

AD-A122 207 RATE CONSTANT OF THE OH + H2O2 YIELD HO2 + H2O REACTION 1/1  
(U) CALIFORNIA UNIV IRVINE DEPT OF CHEMISTRY  
M J MOLINA ET AL. JUL 82 FAA/EE-82-17 DTFA01-80-C-10084

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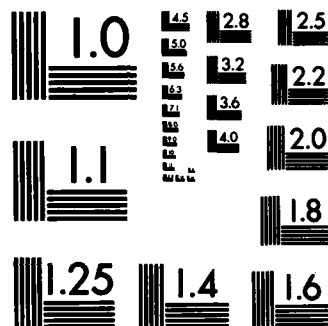
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# Rate Constant of the $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ Reaction



U.S. Department  
of Transportation  
Federal Aviation  
Administration

Office of Environment  
and Energy  
Washington, DC 20591

AD A122207

1982

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Mario J. Molina  
Lusia T. Molina  
Craig A. Smith  
John J. Lamb

July 1982

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for release

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| 1. Report No.<br>FAA-EE-82-17                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 2. Government Accession No.<br>AD-A122207            | 3. Recipient's Catalog No.                                                                                                                            |           |
| 4. Title and Subtitle<br>RATE CONSTANT OF THE<br>$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ REACTION                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                      | 5. Report Date<br>July 1982                                                                                                                           |           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                      | 6. Performing Organization Code                                                                                                                       |           |
| 7. Author(s)<br>Mario J. Molina, Luisa T. Molina<br>Craig A. Smith, John J. Lamb                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                      | 8. Performing Organization Report No.                                                                                                                 |           |
| 9. Performing Organization Name and Address<br>University of California<br>Department of Chemistry<br>Irvine, California 92717                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                      | 10. Work Unit No. (TRAIS)                                                                                                                             |           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                      | 11. Contract or Grant No.<br>DTFA01-80-C-10084                                                                                                        |           |
| 12. Sponsoring Agency Name and Address<br>Department of Transportation<br>Federal Aviation Administration<br>Office of Environment and Energy<br>Air Quality Division<br>Washington, D.C. 20591                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                      | 13. Type of Report and Period Covered<br>Final Report                                                                                                 |           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                      | 14. Sponsoring Agency Code                                                                                                                            |           |
| 15. Supplementary Notes                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                      |                                                                                                                                                       |           |
| 16. Abstract<br><p>Absolute rate constants for the reaction <math>\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}</math> have been measured using the flash photolysis resonance fluorescence technique over the temperature range 241 to 413 K and at 1 atm helium. <math>\text{H}_2\text{O}_2</math> concentrations were measured by ultra-violet and infrared absorption spectrophotometry. The rate constant at 294 K was found to be <math>k_1 = 1.8 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}</math>, in agreement with recent literature values. The results yield a curved Arrhenius plot, with a slight increase in the rate constant at the lower temperatures. ←</p> <p style="text-align: right;">12 to the present</p> |                                                      |                                                                                                                                                       |           |
| 17. Key Words<br>Hydrogen Peroxide, $\text{H}_2\text{O}_2$<br>Hydroxyl Radical, OH<br>Reaction Rate Constant                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                      | 18. Distribution Statement<br>This document is available to the public through the National Technical Information Service Springfield, Virginia 22161 |           |
| 19. Security Classif. (of this report)<br>UNCLASSIFIED                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 20. Security Classif. (of this page)<br>UNCLASSIFIED | 21. No. of Pages<br>23                                                                                                                                | 22. Price |

# ABSTRACT

Absolute rate constants for the reaction  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$  have been measured using the flash photolysis resonance fluorescence technique over the temperature range 241 to 413 K and at 1 atm helium.  $\text{H}_2\text{O}_2$  concentrations were measured by ultra-violet and infrared absorption spectrophotometry. The rate constant at 294 K was found to be  $k_1 = 1.8 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in agreement with recent literature values. The results yield a curved Arrhenius plot, with a slight increase in the rate constant at the lower temperatures.



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## INTRODUCTION

The gas phase reaction of OH with  $\text{H}_2\text{O}_2$  is an important component of the atmospheric  $\text{HO}_x$  cycle:



$\text{H}_2\text{O}_2$  is formed in the atmosphere mainly by the recombination reaction of  $\text{HO}_2$  radicals (reaction 2) and its principal loss processes are reaction with OH radicals (reaction 1) and photodissociation (reaction 3):



In addition, rainout and washout processes represent significant sinks for  $\text{H}_2\text{O}_2$  in the troposphere.

Several previous studies of reaction (1) have been reported: early measurements of the rate constant using steady state photolysis methods (Gorse and Volman, 1972; Meagher and Heicklen, 1979), flash photolysis (Greiner, 1968; Harris and Pitts, 1979), and discharge flow techniques (Hack et al., 1975) gave results in the  $0.62\text{--}1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  range at 298 K. More recently, four measurements by two different methods -- discharge flow (Sridharan et al., 1980; Keyser, 1980) and flash photolysis resonance fluorescence (Wine et al., 1982; Kurylo et al., 1982)

-- yielded rate constants that are about a factor of two larger at 298 K and which showed linear Arrhenius plots, with the rate constant decreasing by ~ 10% at 250 K. In this work we essentially confirm these new rate constant values using the flash photolysis resonance fluorescence technique at 1 atm He; however, we observe a curved Arrhenius plot, with the rate constant increasing below room temperature and becoming 10% larger at 250 K.

## EXPERIMENTAL

### Instrumentation and Chemicals

An all-pyrex jacketed reaction cell with an internal volume of  $\sim 150 \text{ cm}^3$  was used in the experiments. The cell was maintained at constant temperature by flowing a thermostated liquid through the outer jacket surrounding the cell. The temperature was monitored at five different positions on the cell with copper-constantan thermocouples.

OH radicals were produced by flash photolysis of  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$  and/or  $\text{H}_2\text{O}$  using a nitrogen flash-lamp equipped with a Suprasil quartz lens and operated around 15 kV. An adjustable iris was placed in front of the lens to control the amount of photolysis light reaching the cell, which was unfocused. An OH microwave-discharge lamp excited resonance fluorescence in the O-O band of the  $\text{A}^2\Sigma^+-\text{X}^2\Pi$  system ( $\lambda \sim 308 \text{ nm}$ ). This fluorescence was monitored perpendicular to both the flash lamp and the resonance lamp radiation flux by an EMI-9782QA photomultiplier fitted with an interference filter (290-320 nm, 20% T at 307 nm) and a Corning 7-54 filter. The resonance lamp and the photomultiplier were also fitted with quartz lenses which mildly focused the radiation.

The signals, in the form of photon counts, were processed by a signal averager-computer system (Inotech Ultima II, Data General-Nova 3) using a non-linear least-squares routine to analyze the decays. For each decay rate sufficient flashes (usually 400)

were averaged to obtain a well-defined temporal profile of OH concentration over at least 3  $1/e$  times. The residuals and the autocorrelation coefficients were plotted routinely; in no case was there statistical evidence for departures from the single exponential decay expected for pseudo-first order conditions.

In order to avoid accumulation of products and to minimize the decomposition of  $H_2O_2$ , the reactant mixture was flowed through the reaction cell with a linear velocity of about 8 cm  $s^{-1}$ . The flash lamp repetition rate was about 1 Hz, so that the cell was refilled with a fresh reactant mixture for every flash.

$H_2O_2$  was introduced into the system by passing He gas through a glass bubbler containing several milliliters of concentrated  $H_2O_2$  solution at 0°C. For some runs  $HNO_3$  was added in small amounts (5-10 mtorr) in order to provide an alternate more efficient photolytic OH source. A separate bubbler was assembled containing several milliliters of aqueous  $HNO_3$  at 0°C. Helium gas was slowly bubbled through the liquid and the mixture was added to the  $H_2O_2$ /He flow downstream from the UV spectrophotometer. All connections and tubing after the bubblers were either glass or teflon.

Helium gas (Matheson Gas Products) was passed through a molecular sieve trap kept at liquid nitrogen temperature. Hydrogen peroxide (90%, FMC Corporation) was used without further purification. Nitric acid (70%, Mallinckrodt, Analytical Reagent grade) and  $C_2H_6$  (Matheson Gas Products, CP grade) were also used without further purification.

The flow rates were measured using Matheson mass flow meters. Pressures were monitored with an MKS capacitance manometer (0-100 torr range) and with a Bourdon-type Wallace-Tiernan gauge (0-800 torr range).

#### H<sub>2</sub>O<sub>2</sub> Concentration Determination

The H<sub>2</sub>O<sub>2</sub> concentrations were measured using a Perkin-Elmer 552 UV-vis spectrophotometer equipped with a 50 cm cell with folded optics, to give an optical path length of 100 cm. Due to the low partial pressures of H<sub>2</sub>O<sub>2</sub> used (0.8-13 mtorr), this UV measurement was made before the final dilution with He. The absorbance of the room temperature gas mixture was monitored in the 205-220 nm range, and the concentrations were calculated using the absorption cross section data of Molina and Molina (1981).

For most of the runs, the H<sub>2</sub>O<sub>2</sub> concentrations were also measured after the reaction cell by using a Nicolet-7199 Fourier-transform infrared spectrometer (FTIR) equipped with a standard Nicolet data-handling system and a liquid nitrogen cooled HgCdTe detector. A 55 cm long teflon-coated absorption cell with a ~ 6 cm<sup>2</sup> cross section and maintained at room temperature was interfaced to the FTIR. The cell was fitted with internal mirrors and KCl windows, with an optical path of ~ 20 m. The HNO<sub>3</sub> concentrations were also monitored with the FTIR cell. The IR band strengths for H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> were calibrated as described earlier (Molina and Molina, 1981).

The  $\text{H}_2\text{O}_2$  concentrations calculated from UV and IR measurements agreed to within a few percent, except at the highest temperature (413 K), where the discrepancy indicated about 15% decomposition in the resonance fluorescence cell.

### Sensitivity and Control Experiments

The OH detection sensitivity of the resonance fluorescence system was calibrated by photolyzing  $\text{HNO}_3/\text{He}$  mixtures at 222 nm with a KrCl excimer laser whose power was measured with a thermopile: at 1 atm He, this sensitivity was  $\sim 2 \times 10^{-8}$  counts  $\text{cm}^3$  molecule $^{-1}\text{s}^{-1}$ . Using this figure, the initial OH concentration for the flash photolysis runs was estimated to be at most  $10^{12}$  molecule  $\text{cm}^{-3}$ .

Some control experiments were carried out to determine the OH +  $\text{C}_2\text{H}_6$  rate constant in our apparatus, as a function of temperature, using  $\text{HNO}_3$  as an OH photolytic source, and using a  $\text{C}_2\text{H}_6/\text{He}$  mixture analyzed by gas chromatography. The observed rate constant decreased by a factor of two between 298 K and 250 K, and the results agreed to within 10% at these two temperatures with the values recommended by the NASA Panel for Data Evaluation (DeMore et al., 1982).

## RESULTS AND DISCUSSION

### Chemical Kinetics

The  $\text{OH} + \text{H}_2\text{O}_2$  reaction was studied over the temperature range 241-413 K and at a He pressure of 760 torr. A total of twenty-five bimolecular rate constants were measured. The results are shown in Table 1.

All experiments were carried out under pseudo-first order conditions:

$$\ln\{[\text{OH}]_0/[\text{OH}]_t\} = (k_1[\text{H}_2\text{O}_2] + k_d)t \equiv k^I \cdot t$$

where  $k_d$  is the first order rate constant for loss of OH in the absence of  $\text{H}_2\text{O}_2$  and  $k^I$  is the pseudo-first order rate constant.  $k_1$  was obtained from the slope of plots of  $k^I$  vs.  $[\text{H}_2\text{O}_2]$ . A typical OH decay is shown in Figure 1, and Figure 2 shows a typical plot of  $k^I$  vs.  $[\text{H}_2\text{O}_2]$ . The individual rate constants were determined from a linear least squares analysis of these latter plots. The value of the intercept agreed well with the value for  $k_d$  obtained in the absence of  $\text{H}_2\text{O}_2$  (with  $\text{H}_2\text{O}$  as the photolytic source of OH). The uncertainties listed in Table 1 represent one standard deviation, that is, about  $\pm 3\%$  at 294 K. We estimate that systematic errors raise the uncertainty to  $\pm 15\text{-}20\%$  yielding

$$k_1 (294 \text{ K}) = (1.8 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Table 1. Rate Constant Data for the Reaction of OH with H<sub>2</sub>O<sub>2</sub>

| Temperature<br>(K) | Pressure Range<br>H <sub>2</sub> O <sub>2</sub> (mtorr) | Pressure<br>HNO <sub>3</sub> (mtorr) | Number<br>of Runs | $k_1 + 1\sigma$<br>(10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) |
|--------------------|---------------------------------------------------------|--------------------------------------|-------------------|------------------------------------------------------------------------------------------------|
| 241                | 1.3-6.8                                                 | 0                                    | 13                | 2.10 ± 0.13                                                                                    |
| 241                | 2.4-6.0                                                 | 5                                    | 19                | 2.04 ± 0.07                                                                                    |
|                    |                                                         |                                      | Average:          | 2.07 ± 0.10                                                                                    |
| 251                | 0.7-5.6                                                 | 0                                    | 12                | 1.95 ± 0.06                                                                                    |
| 251                | 0.9-9.7                                                 | 0                                    | 10                | 1.90 ± 0.05                                                                                    |
| 251                | 0.9-7.9                                                 | 0                                    | 15                | 1.90 ± 0.05                                                                                    |
|                    |                                                         |                                      | Average:          | 1.92 ± 0.05                                                                                    |
| 294                | 1.1-11.3                                                | 0                                    | 15                | 1.88 ± 0.11                                                                                    |
| 294                | 1.8-7.1                                                 | 0                                    | 22                | 1.86 ± 0.10                                                                                    |
| 294                | 1.9-6.3                                                 | 5                                    | 12                | 1.81 ± 0.06                                                                                    |
| 294                | 1.2-12.0                                                | 0                                    | 11                | 1.85 ± 0.04                                                                                    |
| 294                | 5.0-8.7                                                 | 0                                    | 4                 | 1.71 ± 0.03                                                                                    |
| 294                | 1.7-9.9                                                 | 0                                    | 7                 | 1.81 ± 0.04                                                                                    |
| 294                | 1.3-11.0                                                | 0                                    | 6                 | 1.66 ± 0.05                                                                                    |
| 294                | 1.3-10.6                                                | 0                                    | 6                 | 1.81 ± 0.05                                                                                    |
| 294                | 2.4-8.2                                                 | 0                                    | 4                 | 1.77 ± 0.05                                                                                    |
|                    |                                                         |                                      | Average:          | 1.80 ± 0.06                                                                                    |
| 333                | 2.4-11.8                                                | 0                                    | 21                | 1.66 ± 0.08                                                                                    |
| 333                | 1.1-9.4                                                 | 0                                    | 12                | 1.76 ± 0.08                                                                                    |
| 333                | 0.8-8.3                                                 | 0                                    | 9                 | 1.75 ± 0.04                                                                                    |
|                    |                                                         |                                      | Average:          | 1.72 ± 0.07                                                                                    |
| 365                | 2.9-9.2                                                 | 5                                    | 17                | 1.76 ± 0.13                                                                                    |
| 365                | 2.4-9.8                                                 | 5                                    | 12                | 1.79 ± 0.15                                                                                    |
|                    |                                                         |                                      | Average:          | 1.78 ± 0.14                                                                                    |
| 413                | 2.8-6.8                                                 | 5                                    | 9                 | 2.04 ± 0.30                                                                                    |
| 413                | 2.9-9.2                                                 | 10                                   | 9                 | 1.64 ± 0.12                                                                                    |
|                    |                                                         |                                      | Average:          | 1.84 ± 0.21                                                                                    |

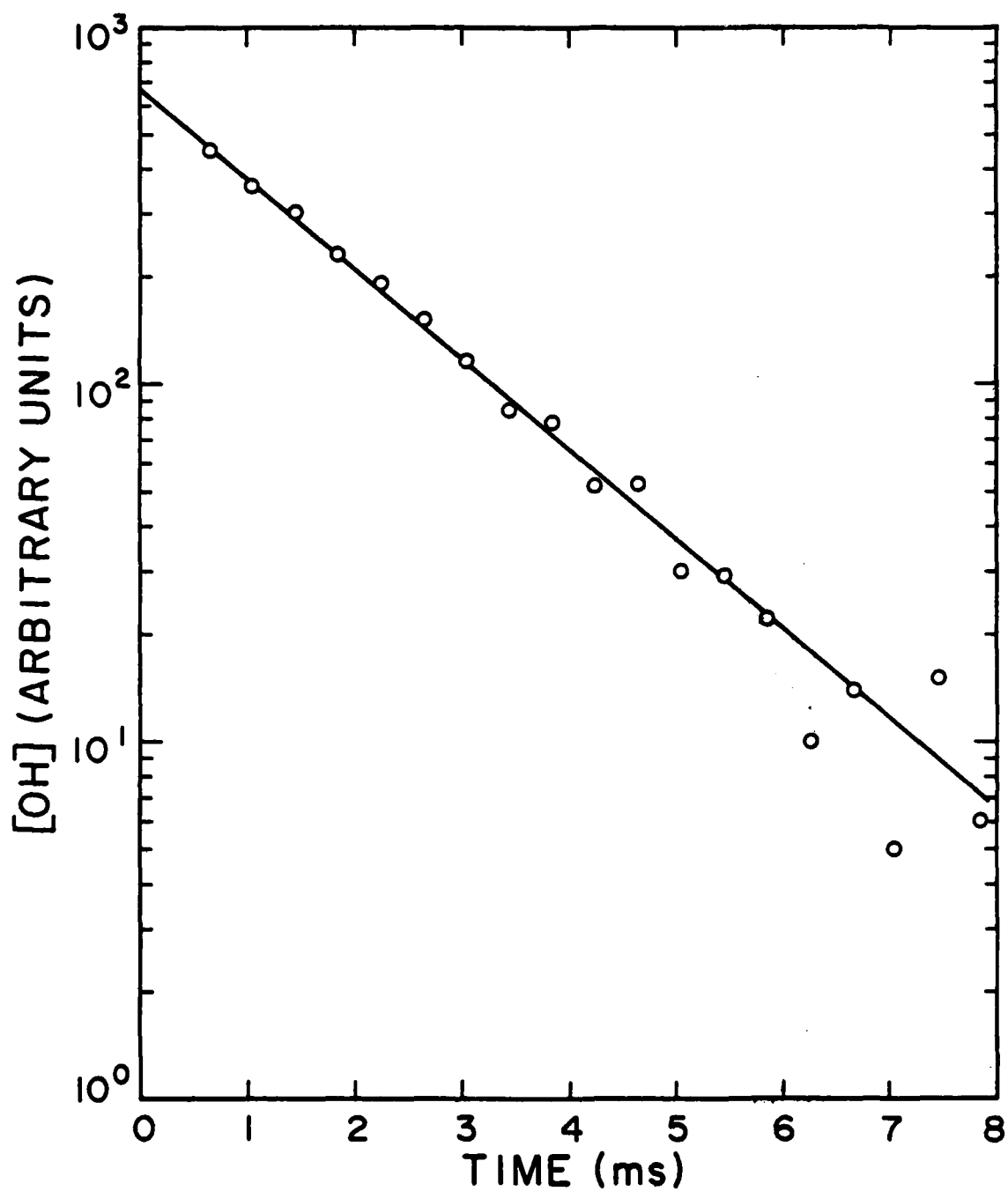


FIGURE 1. Typical OH Temporal Profile following Photolysis of an  $\text{H}_2\text{O}_2/\text{HNO}_3/\text{H}_2\text{O}/\text{He}$  Mixture.  $T = 241 \text{ K}$ ;  $P = 760 \text{ torr}$ ;  $[\text{H}_2\text{O}_2] = 5.3 \text{ mtorr}$ ;  $[\text{HNO}_3] = 4.4 \text{ mtorr}$ .

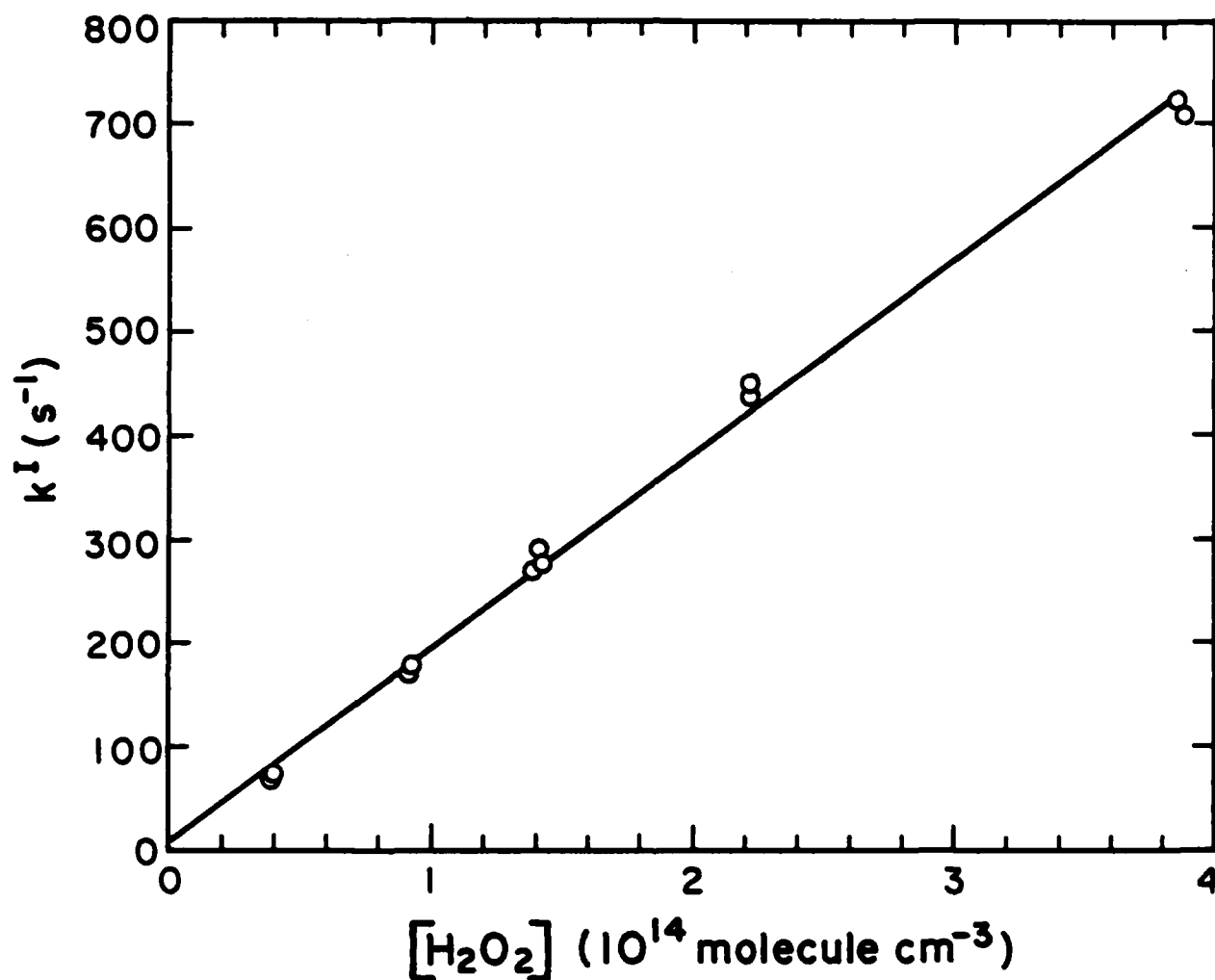


FIGURE 2. Plot of  $k^I$  versus  $[\text{H}_2\text{O}_2]$  at Room Temperature and Atmospheric Pressure (first 294 K entry in Table 1). Line is least squares fit of the experimental points.

For runs containing  $\text{HNO}_3$ , contributions to the observed  $k^I$  from the reaction  $\text{OH} + \text{HNO}_3$  were subtracted out using a rate constant obtained from the Arrhenius Equation  $k = 9.4 \times 10^{15} \exp(778/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , taken from the recommendation of the NASA Panel for Data Evaluation (DeMore et al., 1982). This correction amounted in all cases to less than 10% of the observed pseudo first order rate constant. The addition of  $\text{HNO}_3$  provided about a three-fold increase in the signal to noise ratio for an equivalent number of flashes.

### Secondary Reactions

Given the relatively small radical concentration ( $[\text{OH}]_0 < 10^{12} \text{ cm}^{-3}$ ) complications from secondary reactions should be minimal. As a check, the initial  $[\text{OH}]$  was varied by more than a factor of two by changing the intensity of the photolysis light; no significant change was observed in  $k^I$ . Also, as may be seen in Table I, the addition of  $\text{HNO}_3$  yielded essentially the same results. Furthermore, no departures from an exponential decay in  $\text{OH}$  were evident in any of the experiments.

The fast reaction between H-atoms and  $\text{HO}_2$  radicals is potentially a source of error since  $\text{OH}$  radicals can be regenerated by this route:



Some H-atoms might have been produced by the flash photolysis of water vapor present in our sample in spite of the 165 nm Suprasil

cutoff, but the expected amounts were too small to significantly perturb the OH concentrations: we estimate  $[H]_0/[OH]_0 < 0.3$  for typical runs without  $HNO_3$  added, and  $[H]_0/[OH]_0 < 0.1$  in the presence of  $HNO_3$ . Computer simulations of the kinetics incorporating reaction 4 as well as other potentially interfering secondary reactions confirmed that under our experimental conditions there should have been no significant departures from the simple exponential decay resulting from the  $OH + H_2O_2$  reaction. The results of these simulations essentially duplicate those presented by Kurylo et al., (1982), and hence they will not be repeated here.

#### Temperature Dependence

The temperature dependence of the rate constant for the reaction under study is shown in Figure 3, and also in Figure 4 along with the results of the four groups which have studied this reaction recently.

A linear least-squares fit to our results yields the expression:

$$k = (1.47 \pm 0.20) \times 10^{-12} \exp[(70 \pm 41)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

where the uncertainty represents one standard deviation. However, a clear departure from simple Arrhenius behavior is apparent in the figure, and the results are better fitted by the expression

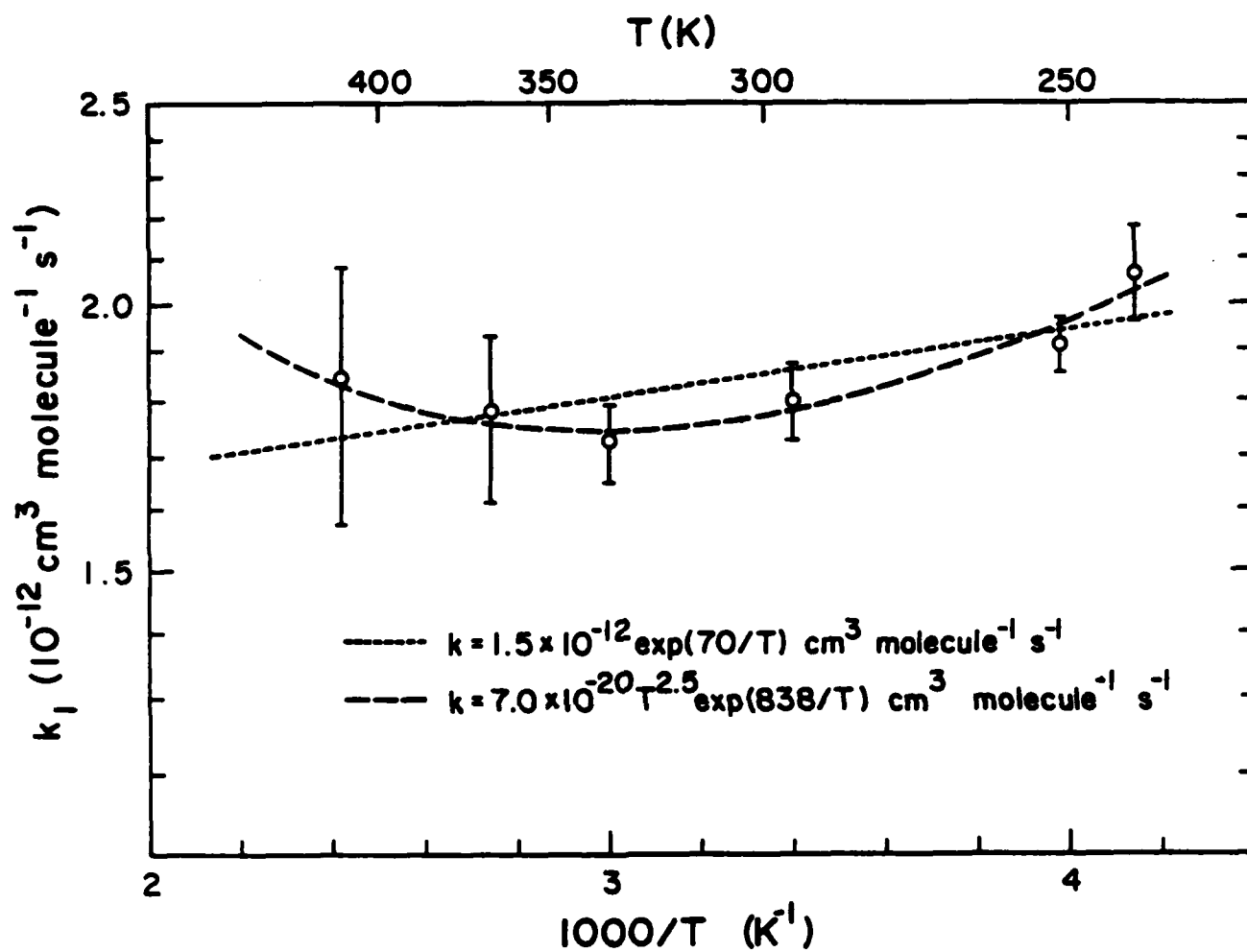


FIGURE 3. Arrhenius Plot from present work:  $\ln(k_1)$  versus  $1/T$ .

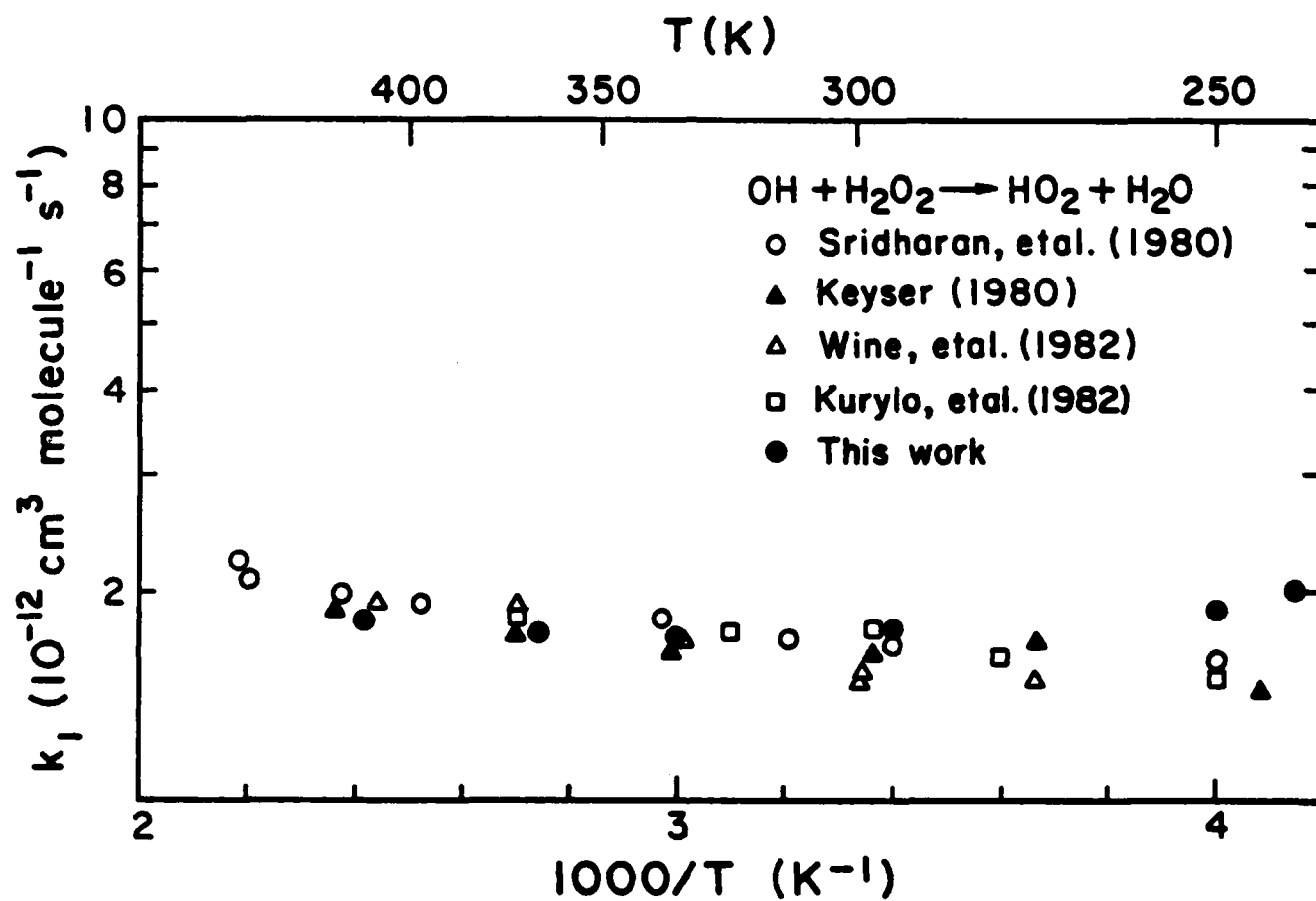
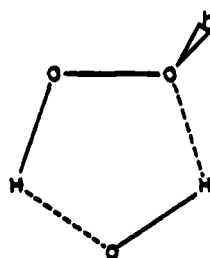


FIGURE 4. Arrhenius Plot of  $k_1$  values from the most recent studies.

$$k = (7.0 \pm 2.0) \times 10^{-20} T^{2.5} \exp[838 \pm 86]/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

As expected, the fit is insensitive to the exact value of the power  $n$  to which  $T$  is raised (the minimum standard deviation was actually obtained for  $n = 2.8$ ). Equation 5 reproduces the experimental rate constant values to within 7%, and equation 6 to within 3%.

Curvature in the Arrhenius plot can be rationalized by assuming the existence of two different reaction mechanisms: a direct H-atom abstraction predominating at the higher temperatures, and an addition mechanism, i.e., a "complex-mode" bimolecular reaction (see, for example, DeMore et al., 1982), predominating at the lower temperatures. Recently Leu and Smith (1982) found similar, even more pronounced curvature in the Arrhenius plot for the reaction  $\text{OH} + \text{H}_2\text{S}$ , which they also interpreted in terms of the dual-mechanism postulate. Thus, it appears that at low temperatures the complex-mode mechanism is quite prevalent for reactions of the OH radical with polar molecules which may form hydrogen bonds, e.g.,  $\text{HNO}_3$ ,  $\text{HNO}_4$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}_2$ , a mechanism which is evidenced by the negative activation energies observed in these reactions (DeMore et al., 1982). The  $\text{H}_2\text{O}_2$  molecule is non-planar; a plausible structure for the intermediate adduct is a hydrogen-bonded five-membered ring:



### Comparison with Other Measurements

Inspection of Table 2 and Figure 4 shows that our measured rate constants for the  $\text{OH} + \text{H}_2\text{O}_2$  reaction at 273 K and above are in very good agreement with those reported most recently (Sridharan et al., 1980; Keyser, 1980; Wine et al., 1982; Kurylo et al., 1982), but are larger by about 25% at 250 K. The discrepancy appears to lie just within the combined error limits. Sridharan et al. suggested a possible leveling off at the low temperature end of their Arrhenius plot, a trend which appears also in the data of Wine et al., and if one ignores the lowest temperature run it is borne out in the data of Keyser as well.

In summary, it is now well established that earlier measurements underestimated the rate constant for the  $\text{OH} + \text{H}_2\text{O}_2$  reaction by about a factor of two for reasons that have been discussed elsewhere at length (Sridharan et al., 1982; Kurylo et al., 1982). The results of the most recent flash photolysis and discharge flow studies are in very good agreement with each other, except possibly at 250 K and below, where our numbers show an increase in the rate constant with decreasing temperatures, indicating the formation of an intermediate hydrogen-bonded addition complex.

Table 2. Comparison of Recent Rate Measurements for the OH +  
H<sub>2</sub>O<sub>2</sub> Reaction

| Temperature<br>(K) | k <sub>1</sub> (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) * |           |           |           |           |
|--------------------|----------------------------------------------------------------------------------------------|-----------|-----------|-----------|-----------|
|                    | (a)                                                                                          | (b)       | (c)       | (d)       | (e) **    |
| 241                | 1.50±0.30                                                                                    | 1.49±0.48 | 1.26±0.29 | 1.49±0.31 | 2.04±0.51 |
| 251                | 1.54±0.30                                                                                    | 1.52±0.39 | 1.31±0.28 | 1.53±0.31 | 1.97±0.46 |
| 294                | 1.69±0.26                                                                                    | 1.64±0.32 | 1.53±0.28 | 1.68±0.30 | 1.79±0.30 |
| 333                | 1.85±0.32                                                                                    | 1.72±0.36 | 1.69±0.34 | 1.79±0.34 | 1.75±0.35 |
| 365                | 1.89±0.36                                                                                    | 1.78±0.45 | 1.81±0.40 | 1.87±0.38 | 1.77±0.41 |
| 413                | 1.99±0.42                                                                                    | 1.85±0.52 | 1.97±0.47 | 1.97±0.42 | 1.85±0.49 |

(a) Sridharan et al. (1980).

(b) Keyser (1980).

(c) Wine et al. (1982).

(d) Kurylo et al. (1982).

(e) This work.

\* Computed from the Arrhenius expression and error bars given by each group. The error bars for T ≠ 294 K were estimated as explained by the NASA Panel for Data Evaluation (DeMore et al., 1982).

\*\* Computed from Equation 6, with an error bar at 294 K of ± 0.3 x 10<sup>-12</sup>, and error bars at other temperatures as above.

#### LITERATURE CITED

DeMore, W.B., D.M. Golden, R.F. Hampson, C.J. Howard, M.J. Kur-  
ylo, M.J. Molina, A.R. Ravishankara, and R.T. Watson (1982), JPL  
Publication 82-57, Jet Propulsion Laboratory, California Insti-  
tute of Technology, Pasadena, California.

Gorse, R.A. and D.H. Volman (1972), Photochemistry of the Gaseous  
Hydrogen Peroxide - Carbon Monoxide System: Rate Constants for  
Hydroxyl Radical Reactions with Hydrogen Peroxide and Isobutane  
by Competitive Kinetics, J. Photochem., 1, 1-10.

Greiner, N.R. (1968), Hydroxyl Radical Kinetics by Kinetic Spec-  
troscopy. III. Reactions with  $H_2O_2$  in the Range 300-458 K, J.  
Phys. Chem., 72, 406-410.

Hack, W., K. Hoyer mann, and H. Gg. Wagner (1975), The Reaction  $NO$   
 $+ HO_2 \rightarrow NO_2 + OH$  with  $OH + H_2O_2 \rightarrow HO_2 + H_2O$  as an  $HO_2$ -Source,  
Int. J. Chem. Kinet. Symp., 1, 329-339.

Harris, G., and J.N. Pitts, Jr. (1979), Rate Constant for the  
Reaction of OH Radicals with Hydrogen Peroxide at 298 K, J. Chem.  
Phys., 70, 2581-2582.

Keyser, L.F. (1980), Absolute Rate Constant of the Reaction  $OH +$   
 $H_2O_2 \rightarrow HO_2 + H_2O$  from 245 to 423 K, J. Phys. Chem., 84, 1659-  
1663.

Kurylo, M.J., J.L. Murphy, G.S. Haller, and K.D. Cornett (1982), A Flash Photolysis Resonance Fluorescence Investigation of the Reaction  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ , Int. J. Chem. Kinet., in press.

Leu, M.-T., and R.A. Smith (1982), Rate Constants for the Gas-Phase Reaction between Hydroxyl and Hydrogen Sulfide over the Temperature Range 228-518 K, J. Phys. Chem., 86, 73-81.

Meagher, J.F. and J. Heicklen (1979), The Photolysis of Hydrogen Peroxide in the Presence of Carbon Monoxide, J. Photochem., 3, 455-466.

Molina, L.T. and M.J. Molina (1981), UV Absorption Cross Sections of  $\text{HO}_2\text{NO}_2$  Vapor, J. Photochem., 15, 97-108.

Sridharan, U.C., B. Reimann, and F. Kaufman (1980), Kinetics of the Reaction  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ , J. Chem. Phys., 73, 1286-1293.

Wine, P.H., D.H. Semmes, and A.R. Ravishankara (1982), A Laser Flash Photolysis Kinetics Study of the Reaction  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ , J. Phys. Chem., in press.