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Kinetic study of the reaction of HO₂ with ozone

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The reaction HO₂ + O₃ \rightarrow OH + 2O₂ has been studied using a discharge-flow system with laser magnetic resonance detection. The rate constant for the reaction was determined directly by monitoring the first-order decay of isotopically labeled H¹⁸O₂ in excess ¹⁶O₃. The data give a curved Arrhenius plot over the temperature range 243 < T < 413 K: $k(T) = (3.8 \pm 2.4) \times 10^{-14} \exp[-(820 \pm 190/T)] \text{ cm}^3 \text{ s}^{-1}$. A more representative fit is obtained with a three parameter expression: $k(T) = (3.2 \pm 5.8) \times 10^{-13} \exp[-(1730 \pm 740)/T] + (1.2 \pm 0.5) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. The error limits are the 95% confidence limits on the coefficients while the accuracy of the measurements is estimated to be about $\pm 20\%$ at each temperature. An analysis of the OH radical product indicates that ¹⁶OH is formed predominately (75 \pm 10)%. The scrambling reactions H¹⁸O₂ + ¹⁶O₃ \rightarrow H¹⁶O₂ + ¹⁸O¹⁸O¹⁶O (1c) and H¹⁸O₂ + ¹⁶O₂ \rightarrow H¹⁶O₂ + ¹⁸O₂ (8) were also examined and found to be slow. Their rate constants are $k_{1c} < 2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 297 and 333 K and $k_8 < 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 297 and 413 K.

(3)

INTRODUCTION

The reaction of HO_2 with ozone plays an important role in a catalytic cycle for ozone destruction:

k.

 $2O_3 \rightarrow 3O_2$.

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{1}$$

$$OH + O_3 \rightarrow HO_2 + O_2$$
 (2)

Net:

Unlike most catalytic cycles involving hydrogen, nitrogen, or chlorine radicals, which require free oxygen atoms for their propagation, the present cycle does not. As a result, this cycle is important in the lower stratosphere and troposphere where the concentration of oxygen atoms is low due to their rapid three-body recombination with O_2 . The rate limiting step in the above cycle is reaction (1) and several modeling studies have demonstrated the importance of k_1 in calculating ozone profiles for the stratosphere.¹⁻³

There is only one published study in which k_1 and its temperature dependence have been directly measured.⁴ The difficulty of measuring k_1 arises from the occurrence of reaction (2) which is a factor of 30 times faster at room temperature. Thus under typical pseudo-first-order conditions, i.e., excess ozone, hydroxyl radicals generated by reaction (1) are rapidly consumed by reaction (2) to regenerate HO₂. This complication makes it very difficult to monitor the change in HO₂ concentration in a kinetic study, therefore most of the measurements of k_1 have been made indirectly.⁵⁻⁷ In the direct measurement of k_1 by Zahniser and Howreaction (1), thus preventing the hydroxyl radicals from participating in any secondary chemistry. The scavenger, chlorotrifluroethene, reacts rapidly with OH $(k = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1})$ but negligibly with HO₂ and ozone at room temperature.⁴ Using the scavenger technique, Zahniser and Howard measured the temperature dependence of k_1 over the range 245–360 K. The temperature range of their study was limited by interference from products of the O₃ + C₂F₃Cl reaction which became significant at temperatures above 360 K. Because of the importance of reaction (1) we thought it

ard, ${}^{4}C_{2}F_{3}Cl$ was used to scavenge the OH radicals formed in

would be worthwhile to carry out a second independent and direct measurement of k_1 . Our goals for these experiments were threefold: (a) to increase the temperature range over which reaction (1) has been studied, (b) to eliminate the complications due to the use of a scavenger, and (c) to provide some insight into the mechanism of this reaction. In order to achieve these goals we have used isotopically labeled $H^{18}O_2$ to study reaction (1). The experimental technique we have used is a discharge flow reactor coupled with laser magnetic resonance (LMR) detection. The LMR technique is particularly well suited for this study since it allows us to distinguish and detect with good sensitivity the various isotopic species (¹⁸OH, ¹⁶OH, H¹⁶O¹⁶O, H¹⁸O¹⁸O, etc.) involved in this reaction:

$$H^{18}O_2 + {}^{16}O_3 \rightarrow {}^{16}OH + {}^{16}O{}^{16}O + {}^{18}O{}^{18}O$$
 (1a)

$$\rightarrow {}^{18}\text{OH} + {}^{16}\text{O}{}^{16}\text{O} + {}^{18}\text{O}{}^{16}\text{O}$$
 (1b)

$$\rightarrow H^{16}O^{16}O + {}^{18}O^{18}O^{16}O.$$
 (1c)

The use of isotopically labeled $H^{18}O_2$ has several advantages. First, it eliminates interference from hydroxyl radicals without having to use the scavenger C₂F₃Cl, since neither the ¹⁸OH nor the ¹⁶OH product is able to regenerate $H^{18}O_2$ via reaction with natural ozone. Thus, monitoring the [$H^{18}O_2$] vs reaction time gives a direct measure of k_1 . Sec-

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ondly, the use of isotopic labeling allows us to obtain information on the mechanism of the reaction from a measurement of the branching ratio for the various channels. We have used this technique to directly measure $k_1(T)$ over the temperature range 245-413 K.

EXPERIMENTAL

The discharge flow/laser magnetic resonance (LMR) system has been described in detail before.⁸ Briefly, the LMR detection scheme works by Zeeman tuning a rotational transition of a paramagnetic molecule into resonance with a fixed frequency far-infrared laser. The intracavity absorption of laser radiation by the molecules causes a decrease in the laser power. A small fraction of the laser radiation is coupled out of the laser cavity and is continuously monitored by a liquid helium cooled, gallium doped germanium bolometer. The output of the bolometer is fed into a lock-in amplifier whose output is displayed on a recorder. The dc magnetic field, which tunes the molecule into resonance, can be varied up to 16 kG and is modulated with a small, typical-1y < 100 G, ac field at a frequency near 1 kHz. Phase sensitive detection at this frequency using the lock-in amplifier vields a first derivative absorption curve.

Two different LMR spectrometers were used in these studies. The kinetic measurements, which required monitoring the $[H^{18}O_2]$ concentration as a function of reaction time, were performed with a water vapor LMR spectrometer operating on the 118.6 μ m H₂O laser line.⁸ Unfortunately, none of the accessible lines of the water vapor laser are in near coincidence with a strong transition in ¹⁸OH, although there are weak transitions that could be detected. Thus, in order to detect ¹⁸OH and ¹⁶OH with high sensitivity, as required for the product analysis, we also used an optically pumped LMR spectrometer.⁸ The particular laser lines used to detect the various radical species are summarized in Table I.

A schematic of the H_2O LMR experimental apparatus is shown in Fig. 1. The 2.54 cm i.d. Pyrex flow tube reactor is jacketed along the 60 cm reaction zone to provide temperature control by circulating either silicone oil (T > 296 K) or ethanol (T < 296 K). The fluid is pumped rapidly through the jacket from a temperature regulated reservoir. Temperature is measured in the reservoir and at the flow tube by



FIG. 1. Schematic of the flow tube and LMR detection system.

Chromel-Alumel thermocouples. For the high temperature studies, the bath is heated and regulated by an electronic servo mechanism which maintains the temperature to within $\pm 1^{\circ}$ of a preset value. For the low temperature studies, liquid N₂ is injected into a copper coil immersed in the ethanol bath. Manual regulation of the liquid N₂ flow achieves temperature control to $\pm 1^{\circ}$.

In order to minimize the loss of radicals, the inner surface of the flow tube was coated with halocarbon wax. However, studies at T > 383 K were conducted in an uncoated flow tube since the halocarbon wax melts at $\simeq 388$ K. Helium (>99.999% purity) was used as a carrier gas, with a typical flow rate of $\simeq 6.5$ STP cm³ s⁻¹ (STP = 1 atm, 273 K). The pressure in the flow tube was between 2.0 and 3.2 Torr, while the average flow velocity ranged from 350 to 800 cm s⁻¹. The oxygen isotope gas was > 98% atomic ¹⁸O.

The $H^{18}O_2$ radicals were generated in a side arm reactor using the following chemistry:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
, (4)

$$CH_2OH + {}^{18}O_2 \rightarrow H^{18}O_2 + H_2CO$$
, (5)

TABLE I. LMR detection i	information.
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Radical	Far infrared laser gas/wavelength	Relative polarization ^a	Magnetic field (kG)	Detection limit (molecule cm ⁻³) ^b
¹⁶ OH	H ₂ O/118.6 μm		14.4	5×10 ⁷
	$CH_3OH/163 \mu m$	σ	3.7	6×10 ⁷
H ¹⁶ O ₂	$H_2O/118.6 \mu m$	π	11.9	4×10 ⁸
-	$CH_3OH/163 \mu m$	σ	2.2	4×10^{8}
¹⁸ OH	$CH_3OH/165 \mu m$	π	20.2	4×10 ⁸
H ¹⁸ O ₂	$H_2O/118.6\mu m$	π	3.8	7×10 ⁸

* σ : Electric field of FIR laser perpendicular to magnetic field. π : Electric field of FIR laser parallel to magnetic

field.

^bDetection limit with $S/N \approx 1$ at 1 s time constant.

where $k_4 = 6.3 \times 10^{-11}$ cm³ s⁻¹⁹ and $k_5 = 9.5 \times 10^{-12}$ $cm^3 s^{-1}$.¹⁰ Chlorine atoms were generated by passing small amounts of Cl₂ seeded in helium through a microwave discharge. The HO₂ source flow rates were as follows: approximately 0.02 STP cm³ s⁻¹ of a 9% Cl₂ in He mixture was carried through the microwave discharge by a 2.0 STP $cm^3 s^{-1}$ flow of He, while the flow of ${}^{18}O_2$ was 0.04 STP cm³ s⁻¹ and the flow of CH₃OH was 0.015 STP $cm^3 s^{-1}$. Of the two types of hydrogen atoms on the methanol, it is thermodynamically more favorable for the chlorine atoms to remove the hydrogen on the carbon moiety.¹¹ The H₂COH radicals thus generated, then undergo reaction with ¹⁸O₂ to produce H¹⁸O₂. The H¹⁸O₂ radical source was operated under conditions such as to ensure that reactions (4) and (5) had gone to completion within the side arm reactor. This was tested by changing the ${}^{18}O_2$ flow rate. As ${}^{18}O_2$ was added, a point was reached where a further increase in ${}^{18}O_2$ flow did not give an appreciable increase in the $H^{18}O_2$ signal. This indicated that the source reaction had gone to completion. A small excess of ¹⁸O₂ was always maintained during the kinetic run.

The $H^{18}O_2$ radical source was operated to produce $H^{18}O_2$ concentrations on the order of 3×10^{11} cm⁻³ in the flow tube. A typical $H^{18}O_2$ signal is shown in Fig. 2. The $H^{18}O_2$ signals were calibrated relative to ¹⁶OH by adding excess $N^{16}O$ just before the detection zone to convert $H^{18}O_2$ to ¹⁶OH by the reactions

$$H^{18}O_2 + N^{16}O \rightarrow {}^{18}OH + {}^{18}ON^{16}O,$$
 (6)

$$^{18}OH + N^{16}O \rightarrow ^{16}OH + N^{18}O$$
, (7)

where $k_6 = 8 \times 10^{-12}$ cm³ s⁻¹⁹ and $k_7 = 2.1 \times 10^{-11}$ cm³ s^{-1.12} The ¹⁶OH signals were calibrated by adding measured amounts of N¹⁶O₂ to excess hydrogen atoms, so that [¹⁶OH] formed is equal to the [N¹⁶O₂] added.

Ozone is added to the flow tube through a moveable inlet. Ozone was generated by flowing O_2 (>99.95% purity) through a commercial ozonizer and collected in a silica gel filled trap at 190 K. After pumping off excess O_2 , the ozone was eluted into the flow tube with helium. The elution



FIG. 2. Part of the LMR spectrum of $H^{18}O_2$ using the 118.6 μ m line of the H_2O laser. The transition used in the kinetic study is indicated by an arrow.

rate was controlled by varying both the helium flow rate and the temperature of the trap between 193 and 273 K. The partial pressure of ozone was determined by absorption at 253.7 nm in a 0.89 cm long cell [σ (253.7 nm) = 1.15×10⁻¹⁷ cm²].¹³ Once the partial pressure of ozone is known, its flow rate is given by

$$F_{\rm O_3} = F_{\rm He} P_{\rm O_3} / (P_T - P_{\rm O_3})$$

where P_T is the total pressure in the absorption cell, F_{He} is the flow of helium through the cell, and P_{O_3} is the partial pressure of ozone as determined by the absorption measurement. Ozone concentrations in the flow tube were typically varied between $(0.1-1) \times 10^{16}$ cm⁻³.

RESULTS

Temperature dependence

Sample first-order H¹⁸O₂ decays as a function of reaction time are shown in Fig. 3. The slopes of such decay plots yield the effective first-order rate constant k_1^I . The bimolecular rate constant k_1 is obtained from the slope of a plot of k_1^I vs [O₃]. Figure 4 shows several such plots for data taken at various temperatures. The plots are linear and the [O₃] was varied by about a factor of 8. Some data exhibit small positive intercepts ($\simeq 1 \text{ s}^{-1}$) which we feel are not significant. The bimolecular rate constants are summarized in Table II. The error limits indicated are two times the standard error obtained from a linear least squares fit to the data. We



FIG. 3. Typical first-order decay plots for $H^{18}O_2$ as a function of reaction time, for various values of $[O_3]$. Conditions were: T = 333 K; v = 565 cm s⁻¹; $[H^{18}O_2]_0 = 3 \times 10^{11}$ cm⁻³; and $[O_3] = 0$ (\Box), 1.15×10^{15} (O), 4.46×10^{15} (Δ), and 7.86×10^{15} cm⁻³ (\oplus).



FIG. 4. Plot of k_1' vs $[O_3]$ for reaction (1) at various temperatures. The lines shown are linear least square fits to the data. T = 413 K (\Box), 333 K (\bigcirc), and 267 K (\triangle).

estimate the overall accuracy of the measurements to be \pm 20% at the 95% confidence level.

The measured values of k_1 from this experiment are plotted in Arrhenius form in Fig. 5 along with the results from other direct studies. The temperature range of our study was from 245 to 413 K. As a consistency check, we have also remeasured the rate coefficient for the $H^{16}O_2 + {}^{16}O_3$ reaction at T = 298 K and T = 333 K using the C_2F_3Cl scavenger. These data points are indicated by triangles in Fig. 5 and agree well with the other data. A weighted (weights = $1/\sigma^2$) nonlinear least squares fit to the $H^{18}O_2$ data gives

$$k_1(T) = (3.82 \pm 2.4) \times 10^{-14}$$

 $\times \exp[-(820 + 190)/T] \text{ cm}^3 \text{ s}^{-1}.$

The indicated error limits are the 95% confidence limits. As can be seen in Fig. 5, the Arrhenius plot for reaction (1) exhibits curvature over the temperature range studied. In order to provide better agreement with the observed data, we have also fit the temperature dependence using an empirical three parameter expression of the form

$$k_1(T) = (3.2 \pm 5.8) \times 10^{-13} \exp[-(1730 \pm 740)/T]$$

+ $(1.2 \pm 0.5) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.

TABLE II. Summary of experimental results for $H^{18}O_2 + {}^{16}O_3$.

<i>T</i> (K)	Number of experiments	$[O_3]$ range (10 ¹⁵ cm ⁻³)	k_1^{a} (10 ⁻¹⁵ cm ³ s ⁻¹)
413	22	0.44- 4.3	6.00 ± 0.32
373	20	1.13- 7.1	3.95 ± 0.35
333	21	1.15-12.0	3.15 + 0.20
297	37	1.35-11.81	2.14 + 0.14
267	12	1.52-10.3	1.60 + 0.10
243	16	1.49-13.0	1.50 ± 0.07

* Error limits are two times the standard error from the least square fits.



FIG. 5. Arrhenius plot for k_1 . This work: (\bullet) H¹⁸O₂ + O₃ and (O) H¹⁶O₂ + O₃; Zahniser and Howard (Ref. 4): (\blacksquare); and Manzanares *et al.* (Ref. 15): (\triangle). The error bars are the 2σ limits derived from the k_1^r vs [O₃] plots. The H¹⁸O₂ data were fit to an Arrhenius expression (solid line) and a three parameter expression (dashed line) as described in the text.

This result is represented by the dashed line in Fig. 5.

The use of isotopically labeled $H^{18}O_2$ creates the possibility of interference from the scrambling reactions:

$$H^{18}O_2 + {}^{16}O_2 \rightarrow H^{16}O_2 + {}^{18}O_2$$

→ $H^{16}O^{18}O + {}^{16}O^{18}O$
→ $H^{18}O^{16}O + {}^{16}O^{18}O$, (8)

since some ${}^{16}O_2$ is always present in ${}^{16}O_3$. We have investigated reaction (8) at 297 and 413 K by measuring the decay of $H^{18}O_2$ as a function of reaction time in excess ${}^{16}O_2$. No reaction was observed and from these measurements we conclude that $k_8 < 3 \times 10^{-17}$ cm³ s⁻¹. Thus, reaction (8) will not influence the result of the present study. Also this shows that the reverse reaction cannot regenerate $H^{18}O_2$ reactant from $H^{16}O_2$ and ${}^{18}O_2$.

Branching ratio determination

The reaction of $H^{18}O_2$ with ozone has at least three possible channels as shown in Eqs. (1a)–(1c). We have tested for $H^{16}O_2$ production in channel (1c), at 297 and 333 K by adding the scavenger C_2F_3Cl to remove hydroxyl radicals. The scavenger blocks the formation of $H^{16}O_2$ via the reaction of OH with ozone. Thus, with the scavenger present, any $H^{16}O_2$ detected must come from reaction (1c). The only

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significant reactions in this experiment are the reactions of O_3 with the two HO₂ species. The integrated rate equation is

$$[\mathbf{H}^{16}\mathbf{O}_2]_t = [\mathbf{H}^{18}\mathbf{O}_2]_0 e^{-k_1[\mathbf{O}_3]t} (1 - e^{-k_{1c}[\mathbf{O}_3]t}).$$

Where $[H^{18}O_2]_0$ is the initial concentration for that species, t is the reaction time, and k_1 is the rate constant for reaction of $H^{16}O_2$ with ozone. Since we did not observe any $H^{16}O_2$, its concentration must be less than our detection limit, $< 5 \times 10^8$ cm⁻³. This gives $k_{1c} \le 2 \times 10^{17}$ cm³ s⁻¹. Other mixed isotope products such as $H^{18}O^{16}O$ and $H^{16}O^{18}O$ are also possible and these channels would contribute to the measured rate coefficient k_1 . The fact that k_1 for $H^{18}O_2$ agrees well with k_1 for $H^{16}O_2$ and that these processes require an unlikely molecular rearrangement lead us to conclude that such reactions are not significant in our experiment.

The determination of the ¹⁸OH vs ¹⁶OH product branching ratio was difficult because of potential interferences from rapid secondary chemistry, particularly scrambling reactions. Efforts to detect ¹⁸OH directly in preliminary experiments were unsuccessful and the magnet power supply failed to operate properly at the high magnetic field strengths required ($H \approx 20 \text{ kG}$). Large [¹⁶OH] were detected as a primary product; therefore, we concentrated our efforts on making quantitative measurements of the ¹⁶OH yield.

In order to minimize the effects of the scrambling reactions, we have determined the branching ratio by observing the initial appearance of ¹⁶OH from reaction (1). By looking at very short times ($t\approx 9\times 10^{-3}$ s) and using minimal [CH₃OH] ([CH₃OH] $\approx 4\times 10^{13}$ cm⁻³), we can overcome the problems arising from secondary chemistry. This set of experiments was conducted in the following manner. The amount of ¹⁶OH produced from a reference reaction, H¹⁶O₂ + ¹⁶O₃, where the yield is 100%, is compared to the ¹⁶OH product yield produced from the reaction H¹⁸O₂ + ¹⁶O₃. This method is successful because reaction (1c) plays a negligible role in the isotope scrambling process. Figure 6 shows the appearance curve for ¹⁶OH pro-



FIG. 6. ¹⁶OH appearance curves for reaction (1) product measurements. ¹⁶OH produced from the reference reaction $H^{16}O_2 + {}^{16}O_3$ (\bigcirc). ¹⁶OH produced from the reaction, $H^{18}O_2 + {}^{16}O_3$ (\square). The experimental conditions were identical for the two data sets: P = 1.0 Torr, T = 297 K, v = 2390cm s⁻¹, $[O_3] = 8.91 \times 10^{14}$, $[He] = 3.16 \times 10^{16}$, $[Cl_2] = 1.1 \times 10^{13}$, $[CH_3OH] = 4.45 \times 10^{13}$, $[{}^{18}O_2] = 4.45 \times 10^{13}$, $[{}^{16}O_2] = 4.45 \times 10^{13}$, $[HO_2]_0 = 6 \times 10^{10}$. All concentrations are in units of cm⁻³.

duced from the reaction of $H^{18}O_2$ with ${}^{16}O_3$ as well as from the reference reaction of $H^{16}O_2$ with ${}^{16}O_3$. Both reactions were conducted under identical conditions. In particular, care was taken to ensure that the $[O_3]_0$ and $[HO_2]_0$ were identical for both measurements. The $[HO_2]$ was calibrated by converting both $H^{18}O_2$ and $H^{16}O_2$ to ${}^{16}OH$ by adding N¹⁶O [see reactions (6) and (7)]. Equal amounts of ${}^{16}OH$ produced from $[H^{16}O_2]_0$ and $[H^{18}O_2]_0$, after adding N¹⁶O, signified that $[H^{16}O_2]_0 = [H^{18}O_2]_0$. By taking the ratio of the $[{}^{16}OH]$ obtained from the two reactions (as shown in Fig. 6), we find that $\approx 80\%$ of reaction (1) proceeds via the ${}^{16}OH$ channel.

In making the branching ratio measurement we must account for possible rapid scrambling reactions. We have investigated the importance of reaction (9a) by measuring the total removal rate of ¹⁸OH by ozone using the less sensitive 79 μ m H₂O laser for ¹⁸OH detection:

$${}^{18}\text{OH} + {}^{16}\text{O}_3 \rightarrow {}^{16}\text{OH} + {}^{18}\text{O}{}^{16}\text{O}{}^{16}\text{O}$$
 (9a)

$$\rightarrow \mathrm{HO}_2 + \mathrm{O}_2 \,. \tag{9b}$$

The rate constant for reaction (9) was determined to be $k_9 = (5.4 \pm 1.0) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at room temperature, which is in good agreement with the reported value for reaction (2) of $k_2 = (6.5 \pm 1.0) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.⁴ This is too slow to play a significant role in the branching ratio measurements.

A second process which could potentially interfere in the OH branching ratio determination is

$$^{8}OH + CH_{3}OH \rightarrow CH_{2}OH + H_{2}^{18}O$$
, (10)

$$CH_2OH + {}^{16}O_3 \rightarrow {}^{16}OH + H_2CO + O_2$$
, (11)

where $k_{10} = 7.5 \times 10^{-13}$ cm³ s⁻¹⁹ and $k_{11} \approx 2.6 \times 10^{-11}$ cm³ s^{-1,14} A computer model was used to assess the influence of these reactions. The reactions used in the model along with their rate coefficients are shown in Table III and the results of sample calculations are displayed in Fig. 7. The lowest curve in the figure represents the amount of ¹⁶OH that is produced if reaction (1) were to proceed exclusively via the ¹⁸OH channel, i.e., 0% ¹⁶OH, with the ¹⁶OH being produced only by reactions (10) and (11). The upper curve in the figure represents the amount of ¹⁶OH that is produced if reaction (1) were to proceed exclusively via the ¹⁶OH product channel. Figure 7 demonstrates that under the experimental conditions used, secondary chemistry is minor and that monitoring ¹⁶OH appearance permits an accurate determination of the branching ratio.

An independent test of the OH product measurement was conducted with a different $H^{18}O_2$ source. In the new source, $H^{18}O_2$ was generated by the following three-body recombination reaction in a high pressure ($P \approx 20$ Torr) side arm reactor:

$$\mathbf{H} + \mathbf{O}_2 + \mathbf{M} \rightarrow \mathbf{H}\mathbf{O}_2 + \mathbf{M} \,. \tag{12}$$

The characteristics of this source have been described previously.⁴ The source has the advantage of not using CH₃OH, although it does use large amounts of ¹⁸O₂. Some results obtained with this HO₂ source are shown in Fig. 8. These measurements indicate that $\simeq 75\%$ of reaction (1) goes via the ¹⁶OH channel. Computer simulations were carried out to confirm that under the conditions used, secondary chemis-

TABLE III. Reactions	s used in	model	ing stuc	ly.'
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	Reaction	Rate constant ^c (cm ³ s ⁻¹)	Reference
1.	$H^{18}O_2 + {}^{16}O_3 \rightarrow H^{18}O + {}^{16}O_2 + {}^{18}O^{16}O$	varied in model	
2.	$H^{18}O_2 + {}^{16}O_3 \rightarrow H^{16}O + {}^{16}O_2 + {}^{18}O_2$	constrained ^d	•••
3.	$H^{16}O_2 + {}^{16}O_3 \rightarrow H^{16}O + {}^{16}O_2 + {}^{16}O_2$	2.1×10^{-15}	this work
4.	$H^{18}O^{16}O + O_3 \rightarrow H^{16}O + {}^{18}O^{16}O + {}^{16}O_2$	2.1×10^{-15}	this work
5.	$H^{18}O_2 + H^{18}O_2 \rightarrow H_2^{18}O_2 + {}^{18}O_2$	1.7×10 ⁻¹²	9 ⁶
6.	$H^{18}O + {}^{16}O_3 \rightarrow H^{18}O^{16}O + {}^{16}O_2$	6.8×10 ⁻¹⁴	4 ^b
7.	$H^{16}O + {}^{16}O_3 \rightarrow H^{16}O_2 + {}^{16}O_2$	6.8×10^{-14}	4
8.	$H^{18}O + CH_3OH \rightarrow CH_2OH + H_2^{18}O$	7.5×10 ⁻¹³	9 ⁶
9.	$H^{16}O + CH_3OH \rightarrow CH_2OH + H_2^{16}O$	7.5×10^{-13}	9
10.	$H^{18}O + H^{18}O_2 \rightarrow H_2^{18}O + {}^{18}O_2$	7.0×10 ⁻¹¹	9 ^ь
11.	$H^{16}O + H^{18}O_2 \rightarrow H_2^{16}O + {}^{18}O_2$	7.0×10^{-11}	9 ⁶
12.	$CH_2OH + {}^{18}O_2 \rightarrow H^{18}O_2 + H_2CO$	9.5×10 ⁻¹²	10 ⁶
13.	$CH_2OH + {}^{16}O_2 \rightarrow H^{16}O_2 + H_2CO$	9.5×10 ⁻¹²	10
14.	$CH_2OH + {}^{16}O_3 \rightarrow {}^{16}OH + {}^{16}O_2 + H_2CO$	2.6×10^{-11}	14
15.	H ¹⁸ O _{wail}	5.0	this work ^b
16.	H ¹⁶ O _{wall}	5.0	this work
17.	H ¹⁸ O _{2wall}	1.5	this work ^b
18.	$H^{16}O_{2wall}$	1.5	this work

* Experimental conditions used are listed in the caption of Fig. 6.

^b The rate constants for reactions involving species containing ¹⁸O have been taken to be equal to the rates for the ¹⁶O species.

^c Units for first order reactions are s^{-1} .

^d The value for this rate constant was constrained such that the sum of the rate constants for the ¹⁸OH and ¹⁶OH channels was 2.14×10^{-15} cm³ s⁻¹.

try was negligible. Thus, by measuring the initial appearance of ¹⁶OH using two different H¹⁸O₂ sources we conclude that reaction (1) goes predominately via the ¹⁶OH channel $(75 \pm 10)\%$ at 297 K.

DISCUSSION

The use of isotopically labeled $H^{18}O_2$ has allowed us to study the reaction $HO_2 + O_3$ with minimal interferences from secondary chemistry. Since the present measurements were made with a species which is different from the most abundant natural isotope of oxygen, the possibility of a kinetic isotope effect must be given some consideration. We expect the effect to be small because of the relatively small isotope mass difference between ¹⁶O and ¹⁸O. An assessment of the magnitude of the effect on the rate coefficient and its temperature coefficient requires information about the reaction surface and transition state which are not known to us.⁴ Two factors indicate that the effect is probably small: (1) the mechanism involves predominantly the transfer of an H atom and (2) the room temperature rate coefficients for both isotopes species are in good agreement. The results of the present study are in reasonable agreement with the earlier work of Zahniser and Howard⁴ and the more recent room temperature measurement of Manzanares *et al.*¹⁵ as



FIG. 7. Computer simulations of ¹⁶OH appearance curves. The reactions used in the simulation are listed in Table III. The experimental conditions are the same as in the caption to Fig. 6. The assumed yields of ¹⁶OH from reaction (1) are indicated on the right. The lines show the computed [¹⁶OH].



FIG. 8. ¹⁶OH appearance curve for reaction (1) using the high pressure $(H + O_2 + M)$ source. ¹⁶OH produced from the reference reaction $H^{16}O_2 + {}^{16}O_3$ (\Box). ¹⁶OH produced from $H^{18}O_2 + {}^{16}O_3$ (O). The experimental conditions were: $v = 2370 \text{ cm s}^{-1}$, T = 298 K, P = 1.0 Torr, $[HO_2]_0 = 5 \times 10^{10}$, $[O_3] = 1.0 \times 10^{15}$, $[He] = 2.72 \times 10^{16}$, $[O_2] = 4.26 \times 10^{15}$. All concentrations are in units of cm⁻³.

shown in Fig. 5. We feel that the curvature of the Arrhenius plot of Fig. 5 may be real. This trend is not as evident in the work of Zahniser and Howard since the temperature range of their study is smaller, but their lowest temperature measurements are parallel to the present results. Clearly, more data are needed at temperatures below 240 K in order to evaluate this apparent curvature. Because of the high HO_2 wall loss at temperatures below 240 K, we were not able to obtain reliable kinetic data in this region.

For the purposes of atmospheric modeling, our three parameter expression should be tested. A four parameter expression with an activation energy on the second term was also fitted to the data, but the activation energy derived from the fit was not significant. In atmospheric model calculations the difference between the two parameter and the three parameter fits will be the greatest at low temperatures. The value of k_1 extrapolated to 200 K, for example, is 6.3×10^{-16} cm³ s⁻¹ from the Arrhenius equation and 1.3×10^{-15} cm³ s⁻¹ from the three parameter expression. This demonstrates that uncertainties are very large beyond our measurement range. Reaction (1) is important in the upper troposphere, lower stratosphere, and in the polar regions where very low temperatures obtain.

One concern from the previous study⁴ of reaction (1)was that the Arrhenius A factor was anomalously low, $A = 1.4 \times 10^{-14}$ cm³ s⁻¹. This was shown to be consistent with a very tight cyclic transition state.⁴ In the present study, the A coefficient from the two parameter fit is about a factor of 3 times larger than the previous value and the first term of the three parameter fit gives an A coefficient that is close to what a conventional transition state model would predict. Unfortunately, the three parameter fit creates a new problem of explaining the second, temperature independent term. It is possible that it is due to the existence of two independent reaction channels. This possibility is consistent with the product analysis which indicates a two channel mechanism at 297 K. A study of the temperature dependence of the product channels would improve our understanding of the mechanism.

The theoretical work of Dupuis *et al.*¹⁶ has shown that in radical reactions involving ozone, e.g., $H + O_3$ and $NO + O_3$, the π orbitals from the terminal oxygen atoms which point out of the plane of the O_3 play a central role in determining the geometry of reactant approach. We postulate that in the reaction under study, the HO₂ radical must approach the O_3 molecule from above or below the O_3 plane. Such a constrained approach geometry is consistent with a low A factor. This hypothesis needs to be explored by accurate *ab initio* calculations.

We expect that the reaction $DO_2 + O_3$ may show a substantial kinetic isotope effect, since the transfer of a hydrogen atom is found to be the primary step in reaction (1). Although very little is known about the reactions of other peroxy radicals with O₃, they also may be quite slow because the analogous hydrogen atom transfer channel is not possible. For example, Simonaitis and Heicklen ¹⁷ reported an upper limit of 2.4×10^{17} cm³ s⁻¹ for CH₃O₂ + O₃.

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