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A Dye Laser Flash Photolysis Kinetics Study of the Reaction of Ground-State Atomic Oxygen with Hydrogen Peroxide[1]

Sir: We would like to report on a recently completed study on the reaction of $O(^3P)$ with hydrogen peroxide over the temperature range 283–368°K. This reaction is of possible significance both in the atmosphere (where H_2O_2 is present as a trace constituent) and in combustion processes, especially H_2–O_2 flames.

A literature survey has shown that only one kinetics study has been reported[2] on this system and that set only an upper limit on the value of the rate constant at 300°K. The experimental difficulties involved with this reaction system are twofold: (1) the quantitative handling of hydrogen peroxide in a gas handling system; and (2) the generation of $O(^3P)$ in the absence of high concentrations of metastable O_2, OH, and HO_2. In the present study, the above problems were greatly minimized by (1) the use of an all-glass gas handling system and a glass reaction cell, and (2) the generation of $O(^3P)$ by the dye laser flash photolysis of ozone in the Chappius band at 6000 Å. The detection technique for atomic oxygen was that of resonance fluorescence and further details on this can be found in previous publications.[3,4] Also described in earlier work is the use of the tunable dye laser as a means of generating a clean source of ground-state atomic oxygen from photolysis of O_3.[5]

In this investigation, the limited temperature range of 283–368°K was defined by the thermal decomposition of H_2O_2 at high temperatures and the low vapor pressure of peroxide below 283°K. In the latter case, the small value of the bimolecular rate constant for reaction 1 at low temperatures was also a contributing factor. Throughout this

$$O(^3P) + H_2O_2 \longrightarrow HO_2 + OH \quad (1)$$
$$\longrightarrow H_2O + O_2$$
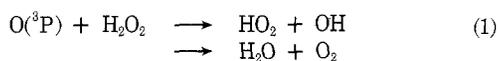
study a major concern was the thermal decomposition of hydrogen peroxide both *via* homogeneous and heterogeneous processes. Accordingly, independent studies were carried out to determine the extent of this problem using a temperature-controlled recording Cary 14 uv spectrophotometer. At 298°K, it was found that H_2O_2 decomposed at a
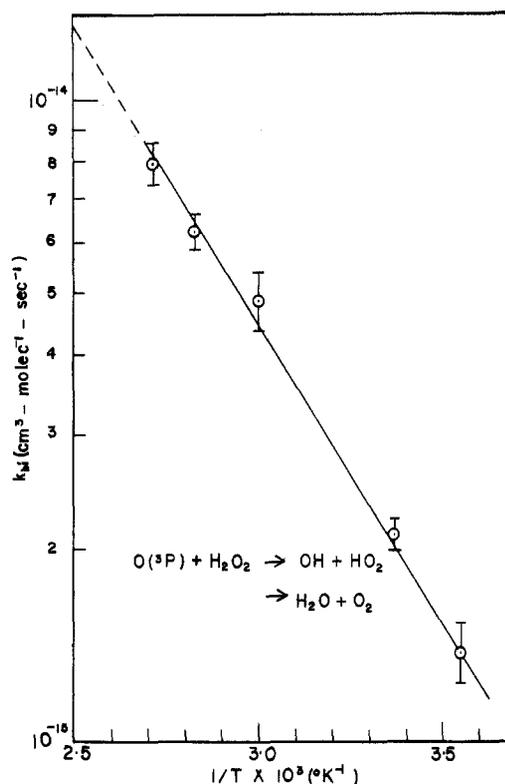

Figure 1. Arrhenius plot of the rate constant for reaction of ground-state atomic oxygen with hydrogen peroxide.

rate of 1%/min. Whereas, at 353°K, the decomposition of H_2O_2 was about 5%/min. In a typical experiment, the reaction mixture remained in the reaction cell for no more than 3 min. Pressure corrections due to decomposition of H_2O_2 were made accordingly.

The hydrogen peroxide used in this study was from Becco Chemical Division and had a purity level of 98%. Ozone was prepared using a ozonator and was stored in a trap filled with silica gel at Dry Ice–acetone temperatures. From uv absorption measurements, it was shown to have a purity of 94%. All pressure measurements of H_2O_2 and O_3 were made using a MKS Baraton pressure gauge.

The results from experiments performed over the temperature range 283–368°K are summarized in Table I. In all cases, the bimolecular rate constant was obtained from the slope of a plot of the pseudo-first-order rate constant, k_1, *vs.* the H_2O_2 concentration. The nonzero value for k_1 at zero H_2O_2 pressure is due to the loss of atomic oxygen by diffusion[3,4] and reaction with O_3.[5] At a fixed temperature this contribution to k_1 was always constant. The bimolecular rate constant for reaction 1 was determined to be $(2.12 \pm 0.33) \times 10^{-15}$ cm³ molecule⁻¹ sec⁻¹ at 298°K. The reported rate constant is based on direct observations of the rate of decay of $O(^3P)$ and thus represents the total bimolecular rate constant for both reaction channels (HO_2 + OH and H_2O + O_2). Over the temperature range 283–368°K, a least-squares fit of the rate data to the Arrhenius equation (see Figure 1) gave the rate expression $k_1 = (2.75 \pm 0.41) \times 10^{-12} \exp\{2125 \pm 261/T\}$.

A consideration of several possible secondary reactions in this system involving O, OH, and HO_2 indicated that none of these processes would have influenced the $O(^3P)$ decay curves. This point was demonstrated experimentally by a variation in the flash intensity [hence $O(^3P)$ con-

TABLE I: Rate Measurements for Reaction of $O(^3P)$ with H_2O_2 over the Temperature Range 283-368°K

Temp, °K	Total pressure (He), Torr	O_3 pressure, mTorr	H_2O_2 pressure, mTorr	First-order decay constant, sec^{-1}	Bimolecular rate constant k_1, cm^3 molecule^{-1} sec$^{-1} \times 10^{15}$
283	50	150	0	46	
	50	150	500	70	
	50	150	800	84	1.39 ± 0.15
298	50	150	0	55	
	50	150	400	80	
	50	150	800	110	$2.12 + 0.12$
333	50	100	300	122	
	50	100	600	166	
	50	100	1200	250	4.89 ± 0.51
353	50	150	190	150	
	50	150	380	184	
	50	150	320	165	
	50	150	570	215	
	50	150	760	230	6.25 ± 0.41
368	50	150	180	161	
	50	150	450	220	
	50	150	900	312	7.97 ± 0.61

centration] by a factor of 5 without observing any significant change in the bimolecular rate constant.

As mentioned earlier, only one other measurement of reaction 1 has been reported, this being an investigation by Foner and Hudson[2] using a mass spectrometric technique. The reaction was studied at 298°K, and yielded only an upper limit for k_1 of $\leq 4 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}. The two measurements, therefore, can be considered to be in good agreement within the assigned uncertainties.

Calculations based on available rate data[6] for reaction 2

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (2)$$
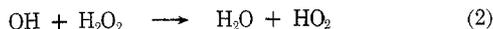
and concentration data for O and OH in the troposphere and stratosphere indicate that reaction 2 is the dominate gas kinetic destruction mechanism for H_2O_2 in the atmo-

sphere. Only in the mid and upper stratosphere could reaction 1 account for possibly as much as 10% of the total loss of H_2O_2 via gas kinetic processes.

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