



Kinetics of the reaction of HO2 with ozone

Mark S. Zahniser and Carleton J. Howard

Citation: The Journal of Chemical Physics **73**, 1620 (1980); doi: 10.1063/1.440343 View online: http://dx.doi.org/10.1063/1.440343 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/73/4?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Kinetic study of the reaction of HO2 with ozone J. Chem. Phys. **87**, 2122 (1987); 10.1063/1.453136

Yields of HO2 in the reaction of hydrogen atoms with ozone J. Chem. Phys. **72**, 3842 (1980); 10.1063/1.439601

Kinetics of the reaction of HO2 with NO2 J. Chem. Phys. **67**, 5258 (1977); 10.1063/1.434703

Absorption Spectrum and Reaction Kinetics of the HO2 Radical in the Gas Phase J. Chem. Phys. **56**, 4426 (1972); 10.1063/1.1677885

Kinetics of the Gas Phase Reaction between Acetylene and Ozone J. Chem. Phys. **21**, 163 (1953); 10.1063/1.1698576



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 130.209.6.50 On: Sat, 20 Dec 2014 11:04:45

Kinetics of the reaction of HO₂ with ozone

Mark S. Zahniser^{a)} and Carleton J. Howard

Aeronomy Laboratory, NOAA Environmental Research Laboratories. Boulder, Colorado 80303 (Received 29 February 1980; accepted 29 April 1980)

Rate constants were measured for the reaction $HO_2 + O_3 \rightarrow OH + 2O_2(k_1)$ using a discharge-flow system with laser magnetic resonance detection of both HO_2 and OH. k_1 was determined directly from the first order decay of HO_2 in excess O_3 when C_2F_3Cl was added to scavenge the OH product and prevent interference from the faster reaction $OH + O_3 \rightarrow HO_2 + O_2(k_2)$. The ratio k_2/k_1 was independently determined from the steady-state $[HO_2]/[OH]$ ratio obtained without C_2F_3Cl . Results from the scavenger method are given by $k_1 = (1.4\pm0.4) \times 10^{-14}$ exp $[-(580\pm100)/T]$ cm³s⁻¹ for 245 K < T < 365K. Results of the ratio measurements are in good agreement with these data when combined with a directly measured value of $k_2 = (6.5\pm1.0) \times 10^{-14}$ cm³s⁻¹ at 300 K. These measurements are compared with other studies and some implications for stratospheric ozone chemistry are discussed.

INTRODUCTION

The importance of odd hydrogen radicals in determining the concentration of stratospheric ozone was recognized first by Hampson¹ and later by Hunt² who calculated the effects of the reaction sequence

 $HO_2 + O_3 - OH + 2O_2 , \qquad (1)$

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

as a catalytic cycle removing odd oxygen in the natural stratosphere. This cycle is particularly important at altitudes below 25 km, since it does not require oxygen atoms as do similar catalytic cycles involving nitrogen oxides³ or chlorine species.⁴ The rate limiting step in this cycle is Reaction (1), and several recent studies have demonstrated the importance of k_1 in calculating ozone profiles for both the natural and perturbed stratosphere.⁵⁻⁷

Although there have been several direct measurements of k_2 , ⁸⁻¹⁰ there have been only indirect studies of k_1 . Simonaitis and Heicklen, ¹¹ DeMore and Tschuikow-Roux, ¹² and DeMore¹³ have measured the ratio $k_1/k_3^{1/2}$, where k_3 is the rate constant for the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 , \qquad (3)$$

by monitoring ozone concentrations in UV photolyzed gas mixtures.

We have used the discharge-flow technique with laser magnetic resonance (LMR) detection of OH and HO₂ to directly determine k_1 over the temperature range 245 to 365 K. The LMR technique is particularly well suited for this study since both reactant and product radicals are readily monitored. This has enabled us also to determine the ratio k_2/k_1 independently by simultaneously measuring the OH and HO₂ concentrations at steady state in the presence of excess ozone.

EXPERIMENTAL

The discharge-flow system and the LMR technique for detecting free radicals in kinetic studies have been de-scribed in detail previously.¹⁴ Several recent modifications are described below and are shown in Fig. 1.

The 2.54 cm i.d. Pyrex flow tube is double-walled along the 60 cm reaction zone to provide temperature control by circulating either dibutylphthalate (300 to 450 K) or ethanol (200 to 300 K) from a thermoregulated reservoir. This fluid is pumped rapidly so that the temperature drop along the flow tube jacket is less than 1 °C. The intersection of the flow tube and the laser tube is also jacketted to provided temperature regulation in the detection region (absorption volume). Temperature is measured in the reservoir and at three points along the flow tube by both platinum resistance thermometers and chromel-alumel thermocouples. The inner surface of the flow tube is coated with phosphoric acid or boric acid and baked under vacuum at 400 K to reduce the loss of radicals at the surface. Helium (analyzed > 99.999%) is used as a carrier gas at a total pressure between 1.5 and 4 Torr, with average linear flow velocities between 400 and 1400 cm s⁻¹.

HO₂ radicals are formed by the reaction

$$H + O_2 + M - HO_2 + M$$
, (4)

where the H atoms are generated in a microwave discharge of trace amounts of H_2 in helium. At normal flow tube pressures, this reaction is not an ideal source of HO_2 since large amounts of OH are produced in the subsequent fast reaction,

$$H + HO_2 \rightarrow 2OH$$
.

OH formation may be reduced, however, by increasing the pressure and the O₂ concentration so that nearly all the H atoms are consumed in Reaction (4). This is accomplished by placing a capillary constriction, 1 mm i.d. and 4 cm long, between the source region and the flow tube. The viscous pressure drop along this capillary is about 20 Torr with flow rates of 2 STP cm³ s⁻¹ O₂ and $0.5 \text{ STP cm}^3 \text{ s}^{-1}$ He. A constriction between the discharge region and the point of O₂ addition prevents O₂ from diffusing into the discharge region. This source provides HO₂ concentrations in the flow tube of $\simeq 10^{11}$ cm^{-3} but only negligible amounts of OH and H (< 10⁹) cm⁻³). There is sufficient residence time ($\simeq 30$ ms) in the high pressure source to assure that any excited HO₂ produced in Reaction (4) will be collisionally relaxed before entering the flow tube. The HO, source is located either on a fixed side inlet at the upstream end of the flow tube or it is affixed to the end of a moveable 7 mm

^{a)}NOAA NRC Postdoctoral Fellow, 1977 to 1979. Present address: Aerodyne Research Inc., Bedford, MA 01730.



FIG. 1. Flow tube reactor with laser magnetic resonance detection system.

i.d., 1 m long, Pyrex tube attached to the flow tube with an O-ring seal. The moveable source is used to determine directly the surface loss rate constant k_w of HO₂ radicals in the flow tube. All surfaces of the source except the discharge region are coated with phosphoric acid.

For the steady-state ratio measurements and for the $OH + O_3$ reaction measurements, OH radicals are produced by the reaction

 $H + NO_2 - OH + NO$.

The H atoms are produced by a microwave discharge or by thermal dissociation and NO₂ is added to the flow tube with the carrier gas. Alternatively, in some experiments OH is formed at the end of a moveable 9 mm o.d. injector where H is added through an inner concentric 6 mm o.d. tube and NO₂ is added through the outer tube. With $[NO_2] \simeq 5 \times 10^{12} \text{ cm}^{-3} > 50 \times [H]$, the reaction is complete in the first few centimeters of the flow tube yet only small amounts of NO are produced. Large concentrations of NO would be a serious interference in this study since the reaction

$$NO + HO_2 - OH + NO_2$$
 (5)

rapidly converts HO₂ to OH $(k_5 = 8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1})$.¹⁵ The NO₂ is purified by vacuum distillation at 196 K to obtain a white solid with NO impurity levels, <1%, as determined by direct observation with LMR in the flow tube. The helium which passes through the microwave discharge is trapped with molecular sieves at 77 K to remove any H₂O or other precursors of atomic oxygen which would react with NO₂ to produce NO. Since NO₂ is detected directly with LMR, the amount of NO produced from NO₂ by reaction with atoms or radicals produced in the discharge is also determined by observing the change in the NO₂ signal with the discharge on and off. This establishes an upper limit to the [NO] in the system of $1 \times 10^{11} \text{ cm}^{-3}$.

The 118.6 μ m line of an H₂O laser is suitable for detecting both OH and HO₂, and switching from one species to the other requires only a change in the magnetic field. The $(4_{3,1} - 5_{2,4})\Delta M_J = 0, M_J = \frac{3}{2}$ transition at 11.9 kG¹⁶ is used for HO₂ in this work since it is one of the strongest lines and is free from interference by other species, namely OH and O₂. The $(J = \frac{5}{2} - J = \frac{3}{2})\Delta M_J = 0, M_J = \frac{3}{2}$ rotational transition at 14.4 kG is used to detect OH($X^2\Pi_{3/2}$). Detection is specific for ground state transitions for both radicals.

The OH signal is calibrated by adding measured amounts of NO₂, $\simeq 10^{11}$ cm⁻³, to excess H atoms, $\simeq 10^{13}$ cm⁻³, so that [OH] formed is equal to [NO₂] added. The HO₂ signal is calibrated relative to OH by adding NO just before the detection point to convert HO₂ to OH via Reaction (5). Radical concentrations are kept low, $\simeq 10^{10}$ cm⁻³, so that secondary reactions such as OH + HO₂ \rightarrow H₂O + O₂ are negligible. The resulting detection limits with a signal to noise ratio of unity for a 1 s time constant are about 1×10^6 and 5×10^8 molecule cm⁻³ for OH and HO₂, respectively. A typical signal trace for HO₂ is shown in Fig. 2.

The end of the flow tube is positioned as close to the detection point as possible without disturbing the laser beam. The residence time of the radicals from the end of the flow tube to the detection point has been minimized by (1) minimizing the inside diameter of the laser cavity (50 mm) in the detection region and (2) adding N₂ to the laser cavity on both sides of the detection region to increase the velocity through the detection zone. The residence time in the detection region is about 5 ms for a flow tube velocity of 1000 cm s⁻¹.

Ozone is added to the flow tube either through a fixed





100 G

inlet at the upstream end of the reaction zone or through the moveable reactant tube so that the injection point may be varied from 3 to 50 cm upstream of the detection point. Ozone concentrations, 10^{14} to 10^{16} cm⁻³, are small compared to the helium carrier gas, 5×10^{16} to 10^{17} cm⁻³, but much larger than the radical concentrations, $< 10^{11}$ cm⁻³, so that the kinetics are pseudo-firstorder.

Ozone is generated by flowing O_2 (> 99.95% purity) through an ac discharge at atmospheric pressure and collected on silica gel at 150 K. After pumping off the O_2 at 196 K, the ozone is eluted into the flow tube with helium. The elution rate is controlled by varying both the helium flow rate and the temperature of the trap. The ozone flow rate is determined by UV absorption at 253.7 nm in a 1.04 cm path cell. The partial pressure of O3 is calculated using Beer's law and the absorption cross section of $1.15 \times 10^{-17} \text{ cm}^2$ measured by DeMore and Raper.¹⁷ The total pressure in the cell, 5-15 Torr, is measured with a capacitance manometer. The cell temperature, which is about 5°C above room temperature due to heating by the mercury pen lamp, is measured in the gas with a platinum resistance thermometer. The ozone is purified before each use by pumping on the silica gel until the O_3 pressure determined by UV absorption agrees within 1% with the total pressure in the cell. Thermal decomposition of O_3 in the stainless steel tubing or in the flow tube is negligible. This is verified by sampling the flow tube gas downstream of the reaction zone through a second UV absorption cell with a 30 cm path length. The two measurements agree within 3%for flow tube temperatures from 220 to 450 K.

RESULTS

A. Direct measurement for k_1

There is no significant change in $[HO_2]$ when O_3 is added, although the formation of a small amount of OH



FIG. 3. First-order decay plots for HO₂+O₃. Conditions are (concentrations in units of 10^{15} cm⁻³): (a) T = 245 K, $\overline{v} = 410$ cm s⁻¹, [O₃] = 16.1, [C₂F₃Cl] = 5.0, [O₂] = 31.7, [He] = 33.6; (b) T = 343 K, $\overline{v} = 503$ cm s⁻¹, [O₃] = 3.9, [C₂F₃Cl] = 4.0, [O₂] = 23.0, [He] = 24.3. Square symbols at the top of each figure are same conditions except [O₃] = 0. First order rate constants are indicated on each line.



FIG. 4. First order rate constants for Reaction (1) vs $[O_3]$. Lines are linear least squares fits.

product is observed. This indicates that the radicals are in steady state whereby HO₂ is regenerated by Reaction (2) as rapidly as it is removed in Reaction (1). The decay of HO₂ due to Reaction (1) is observed only when an OH scavenger, trifluorochloroethylene, is added to the system. C₂F₃Cl reacts rapidly with OH with a rate constant¹⁸ of 6×10^{-12} cm³s⁻¹ but negligibly with HO₂ at the concentrations used, $\simeq 5 \times 10^{15}$ cm⁻³.

Sample first-order HO₂ decay plots are shown in Fig. 3. In these experiments HO₂ is added through the moveable inlet while O₃ and C₂F₃Cl are added through fixed inlets at the upstream end of the reaction zone. Linearity over nearly a factor of 10 in [HO₂] decay indicates that the OH product is effectively removed by the scavenger. This is confirmed by the direct observation of [OH] $< 10^7$ cm⁻³ under these conditions. The slopes of the plots in Fig. 3(b) are constant over a factor of 15 change in initial [HO₂] indicating that there are no secondary reactions of the OH + C₂F₃Cl reaction product with HO₂.

The data indicated by square symbols in Fig. 3 are obtained when no O_3 is added. These give a direct measurement of the wall loss of HO₂ and indicate that the reaction HO₂ + C₂F₃Cl is negligible. The first-order wall rate constant k_w increases with decreasing temperature from 0.5 s⁻¹ at 360 K to 2.5 s⁻¹ at 245 K. Below 240 K it increases rapidly to >10 s⁻¹. k_w is measured in the presence C₂F₃Cl after each run and subtracted from the total first-order decay to obtain $k_1^I = k_{tot}^I - k_w$. Note that this analysis method differs from that for the fixed radical source-variable reactant inlet configuration in which the wall loss term does not enter explicitly into the data analysis.¹⁹

The bimolecular rate constant k_1 is obtained from the slope of a plot of k_1^I versus $[O_3]$ as shown in Fig. 4. Each plot is linear for $[O_3]$ variations of about a factor of 7 and has a negligible intercept. The results are summarized in Table I. The error limits are experimental precision, 2σ limits. When combined with estimates of systematic errors, the overall uncertainty at each temperature is $\pm 20\%$.

The addition of C_2F_3Cl creates several possibilities for interference which must be considered: (1) The re-

TABLE I. Results for the reaction $HO_2 + O_3 \rightarrow OH + 2O_2$.

<i>T</i> (K)	Number of experiments	[O ₃] range (10 ¹⁵ cm ⁻³)	k_1^a (10 ⁻¹⁵ cm ³ s ⁻¹)		
245	11	2.4-15	1.38 ± 0.08		
267	12	2.6-9.9	1.47 ± 0.20		
298	48	1.4 - 10.0	1.98 ± 0.22		
345	19	1.7 - 11.6	2.74 ± 0.24		
365	15	1.4 - 10.5	2.74 ± 0.18		

^aErrors are 2σ from linear least-squares slopes of k_1^f vs $[O_3]$ plots.

action of C₂F₃Cl with HO₂ is measured directly and found to be negligible. Even at 400 K there is no noticeable decay of HO₂ for $[C_2F_3C1] = 6 \times 10^{15} \text{ cm}^{-3}$. This gives an upper limit for $k (HO_2 + C_2F_3Cl) < 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. (2) The possibility of a secondary reaction between the products from the $C_2F_3Cl + OH$ reaction and HO_2 may be discounted due to the low radical concentrations employed and the invariance of the observed rate constant with initial $[HO_2]$ as in Fig. 3(b). (3) The possibility that products of the $C_2F_3Cl + OH$ reaction could react with O_3 to reform HO_2 is unlikely since it would result in HO2 first-order decay plot curvature which is not observed. (4) The possibility that HO_2 reacts with a product of a $C_2F_3Cl + O_3$ reaction is unlikely over the temperature range of this study, since there is no dependence of the second order rate constant on $[O_3]$ as is indicated by linearity of the plots in Fig. 4. As a further test, $[C_2F_3C_1]$ is varied for a constant $[O_3]$ as shown in Fig. 5. For temperatures less than 360 K the rate constant k_1 is independent of $[C_2F_3C1]$ above a minimum concentration necessary to remove OH. For temperatures greater than 400 K, however, k_1 increases with $[C_2F_3Cl]$. This increase is believed to be due to HO, removal by a product of a strongly temperature dependent ozone- C_2F_3Cl reaction. No data are used for T > 360 K.

The measured values of k_1 are plotted in Arrhenius form in Fig. 6. The temperature range, 245 to 360 K,



FIG. 5. Dependence of k_1 on $[C_2F_3Cl]$. Solid lines are least squares fits. Slopes are not significantly different from zero except at 407 K. The observed rate constant goes to zero when $[C_2F_3Cl] = 0$ as indicated by dashed line at 345 K.



FIG. 6. Arrhenius plot for k_1 . Our data from Table I(0) is shown with error bars. Comparison is made with ratio measurements of Simonaitis and Heicklen (Ref. 11), DeMore, and Tschuikow-Roux (Ref. 12) and DeMore (Ref. 13) where the solid lines are based on a temperature independent $k_3 = 3 \times 10^{-12}$ cm³ s⁻¹ and the dashed lines are based on the temperature dependent value for k_3 of Cox and Burrows (Ref. 22). Also shown is the upper limit of Anderson and Kaufman (Ref. 8).

is limited on the higher end by interference from the $C_2F_3Cl + O_3$ reaction and on the lower end by the large surface loss of HO₂. A least squares fit to the data gives

$$k_1 = (1.4 \pm 0.4) \times 10^{-14} \exp[-(580 \pm 100)/T] \text{ cm}^3 \text{ s}^-$$

where the values for k_1 are weighted according to the number of experiments at each temperature. The error limits include estimates of systematic errors and are larger than the statistical uncertainties which are $\simeq 4\%$ based on 103 degrees of freedom.

B. The ratio k_2/k_1

Measurements of [OH] and $[HO_2]$ at steady state give an independent determination of the ratio of rate constants for Reactions (1) and (2). The approach to steady state is shown in Fig. 7. In this experiment OH is added through the moveable inlet. At longer reaction times the production and removal rates for OH and HO₂ are equal and the rate constant ratio is given,

$$k_2/k_1 = [HO_2]/[OH]$$
.

This analysis assumes that there are no other loss processes for the radicals. The wall loss for HO₂ is small, $k_w < 2 \, \mathrm{s}^{-1}$, for $T \ge 300 \, \mathrm{K}$. The loss of HO_x = OH + HO₂ due to the larger OH wall reaction, $k_w(OH) = 15 \, \mathrm{s}^{-1}$, is insignificant since at steady state more than 97% of the HO_x radicals are in the form of HO₂. This is shown in Fig. 7, where there is no decline of either [OH] or [HO₂] at steady state. The effects of wall loss on the ratio values have been tested by a computer simulation of the Reactions (1) and (2) with first-order losses of OH and HO₂. The input ratio k_2/k_1 is compared to the computed values of $[HO_2]/[OH]$ at steady state for different combinations of [O₃], $k_w(OH)$, and $k_w(HO_2)$. Under

1623



FIG. 7. Decay of OH and formation of HO₂ showing approach to steady state. OH is formed in a moveable injector source from H+NO₂. Conditions are T = 368 K, $\overline{v} = 880$ cm s⁻¹, [He] = 4. 3×10^{16} cm⁻³ and [O₃] = 1.0 \times 10^{15} cm⁻³. Dashed curves are calculated using $k_2 = 1.45 \times 10^{-13}$ cm³ s⁻¹, $k_1 = 3.4 \times 10^{-15}$ cm³ s⁻¹, k_w (OH) = 17 s⁻¹ and k_w (HO₂) = 0. The negative distance corresponds to reaction in the laser cavity and is equivalent to 8 cm of flow tube distance.

the conditions of our experiments where $k_2[O_3] \gg k_w(OH)$, errors due to wall losses in determining k_2/k_1 are <10%.

The steady-state $[HO_2]/[OH]$ ratios are measured by starting with either OH or HO₂ radicals. HO₂ is formed by the fixed H + O₂ + M source described previously and OH is formed by the reactions of H with either NO₂ or O₃. Measurements are always taken under conditions of sufficient O₃ and reaction time to reach steady state as determined by the criterion $(k_1 + k_2)[O_3]z/\bar{v} > 4$, where z is the reaction distance and \bar{v} is the flow velocity.

Results of these ratio measurements are summarized in Table II. The relatively large scatter in these values is somewhat surprising, since in principle one should be able to measure the ratio with better precision than either of the individual rate constants due to cancellation of most experimental parameters. The ratio measurements, however, depend on an absolute calibration of the LMR detection ratio for OH and HO_2 which is a sensitive function of magnetic field modulation amplitude and line pressure broadening. These effects cause an additional uncertainty in the ratio measurements even though the sensitivity calibrations are made under conditions matching the ratio measurements as closely as possible.

It is possible that there is interference in the ratio measurements from vibrationally excited OH or HO₂. Excited states produced initially in the radical formation reactions are quenched by wall collisions as is indicated by observing the same $[HO_2]/[OH]$ ratio with either $H + O_3$ or $H + NO_2$ as the OH source: the former produces vibrationally excited OH up to v = 9. However, both Reactions (1) and (2) are sufficiently exothermic, $-\Delta H = 25$ and 43 kcal/mol, respectively, to produce vibrationally excited OH and HO_2 . Rate constants for $OH(v \ge 0) + O_3$ are 10 to 100 times faster^{20,21} than for v = 0 and at large $[O_3]$ these rates are faster than deactivation by wall collisions, especially in the large diameter detection region. With $[O_3] > 10^{16} \text{ cm}^{-3}$ we observe an increase of 10% to 20% in $[HO_2]/[OH]$ and a decrease in the observed LMR signals for both OH and HO₂. However, this effect cannot be ascribed unambiguously to the formation of undetected vibrationally excited species, since the detection sensitivity may be affected by pressure broadening due to high O_3 concentrations.

To obtain k_1 from the ratio measurements, we have measured k_2 directly at 300 K from the first order decay of OH, formed by H + NO₂, when O₃ is added through the moveable injector. Only the initial slopes, [OH]/ [OH]₀>0.2, are used so that interference from Reaction (1) is negligible. First-order rate constants are plotted versus [O₃] in Fig. 8. The slope of this plot gives k_2 = (6.5±1.0)×10⁻¹⁴ cm³ s⁻¹ where the error limit includes an estimate of systematic errors.

Combining this value for k_2 with the average of 12

TABLE II. $k_2/$	'k ₁ ratio	measurements.
------------------	-----------------------	---------------

1.

Т (К)	Radical generation method	O ₃ (10 ¹⁵ cm ⁻³)	<i>z</i> (cm)	<i>v</i> (cm s ⁻¹)	Measured steady state [HO ₂]/[OH] ^ª	Calculated ^b k_2/k_1
300	$H + O_2 + M$	2 – 5	70	800	30 ± 5	
	$H + NO_2$	3 - 8	40	530	38 ± 5	32
H+O	$H + O_3$	5	40	400	37 ± 10	
368	$H + NO_2$	1	50	880	47 ± 7	40
373	$H + NO_2$	2	40	1260	60 ± 10	41
423	$H + NO_2$	1.3	40	1410	63 ± 10	46

^aRatios are based on measured HO₂ and OH signals and calculated for a detector response ratio $R_{OH}/R_{HO_2} = 650 \pm 100$. Errors represent the range from the median of several measurements.

^bThese ratios are calculated assuming $k_1 = 1.4 \times 10^{-14} \exp(-580/T) \text{ cm}^3 \text{ s}^{-1}$ (this work), k_2

=6.5×10⁻¹⁴ cm³ s⁻¹ at 300 K (this work), and $k_2 \propto \exp\{-950/T\}$ (Refs. 8 and 10).



FIG. 8. Plot of first order rate constants vs $[O_3]$ for the reaction OH+O₃ \rightarrow HO₂+O₂ at T=300 K.

ratio measurements gives $k_1 = (1.8 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 300 K which is in agreement with the directly measured value for k_1 using the OH scavenger method. Agreement is less satisfactory between the steady state ratios of $[HO_2]/[OH]$ and the directly measured values of k_2 and k_1 over the temperature range 368 to 423 K as shown in Table II, where the values for k_2 are obtained by combining the room temperature measurement from this study with the temperature dependence obtained by Anderson and Kaufman⁸ and Ravishankara et al.¹⁰ $[\exp(-950/T)]$. The direct measurement of Ravishankara et al. $(k_2 = 1.8 \times 10^{-12} \exp(-930/T) \text{ cm}^3 \text{ s}^{-1}$ for 238 < T < 357 K) gives better agreement with the observed ratios at high temperatures but gives poor agreement at 300 K. Our preliminary study of the temperature dependence of k_2 for the range $210 \le T \le 423$ K gives a curved Arrhenius plot with $k_2 \propto T^4$. Values of the ratio k_2/k_1 calculated with these data give good agreement with the directly measured values shown in Table II.

DISCUSSION

Results for k_1 are compared in Table III and Fig. 6 with O₃ photolysis studies which determine the ratio $k_1/k_3^{1/2}$, where k_3 is the rate constant for the HO₂ + HO₂

reaction. The values of Simonaitis and Heicklen¹¹ and DeMore and Tschuikow-Roux¹² are a factor of 2 less than this study at 300 K and have a much greater temperature dependence when combined with a temperature independent value of $k_3 = 3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Recent measurements by Cox and Burrows²² of k_3 at atmospheric pressure give a negative temperature dependence, $k_3 = 3.8 \times 10^{-14}$ $\times \exp(+1250/T)$ cm³s⁻¹, which brings the ratio measurements into better agreement with this study. Cox and Burrows²² also observe an increase of k_3 upon addition of water vapor. This increase is greater at lower temperatures and would have the effect of further decreasing the temperature dependence for k_1 from the DeMore and Tschuikow-Roux study in which H₂O was present. DeMore¹³ has recently repeated these ratio measurements using a smaller photolysis cell with more uniform light absorption and with $H_2/O_2/O_3$ rather than H_2O/O_2 mixtures. These results, when combined with k_3 from the Cox and Burrows study, are in excellent agreement with our direct measurements for both the activation energy and the A factor. The agreement implies there is no change in k_1 with pressure from 2 Torr of this study to one atmosphere of the DeMore¹³ and Cox and Burrows²² measurements.

The A factor for k_1 is anomalously low for a simple atom transfer mechanism. One possible explanation is a tight, low entropy, transition state. The A factor may be estimated from transition state theory using the group additivity methods of Benson²³ to obtain the standard entropy of the transition state S^{\ddagger} . This gives $A = (e^{2}kT/$ h) $\exp(\Delta S^{\ddagger}/R) = 4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for the open chain H-O₅ complex, which is a factor of 30 greater than the experimental value. Going from this structure to a six-member ring converts three internal rotations into three low frequency ring distortion modes. Assuming frequencies of about 200 cm⁻¹ for the latter, ring closure lowers S⁷ by $\simeq 9$ eu which decreases A by a factor of $\simeq 80$. Unfortunately, there is no independent evidence that indicates whether such a restrictive geometry is indeed a realistic picture of the transition state. A similar anomaly is found for the OH + HNO₃ reaction, where $A = 9 \times 10^{-14}$ $cm^{3}s^{-1}.^{24}$

The value for k_2 is compared with previous measurements in Table IV. At 300 K the value from this study is $\simeq 20\%$ less than that of Ravishankara *et al.*¹⁰ but $\simeq 20\%$ greater than that of Anderson and Kaufman.⁸ The

TABLE III. C	comparison of rate	constants and Arrhenius	parameters for HO	$y_2 + 0_2$	3-→OH + 2O2	2.
--------------	--------------------	-------------------------	-------------------	-------------	-------------	----

Reference	Method	T range (K)	$A (10^{-14} \text{ cm}^3 \text{ s}^{-1})$	<i>E /R</i> (K)	$k_1(300 \text{ K})$ (10 ⁻¹⁵ cm ³ s ⁻¹)
This work	DF-LMR	245-365	1.4	580	2.0
Simonaitis and Heicklen ¹¹	H ₂ /O ₂ /O ₃ photolysis ^a	225-298	0.4 (3.3)	380(1000)	1.0(1.1)
DeMore and Tschuikow-Roux ¹²	H_2O/O_2 photolysis ^a	273-342	2.1(20)	940(1560)	0.9(1.1)
DeMore ¹³	$H_2/O_2/O_3$ photolysis ^a	230-334	1.2(11)	600(1220)	1.7(1.9)

^aAuthors measure the ratio $k_1/(k_3)^{1/2}$. Values for k_1 are based on $k_3 = 3.8 \times 10^{-14} \exp(+1250/T) \text{ cm}^3 \text{ s}^{-1}$ of Cox and Burrows.²² Values in parentheses are for a temperature independent $k_3 = 3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

J. Chem. Phys., Vol. 73, No. 4, 15 August 1980

Reference	Method ²	T range (K)	A (10 ⁻¹² cm ³ s ⁻¹)	<i>E /R</i> (K)	$k_2 (300 \text{ K})$ (10 ⁻¹⁴ cm ³ s ⁻¹)
This work	DF-LMR				6.5
Ravishankara <i>et al</i> . ¹⁰	FP-RF	238-357	1.8	930	8.2
Chang and Kaufman ²⁶	DF-RF	295			6-6.5
DeMore ^{27(b)}	Steady- state ratio	271-333	4.5	1230	7.4
Kurylo ^{9 (c)}	FP-RF	298			6.1
Anderson and Kaufman ^{8(c)}	DF-RF	220-450	1.2	950	5.2

TABLE IV. Comparison of rate constants and Arrhenius parameters for $OH + O_3 \rightarrow HO_2 + O_2$.

^aDF, discharge flow; FP, flash photolysis, RF, resonance fluorescence, LMR, laser magnetic resonance.

^bBased on $k(OH + CO) = 2.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (Ref. 27) assumed to be temperature independent.

^cValues decreased by 8% due to correction in O₃ absorption measurements as noted in Ref. 25.

latter value and that of Kurylo⁹ have been decreased by 8% due to a correction in the O₃ absorption measurements.²⁵ In the Anderson and Kaufman study it is possible that NO concentrations, produced by the OH source reaction, were sufficiently large to cause an underestimation of k_2 due to NO + HO₂ (Reaction 5). Although they estimated the effect of this reaction to be negligible, its rate constant, k_5 , has subsequently been found to be much faster than previous measurements indicated.¹⁵ Chang and Kaufman²⁶ recently reported discharge flowresonance fluorescence measurements of k_2 in the range $(6-6.5) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. The relative rate measurement of k_2 by DeMore²⁷ is in agreement with the direct studies if the pressure dependence of the reference reaction is considered, $k(OH + CO) = 2.7 \times 10^{-13}$ cm³s⁻¹ at 730 Torr with O₂ present, as reported by Biermann et al.²⁸

The value for k_1 in this study is a factor of 5 times greater at 220 K than previous values used in modeling calculations for atmospheric chemistry.²⁹ This decreases the calculated stratospheric O₃ column density below 25 km since Reaction (1) is the rate limiting step in the HO, catalytic cycle, Reactions (1) and (2). The larger rate constant also shifts the calculated $HO_x (= HO_2)$ +OH) balance towards larger [OH] in the lower stratosphere. This decreases the effectiveness of the NO_x catalytic cycle for O3 removal since OH provides the major sink for NO_x via reaction with NO_2 to form HNO_3 . The effect is the opposite for O_3 destruction by ClO_x since the reaction of OH with HCl produces catalytically active Cl atoms which results in a larger calculated decrease in O₃ due to stratospheric injections of chlorine containing compounds.

ACKNOWLEDGMENT

This work was supported in part by the Chemical Manufacturers Association Technical Panel on Fluorocarbon Research.

- ¹J. Hampson, Tech Note 1627/64, Canadian Armament Research Development Establishment, 1964).
- ²B. G. Hunt, J. Geophys. Res. 71, 1385 (1966).
- ³P. J. Crutzen, Quart. J. Roy. Met. Soc. 96, 320 (1970); H.
- S. Johnston, Science 173, 517 (1971).

- ⁴R. S. Stolarski and R. J. Cicerone, Can. J. Chem. 52, 1610 (1974); M. J. Molina and F. S. Rowland, Nature (London) 249, 810 (1974).
- ⁵W. H. Duewer, D. J. Wuebbles, H. W. Ellsaesser, and J. S. Chang, J. Geophys. Res. 82, 935 (1977).
- ⁶P. J. Crutzen and C. J. Howard, Pure Appl. Geophys. 116, 497 (1978).
- ⁷R. C. Whitten, W. J. Borucki, L. A. Capone, and R. P. Turco, Nature (London) **275**, 523 (1978); R. P. Turco, R. C. Whitten, I. G. Poppoff, and L. A. Capone, *ibid.* **276**, 805 (1978).
- ⁸J. G. Anderson and F. Kaufman, Chem. Phys. Lett. 19, 483 (1973).
- ⁹M. J. Kurylo, Chem. Phys. Lett. 23, 467 (1973).
- ¹⁰A. R. Ravishankara, P. H. Wine, and A. O. Langford, J. Chem. Phys. 70, 984 (1979).
- ¹¹R. Simonaitis and J. Heicklen, J. Phys. Chem. 77, 1932 (1973).
- ¹²W. B. De More and E. Tschuikow-Roux, J. Phys. Chem. 78, 1447 (1974).
- ¹³W. B. DeMore, J. Phys. Chem. 83, 1113 (1979).
- ¹⁴C. J. Howard and K. M. Evenson, J. Chem. Phys. 61, 1943 (1974).
- ¹⁵C. J. Howard, J. Chem. Phys. 71, 2352 (1979).
- $^{16}\mbox{J.}$ T. Hougen, H. E. Radford, K. M. Evenson, and C. J.
- Howard, J. Mol. Spectrosc. 56, 210 (1975).
- ¹⁷W. B. DeMore and O. Raper, J. Phys. Chem. 68, 412 (1964).
- ¹⁸C. J. Howard, J. Chem. Phys. 65, 4771 (1976).
- ¹⁹A. A. Westenberg and N. deHaas, J. Chem. Phys. **46**, 490 (1967).
- ²⁰G. E. Streit and H. S. Johnston, J. Chem. Phys. 64, 95 (1976).
- ²¹R. N. Coltharp, S. D. Worley, and A. E. Potter, Appl. Opt. **10**, 1786 (1971).
- ²²R. A. Cox and J. P. Burrows, J. Phys. Chem. 83, 2560 (1979).
- ²³S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976), pp. 26-28.
- ²⁴J. J. Margitan, F. Kaufman, and J. G. Anderson, Int. J. Chem. Kinetics, Symposium 1, 281 (1975).
- ²⁵R. F. Hampton, Jr. and D. Garvin, Eds., Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977, Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).
- ²⁶J. S. Chang and F. Kaufman, J. Phys. Chem. 82, 1683 (1978).
- ²⁷W. B. DeMore, Int. J. Chem. Kinet., Symposium 1, 273 (1975).
- ²⁸H. W. Biermann, C. Zetzsch, and F. Stuhl, Ber. Bunsenges. Phys. Chem. 82, 633 (1978).
- ²⁹R. D. Hudson, Ed., Chlorofluoromethanes and the Stratosphere, NASA Reference Publication 1010 (1977).

J. Chem. Phys., Vol. 73, No. 4, 15 August 1980