

Mechanistic Investigation of the HO + HO₂ Reaction

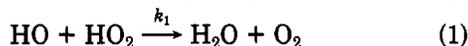
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A steady-state photolysis experiment including mass-spectrometric end-product analysis was used to conduct a mechanistic investigation of the H¹⁸O + HO₂ reaction system. The results obtained do not support the existence of a linear adduct reaction intermediate as suggested by a proposed pressure dependence for the title reaction: HO + HO₂ → H₂O + O₂ (*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 cm³ molecule⁻¹ s⁻¹.

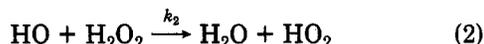
Introduction

The reaction between hydroxyl (HO) and hydroperoxyl (HO₂) 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 troposphere, stratosphere, and mesosphere. HO_x species, in turn, play a major role in the reaction cycles currently used to describe 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



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 + HONO₂, and HO + HO₂NO₂)^{4,5} have somewhat reduced the model sensitivity to *k*₁, the existing uncertainties still merit resolution.

Two recent evaluations⁶ 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 cm³ 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 cm³ molecule⁻¹ s⁻¹.¹¹⁻¹³ A very recent low-pressure study¹⁴ has however resulted in a *k*₁ value near 7 × 10⁻¹¹ cm³ 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



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 cm³ 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,

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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., 10⁴–10⁵ vibrational lifetimes). Such stability (lifetime) is neither calculable from theoretical considerations¹⁷ nor consistent with the heat of formation of noncyclic H₂O₃ estimated by Nangia and Benson¹⁸ to be –15.7 kcal mol⁻¹. Currently there is no published estimate of the stability of a cyclic (hydrogen-bonded) H₂O₃ complex. Nevertheless, in view of the indication that lower-pressure studies yield a lower value 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 H¹⁸O and HO₂. For these reactants, a simple bimolecular abstraction mecha-

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(3) R. S. Stolarski, "Latest Determination of Modeling Uncertainties Due to Chemistry", presented at the 4th Meeting of the HAPP Scientific Advisory Committee, Federal Aviation Administration, Washington, DC, Dec 1980.

(4) P. H. Wine, A. R. Ravishankara, N. M. Kreutter, R. C. Shah, J. M. Nicovich, and R. L. Thompson, *J. Geophys. Res.*, **86**, 1105 (1981).

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(7) 1 torr = 133.32 Pa = 9.6587 × 10¹⁸/T(K) molecules cm⁻³.

(8) (a) J. P. Burrows, G. W. Harris, and B. A. Thrush, *Nature (London)*, **267**, 233 (1977); (b) J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, *Proc. R. Soc. London, Ser. A*, **368**, 463 (1979).

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(12) (a) W. B. DeMore and E. Tschuikow-Roux, *J. Phys. Chem.*, **78**, 1447 (1974); (b) W. B. DeMore, *Ibid.*, **83**, 1113 (1979).

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(14) L. F. Keyser, "Kinetics of the Reaction OH + HO₂ → H₂O + O₂", presented at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981.

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nism should yield exclusively H₂¹⁸O and O₂ as products. However, the adduct intermediate (H¹⁸OOOH), which yields products *only* after rearrangement, has near equal probability for producing H₂¹⁸O + O₂ and H₂O + ^{16,18}O₂. Significant production of ^{16,18}O₂ in such an experiment would therefore suggest the participation of a linear adduct intermediate consistent with a pressure dependence for *k*₁.

The experiments consisted of the steady-state photolysis of H₂¹⁸O + O₂ gas mixtures in the presence of an atmosphere of inert diluent gas (SF₆). While small yields of ^{16,18}O₂ were observed, these can be explained by a reaction mechanism which does not include formation of an H¹⁸OOOH 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.

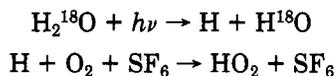
Experimental Section

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 photomultiplier-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 H₂O₂ produced from either HO or HO₂ self-reaction (ε = 7.9 atm⁻¹ cm⁻¹ at λ = 213.9 nm).²¹

The Hg lamp-50-cm³ 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 ε_{*x*}/ε_{C₂H₄}. 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 H₂¹⁸O, 1 torr of O₂, 750 torr of SF₆), H¹⁸O and HO₂ radicals were generated by the reaction sequence



After a measured photolysis time (typically 5–9 min) the condensable products (including SF₆ and H₂¹⁸O) were removed via liquid-N₂ trapping and the residual gas was

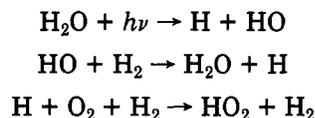
TABLE I: Absorption Coefficients for Mercury Lamp Experiments

species	ε(296 K), atm ⁻¹ cm ⁻¹	
	λ = 184.9 nm	λ = 253.7 nm
C ₂ H ₄	7.5 ^{a,b,c}	
H ₂ O	2.1 ^d	<10 ^{-3 e}
O ₂	0.29 ^{d,f}	<10 ^{-5 g}
O ₃	17.1 ^g	283 ^{h,i}
H ₂ O ₂	28 ^j	1.9 ^{k,l}
HO ₂	94.7 ^m	14.2 ⁿ

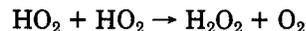
^a K. Watanabe, *J. Chem. Phys.*, 40, 558 (1964). ^b L. C. Glasgow and P. Potzinger, *J. Phys. Chem.*, 76, 138 (1972). ^c Measured during the course of this work to be 7.44 ± 0.11. ^d W. B. DeMore, *Science*, 180, 735 (1973). ^e B. A. Thompson, P. Harteck, and R. R. Reeves, *J. Geophys. Res.*, 68, 6431 (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).

analyzed mass-spectrometrically to determine the ^{16,18}O₂ abundance. Absolute concentrations of ^{16,18}O₂ (mass 34) were determined relative to ^{16,17}O₂ (mass 33) whose concentration in turn was calculated from its natural abundance in the 1 torr of O₂ 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 O₃ production in the optically thin photolysis of O₂ in N₂. For such measurements, the Hg lamp-50-cm³ cell was attached to a 1-m absorption cell to observe the O₃ absorption at 253.7 nm. Excellent agreement was obtained between measured O₃ and that predicted by the C₂H₄ actinometry. Attempts to measure H₂O₂ produced in the H₂¹⁸O/O₂/SF₆ system were hindered by the low H₂O₂ absorption coefficient at 213.9 nm (a wavelength chosen for minimal interference from either H₂O or O₂ absorption). Thus, to enhance H₂O₂ production, we conducted a number of experiments on mixtures consisting of 1–2 torr of O₂, 1–16 torr of H₂O, and 440–640 torr of H₂. For these experiments a xenon photolysis source (λ = 147 nm) coupled to the sapphire-windowed Pyrex cell was used. HO₂ radicals were thus generated by



Because of the larger photon flux at 147 nm as well as the higher H₂O absorption coefficient²³ at this wavelength, the HO₂ formation rate was nearly 2 orders of magnitude greater than in the Hg lamp experiments. This was easily observable in the increased amount of H₂O₂ produced by the reaction



In this system O₃ was also formed via O₂ photodissociation²⁴ followed by O + O₂ combination. In order to remove

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any chemical complexity due to O₃, a 253.7-nm Hg lamp was used simultaneously with the Xe lamp. Thus, any ozone produced was immediately photolyzed to O₂ + O(¹D). The O(¹D) was converted rapidly into H and HO via reactions with H₂ and H₂O, and the above reaction sequence again predominates. Thus, by monitoring H₂O₂ production, we were able to investigate the possibility of heterogeneous wall removal of H₂O₂ in our experiments.

The gases used in this study had the following stated minimum purities: H₂¹⁸O, 99 at. % ¹⁸O; O₂, 99.99%; H₂, 99.999%; and SF₆, 99.99%. They were used without further purification, all metering being done through a high-vacuum manifold.

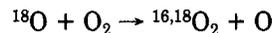
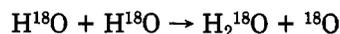
Results and Discussion

As stated previously, attempts to measure H₂O₂ 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 H₂O₂ consistently appeared to be at least a factor of 2 smaller than predicted by the photolysis lamp flux ($\phi_{\text{H}_2\text{O}_2} \approx 0.5$). The Xe lamp experiments also gave reproducible quantum yields for H₂O₂ between 0.25 and 0.33 independent of photolysis mixture composition. This observation is nearly identical with that of Cox and Burrows²⁵ 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 H₂O₂ 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 H₂O₂ quantum yield. One would have expected H₂O to have an important role as a complexing agent for those reactions or photolyses occurring on the walls. In addition, this same change in H₂O 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}O₂ 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}O₂ 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}O₂ (via the linear complexation mechanism) predicted yields of ^{16,18}O₂ 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

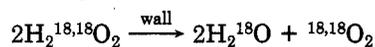
(i.e., direct abstraction assumed), the model still predicted formation of ^{16,18}O₂ but with a much lower yield. In this case, ^{16,18}O₂ formed in the reaction sequence



accounts for virtually all of the ^{16,18}O₂ observed.

Since, to a first approximation, the ¹⁸O (and hence ^{16,18}O₂) concentration depends on [H¹⁸O]², we felt that the ^{16,18}O₂ yield could provide information on the rate constants for those reactions controlling H¹⁸O (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 H¹⁸O and HO₂ were 3×10^{11} molecules/cm³. 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 H¹⁸O concentration was controlled by self-reaction (combination and disproportionation), reaction with HO₂, and reaction with hydrogen peroxide. The latter fate proved particularly interesting since nearly half of the H₂O₂ formed comes from HO + HO combination and hence is present as H₂^{18,18}O₂. This doubly labeled peroxide ultimately is converted into H^{18,18}O₂ via reaction with various radicals (primarily HO). The H^{18,18}O₂ then generates ^{18,18}O₂ through further reactions. In fact, the model predicts a yield of ^{18,18}O₂ nearly equal to that of ^{16,18}O₂. While there was indeed some ^{18,18}O₂ observed experimentally, its yield was consistently 1 order of magnitude less than that of ^{16,18}O₂. Since the only source of ^{18,18}O₂ in our kinetic scheme is H₂^{18,18}O₂, we attribute the deficiency of ^{18,18}O₂ to a heterogeneous sink for hydrogen peroxide in the experimental assembly. This interpretation is supported by our observations on the yield of H₂O₂ in the flowing photolysis experiments (discussed earlier). While we cannot specify exactly the products of H₂O₂ heterogeneous removal, the deficiency of ^{18,18}O₂ suggests that the process



is of minor importance in our system. Since, at atmospheric pressures, a heterogeneous removal would be diffusion controlled, we included such a calculated rate²⁷ for loss of H₂O₂ 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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(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 ¹⁸ O + hν → H + H ¹⁸ O	see text	H + HO ₂ → HO + HO	3.2 × 10 ^{-11c}
H + O ₂ → HO ₂	3.7 × 10 ⁻¹²	H + HO ₂ → H ₂ + O ₂	1.4 × 10 ^{-11c}
H ¹⁸ O + H ¹⁸ O → H ₂ ^{18,18} O + ¹⁸ O	1.8 × 10 ⁻¹²	^{18,18} O ₂ + hν → ¹⁸ O + ¹⁸ O	see text
H ¹⁸ O + H ¹⁸ O → H ₂ ^{18,18} O ₂	3.7 × 10 ⁻¹²	O + H ¹⁸ O → H + ^{16,18} O ₂	3.3 × 10 ⁻¹¹
H ¹⁸ O + HO ₂ → H ₂ ¹⁸ O + O ₂	see text	O + HO → H + O ₂	3.3 × 10 ⁻¹¹
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	4.5 × 10 ^{-12a}	¹⁸ O + H ¹⁸ O → H + ^{18,18} O ₂	3.3 × 10 ⁻¹¹
¹⁸ O + O ₂ → ^{16,18} O ₂ + O	1.7 × 10 ^{-12b}	¹⁸ O + HO → H + ^{16,18} O ₂	3.3 × 10 ⁻¹¹
O ₂ + hν → O + O	see text	O + HO ₂ → HO + O ₂	3.5 × 10 ⁻¹¹
^{16,18} O ₂ + hν → O + ¹⁸ O	see text	O + H ^{16,18} O ₂ → HO + ^{16,18} O ₂	3.5 × 10 ⁻¹¹
¹⁸ O + O ₂ → ¹⁸ O ₃	7.4 × 10 ⁻¹⁴	O + H ^{18,18} O ₂ → HO + ^{18,18} O ₂	3.5 × 10 ⁻¹¹
O + O ₂ → O ₃	7.4 × 10 ⁻¹⁴	¹⁸ O + HO ₂ → H ¹⁸ O + O ₂	3.5 × 10 ⁻¹¹
¹⁸ O ₃ + hν → O ₂ + ¹⁸ O(1D)	see text	¹⁸ O + H ^{16,18} O ₂ → H ¹⁸ O + ^{16,18} O ₂	3.5 × 10 ⁻¹¹
¹⁸ O ₃ + hν → ^{16,18} O ₂ + O(1D)	see text	O + H ^{18,18} O ₂ → HO + ^{18,18} O ₂	3.5 × 10 ⁻¹¹
¹⁸ O(1D) + H ₂ ¹⁸ O → H ¹⁸ O + H ¹⁸ O	2.3 × 10 ⁻¹⁰	¹⁸ O + HO ₂ → H ¹⁸ O + O ₂	3.5 × 10 ⁻¹¹
O(1D) + H ₂ ¹⁸ O → H ¹⁸ O + HO	2.3 × 10 ⁻¹⁰	¹⁸ O + H ^{16,18} O ₂ → H ¹⁸ O + ^{16,18} O ₂	3.5 × 10 ⁻¹¹
O ₃ + hν → O ₂ + O(1D)	see text	¹⁸ O + H ^{18,18} O ₂ → H ¹⁸ O + ^{18,18} O ₂	3.5 × 10 ⁻¹¹
H ₂ ^{18,18} O ₂ + hν → H ¹⁸ O + H ¹⁸ O	see text	H ¹⁸ O + H ^{16,18} O ₂ → H ₂ ¹⁸ O + ^{16,18} O ₂	see text
H ₂ O ₂ + hν → HO + HO	see text	H ¹⁸ O + H ^{18,18} O ₂ → H ¹⁸ O + ^{18,18} O ₂	see text
HO + HO → H ₂ O + O	1.8 × 10 ⁻¹²	HO + H ^{16,18} O ₂ → H ₂ O + ^{16,18} O ₂	see text
HO + HO → H ₂ O ₂	3.7 × 10 ⁻¹²	HO + H ^{18,18} O ₂ → H ₂ O + ^{18,18} O ₂	see text
HO + H ¹⁸ O → H ₂ O + ¹⁸ O	9.0 × 10 ⁻¹³	HO ₂ + H ^{16,18} O ₂ → H ₂ O ₂ + ^{16,18} O ₂	2.25 × 10 ^{-12a}
HO + H ¹⁸ O → H ₂ ¹⁸ O + O	9.0 × 10 ⁻¹³	HO ₂ + H ^{16,18} O ₂ → H ₂ ^{16,18} O ₂ + O ₂	2.25 × 10 ^{-12a}
HO + H ¹⁸ O → H ₂ ^{16,18} O ₂	3.7 × 10 ⁻¹²	HO ₂ + H ^{18,18} O ₂ → H ₂ O ₂ + ^{18,18} O ₂	2.25 × 10 ^{-12a}
HO + HO ₂ → H ₂ O + O ₂	see text	HO ₂ + H ^{18,18} O ₂ → H ₂ ^{18,18} O ₂ + O ₂	2.25 × 10 ^{-12a}
H ₂ O + hν → H + HO	see text	H ^{16,18} O ₂ + H ^{16,18} O ₂ → H ₂ ^{16,18} O ₂ + ^{16,18} O ₂	4.5 × 10 ^{-12a}
H ₂ ^{16,18} O ₂ + hν → HO + H ¹⁸ O	see text	H ^{16,18} O ₂ + H ^{18,18} O ₂ → H ₂ ^{16,18} O ₂ + ^{18,18} O ₂	2.25 × 10 ^{-12a}
H + O ₃ → HO + O ₂	2.9 × 10 ⁻¹¹	H ^{16,18} O ₂ + H ^{18,18} O ₂ → H ₂ ^{16,18} O ₂ + ^{16,18} O ₂	2.25 × 10 ^{-12a}
H + ¹⁸ O ₃ → HO + ^{16,18} O ₂	1.45 × 10 ⁻¹¹	H ^{18,18} O ₂ + H ^{18,18} O ₂ → H ₂ ^{18,18} O ₂ + ^{18,18} O ₂	4.5 × 10 ^{-12a}
H + ¹⁸ O ₃ → H ¹⁸ O + O ₂	1.45 × 10 ⁻¹¹	O + ¹⁸ O ₃ → O ₂ + ^{16,18} O ₂	8.8 × 10 ⁻¹⁵
H ¹⁸ O + H ₂ ^{18,18} O ₂ → H ₂ ¹⁸ O + H ^{18,18} O ₂	1.7 × 10 ⁻¹²	O + O ₃ → O ₂ + O ₂	8.8 × 10 ⁻¹⁵
H ¹⁸ O + H ₂ ^{16,18} O ₂ → H ₂ ¹⁸ O + H ^{16,18} O ₂	1.7 × 10 ⁻¹²	¹⁸ O + ¹⁸ O ₃ → ^{16,18} O ₂ + ^{16,18} O ₂	4.4 × 10 ⁻¹⁵
H ¹⁸ O + H ₂ ¹⁸ O ₃ → H ₂ ¹⁸ O + HO ₂	1.7 × 10 ⁻¹²	¹⁸ O + ¹⁸ O ₃ → ^{18,18} O ₂ + O ₂	4.4 × 10 ⁻¹⁵
HO + H ₂ ^{18,18} O ₂ → H ₂ O + H ^{18,18} O ₂	1.7 × 10 ⁻¹²	¹⁸ O + O ₃ → ^{16,18} O ₂ + O ₂	8.8 × 10 ⁻¹⁵
HO + H ₂ ^{16,18} O ₂ → H ₂ O + H ^{16,18} O ₂	1.7 × 10 ⁻¹²	H + ^{16,18} O ₃ → H ^{16,18} O ₂ + O	3.7 × 10 ⁻¹²
HO + H ₂ O ₂ → H ₂ O + HO ₂	1.7 × 10 ⁻¹²	H + ^{18,18} O ₃ → H ^{18,18} O ₂ + O	3.7 × 10 ⁻¹²
H ¹⁸ O + ¹⁸ O ₃ → H ^{18,18} O ₂ + O ₂	3.4 × 10 ⁻¹⁴	HO ₂ + hν → HO + O	see text
H ¹⁸ O + ¹⁸ O ₃ → H ^{16,18} O ₂ + ^{16,18} O ₂	3.4 × 10 ⁻¹⁴	H ^{16,18} O ₂ + hν → HO + ¹⁸ O	see text
H ¹⁶ O + O ₃ → H ^{16,18} O ₂ + O ₂	6.8 × 10 ⁻¹⁴	H ^{16,18} O ₂ + hν → H ¹⁸ O + O	see text
HO + ¹⁸ O ₃ → H ^{16,18} O ₂ + O ₂	3.4 × 10 ⁻¹⁴	H ^{18,18} O ₂ + hν → H ¹⁸ O + ¹⁸ O	see text
HO + ¹⁸ O ₃ → HO ₂ + ^{16,18} O ₂	3.4 × 10 ⁻¹⁴	¹⁸ O + ^{16,18} O ₂ → O + ^{18,18} O ₂	8.5 × 10 ^{-13b}
HO + O ₃ → HO ₂ + O ₂	6.8 × 10 ⁻¹⁴	O + ^{16,18} O ₂ → ¹⁸ O + O ₂	8.5 × 10 ^{-13b}
H + H ^{18,18} O ₂ → H ¹⁸ O + H ¹⁸ O	3.2 × 10 ^{-11c}	O + ^{18,18} O ₂ → ¹⁸ O + ^{16,18} O ₂	1.7 × 10 ^{-12b}
H + H ^{18,18} O ₂ → H ₂ + ^{18,18} O ₂	1.4 × 10 ^{-11c}	H ₂ O ₂ → wall	see text
H + H ^{16,18} O ₂ → HO + H ¹⁸ O	3.2 × 10 ^{-11c}	H ₂ ^{16,18} O ₂ → wall	see text
H + H ^{16,18} O ₂ → H ₂ + ^{16,18} O ₂	1.4 × 10 ^{-11c}	H ₂ ^{18,18} O ₂ → 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 H₂O₂ are relatively slow. Nevertheless, when such processes for H₂O₂ are included, there is a marked reduction in ^{18,18}O₂ to the point where the predicted ^{16,18}O₂/^{18,18}O₂ ratio is within experimental error of the observed ratio.²⁸

With the model constrained to agree with our observed limited production of ^{18,18}O₂ (and low yields of H₂O₂), the sensitivity of the ^{16,18}O₂ 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}O₂; the lower the value of *k*₁, the higher the calculated yield of ^{16,18}O₂. 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}O₂] is excellent for *k*₁ values near 2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and high by factors of 2–3 for *k*₁ values as low as 4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. When one includes the measurement uncertainties (as well as allowing for as much as a factor of 2

TABLE III: Measured and Predicted ^{16,18}O₂ Production

10 ⁶ <i>J</i> , s ⁻¹	<i>t</i> , s	[^{16,18} O ₂], molecules cm ⁻³		
		calcd		measured ^a
		<i>k</i> ₁ = 4 × 10 ⁻¹¹	<i>k</i> ₁ = 2 × 10 ⁻¹⁰	
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 ε_x[X]/ε_{C₂H₄} to obtain photolytic decomposition rates for species *x*.

uncertainty in the H₂O₂ loss rate) in this comparison, our conclusions must encompass a range of *k*₁ values.

Simply stated, then, the results of this investigation indicate the following: (1) The absence of significant direct production of ^{16,18}O₂ in the reaction of H¹⁸O with HO₂ does

(28) Absolute yields of ^{16,18}O₂ were in the range of 1–5 mtorr. Because of accuracy limitations in measuring ^{18,18}O₂ at partial pressures 1 order of magnitude below this, the ratio ^{16,18}O₂/^{18,18}O₂ 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.

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One-Electron Transfer Reactions Involving Zinc and Cobalt Porphyrins in Aqueous Solutions¹

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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 $ZnP^{\cdot -}$. 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 $ZnP^{\cdot +}$. 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 $ZnP^{\cdot -}$ 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 $ZnP^{\cdot +}$ ($k \approx 10^8$ – 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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