3674 J. Phys. Chem. 1981, 85, 3674-3678

Mechanistic Investigation of the HO + HO_2 Reaction

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A steady-state photolysis experiment including mass-spectrometeric end-product analysis was used to conduct a mechanistic investigation of the $H^{18}O + HO_2$ reaction system. The results obtained do not support the existence of a linear adduct reaction intermediate as suggested by a proposed pressure dependence for the title reaction: $HO + HO_2 \rightarrow H_2O + O_2$ (k_1). An elaborate modeling analysis of the experiment best matches the observed product yields for values of k_1 in the range 1×10^{-10}–2×10^{-10} cm^3 molecule^{-1} s^{-1}.

Introduction

The reaction between hydroxyl (HO) and hydroperoxyl (HO_2) radicals has been shown via computer models to be very important in controlling the concentration of odd-hydrogen species (HO_x) in the earth's troposhere, stratosphere, and mesosphere. HO_x species, in turn, play a major role in the reaction cycles currently used to described stratospheric ozone perturbations by the catalytic activity of atomic chlorine or odd nitrogen (NO_x). More specifically, calculations of the magnitude of such perturbations are quite sensitive to uncertainties in the rate constant for reaction 1.[1-3] This sensitivity, coupled with the large

$$HO + HO_2 \xrightarrow{k_1} H_2O + O_2 \qquad (1)$$

variance in values reported for k_1, has made this reaction responsible for a major part of the stratospheric modeling uncertainty attributable to known chemistry. While recent revisions in the rate constants for two other important reactions (HO + $HONO_2$, and HO + HO_2NO_2)[4,5] have somewhat reduced the model sensitivity to k_1, the existing uncertainties still merit resolution.

Two recent evaluations[6] of the rate data for reaction 1 acknowledge significant disparity in the sets of reported room-temperature rate constants. The studies, until recently, have fallen essentially into two categories: low-pressure investigations ($p < 5$ torr)[7] yielding k_1 values in the 2×10^{-11}–5×10^{-11} cm^3 molecule^{-1} s^{-1} range,[8-10] and high-pressure experiments (p = 700–1200 torr) in which k_1 calculations fall between 10×10^{-11} and 20×10^{-11} cm^3 molecule^{-1} s^{-1}.[11-13] A very recent low-pressure study[14] has however resulted in a k_1 value near 7×10^{-11} cm^3 molecule^{-1} s^{-1}. These differences have given rise to speculation about a possible pressure dependence for reaction 1 although direct evidence from any one study is lacking. In the interim, certain of the earlier low-pressure studies have been called into question because of a significant change in the rate constant for reaction 2.[15,16] The k_1 value from

$$HO + H_2O_2 \xrightarrow{k_2} H_2O + HO_2 \qquad (2)$$

ref 8, for example, was calculated from measurements of the ratio k_1/k_2. The recent upward revision in k_2 changes the value calculated for k_1 from 5.1×10^{-11} to nearly 11×10^{-11} cm^3 molecule^{-1} s^{-1}. Two sets of experiments reported in ref 10 are also critically dependent upon k_2. Unfortunately, the revision in k_2 leads to severe inconsistencies in the data analysis (with k_1 values from one set increasing and those from the other decreasing). Thus, there still remains some uncertainty about the correct value of k_1 to be used in atmospheric modeling calculations as well as the question of a k_1 pressure dependence.

A pressure dependence for reaction 1 in the 10–100-torr region implies the existence of a reaction intermediate having a lifetime between 10^{-8} and 10^{-9} s (i.e., 10^4–10^5 vibrational lifetimes). Such stability (lifetime) is neither calculable from theoretical considerations[17] nor consistent with the heat of formation of noncyclic H_2O_3 estimated by Nangia and Benson[18] to be −15.7 kcal mol^{-1}. Currently there is no published estimate of the stability of a cyclic (hydrogen-bonded) H_2O_3 complex. Nevertheless, in view of the indication that lower-pressure studies yield a lower vlaue for k_1, there remains a strong need for experimental verification of a pressure dependence or lack thereof.

The present study was motivated by the possibility of inferring the existence of a stable HOOOH adduct via an isotopic labeling experiment involving $H^{18}O$ and HO_2. For these reactants, a simple bimolecular abstraction mecha-

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(16) U. C. Sridharan, B. Reimann, and F. Kaufman, *J. Chem. Phys.*, **73**, 1286 (1980).

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nism should yield exclusively $H_2{}^{18}O$ and O_2 as products. However, the adduct intermediate ($H^{18}OOOH$), which yields products *only* after rearrangement, has near equal probability for producing $H_2{}^{18}O + O_2$ and $H_2O + {}^{16,18}O_2$. Significant production of ${}^{16,18}O_2$ in such an experiment would therefore sduggest the participation of a linear adduct intermediate consistent with a pressure dependence for k_1.

The experiments consisted of the steady-state photolysis of $H_2{}^{18}O + O_2$ gas mixtures in the presence of an atmosphere of inert diluent gas (SF_6). While small yields of ${}^{16,18}O_2$ were observed, these can be explained by a reaction mechanism which does not include formation of an $H^{18}OOOH$ addition complex. As such, the results do not support a pressure dependence for reaction 1. The details of the investigation including extensive computer modeling for interpreting the results are presented herein.

Experimental Section

The primary photolysis source used for these experiments was a microwave-powered, low-pressure mercury lamp.[19] The lamp intensity at the 184.9-nm resonance line was determined to be 2.5% of that at 253.7 nm by using a calibrated photomuliplier–vacuum UV monochromator assembly. This ratio was essentially invariant over the lamp power settings used. A few experiments were also conducted with a microwave-operated, low-pressure xenon lamp (λ = 147 nm) as described by Okabe.[20]

Two different photolysis cells were also used. The primary apparatus (used essentially for the Hg lamp runs) was a 5-cm diameter cylindrical Suprasil cell (2.5 cm long). The Hg lamp was sealed to this cell through a vacuum UV grade quartz window. A second (1.5 cm diameter, 3.4 cm long) Pyrex cell equipped with sapphire windows was used for the 147-nm photolysis. Both cells could be used in either static or slow-flow experiments. In the latter case the photolysis cells were connected to one of several long-path (~1 m) absorption cells for optical monitoring of the H_2O_2 produced from either HO or HO_2 self-reaction (ϵ = 7.9 atm^{-1} cm^{-1} at λ = 213.9 nm).[21]

The Hg lamp–50-cm^3 cell combination was characterized over a wide range of lamp power settings by using ethylene actinometry.[19,22] For such calibrations, the acetylene production per unit photolysis time was measured under optically thin conditions. *J* values (photolysis rates) for any absorbing species x can be calculated by multiplying the acetylene production rate by the ratio $\epsilon_x/\epsilon_{C_2H_4}$. Such a procedure takes into account any additional photolysis due to scattered or reflected radiation. Absorption coefficients used for modeling the Hg lamp experiments are given in Table I.

Gas mixtures were prepared manometrically in glass storage bulbs before their admission to the photolysis cells. Under typical experimental conditions (10 torr of $H_2{}^{18}O$, 1 torr of O_2, 750 torr of SF_6), $H^{18}O$ and HO_2 radicals were generated by the reaction sequence

$$H_2{}^{18}O + h\nu \rightarrow H + H^{18}O$$

$$H + O_2 + SF_6 \rightarrow HO_2 + SF_6$$

TABLE I: Absorption Coefficients for Mercury Lamp Experiments

	ϵ(296 K), atm^{-1} cm^{-1}	
species	λ = 184.9 nm	λ = 253.7 nm
C_2H_4	7.5[a,b,c]	
H_2O	2.1[d]	$<10^{-3}$ [e]
O_2	0.29[d,f]	$<10^{-5}$ [g]
O_3	17.1[g]	283[h,i]
H_2O_2	28[j]	1.9[k,l]
HO_2	94.7[m]	14.2[n]

[a] K. Watanabe, *J. Chem. Phys.*, **40**, 558 (1964). [b] L. C. Glasgow and P. Potzinger, *J. Phys. Chem.*, **76**, 138 (1972). [c] Measured during the course of this work to be 7.44 ± 0.11. [d] W. B. DeMore, *Science*, **180**, 735 (1973). [e] B. A. Thompson, P. Harteck, and R. R. Reeves, *J. Geophys. Res.*, **68**, 6431 (1963). [f] Measured during the course of this work to be 0.28 ± 0.01. [g] R. D. Hudson, *Can. J. Chem.*, **52**, 1465 (1974). [h] E. C. Y. Inn and Y. Tanaka, *J. Opt. Soc. Am.*, **43**, 870 (1953). [i] A. G. Hearn, *Proc. Phys. Soc.*, **7**, 932 (1961). [j] Reference 23. [k] L. T. Molina, S. D. Schinke, and M. J. Molina, *Geophys. Res. Lett.*, **4**, 580 (1977). [l] Reference 21. [m] T. T. Paukert and H. S. Johnston, *J. Chem. Phys.*, **56**, 2824 (1972). [n] H. Kijewski and J. Troe, *Helv. Chim. Acta*, **55**, 205 (1972).

After a measured photolysis time (typically 5–9 min) the condensable products (including SF_6 and $H_2{}^{18}O$) were removed via liquid-N_2 trapping and the residual gas was analyzed mass-spectrometrically to determine the ${}^{16,18}O_2$ abundance. Absolute concentrations of ${}^{16,18}O_2$ (mass 34) were determined relative to ${}^{16,17}O_2$ (mass 33) whose concentration in turn was calculated from its natural abundance in the 1 torr of O_2 present in the photolysis mixtures. Each photolysis experiment was performed at least twice to check the reproducibility of the results (better than 10%). Similarly, two or three separate mass-spectrometer injections were made from each experiment to verify that the consistency of the analysis was well within 5%.

The ethylene actinometry measurements on this cell arrangement were verified by monitoring O_3 production in the optically thin photolysis of O_2 in N_2. For such measurements, the Hg lamp–50-cm^3 cell was attached to a 1-m absorption cell to observe the O_3 absorption at 253.7 nm. Excellent agreement was obtained between measured O_3 and that predicted by the C_2H_4 actinometry. Attempts to measure H_2O_2 produced in the $H_2{}^{18}O/O_2/SF_6$ system were hindered by the low H_2O_2 absorption coefficient at 213.9 nm (a wavelength chosen for minimal interference from either H_2O or O_2 absorption). Thus, to enhance H_2O_2 production, we conducted a number of experiments on mixtures consisting of 1–2 torr of O_2, 1–16 torr of H_2O, and 440–640 torr of H_2. For these experiments a xenon photolysis source (λ = 147 nm) coupled to the sapphire-windowed Pyrex cell was used. HO_2 radicals were thus generated by

$$H_2O + h\nu \rightarrow H + HO$$

$$HO + H_2 \rightarrow H_2O + H$$

$$H + O_2 + H_2 \rightarrow HO_2 + H_2$$

Because of the larger photon flux at 147 nm as well as the higher H_2O absorption coefficient[23] at this wavelength, the HO_2 formation rate was nearly 2 orders of magnitude greater than in the Hg lamp experiments. This was easily observable in the increased amount of H_2O_2 produced by the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

In this system O_3 was also formed via O_2 photodissociation[24] followed by O + O_2 combination. In order to remove

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[19] H. D. Beckey, W. Groth, H. Okabe, and H. J. Rommel, *Z. Naturforsch. A*, **19**, 1511 (1964).

[20] H. Okabe, *J. Opt. Soc. Am.*, **54**, 478 (1964).

[21] C. L. Lin, N. K. Rohatgi, and W. B. DeMore, *Geophys. Res. Lett.*, **5**, 113 (1978).

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any chemical complexity due to O_3, a 253.7-nm Hg lamp was used simultaneously with the Xe lamp. Thus, any ozone produced was immediately photolyzed to $O_2 + O(^1D)$. The $O(^1D)$ was converted rapidly into H and HO via reactions with H_2 and H_2O, and the above reaction sequence again predominates. Thus, by monitoring H_2O_2 production, we were able to investigate the possibility of heterogeneous wall removal of H_2O_2 in our experiments.

The gases used in this study had the following stated minimum purities: $H_2{}^{18}O$, 99 at. % ^{18}O; O_2, 99.99%; H_2, 99.999%; and SF_6, 99.99%. They were used without further purification, all metering being done through a high-vacuum manifold.

Results and Discussion

As stated previously, attempts to measure H_2O_2 production in the Hg lamp experiments were complicated by its slow production rate and low detection sensitivity. Within the limits of the measurements, however, the H_2O_2 consistently appeared to be at least a factor of 2 smaller than predicted by the photolysis lamp flux ($\phi_{H_2O_2} \approx 0.5$). The Xe lamp experiments also gave reproducible quantum yields for H_2O_2 between 0.25 and 0.33 independent of photolysis mixture composition. This observation is nearly identical with that of Cox and Burrows[25] in a chemically similar system. We have interpreted these results in our system as indicative of a wall loss of the hydrogen peroxide. Given that the Xe lamp experiments utilized a cell having twice the surface-to-volume ratio as the cell in the Hg lamp runs, it is not surprising that the former gave lower H_2O_2 quantum yields.

In order to assess the homogeneity of both the photolysis and the radical reactions, we varied the partial pressure of water vapor (in the Xe lamp experiments) from 1 to 16 torr without any measurable change in H_2O_2 quantum yield. One would have expected H_2O to have an important role as a complexing agent for those reactions or photolyses occurring on the walls. In addition, this same change in H_2O concentration causes the percent light absorbed to vary from 10 to 80. This in turn produces a marked change in effective photolysis volume. Yet no chemical changes were observed. In these latter experiments the photolysis rate was calculated from ethylene actinometry measurements made on mixtures of similar optical thickness.

With this background of observational data, the mercury photolysis experiments were performed on the isotopically labeled system and the yields of $^{16,18}O_2$ carefully catalogued. It should be emphasized that, because of the small absorption coefficient of water at 184.9 nm, these experiments always employed optically thin photolysis conditions. Thus, radical concentrations were uniform throughout the photolysis volume. The mass-spectrometric analysis did indeed indicate a yield of $^{16,18}O_2$ which was dependent on both the photolysis intensity and duration. However, a simple modeling analysis in which one half of reaction 1 was assigned to produce $^{16,18}O_2$ (via the linear complexation mechanism) predicted yields of $^{16,18}O_2$ 20–30 times greater than those observed. At first glance, this observation would appear to indicate that, at most, 3–5% of reaction 1 can proceed through the adduct channel postulated. Further modeling calculations, however, were able to demonstrate that the assumption of a linear adduct intermediate (i.e., pressure dependence) is not needed at all to explain these results. For example, when the direct formation channel was eliminated from the mechanism (i.e., direct abstraction assumed), the model still predicted formation of $^{16,18}O_2$ but with a much lower yield. In this case, $^{16,18}O_2$ formed in the reaction sequence

$$H^{18}O + H^{18}O \rightarrow H_2{}^{18}O + {}^{18}O$$

$$^{18}O + O_2 \rightarrow {}^{16,18}O_2 + O$$

accounts for virtually all of the $^{16,18}O_2$ observed.

Since, to a first approximation, the ^{18}O (and hence $^{16,18}O_2$) concentration depends on $[H^{18}O]^2$, we felt that the $^{16,18}O_2$ yield could provide information on the rate constants for those reactions controlling $H^{18}O$ (specifically reaction 1). In order to assess this possibility, we had to incorporate a far more extensive set of reactions into the model. These are listed in Table II along with their rate constants. The latter (except where noted) are taken from ref 6a. The various photodissociation rates were calculated from the absorption coefficients listed in Table I, and light flux values determined from actinometry measurements for each experiment. While the list of reactions at first glance appears overwhelming, it should be noted that, aside from photolysis, only 13 different homogeneous reactions are included. Because of the potential for isotopic scrambling via secondary reactions, reactions of the isotopic variants of each species were also included. Many of these, in fact, were shown to have little effect on the modeling results.[26] The modeling program generates the concentrations of all reacting species and products at any times chosen after initiation of photolysis. Typical steady-state concentrations of $H^{18}O$ and HO_2 were 3×10^{11} molecules/cm^3. Concentrations of all other radicals were calculated to be at least 1 order of magnitude lower. As will be discussed below, only the concentrations of the isotopically labeled molecular oxygens relate to the experimental observations.

The calculations indicated that the $H^{18}O$ concentration was controlled by self-reaction (combination and disproportionation), reaction with HO_2, and reaction with hydrogen peroxide. The latter fate proved particularly interesting since nearly half of the H_2O_2 formed comes from HO + HO combination and hence is present as $H_2{}^{18,18}O_2$. This doubly labeled peroxide ultimately is converted into $H^{18,18}O_2$ via reaction with various radicals (primarily HO). The $H^{18,18}O_2$ then generates $^{18,18}O_2$ through further reactions. In fact, the model predicts a yield of $^{18,18}O_2$ nearly equal to that of $^{16,18}O_2$. While there was indeed some $^{18,18}O_2$ observed experimentally, its yield was consistently 1 order of magnitude less than that of $^{16,18}O_2$. Since the only source of $^{18,18}O_2$ in our kinetic scheme is $H_2{}^{18,18}O_2$, we attribute the deficiency of $^{18,18}O_2$ to a heterogeneous sink for hydrogen peroxide in the experimental assembly. This interpretation is supported by our observations on the yield of H_2O_2 in the flowing photolysis experiments (discussed earlier). While we cannot specify exactly the products of H_2O_2 heterogeneous removal, the deficiency of $^{18,18}O_2$ suggests that the process

$$2H_2{}^{18,18}O_2 \xrightarrow{\text{wall}} 2H_2{}^{18}O + {}^{18,18}O_2$$

is of minor importance in our system. Since, at atmospheric pressures, a heterogeneous removal would be diffusion controlled, we included such a calculated rate[27] for loss of H_2O_2 in Table II. The modeling results are fairly insensitive to values of the first-order diffusion rate greater than several s^{-1} since the rates of homogeneous reaction

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(25) R. A. Cox and J. P. Burrows, *J. Phys. Chem.*, **83**, 2560 (1979).

(26) The modeling calculations were performed by using an adaptation of a program package reported in R. L. Brown, "A Computer Program for Solving Systems of Chemical Rate Equations", NBSIR 76-1055, National Bureau of Standards, Washington, DC.

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TABLE II: Reaction Mechanism Used for Modeling Analysis

reaction	rate constant, cm^3 $molecule^{-1}$ s^{-1}	reaction	rate constant, cm^3 $molecule^{-1}$ s^{-1}
$H_2{}^{18}O + h\nu \rightarrow H + H^{18}O$	see text	$H + HO_2 \rightarrow HO + HO$	3.2×10^{-11c}
$H + O_2 \rightarrow HO_2$	3.7×10^{-12}	$H + HO_2 \rightarrow H_2 + O_2$	1.4×10^{-11c}
$H^{18}O + H^{18}O \rightarrow H_2{}^{18}O + {}^{18}O$	1.8×10^{-12}	${}^{18,18}O_2 + h\nu \rightarrow {}^{18}O + {}^{18}O$	see text
$H^{18}O + H^{18}O \rightarrow H_2{}^{18,18}O_2$	3.7×10^{-12}	$O + H^{18}O \rightarrow H + {}^{16,18}O_2$	3.3×10^{-11}
$H^{18}O + HO_2 \rightarrow H_2{}^{18}O + O_2$	see text	$O + HO \rightarrow H + O_2$	3.3×10^{-11}
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	4.5×10^{-12a}	${}^{18}O + H^{18}O \rightarrow H + {}^{18,18}O_2$	3.3×10^{-11}
${}^{18}O + O_2 \rightarrow {}^{16,18}O_2 + O$	1.7×10^{-12b}	${}^{18}O + HO \rightarrow H + {}^{16,18}O_2$	3.3×10^{-11}
$O_2 + h\nu \rightarrow O + O$	see text	$O + HO_2 \rightarrow HO + O_2$	3.5×10^{-11}
${}^{16,18}O_2 + h\nu \rightarrow O + {}^{18}O$	see text	$O + H^{16,18}O_2 \rightarrow HO + {}^{16,18}O_2$	3.5×10^{-11}
${}^{18}O + O_2 \rightarrow {}^{18}O_3$	7.4×10^{-14}	$O + H^{18,18}O_2 \rightarrow HO + {}^{18,18}O_2$	3.5×10^{-11}
$O + O_2 \rightarrow O_3$	7.4×10^{-14}	${}^{18}O + HO_2 \rightarrow H^{18}O + O_2$	3.5×10^{-11}
${}^{18}O_3 + h\nu \rightarrow O_2 + {}^{18}O({}^1D)$	see text	${}^{18}O + H^{16,18}O_2 \rightarrow H^{18}O + {}^{16,18}O_2$	3.5×10^{-11}
${}^{18}O_3 + h\nu \rightarrow {}^{16,18}O_2 + O({}^1D)$	see text	$O + H^{18,18}O_2 \rightarrow HO + {}^{18,18}O_2$	3.5×10^{-11}
${}^{18}O({}^1D) + H_2{}^{18}O \rightarrow H^{18}O + H^{18}O$	2.3×10^{-10}	${}^{18}O + HO_2 \rightarrow H^{18}O + O_2$	3.5×10^{-11}
$O({}^1D) + H_2{}^{18}O \rightarrow H^{18}O + HO$	2.3×10^{-10}	${}^{18}O + H^{16,18}O_2 \rightarrow H^{18}O + {}^{16,18}O_2$	3.5×10^{-11}
$O_3 + h\nu \rightarrow O_2 + O({}^1D)$	see text	${}^{18}O + H^{18,18}O_2 \rightarrow H^{18}O + {}^{18,18}O_2$	3.5×10^{-11}
$H_2{}^{18,18}O_2 + h\nu \rightarrow H^{18}O + H^{18}O$	see text	$H^{18}O + H^{16,18}O_2 \rightarrow H_2{}^{18}O + {}^{16,18}O_2$	see text
$H_2O_2 + h\nu \rightarrow HO + HO$	see text	$H^{18}O + H^{18,18}O_2 \rightarrow H_2{}^{18}O + {}^{18,18}O_2$	see text
$HO + HO \rightarrow H_2O + O$	1.8×10^{-12}	$HO + H^{16,18}O_2 \rightarrow H_2O + {}^{16,18}O_2$	see text
$HO + HO \rightarrow H_2O_2$	3.7×10^{-12}	$HO + H^{18,18}O_2 \rightarrow H_2O + {}^{18,18}O_2$	see text
$HO + H^{18}O \rightarrow H_2O + {}^{18}O$	9.0×10^{-13}	$HO_2 + H^{16,18}O_2 \rightarrow H_2O_2 + {}^{16,18}O_2$	2.25×10^{-12a}
$HO + H^{18}O \rightarrow H_2{}^{18}O + O$	9.0×10^{-13}	$HO_2 + H^{16,18}O_2 \rightarrow H_2{}^{16,18}O_2 + O_2$	2.25×10^{-12a}
$HO + H^{18}O \rightarrow H_2{}^{16,18}O_2$	3.7×10^{-12}	$HO_2 + H^{18,18}O_2 \rightarrow H_2O_2 + {}^{18,18}O_2$	2.25×10^{-12a}
$HO + HO_2 \rightarrow H_2O + O_2$	see text	$HO_2 + H^{18,18}O_2 \rightarrow H_2{}^{18,18}O_2 + O_2$	2.25×10^{-12a}
$H_2O + h\nu \rightarrow H + HO$	see text	$H^{16,18}O_2 + H^{16,18}O_2 \rightarrow H_2{}^{16,18}O_2 + {}^{16,18}O_2$	4.5×10^{-12a}
$H_2{}^{16,18}O_2 + h\nu \rightarrow HO + H^{18}O$	see text	$H^{16,18}O_2 + H^{18,18}O_2 \rightarrow H_2{}^{16,18}O_2 + {}^{18,18}O_2$	2.25×10^{-12a}
$H + O_3 \rightarrow HO + O_2$	2.9×10^{-11}	$H^{16,18}O_2 + H^{18,18}O_2 \rightarrow H_2{}^{18,18}O_2 + {}^{16,18}O_2$	2.25×10^{-12a}
$H + {}^{18}O_3 \rightarrow HO + {}^{16,18}O_2$	1.45×10^{-11}	$H^{18,18}O_2 + H^{18,18}O_2 \rightarrow H_2{}^{18,18}O_2 + {}^{18,18}O_2$	4.5×10^{-12a}
$H + {}^{18}O_3 \rightarrow H^{18}O + O_2$	1.45×10^{-11}	$O + {}^{18}O_3 \rightarrow O_2 + {}^{16,18}O_2$	8.8×10^{-15}
$H^{18}O + H_2{}^{18,18}O_2 \rightarrow H_2{}^{18}O + H^{18,18}O_2$	1.7×10^{-12}	$O + O_3 \rightarrow O_2 + O_2$	8.8×10^{-15}
$H^{18}O + H_2{}^{16,18}O_2 \rightarrow H_2{}^{18}O + H^{16,18}O_2$	1.7×10^{-12}	${}^{18}O + {}^{18}O_3 \rightarrow {}^{16,18}O_2 + {}^{16,18}O_2$	4.4×10^{-15}
$H^{18}O + H_2O_2 \rightarrow H_2{}^{18}O + HO_2$	1.7×10^{-12}	${}^{18}O + {}^{18}O_3 \rightarrow {}^{18,18}O_2 + O_2$	4.4×10^{-15}
$HO + H_2{}^{18,18}O_2 \rightarrow H_2O + H^{18,18}O_2$	1.7×10^{-12}	${}^{18}O + O_3 \rightarrow {}^{16,18}O_2 + O_2$	8.8×10^{-15}
$HO + H_2{}^{16,18}O_2 \rightarrow H_2O + H^{16,18}O_2$	1.7×10^{-12}	$H + {}^{16,18}O_2 \rightarrow H^{16,18}O_2$	3.7×10^{-12}
$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}	$H + {}^{18,18}O_2 \rightarrow H^{18,18}O_2$	3.7×10^{-12}
$H^{18}O + {}^{18}O_3 \rightarrow H^{18,18}O_2 + O_2$	3.4×10^{-14}	$HO_2 + h\nu \rightarrow HO + O$	see text
$H^{18}O + {}^{18}O_3 \rightarrow H^{16,18}O_2 + {}^{16,18}O_2$	3.4×10^{-14}	$H^{16,18}O_2 + h\nu \rightarrow HO + {}^{18}O$	see text
$H^{18}O + O_3 \rightarrow H^{16,18}O_2 + O_2$	6.8×10^{-14}	$H^{16,18}O_2 + h\nu \rightarrow H^{18}O + O$	see text
$HO + {}^{18}O_3 \rightarrow H^{16,18}O_2 + O_2$	3.4×10^{-14}	$H^{18,18}O_2 + h\nu \rightarrow H^{18}O + {}^{18}O$	see text
$HO + {}^{18}O_3 \rightarrow HO_2 + {}^{16,18}O_2$	3.4×10^{-14}	${}^{18}O + {}^{16,18}O_2 \rightarrow O + {}^{18,18}O_2$	8.5×10^{-13b}
$HO + O_3 \rightarrow HO_2 + O_2$	6.8×10^{-14}	$O + {}^{16,18}O_2 \rightarrow {}^{18}O + O_2$	8.5×10^{-13b}
$H + H^{18,18}O_2 \rightarrow H^{18}O + H^{18}O$	3.2×10^{-11c}	$O + {}^{18,18}O_2 \rightarrow {}^{18}O + {}^{16,18}O_2$	1.7×10^{-12b}
$H + H^{18,18}O_2 \rightarrow H_2 + {}^{18,18}O_2$	1.4×10^{-11c}	$H_2O_2 \rightarrow$ wall	see text
$H + H^{16,18}O_2 \rightarrow HO + H^{18}O$	3.2×10^{-11c}	$H_2{}^{16,18}O_2 \rightarrow$ wall	see text
$H + H^{16,18}O_2 \rightarrow H_2 + {}^{16,18}O_2$	1.4×10^{-11c}	$H_2{}^{18,18}O_2 \rightarrow$ wall	see text

[a] This rate constant includes the effect of 10 torr of water vapor as given in ref 12b. [b] W. Brennen and H. Niki, *J. Chem. Phys.*, 42, 3725 (1965). [c] Reference 6b.

of H_2O_2 are relatively slow. Nevertheless, when such processes for H_2O_2 are included, there is a marked reduction in ${}^{18,18}O_2$ to the point where the predicted ${}^{16,18}O_2/{}^{18,18}O_2$ ratio is within experimental error of the observed ratio.[28]

With the model constrained to agree with our *observed* limited production of ${}^{18,18}O_2$ (and low yields of H_2O_2), the sensitivity of the ${}^{16,18}O_2$ production to k_1 values was investigated. We observed that a factor of 5 variation in k_1 generated a 3.5–4-fold change in predicted ${}^{16,18}O_2$; the lower the value of k_1, the higher the calculated yield of ${}^{16,18}O_2$. The extreme limits of this comparison are shown in Table III for all of the various experimental photolysis intensities (J) and durations (t). As can be seen, agreement between calculated and measured values of $[{}^{16,18}O_2]$ is excellent for k_1 values near 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and high by factors of 2–3 for k_1 values as low as 4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. When one includes the measurement uncertainties (as well as allowing for as much as a factor of 2 uncertainty in the H_2O_2 loss rate) in this comparison, our conclusions must encompass a range of k_1 values.

TABLE III: Measured and Predicted ${}^{16,18}O_2$ Production

$10^6 J$,[b] s^{-1}	t, s	$[{}^{16,18}O_2]$, molecules cm^{-3}		
		calcd		
		$k_1 = 4 \times 10^{-11}$	$k_1 = 2 \times 10^{-10}$	measured[a]
80	300	1.1×10^{14}	4.0×10^{13}	4.5×10^{13}
80	540	1.9×10^{14}	7.3×10^{13}	8.1×10^{13}
100	360	1.6×10^{14}	6.0×10^{13}	5.9×10^{13}
300	300	3.8×10^{14}	1.5×10^{14}	1.4×10^{14}
450	300	5.8×10^{14}	2.2×10^{14}	1.7×10^{14}

[a] Values shown are averages of two to three mass-spectrometric determinations from each of several photolysis experiments. [b] These photolysis flux values are calculated for ethylene. They must be multiplied by $\epsilon_X[X]/\epsilon_{C_2H_4}$ to obtain photolytic decomposition rates for species X.

Simply stated, then, the results of this investigation indicate the following: (1) The absence of significant direct production of ${}^{16,18}O_2$ in the reaction of $H^{18}O$ with HO_2 does

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[28] Absolute yields of ${}^{16,18}O_2$ were in the range of 1–5 mtorr. Because of accuracy limitations in measuring ${}^{18,18}O_2$ at partial pressures 1 order of magnitude below this, the ratio ${}^{16,18}O_2/{}^{18,18}O_2$ is simply stated as ≥10.

not support the existence of a linear adduct reaction intermediate and thus calls into question the suggestion of a pressure dependence for k_1. A cyclic (hydrogen-bonded) intermediate would not require rearrangement prior to product formation and thus might not yield isotopically labeled O_2. However, under such circumstances, the need for collisional stabilization is not readily explainable and the mechanism is indistinguishable from direct abstraction. (2) Detailed modeling calculations of the steady-state photolysis system predict yields of $^{16,18}O_2$ in very good agreement with those determined experimentally only if k_1 values between 1×10^{-10} and 2×10^{-10} cm^3 molecule^{-1} s^{-1} are used. The use of values for k_1 much below 1×10^{-10} cm^3 molecule^{-1} s^{-1} in the modeling calculations results in predicted $^{16,18}O_2$ yields greatly exceeding those which we observe.

Acknowledgment. We gratefully acknowledge the assistance of Dr. R. L. Brown in modifying the computer modeling package used in this analysis. This work was supported in part by the FAA/High Altitude Pollution Program of the Department of Transportation and the Fluorocarbon Research Program of the Chemical Manufacturers Association.

One-Electron Transfer Reactions Involving Zinc and Cobalt Porphyrins in Aqueous Solutions[1]

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Zn and Co complexes of the water soluble porphyrins (P) TPPS (tetra(4-sulfonatophenyl)porphyrin), TAPP (tetra(4-(*N*,*N*,*N*-trimethylamino)phenyl)porphyrin), and TMPyP (tetra(4-*N*-methylpyridyl)porphyrin) were studied by steady-state and pulse radiolysis. ZnP are reduced with e_{aq}^- ($k \approx 10^{10}$ M^{-1} s^{-1}), $(CH_3)_2\dot{C}OH$ ($k = 8 \times 10^7$–2×10^9 M^{-1} s^{-1}), and $(CH_3)_2\dot{C}O^-$ ($k = 1 \times 10^9$–7×10^9 M^{-1} s^{-1}) to yield the anion radicals $Zn\dot{P}^-$. The rate of reduction increases in the order ZnTPPS < ZnTAPP < ZnTMPyP. All the anion radicals exhibit broad absorption maxima around 700–730 nm. These porphyrins are also oxidized by Br_2^- ($k \approx 10^9$ M^{-1} s^{-1}) and by $\dot{C}H_2CHO$ ($k \sim 10^8$ M^{-1} s^{-1}) to yield the cation radicals $Zn\dot{P}^+$. The latter radicals exhibit broad absorptions at 650–700 nm. One-electron reduction of $Co^{III}P$ by e_{aq}^- ($k \sim 10^{10}$ M^{-1} s^{-1}) or $(CH_3)_2\dot{C}O^-$ ($k \sim 10^9$ M^{-1} s^{-1}) yields $Co^{II}P$. Br_2^- and $\dot{C}H_2CHO$ oxidize $Co^{II}P$ rapidly ($k \sim 10^9$ M^{-1} s^{-1}) into $Co^{III}P$. All $Zn\dot{P}^-$ studied transfer an electron to all three $Co^{III}P$. The rate constants vary between 10^7 and 10^9 M^{-1} s^{-1} and are affected by the redox potentials and by the electrostatic charge of the reacting species. The effect of charge is much smaller than expected for multiply charged species and indicates that the reactants are influenced only by one or two charges at the site of interaction. Rate constants for one-electron oxidation of $Co^{II}TPPS$ by $Zn\dot{P}^+$ ($k \approx 10^8$–10^9 M^{-1} s^{-1}) follow a similar pattern.

Introduction

One-electron transfer reactions of porphyrins can be conveniently studied by pulse radiolysis. With water-insoluble porphyrins, one-electron reduction can be carried out by irradiation in alcohols,[2] and one-electron oxidation by irradiation in dichloroethane.[3,4] Water soluble porphyrins can be reduced[2,5-7] by e_{aq}^-, $(CH_3)_2\dot{C}OH$, or $\dot{C}O_2^-$ and may be oxidized, e.g., by Br_2^- [8] or $\dot{C}H_2CHO$.[9] Thus it is possible by pulse radiolysis to produce anion and cation radicals of porphyrins under various conditions,[2-5,10-12] and to study their electron-transfer reactions with other electron acceptors or donors.

Rate constants of electron transfer from porphyrin anion radicals to several quinones were found to be in the range of 10^7–10^9 M^{-1} s^{-1}.[2] They vary according to variations in redox potentials as expected from the Marcus relation.[13] More recently, one-electron oxidation of $Co^{II}TPP$ and chlorophyll a by various metalloporphyrin cation radicals were studied in dichloroethane in the presence of pyridine.[4] The rate constants for these reactions were found to be mostly in the range of 3×10^8–5×10^8 M^{-1} s^{-1}, i.e., practically unaffected by redox potential differences and yet much lower than the diffusion-controlled limit. These findings suggested that the pyridine ligated to the metal

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[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2258 from the Notre Dame Radiation Laboratory.

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