 times smaller than those based on $O(^3P)$ decay with $[H_2O_2]_0 \simeq [O]_0$. On the other hand, the rate constant for



is sufficiently large [9–11] that even if $[OH]$ is two to three orders of mag-

TABLE I. Kinetic data for the reaction of $O(^3P)$ With H_2O_2 .

T (K)	P (Torr)	v (cm s ⁻¹)	$[H_2O_2]_0$ (Mol L ⁻¹)	$\frac{[H_2O_2]_0}{[O]_0}$	k_e^* (L Mol ⁻¹ s ⁻¹)
349	1.60	375	1.06×10^{-6}	82.1	1.32×10^7
349	1.71	342	1.17×10^{-6}	220	0.919×10^7
348	1.28	727	1.52×10^{-6}	8.26	2.07×10^7
348	1.28	727	1.67×10^{-6}	11.7	1.88×10^7
343	1.28	707	0.847×10^{-6}	22.5	1.97×10^7
343	1.31	691	1.06×10^{-6}	27.5	1.81×10^7
343	1.28	710	0.802×10^{-6}	21.4	1.77×10^7
343	1.28	707	0.826×10^{-6}	21.9	1.72×10^7
337	1.21	761	1.66×10^{-6}	11.8	1.93×10^7
334	1.20	757	2.02×10^{-6}	17.4	1.74×10^7
331	1.31	707	2.22×10^{-6}	91.7	0.934×10^7
328	1.23	713	1.22×10^{-6}	5.17	1.43×10^7
321	1.20	731	2.46×10^{-6}	20.5	1.11×10^7
316	1.20	692	1.06×10^{-6}	6.35	1.00×10^7
303	1.29	633	1.39×10^{-6}	36.5	0.580×10^7
303	1.29	625	1.32×10^{-6}	34.3	0.669×10^7
303	0.996	695	0.551×10^{-6}	12.0	0.666×10^7
302	0.951	687	0.694×10^{-6}	19.0	0.858×10^7
302	0.874	634	0.752×10^{-6}	93.6	0.487×10^7

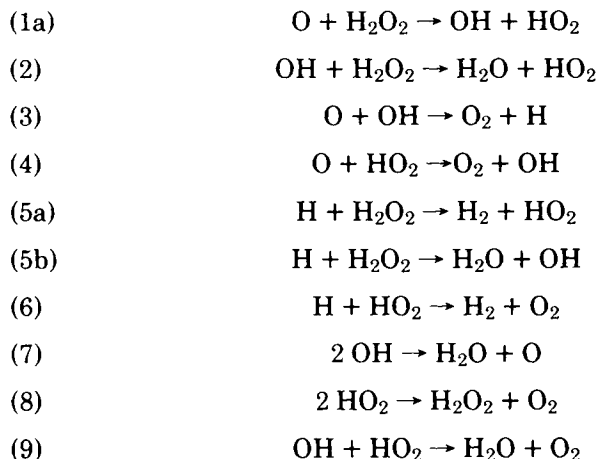
* These are not absolute rate constants. The uncertainty in the rate constants, based on separate experiments in which $[H_2O_2]_0/[O]_0$ and the temperature were held constant and other parameters were varied, is approximately $\pm 8\%$.

nitide smaller than $[O]$, loss of H_2O_2 via reaction (2) will be significant relative to that via reaction (1). Moreover, even if $[H_2O_2]/[OH] \sim 10^4$, the rate of loss of $O(^3P)$ via



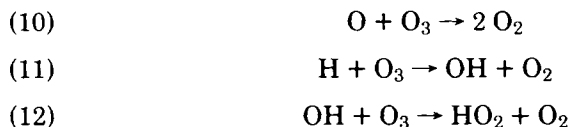
will be comparable to that via reaction (1). The importance of reaction (3) at even very short reaction times is indicated by the observation [3] of concentrations of H atoms amounting to about 40% of the $O(^3P)$ consumed at reaction times as short as 9 ms. Thus even at short reaction times it is not clear that a stoichiometric coefficient of 2.5 indicates equal probability for reactions (1a) and (1b).

To deduce a mechanism which would adequately describe both our results and those in the literature, a set of 18 reactions involving H, OH, HO₂, O₂, O₃, and H₂O₂ was used. The appropriate rate equations were solved numerically using rate constants found in [4] and [10–12]. Reactions were rejected if they caused less than 0.1% change in the rate constant calculated from the predicted O(³P) decays. As in the experimental work, only the initial linear portion of the O(³P) first-order decay was used. The calculations were done for a range of reactant concentrations and temperatures comparable to our conditions and to those of [3] and [4]. The final set of reactions selected on this basis for the mechanism is



As will be seen, it was not necessary to include reaction (1b) to account successfully for the available experimental data. The rate constants used in these calculations were obtained from [4] and [10–12].

The above mechanism was tested by using it to calculate O(³P) decays under the conditions employed in our work and in that of [3] and [4]. As far as possible, the method used to extract rate constants from the calculated O(³P) decays was the same as that used in the original work. Thus in comparing the calculations with the O₃ photolysis work of [4], the reactions



were added to the mechanism and the rate of loss of O(³P) was determined both in the presence and in the absence of H₂O₂, using rate constants from [12]. The mechanism is consistent with their finding that the amount of O₃ used in their work did not interfere with the reaction being studied. In our calculations for each of their experimental conditions, the rate constant

predicted by the mechanism was independent of the presence or absence of O_3 . The predicted rate constants agreed to within a few percent with their experimental values as long as the ratio $[H_2O_2]_0/[O]_0$ was at least 10^3 . This implies a concentration of about $10^{-9}M$ or less for $O(^3P)$, which seems reasonable for their experimental methods (photolysis of O_3 with measurement of $O(^3P)$ by resonance fluorescence). The computed Arrhenius plot and that obtained from their data are compared in Figure 2.

The rate constants predicted by the mechanism for conditions comparable to those used in [3] agree well with their experimental values at temperatures below about 500 K (Fig. 2). The first-order plots of $O(^3P)$ consumption showed pronounced downward curvature at conversions greater than about 20%, in essential agreement both with their work and our own. Above 500 K the mechanism continued to give excellent Arrhenius behavior, in contrast with the upward curvature of the Arrhenius plot in [3]. The source of this curvature is unclear.

The rate constants calculated from the mechanism for our experimental conditions were also in satisfactory agreement with experiment (Figs. 1 and 2). The mechanism also successfully described the variation in the experimental rate constant with $[H_2O_2]_0/[O]_0$ (Fig. 1).

The sensitivity of our calculations to the numerical values of the rate constants for the reactions in the mechanisms was tested by systematically increasing and then decreasing the rate constants for all but reaction (1a) by a factor of 10. The calculated initial rate of loss of $O(^3P)$ was then used to determine the overall rate constant. These calculations were done for temperatures of 300 and 350 K and for a $[H_2O_2]_0/[O]_0$ ratio of 10 since a relatively small ratio such as this should correspond to those of our experimental conditions in which secondary reactions were most important. Only k_2 to k_5 inclusive caused more than 5% variation in the overall rate constant, and of these k_4 had by far the greatest influence. Even so, the overall rate constant varied by only 10% when the results obtained with the largest value of k_4 in the literature [11] are compared with those using the smallest value of k_4 [9].

The mechanism postulated here for the reaction of $O(^3P)$ with H_2O_2 accounts satisfactorily for the major features of the reaction of $O(^3P)$ with H_2O_2 described in our work and in the literature. It also satisfactorily reproduces the experimental rate constants obtained over a very wide range of the $[H_2O_2]_0/[O]_0$ ratio. Calculations in which reaction (1b) was allowed to participate while keeping $k_{1a} + k_{1b}$ constant invariably gave poorer agreement with experiment. It therefore seems safe to conclude that reaction (1a) is the predominant initiation step. This is as might be expected in view of the relatively large amount of rearrangement required in the activated state to give the products of reaction (1b) and in view of the evident importance of free radical intermediates [3] in the overall reaction. It also seems reasonable to recommend the Arrhenius expression given in

[4] as an accurate description of the temperature dependence of the rate constant for the reaction of $O(^3P)$ with H_2O_2 .

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