

Kinetics of $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$: Implications for Stratospheric H_2O_2

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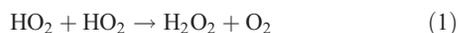
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[1] The reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ (1) has been studied at 100 Torr and 222 K to 295 K. Experiments employing photolysis of $\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2/\text{N}_2$ and $\text{F}_2/\text{H}_2/\text{O}_2/\text{N}_2$ gas mixtures to produce HO_2 confirmed that methanol enhanced the observed reaction rate. At 100 Torr, zero methanol, $k_1 = (8.8 \pm 0.9) 10^{-13} \times \exp[(210 \pm 26)/T]$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ uncertainties), which agrees with current recommendations at 295 K but is nearly 2 times slower at 231 K. The general expression for k_1 , which includes the dependence on bath gas density, is $k_1 = (1.5 \pm 0.2) \times 10^{-12} \times \exp[(19 \pm 31)/T] + 1.7 \times 10^{-33} \times [\text{M}] \times \exp[1000/T]$, where the second term is taken from the JPL00-3 recommendation. The revised rate largely accounts for a discrepancy between modeled and measured $[\text{H}_2\text{O}_2]$ 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 H_2O_2 is the reaction



Reaction (1) is an important sink for HO_x in the troposphere because H_2O_2 is scavenged by aerosols and clouds. In the stratosphere, H_2O_2 serves as a temporary reservoir for HO_x .

[3] Remote measurements of stratospheric $[\text{H}_2\text{O}_2]$ have indicated that our understanding of the H_2O_2 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 $[\text{H}_2\text{O}_2]$ in the lower to middle stratosphere. This has prompted researchers to explore previously unrecognized loss processes for H_2O_2 such as the $\text{H}_2\text{O}_2 + \text{O}_3$ 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 CH_3OH as a

precursor for HO_2 . It has been demonstrated that the observed rate of reaction (1) is enhanced in the presence of CH_3OH , H_2O , and NH_3 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 k_1 as the rate constant for reaction (1) in the limit of zero added methanol and derived $k_1(T)$ at 100 Torr of combined O_2 (40%) and N_2 (60%). The temperature dependence of the methanol enhancement effect was also measured. The new value of $k_1(T)$ was used to compare measured volume mixing ratio (VMR) profiles of stratospheric H_2O_2 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, HO_2 was generated in a 2-m long temperature-controlled flow cell by laser photolysis at 308 nm of either Cl_2 or F_2 in the gas mixtures $\text{CH}_3\text{OH}/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{O}_2/\text{N}_2$, respectively. The laser fluence was $120 \text{ mJ pulse}^{-1}$. HO_2 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 $[\text{HO}_2]$, 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. N_2 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 CH_3O_2 and $\text{CH}_3\text{CH}_2\text{O}_2$ 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 N_2 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. HO_2 was detected by UV absorbance at 220.00 nm. The rate of decay was corrected to account for the time-dependent

Table 1. Experimental Conditions

HO ₂ Source	[Cl ₂] 10 ¹⁵ cm ⁻³	[F ₂] 10 ¹⁶ cm ⁻³	[CH ₃ OH] 10 ¹⁴ cm ⁻³	[H ₂] 10 ¹⁷ cm ⁻³	"[O ₂] 10 ¹⁸ cm ⁻³	[N ₂] 10 ¹⁸ cm ⁻³
Cl + CH ₃ OH → HCl + CH ₂ OH	9–11		2–130		1.2–1.4	1.8–2
CH ₂ OH + O ₂ → HO ₂ + HCHO						
F + H ₂ → HF + H		7.5–8.5		3–20	0.3–2	0.5–1.5
H + O ₂ + M → HO ₂ + M						
Purities (All gases from AirProducts)	99.5%	97.0%	HPLC J.T. Baker	99.999%	99.996%	99.9993%

absorbance by H₂O₂, a product of reaction (1) [Kircher and Sander, 1984]. The value used for the cross-sections of HO₂ and H₂O₂ at 220.00 nm were $3.41 \cdot 10^{-18} \text{ cm}^2$ [Tyndall et al., 2001] and $2.58 \cdot 10^{-19} \text{ cm}^2$ [DeMore et al., 1997], respectively. Both cross-sections were assumed to be independent of temperature and pressure.

[9] We defined k_{obs} as the second-order rate constant, measured in the presence of methanol, and corrected for absorbance of H₂O₂. In each experiment, we measured the HO₂ decay over 38 milliseconds. At a given temperature and methanol concentration, k_{obs} was determined from the average of 3 individual experiments. At each temperature, k_{obs} was measured at 5 to 10 different methanol concentrations. As shown below, k_{obs} was linearly dependent on [CH₃OH]. We expressed the enhancement due to methanol as

$$k_{\text{obs}} = k_1 + k'' \cdot [\text{CH}_3\text{OH}] \quad (2)$$

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_{obs} vs. [CH₃OH]. From the fit, k_1 was determined from the y-intercept and k'' was determined from the slope.

[10] The uncertainty (2σ) in k_{obs} due to the statistical noise in the UV signal was 2% while the uncertainty in determining [CH₃OH], 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_{obs} and [CH₃OH] was not well described by equation (2) at 222 K. This was correlated with slight deviations from second-order rate behavior at high [CH₃OH].

[11] 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).

[12] The effects of secondary reactions were considered as a possible cause for the observed rate enhancement. At all temperatures, the maximum [HO₂] did not change for [CH₃OH] > $1 \cdot 10^{15} \text{ molecules cm}^{-3}$; at the lowest [CH₃OH] employed, maximum

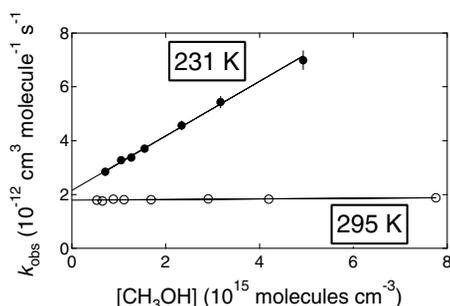


Figure 1. Plot of k_{obs} as a function of [CH₃OH] at 231 K (●) and 295 K (●). Error bars represent 2σ uncertainties in the measurement precision (see text).

[HO₂] decreased by 10%. Competing secondary reactions such as Cl + O₂ and Cl + HO₂ would account for the decrease in maximum [HO₂]. 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 [CH₃OH] > $1 \cdot 10^{15} \text{ molecules cm}^{-3}$. There was no discernable difference in the slope of k_{obs} vs. [CH₃OH] above and below this methanol concentration.

3. Laboratory Results and Discussion

[13] 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_{obs} when [CH₃OH] was varied over the range (1 to 5) $\cdot 10^{15} \text{ molecules cm}^{-3}$. At 231 K, k_{obs} more than doubled over the same range of [CH₃OH].

[14] 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 (2σ) of A and E_a/R for k_1 were $(8.8 \pm 0.9) \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(-210 \pm 26) \text{ K}$, respectively.

[15] In order to validate the approach used in the derivation of k_1 , 308-nm photolysis of F₂/H₂/O₂/N₂ mixtures was used to produce HO₂. 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 FO₂ were determined to be negligible.

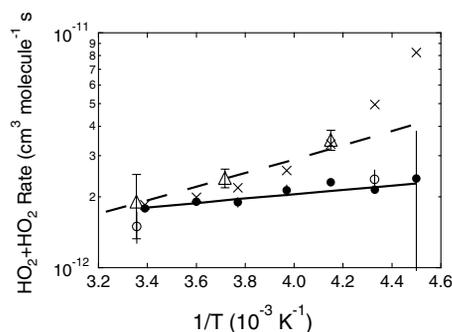


Figure 2. Plot of the rate constant of reaction (1) as a function of inverse temperature at 100 Torr. Filled circles are k_1 values from experiments using Cl₂/CH₃OH/O₂/N₂ at 100 Torr. The solid line is the fit to these values. Values of k_1 obtained using F₂/H₂/O₂/N₂ are denoted by open circles. The dashed line is the JPL00-3 recommendation for k_1 at 100 Torr. Also shown are calculated k_{obs} values using k_1 and k'' measured in the present study and [CH₃OH] = $3 \cdot 10^{15} \text{ molecules cm}^{-3}$ denoted by (×). The results of Kircher and Sander are represented by (Δ). Error bars (2σ) for Kircher and Sander are capped. Error bars for the present study are not capped.

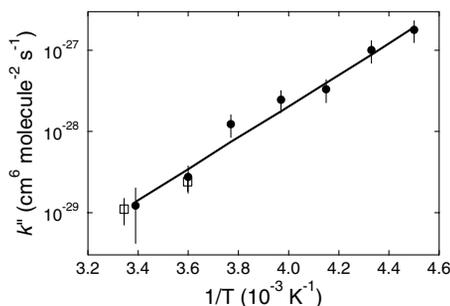


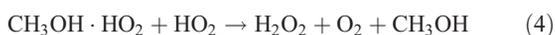
Figure 3. Plot of k'' as a function of inverse temperature from the present study at 100 Torr (●) and from the *Andersson et al.* study at 760 Torr (□). Error bars are 2σ .

[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 $[\text{CH}_3\text{OH}] = (1 \text{ to } 5) \cdot 10^{15} \text{ molecules cm}^{-3}$. The discrepancy between our results and those of *KS* can be explained by taking into account the enhancement in k_{obs} by methanol. In Figure 2, we plot $k_{\text{obs}}(T)$, calculated for $[\text{CH}_3\text{OH}] = 3 \cdot 10^{15} \text{ molecules cm}^{-3}$, using the values for k_1 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_1 indirectly from reactions initiated by $\text{Cl} + \text{C}_2\text{H}_6$ and has not influenced current recommendations. *Maricq and Sente* [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_1 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 $[\text{HO}_2]$ 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 $(2.5 \pm 5.9) \cdot 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $(-4570 \pm 240) \text{ K}$, 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_3OH , H_2O , 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



where $k_4 > k_1$. The temperature dependence of k'' can be shown to result from the enthalpy change due to equilibrium (3) *Mozurke-*

wich and Benson [1985]. The measured E_a/R for k'' in the our experiment was equivalent to $(-9.08 \pm 0.48) \text{ kcal mol}^{-1}$, 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_0 and k' are the bimolecular and termolecular components, respectively. For the model calculations discussed below, we obtained k_0 from equation (5) using the JPL97-4 recommended $k' = 1.7 \cdot 10^{-33} \cdot [\text{M}] \cdot \exp[1000/T]$ 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 $k_0(T)$: $A = (1.5 \pm 0.2) \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_a/R = (-19 \pm 31) \text{ K}$.

4. Atmospheric Implications

[21] Measurements of H_2O_2 from space using infrared spectroscopy are potentially a powerful way to ascertain $[\text{HO}_x]$ in the lower stratosphere and upper troposphere. In these regions of the atmosphere, loss of H_2O_2 by photolysis



is nearly an order of magnitude greater than other combined gas phase loss processes. Assuming reaction (1) is the dominant source of H_2O_2 , the relationship

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

can be established between $[\text{HO}_2]$ and $[\text{H}_2\text{O}_2]$, where J_6 is the photolysis rate of H_2O_2 . This relationship is sensitive to $k_0 + k' \cdot [\text{M}]$, the rate coefficient of $\text{HO}_2 + \text{HO}_2$.

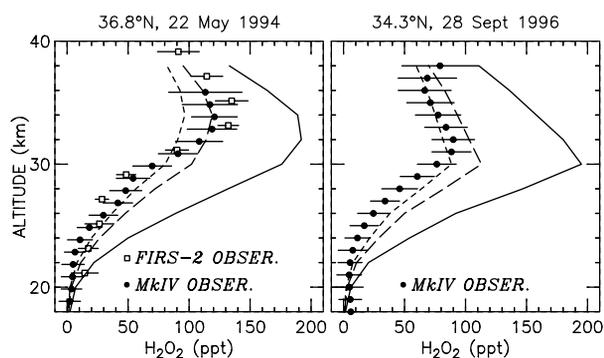


Figure 4. Measured and modeled profiles of H_2O_2 VMR for two seasons near Ft. Sumner, NM (34.5°N), as indicated at the top of each panel. Error bars represent 1σ uncertainty for the measured profiles. The solid lines show calculated $[\text{H}_2\text{O}_2]$ profiles using JPL00-3 kinetics (Model JPL00-3). The long dashed lines show profiles found using the new rate coefficient for $\text{HO}_2 + \text{HO}_2$ and JPL00-3 kinetics for all other reactions (Model A). The short dashed lines show profiles using the new rate coefficient for $\text{HO}_2 + \text{HO}_2$, JPL97-4 coefficients for $\text{OH} + \text{O}_3$ and $\text{HO}_2 + \text{O}_3$, 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 H₂O₂ – HO_x photochemistry by comparing calculations using a constrained photochemical steady state model with observed profiles of H₂O₂. Profiles of H₂O₂, shown in Figure 4, were obtained by two balloon-borne Fourier transform spectrometers: the Harvard-Smithsonian FIRS-2 instrument that senses H₂O₂ 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].

[23] Three sets of model calculations are shown in Figure 4 to illustrate the sensitivity of calculated H₂O₂ to certain kinetic parameters that govern HO_x. The model calculations were constrained by measurements of temperature, O₃, H₂O, CH₄, 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 HO₂ + HO₂ 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 O₃ + OH (reaction (7)) and O₃ + HO₂ (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 [HO₂], and therefore [H₂O₂] via the HO₂ + HO₂ 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 [HO₂] and better agreement with measured [HO₂]/[OH] in the lower stratosphere [Lanzendorf *et al.*, 2001].

[24] Use of the new rate for HO₂ + HO₂ (Models A and B) in the photochemical simulation leads to significantly better agreement with measured H₂O₂ than is found using JPL00-3 kinetics (Figure 4). Changes to the rates of reactions (7) and (8) have a smaller effect on calculated H₂O₂ than the effect due to using the new rate of HO₂ + HO₂. Nonetheless, use of JPL97-4 rates for reactions (7) and (8) together with the new rate for HO₂ + HO₂ leads to slightly better overall agreement with measured H₂O₂ than is found using JPL00-3 rates for reactions (7) and (8). Because our new rate for HO₂ + HO₂ 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 HO₂ + HO₂, the kinetics governing the production and loss of H₂O₂ are well understood and that remote measurements of [H₂O₂] can therefore be used to infer stratospheric [HO_x] and to place strong constraints on upper tropospheric [NO_x].

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