Kinetics of HO₂ + HO₂ \rightarrow H₂O₂ + O₂: Implications for Stratospheric H₂O₂

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[1] The reaction HO₂ + HO₂ \rightarrow H₂O₂ + O₂ (1) has been studied at 100 Torr and 222 K to 295 K. Experiments employing photolysis of Cl₂/CH₃OH/O₂/N₂ and F₂/H₂O₂/N₂ gas mixtures to produce HO₂ confirmed that methanol enhanced the observed reaction rate. At 100 Torr, zero methanol, k₁ = (8.8 ± 0.9) \times 10^{-13} \times \exp(210 ± 26)/T cm³ molecule⁻¹ s⁻¹ (2σ uncertainties), which agrees with current recommendations at 295 K but is nearly 2 times slower at 211 K. The general expression for k₁, which includes the dependence on bath gas density, is k₁ = (1.5 ± 0.2) \times 10^{-12} \times \exp[(19 ± 31)/T] + 1.7 \times 10^{-33} \times [M] \times \exp[1000/T], where the second term is taken from the JPL00-3 recommendation. The revised rate largely accounts for a discrepancy between modeled and measured [H₂O₂] in the lower to middle stratosphere.

INDEX TERMS: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituents sources and sinks; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry

1. Introduction

[2] The principal source of upper tropospheric and stratospheric H₂O₂ is the reaction

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \] (1)

Reaction (1) is an important sink for HO₅ in the troposphere because H₂O₂ is scavenged by aerosols and clouds. In the stratosphere, H₂O₂ serves as a temporary reservoir for HO₅.

[3] Remote measurements of stratospheric [H₂O₂] have indicated that our understanding of the H₂O₂ budget is incomplete. Measurements, shown below, by the balloon-borne MKIV and FIRS-2 spectrometers indicate that photochemical models employing recommended rate constants significantly over-estimate [H₂O₂] in the lower to middle stratosphere. This has prompted researchers to explore previously unrecognized loss processes for H₂O₂ such as the H₂O₂ + O₃ reaction [Wallington et al., 1998]. So far, laboratory studies have been unable to explain the discrepancy.

[4] Reaction (1) has been widely studied (see references in [DeMore et al., 1997]). However, there are comparatively few studies below 273 K. The NASA [DeMore et al., 1997] and IUPAC [Atkinson et al., 1997] recommendations at low temperatures have been influenced by studies that employed CH₃OH as a precursor for HO₂. It has been demonstrated that the observed rate of reaction (1) is enhanced in the presence of CH₃OH, H₂O, and NH₃ and that this rate enhancement is more pronounced at low temperatures [Andersson et al., 1988; Kircher and Sander, 1984; Lii et al., 1980]. The effect of methanol has been the subject of only one study, at 278 K and 299 K.

[5] In the present study, the effect of methanol on reaction (1) was examined over the temperature range 222 K to 295 K. We defined k₁ as the rate constant for reaction (1) in the limit of zero added methanol and derived k₁(T) at 100 Torr of combined O₂ (40%) and N₂ (60%). The temperature dependence of the methanol enhancement effect was also measured. The new value of k₁(T) was used to compare measured volume mixing ratio (VMR) profiles of stratospheric H₂O₂ with model calculations.

2. Experimental Details

[6] The experiments were performed in a pulsed laser photolysis kinetic spectroscopy apparatus described in detail elsewhere (L. E. Christensen et al., manuscript in preparation, 2002A). Briefly, HO₂ was generated in a 2-m long temperature-controlled flow cell by laser photolysis at 308 nm of either Cl₂ or F₂ in the gas mixtures CH₃OH/O₂/N₂ and H₂O₂/N₂, respectively. The laser fluence was 120 mJ pulse⁻¹. HO₂ decay curves were monitored simultaneously by UV and near-IR diode laser spectroscopy. The measurements made in the UV are the subject of this paper. The near-IR measurements of [HO₂], which did not contain any spectral interference from other species and supported the UV measurements, will be discussed in a subsequent paper (L. E. Christensen et al., manuscript in preparation, 2002B). The concentrations and specifications of the gases and methanol are listed in Table 1.

[7] The photolysis beam traveled coaxially through the reaction cell (5-cm diameter) resulting in a photolysis volume with a cross-section of 1 cm by 2 cm. Reagent gases were mixed and cooled prior to entering the middle of the reaction cell. N₂ buffer gas was flowed into both ends of the cell, constraining the reagent gases to an evenly mixed 134-cm long region. This was verified from measurements of gases with flow-meter calibrated concentrations and known cross-sections and further verified by examinations of second-order reactions involving CH₃O₂ and CH₃CH₂O₂ which yielded results consistent with observations made by prior investigators. The residence time of the gas was 3 seconds, and a photolysis flash occurred every 3.5 seconds. Methanol was added to the cell by bubbling N₂ through liquid methanol that was situated in a temperature-controlled bath.

[8] Light from a 150-W deuterium lamp was propagated collinearly with the photolysis beam and made a single pass of path length 134 cm. HO₂ was detected by UV absorbance at 220.00 nm. The rate of decay was corrected to account for the time-dependent
The relationship between and temperature of the bath surrounding the methanol, was 5% which in turn was due to the fluctuations in measured gas flows. Uncertainty in temperature (±1 K).

The uncertainty in determining \([\text{CH}_3\text{OH}]\), deviations from second-order rate behavior at high \([\text{CH}_3\text{OH}]\). As shown below, \(k_{\text{obs}}\) was determined from the average of 3 individual experiments. At each temperature, \(k_{\text{obs}}\) was determined at 5 to 10 different methanol concentrations. As shown below, \(k_{\text{obs}}\) was linearly dependent on \([\text{CH}_3\text{OH}]\). We expressed the enhancement due to methanol as

\[
k_{\text{obs}} = k_1 + k'' \cdot [\text{CH}_3\text{OH}] \tag{2}
\]

where \(k_1\) is the rate constant of reaction (1) in the limit of zero methanol, \(k''\) is the enhancement factor due to the presence of methanol. Equation (2) was fit to \(k_{\text{obs}}\) vs. [CH\(_3\)OH]. From the fit, \(k_1\) was determined from the y-intercept and \(k''\) was determined from the slope.

The uncertainty (2\(\sigma\)) in \(k_{\text{obs}}\) due to the statistical noise in the UV signal was 2% while the uncertainty in determining \([\text{CH}_3\text{OH}]\), which in turn was due to the fluctuations in measured gas flows and temperature of the bath surrounding the methanol, was 5%. The relationship between \(k_{\text{obs}}\) and \([\text{CH}_3\text{OH}]\) was not well described by equation (2) at 222 K. This was correlated with slight deviations from second-order rate behavior at high \([\text{CH}_3\text{OH}]\).

Seven different temperatures, from 222 K to 295 K, were investigated. The temperature dependences of \(k_1\) and \(k''\) were fit to the Arrhenius expression \(k(T) = A \cdot \exp(-(E_a/R)/T)\) using weighted non-linear least-squares fitting. Weights were the uncertainties derived from the linear fitting of \(k_1\) and \(k''\) and the uncertainty in temperature (±1 K).

The effects of secondary reactions were considered as a possible cause for the observed rate enhancement. At all temperatures, the maximum \([\text{HO}_2]\) did not change for \([\text{CH}_3\text{OH}] > 1 \cdot 10^{15} \text{ molecules cm}^{-3}\); at the lowest \([\text{CH}_3\text{OH}]\) employed, maximum \([\text{HO}_2]\) decreased by 10%. Competing secondary reactions such as \(\text{Cl} + \text{O}_2\) and \(\text{Cl} + \text{HO}_2\) would account for the decrease in maximum \([\text{HO}_2]\). The kinetics modeling program FACSIMILE [Curtis and Sweetenham, 1987] was employed to ascertain the effects of these secondary reactions. It was found that their effects were negligible. More than half of the experiments were done with \([\text{CH}_3\text{OH}] > 1.0 \cdot 10^{15} \text{ molecules cm}^{-3}\). There was no discernable difference in the slope of \(k_{\text{obs}}\) vs. \([\text{CH}_3\text{OH}]\) above and below this methanol concentration.

### Laboratory Results and Discussion

The dramatic effect of methanol on the observed rate constant is demonstrated in Figure 1. At 295 K, there was very little change in \(k_{\text{obs}}\) when \([\text{CH}_3\text{OH}]\) was varied over the range (1 to 5) \(\cdot 10^{15} \text{ molecules cm}^{-3}\). At 231 K, \(k_{\text{obs}}\) more than doubled over the same range of \([\text{CH}_3\text{OH}]\).

Figure 2 compares the temperature dependence of \(k_1\) with the JPL00-3 recommended values at 100 Torr. At 295 K, our results are within 7% of the current recommended values, but at 231 K, we find that the rate constant is only 59% of the current recommended value. Our measured values (2\(\sigma\)) of \(A\) and \(E_a/R\) for \(k_1\) were (8.8 ± 0.9) \(\cdot 10^{-13} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}\) and (−210 ± 26) K, respectively.

In order to validate the approach used in the derivation of \(k_1\), 308-nm photolysis of \(\text{F}_2/\text{H}_2/\text{O}_2/\text{N}_2\) mixtures was used to produce \(\text{HO}_2\). These experiments were conducted at two temperatures, 231 K and 295 K. The results, plotted in Figure 2, show that \(k_1\) values obtained by extrapolating to zero methanol were statistically consistent with \(k_1\) in the absence of methanol. Possible interferences from \(\text{FO}_2\) were determined to be negligible.

### Table 1. Experimental Conditions

<table>
<thead>
<tr>
<th>HO(_2) Source</th>
<th>([\text{Cl}_2]) (10^{14} \text{ cm}^{-3})</th>
<th>([\text{F}_2]) (10^{15} \text{ cm}^{-3})</th>
<th>([\text{CH}_3\text{OH}]) (10^{14} \text{ cm}^{-3})</th>
<th>([\text{H}_2]) (10^{15} \text{ cm}^{-3})</th>
<th>([\text{O}_2]) (10^{15} \text{ cm}^{-3})</th>
<th>([\text{N}_2]) (10^{15} \text{ cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{HCl} + \text{CH}_2\text{OH})</td>
<td>9–11</td>
<td>2–130</td>
<td>1.2–1.4</td>
<td>1.8–2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H})</td>
<td>7.5–8.5</td>
<td>3–20</td>
<td>0.3–2</td>
<td>0.5–1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purities (All gases from AirProducts)</td>
<td>99.5%</td>
<td>97.0%</td>
<td>HPLC</td>
<td>99.999%</td>
<td>99.996%</td>
<td>99.9993%</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)  
**Figure 1.** Plot of \(k_{\text{obs}}\) as a function of \([\text{CH}_3\text{OH}]\) at 231 K (●) and 295 K (●). Error bars represent 2\(\sigma\) uncertainties in the measurement precision (see text).

![Figure 2](image2.png)  
**Figure 2.** Plot of the rate constant of reaction (1) as a function of inverse temperature at 100 Torr. Filled circles are \(k_1\) values from experiments using \(\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2/\text{N}_2\) at 100 Torr. The solid line is the fit to these values. Values of \(k_1\) obtained using \(\text{F}_2/\text{H}_2/\text{O}_2/\text{N}_2\) are denoted by open circles. The dashed line is the JPL00-3 recommendation for \(k_1\) at 100 Torr. Also shown are calculated \(k_{\text{obs}}\) values using \(k_1\) and \(k''\) measured in the present study and \([\text{CH}_3\text{OH}] = 3 \cdot 10^{15} \text{ molecules cm}^{-3}\) denoted by (∆). Error bars (2\(\sigma\)) for Kircher and Sander are represented by (x). Error bars for the present study are not capped.
[16] Our measured temperature dependence leads to a negative $E_a$ that is half that reported by prior investigators. The study by Kircher and Sander [1984] (KS) is similar to the JPL and IUPAC recommendations and has influenced the recommendations for temperatures below 273 K. Their study was conducted between 240 K and 417 K and employed $[\text{CH}_3\text{OH}] = (1$ to $5) \times 10^{15}$ molecules cm$^{-3}$. The discrepancy between our results and those of KS can be explained by taking into account the enhancement in $k_{\text{obs}}$ by methanol. In Figure 2, we plot $k_{\text{obs}}(T)$, calculated for $[\text{CH}_3\text{OH}] = 3 \times 10^{15}$ molecules cm$^{-3}$, using the values for $k_i$ and $k'$ measured in the present experiment. The plot demonstrates that we obtain the same observed reaction rate as KS under the same experimental conditions. The plot also shows that at temperatures below 240 K, the calculated rate constant begins to diverge from the recommended values. At 220 K, the calculated values are 2 times larger.

[17] To date, there are five published experimental studies of reaction (1) at temperatures below 273 K. Studies conducted by KS, Lightfoot et al. [1990] and Takacs and Howard [1986] employed methanol. A study by Dobis and Benson [1993] inferred $k_i$ indirectly from reactions initiated by Cl + C$_2$H$_5$ and has not influenced current recommendations. Maricq and Scente [1994] studied reaction (1) in the absence of methanol. They utilized $\text{F}_2/\text{H}_2\text{O}_2/\text{N}_2$ gas mixtures at 200 Torr and reported results similar to the current recommendations but in disagreement with our results at low temperatures. At 222 K, their results agree with current recommendations of KS, and are 40% higher than our value of $k_i$ at zero-added methanol after extrapolating to 100 Torr using the JPL recommended pressure-dependence. They analyzed HO$_2$ decays over a shorter time period, when competing reactions are more important, and formed higher maximum [HO$_2$] than in our experiment.

[18] An Arrhenius plot for $k'$ is shown in Figure 3. The measured $A$ and $E_a/R$ values (2σ) for $k'$ were $2.5 \pm 5.9 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $(-4570 \pm 240)$ K, respectively. Also plotted in Figure 3 are measurements of $k'$ by Andersson et al. [1988] which agree favorably with our results at the two temperatures they investigated, 278 K and 299 K.

[19] The rate enhancement due to methanol can be explained in terms of a hydrogen-bonded complex. Prior investigators of the rate enhancement by CH$_3$OH, H$_2$O, and NH$_3$ on reaction (1) have postulated that the effect is due to a hydrogen-bonded complex that reacts with HO$_2$ faster than HO$_2$ reacts with itself [Andersson et al., 1988; Kircher and Sander, 1984; Lii et al., 1980]. For methanol, the scheme can be described as

$$\text{CH}_3\text{OH} + \text{HO}_2 \leftrightarrow \text{CH}_3\text{OH} \cdot \text{HO}_2 \quad (3)$$

$$\text{CH}_3\text{OH} \cdot \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{CH}_3\text{OH} \quad (4)$$

where $k_2 > k_i$. The temperature dependence of $k'$ can be shown to result from the enthalpy change due to equilibrium (3) Mozurkevich and Benson [1985]. The measured $E_a/R$ for $k''$ in the our experiment was equivalent to $(-9.08 \pm 0.48)$ kcal mol$^{-1}$, which is consistent with the stabilization energy of a strongly hydrogen-bonded complex (L. E. Christensen et al., manuscript in preparation, 2002B).

[20] Reaction (1) proceeds via a complex potential energy surface and displays pressure-dependent behavior. Both the NASA and IUPAC recommendations separate the expression for the overall rate constant into two terms, i.e.

$$k_1 = k_0 + k' \cdot [\text{M}] \quad (5)$$

where $k_i$ and $k'$ are the bimolecular and termolecular components, respectively. For the model calculations discussed below, we obtained $k_i$ from equation (5) using the JPL97-4 recommended $k' = 1.7 \times 10^{-33}$ [M] · exp[1000/T] where the suggested uncertainty factor is 1.3 and 2 at 298 K and 220 K, respectively (see [DeMore et al., 1997] for an explanation of the uncertainty factor). The following best-fit parameters (2σ) were obtained for $k_i(T)$: $A = (1.5 \pm 0.2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $E_a/R = (-19 \pm 31)$ K.

4. Atmospheric Implications

[21] Measurements of H$_2$O$_2$ from space using infrared spectroscopy are potentially a powerful way to ascertain [HO$_2$] in the lower stratosphere and upper troposphere. In these regions of the atmosphere, loss of H$_2$O$_2$ by photolysis

$$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH} \quad (6)$$
is nearly an order of magnitude greater than other combined gas phase loss processes. Assuming reaction (1) is the dominant source of H$_2$O$_2$, the relationship

$$\left\{ [\text{HO}_2]^2 \right\}_{24\text{-hr avg}} = \frac{J_6 \cdot [\text{H}_2\text{O}_2]}{k_0 + k' \cdot [\text{M}]}$$

can be established between [HO$_2$] and [H$_2$O$_2$], where $J_6$ is the photolysis rate of H$_2$O$_2$. This relationship is sensitive to $k_i + k' \cdot [\text{M}]$, the rate coefficient of HO$_2$ + HO$_2$.

![Figure 4](https://example.com/fig4.png)

**Figure 4.** Measured and modeled profiles of H$_2$O$_2$ VMR for two seasons near Ft. Sumner, NM (34.5°N), as indicated at the top of each panel. Error bars represent 1σ uncertainty for the measured profiles. The solid lines show calculated [H$_2$O$_2$] profiles using JPL00-3 kinetics (Model JPL00-3). The long dashed lines show profiles found using the new rate coefficient for HO$_2$ + HO$_2$ and JPL00-3 kinetics for all other reactions (Model A). The short dashed lines show profiles using the new rate coefficient for HO$_2$ + HO$_2$, JPL97-4 coefficients for OH + O$_3$ and HO$_2$ + O$_3$, and JPL00-3 kinetics for all other reactions (Model B). The left and right panels depict results for spring and fall, respectively.
[22] We tested our understanding of H$_2$O$_2$ – HO$_2$ photochemistry by comparing calculations using a constrained photochemical steady state model with observed profiles of H$_2$O$_2$. Profiles of H$_2$O$_2$, shown in Figure 4, were obtained by two balloon-borne Fourier transform spectrometers: the Harvard-Smithsonian FIRS-2 instrument that senses H$_2$O$_2$ thermal emission from 80 cm$^{-1}$ to 170 cm$^{-1}$ [Jucks et al., 1998] and the JPL MKIV instrument that uses mid-IR solar occultation [Sen et al., 1998].

Three sets of model calculations are shown in Figure 4 to illustrate the sensitivity of calculated H$_2$O$_2$ to certain kinetic parameters that govern HO$_2$. The model calculations were constrained by measurements of temperature, O$_3$, H$_2$O, CH$_4$, NO$_y$, and Cl$_y$ as well as profiles of sulfate aerosol surface area appropriate for the time of measurement [Sen et al., 1998] (K. W. Jucks et al., manuscript in preparation, 2002). One calculation, denoted JPL00-3, used the current recommended rate constants [Sander et al., 2000]. A second calculation, denoted Model A, used JPL00-3 rate coefficients and the rate of HO$_2$ + H$_2$O from this study. A third calculation, denoted Model B, is identical to Model A except rate constants from the JPL97-4 evaluation were used for O$_3$ + OH (reaction 7) and O$_3$ + HO$_2$ (reaction 8). From the upper troposphere to the middle stratosphere, the partitioning of HO$_x$ is mainly controlled by reactions (7) and (8). These reactions affect calculated [HO$_2$], and therefore [H$_2$O$_2$] via the HO$_2$ + HO$_2$ reaction. We include reactions (7) and (8) in our sensitivity study because the recommended rates have recently changed. We note that at low temperatures, JPL97-4 rates for these reactions lead to lower calculated [HO$_2$] and better overall agreement with measured [HO$_2$]/[OH] in the lower stratosphere [Lanzendorf et al., 2001].

[24] Use of the new rate for HO$_2$ + H$_2$O (Models A and B) in the photochemical simulation leads to significantly better agreement with measured H$_2$O$_2$ than is found using JPL00-3 kinetics (Figure 4). Changes to the rates of reactions (7) and (8) have a smaller effect on calculated H$_2$O$_2$ than the effect due to using the new rate of HO$_2$ + HO$_2$. Nonetheless, use of JPL97-4 rates for reactions (7) and (8) together with the new rate for HO$_2$ + HO$_2$ leads to slightly better overall agreement with measured H$_2$O$_2$ than is found using JPL00-3 rates for reactions (7) and (8). Because our new rate for HO$_2$ + HO$_2$ differs from the current recommendation mainly at low temperatures, the impact on model calculations will be small for both the middle troposphere and the upper stratosphere. The comparisons in Figure 4 suggest that, using the new rate coefficient for HO$_2$ + HO$_2$, the kinetics governing the production and loss of H$_2$O$_2$ are well understood and that remote measurements of [H$_2$O$_2$] can therefore be used to infer stratospheric [HO$_2$] and to place strong constraints on upper tropospheric [NO$_y$].

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References