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The rate constant for the reaction $OH + ClO \rightarrow Products$ (1) was measured in a discharge flow tube under pseudo-first order conditions in OH. OH was monitored via the resonance fluorescence detection scheme. The measurements were made at low pressures (~1 Torr) and at temperatures between 248 and 335 K. The measured rate coefficients, corrected for the interference due to OH regeneration via the reaction $Cl + HO_2 \rightarrow OH + ClO$, were found to be nearly temperature independent with a mean value of $(1.17 \pm 0.33) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

INTRODUCTION

OH and ClO are two very important radical species in the stratosphere. OH engages in many ozone destruction cycles as well as reactions which convert inactive species to active species (for example, $OH + HCl - H_2O$ + Cl) and active species into inactive or less active species (for example, $OH + NO_2 + M - HNO_3 + M$ and $OH + HO_2 - H_2O + O_2$). Similarly, ClO engages in ozone destruction cycles as well as other reactions which control the concentration of many reactive radical species. The reaction of OH with ClO,

$$OH + CIO - HO_2 + CI$$
(1a)

$$- HCl + O_2$$
, (1b)

is of interest since this reaction has the potential for being a sink for both OH and ClO, if the branching ratio for reaction (1b) is large. Furthermore, predicted ratios of HO₂ to OH and ClO to Cl depend upon both the rate constant and branching ratio for reaction (1). Since calculated stratospheric ozone perturbations depend upon both $[HO_2]/[OH]$ and [ClO]/[Cl], it is important to characterize reaction (1) as completely as possible.

Leu and Lin¹ measured the net rate coefficient $k_1 = k_{1a} + k_{1b}$ at 298 K to be $(9.1 \pm 1.3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ using a discharge flow tube. In addition, they estimate the upper limit for the branching ratio k_{1b}/k_1 to be 35%. To verify the results of Leu and Lin at 298 K and to obtain the value of k_1 at stratospheric temperatures, we have measured k_1 as a function of temperature using a discharge flow—OH resonance fluorescence apparatus. The results of this investigation are presented here.

EXPERIMENTAL

A discharge flow apparatus shown in Fig. 1 was used to study the kinetics of reaction (1). The concentration of OH was monitored as a function of reaction time in excess ClO using resonance fluorescence detection. Since this condition ensured pseudo-first order kinetics in OH, the only species whose absolute concentration had to be known was ClO. The ClO concentration was assumed to be equal to the measured concentration of O₃ added to an excess of Cl atoms since reaction with Cl rapidly and quantitatively converts O₃ to ClO. ClO was introduced into a flow tube (1 in. i.d.) via a (3/8 in. o.d.) movable injector while OH was prepared in the main body of the flow tube via the standard technique of H atom titration with NO_2 :

 $H + NO_2 \rightarrow OH + NO$. (2)

H atoms were produced via a microwave discharge of a small amount of H_2 in He. The flow tube was coated with halocarbon wax to decrease the wall loss of OH.

The detector section of the flow tube consisted of a 2, 6 cm diameter brass tube whose inside was coated with FEP teflon and overcoated with halocarbon wax. This tube was connected to the glass flow tube using Viton o rings on one side and to a pump through a large glass trap on the other side. A thermocouple could be introduced from the pump end of the detector section into the flow tube such that the gas temperature in the flow tube could be directly measured. The detector section had eight ports, two sets of four each. The first set of four was used for resonance fluorescence detection of OH. The output of OH resonance lamp was collimated by a series of apertures and then focused onto the opposite exit port into a light trap. The resonance fluorescence emission was collected at 90° to the incident beam by a 1 in. focal length quartz lens and then focused on to the photocathode of a photomultiplier tube (RCA 8850). A bandpass filter (center wavelength-309 nm, FWHM-10 nm) and a stack of UV broad band filters (7-54) were placed between the PM tube and the lens to isolate emission due to OH $[A^2\Sigma(v=0) - X^2\Pi(v=0)]$. The output of the photomultiplier tube was amplified and counted using a pulse counter. In preliminary experiments, it was determined that $\sim 5 \times 10^8$ OH/cm³ could be detected with a S/N = 1 for a 1s integration. The second set of ports were used for monitoring Cl atoms via the chemiluminescent recombination reaction

$$Cl + Cl - Cl_2 + h\nu(\lambda > 500 \text{ nm})$$
 (3)

The chemiluminescence was monitored using a red sensitive PM tube (Hamamatsu R928P) and a broadband red filter (OG-610). The output of the PM tube was measured by an electrometer.

All gas flows were controlled by needle values and measured using calibrated mass flow meters. The diluent was added upstream of all other inlets in the flow tube. The pressure in the flow tube was measured in two places, upstream near the OH production region



FIG. 1. Schematic diagram of the discharge flow-OH resonance fluorescence apparatus. PM1, F1, and F2 combination was used for OH detection. PM2 and F3 combination was used for Cl atom detection.

and downstream near the detector. There was very little difference in pressure between the two ports. All concentrations were calculated based on the measured mass flow rates, pressure in the flow tube, and the known concentrations in the source mixtures. The concentrations of O_3 and NO_2 in the source mixtures were measured by absorption at 253.7 and 365 nm, respectively. These concentrations were known to better than 5% accuracy. The Cl₂ source mixture was prepared manometrically while a 0.1% H₂/He mixture was purchased from Matheson gas products and used as supplied.

All gases except O_3 were obtained from Matheson gas products and had the following stated purity levels: He>99.9995%, Cl₂>99.96%, H₂>99.9995%, NO₂>99.5%. O₃ was prepared by using an ozonizer and stored on silica gel at 197 K. Before use, O₃ was liquified in a bulb at 77 K and all O₂ pumped out. NO₂ was mixed with excess high purity O₂ to convert NO into NO₂ and then O₂ was pumped away while freezing NO₂ at 197 K. Cl₂ was degassed before use.

The discharge flow tube was tightly wrapped with copper tubing and then covered with thermally insulating material. By circulating hot or cold fluids from temperature controlled baths through the copper coils, the temperature in the flow tube was controlled to within ± 1 K. The temperature of the gas in the flow tube was measured just before and just after the experiments. The detector section was always maintained at room temperature.

Since the flow tube apparatus was newly assembled and "untested," we used it to measure the well known rate coefficient² for the reaction

$$OH + HC1 \xrightarrow{R_4} H_2O + C1 . \tag{4}$$

Our measured value of k_4 agreed with the evaluated results² to within 10% at both 298 (7.1×10⁻¹³ cm³ molecule⁻¹ s⁻¹) and 248 K (5.1×10⁻¹³ cm^3 molecule⁻¹ s⁻¹). This close agreement suggests the lack of any major systematic errors in the apparatus.

Before investigating the reaction of OH with ClO, it was necessary to measure the rate coefficients for the reactions of OH with Cl_2 and Cl:

$$OH + Cl_2 \rightarrow Products$$
, (5)

$$QH + Cl \rightarrow Products$$
, (6)

since both of these species were present in great excess over ClO. Reactions (5) and (6) were studied under pseudo-first order conditions with Cl₂ or Cl in excess over OH. The experimental procedure employed to carry out the measurements was the same as that for reaction (1) and is described below. It was found that k_5 was ~ 7. 4×10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ while $k_6 < 5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. In the case of k_6 , the absolute concentration of Cl atoms was not known accurately and the quoted upper limit is an estimate. Our value of k_5 compares very well with the value $(5.5 \pm 0.3) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, measured by Leu and Lin.¹

The experimental procedure employed to study reaction (1) was as follows: the flow tube was conditioned by flowing OH through it for approximately 10 min before measurements were made. The background resonance counts were obtained by turning off the H atom discharge and compared with the signal obtained when H atom source was on and NO_2 not added to the tube. It was found that small amounts (~1% of the total) OH were produced even in the absence of added NO, due to either the discharge source or the reaction of H atoms with the walls. Once the background counts were measured, $\sim 5-10 \times 10^{10}$ OH cm⁻³ was generated and the signal measured. Then Cl₂ was added to the flow tube and the microwave discharge was turned on to convert Cl₂ to Cl atoms. As mentioned above, the OH signal was not reduced due to reaction with either Cl or Cl₂. A known concentration of O_3 was added to the stream of Cl atoms, all the while making sure that there was an excess of Cl

atoms as indicated by the chemiluminescence signal. The distance between the point of O₃ addition to Cl atoms and to the end of the injector was ~ 1 m, which ensured both complete conversion of O_3 to Cl and the thermalization of ClO. The decrease in OH signal due to reaction with ClO was then measured. Following this measurement, the ClO concentration was changed by altering the O_3 concentration, and the OH signal was remeasured. Typically five O_3 concentrations (i.e., ClO concentrations) were employed. Finally, the OH source was turned off to remeasure background. Following these measurements, the injector was moved to a different position and the whole experiment repeated. Usually, five injector positions (i.e., reaction times) were employed to span at least two 1/e times. In all these experiments the loss in ClO due to the reaction ClO + ClO - products was less than 3% and hence essentially constant. It is expected that there would be no other loss process for ClO in our system. During all measurements, care was taken to maintain constant pressure and constant flow velocity. The flow velocity was in the range ~ 1300-1700 cm s⁻¹ in all experiments.

RESULTS AND DISCUSSION

As mentioned earlier, all kinetics experiments were carried out under pseudo-first order conditions with [ClO] in excess over [OH]. Therefore, [OH] should follow simple first order kinetics, i.e.,

$$[OH]_t = [OH]_0 \exp(-k_t [ClO]t) , \qquad (I)$$

where $t = d/\overline{v}$, d is the distance from the tip of the injector to the detector, \overline{v} is the linear gas flow velocity in the tube, and $[OH]_0$ is the concentration of OH in the absence of ClO (and the presence of Cl₂). Equation (I) can be rearranged to yield



FIG. 2. Plot of $\ln[OH]_0/[OH]$ vs [CIO] at one value of d, the distance of the CIO injector tip from the detection zone. The circles are the measured values. The triangles were obtained by correcting the measured data using the procedure described in the text for the interference due to reaction (7).



FIG. 3. Plot of ln[OH] vs d at one value of [ClO]. The circles are measured values. The triangles were obtained by correcting the measured data using the procedure described in the text for the interference due to reaction (7). The slope of the plots yield k' values.

$$\ln \frac{[OH]_0}{[OH]} = k_0 [CIO] d/\bar{v} . \tag{II}$$

Figure 2 shows a plot of $\ln[OH]_0/[OH]$ vs [CIO] at a fixed value of d and \overline{v} ; the plot is linear. \overline{v} was calculated from the net mass flow of gases through the tube, the pressure in the tube, and the area of cross section of the tube. Since [ClO] was known, k_1 could be calculated from the plot in Fig. 1. Such measurements were carried out at various values of d. Alternatively, at a fixed concentration of ClO, the concentrations of detected OH at various reaction times, i.e., at various values of d at a fixed \bar{v} , were measured. One such plot is shown in Fig. 3. The slope of the line gives the pseudo-first order rate constant $k' = k_i[ClO]$. Values of k' at various values of [CIO] were measured and then k' vs [CIO] plots (such as the one shown in Fig. 4) were generated. k_1 values were obtained from the slopes of these plots. In the absence of ClO, k' should be zero. However, we measured a negative value $\sim -2 \text{ s}^{-1}$. This is interpreted to represent the increased wall loss as the injector was thrust farther into the flow tube. It was found that the value of k_1 obtained by this method agreed well with that calculated at fixed values of d. However, since the wall loss on the injector could be varying to some degree, we preferred using the method of fixed d. All the values reported here were calculated by this method.

 k_1 was measured at five temperatures ranging from



FIG. 4. Plot of k' vs [ClO]. k' values were obtained from plots such as those in Fig. 3. The circles and triangles have the same meaning as in Figs. 2 and 3. The slope of the plots yields k_1 values.

248 to 335 K. The obtained values, along with the overall error limits (95% confidence limit including random errors and estimates of systematic errors), are shown in Table I. The usual testing for the presence of complicating secondary reactions, variations of $[OH]_0$, \overline{v} , $[Cl]_0$, and pressure (1.0 to 4 Torr), were carried out and found to have no effect on the measured value of k_1 . This invariance was interpreted to mean that no secondary reactions were affecting our measured value of k_1 , since HO₂, the reaction product, was expected to be quickly converted to nonreactive HCl via the reaction³⁻⁶

$$Cl + HO_2 - HCl + O_2 . \tag{7}$$

In fact, the choice of this particular chemical system was due to its simplicity and the fact that CIO concentration need not be directly measured. However, it has been recently discovered⁷ that reaction (7) has multiple product channels, i.e.,

$$Cl + HO_2 - HCl + O_2$$
(7a)

$$\rightarrow$$
 OH + ClO . (7b)

The effect of reaction (7b) on our experiments is the regeneration of OH, thereby leading to an erroneously low value of k_1 . However, since the Cl atom concentration was much greater than that of ClO, it is possible to obtain an analytical solution for the temporal behavior of OH in this system [i.e., reaction (1), followed by reactions (7a) and (7b)]:

$$[OH] = \frac{[OH]_0}{(\alpha^2 - 4\beta)^{1/2}} \left\{ (k_7[C1] + \lambda_1) e^{\lambda_1 t} - (k_7[C1] + \lambda_2) e^{\lambda_2 t} \right\}, \qquad (III)$$

where

$$\begin{split} &\alpha = k_1 [\text{CIO}] + k_1 [\text{CI}] ,\\ &\beta = \left\{ (k_7 [\text{CI}]) \times (k_1 [\text{CIO}]) \right\} - \left\{ (k_{1a} [\text{CIO}]) \times (k_{7b} [\text{CI}]) \right\} ,\\ &\lambda_1 = \frac{-\alpha + (\alpha^2 - 4\beta)^{1/2}}{2} \quad , \end{split}$$

$$\lambda_2 = \frac{-\alpha - (\alpha^2 - 4\beta)^{1/2}}{2}$$

The measured value of [OH] actually followed Eq. (II) while we assumed Eq. (I) to be valid. Therefore, the measured value of $[OH]_0/[OH]$ can be corrected by using the values of k_{7a} and k_{7b} obtained by Lee and Howard⁷:

$$k_{7a} = (1.8 \pm 0.5) \times 10^{-11}$$

 $\times \exp[(170 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IV)

and

$$k_{7b} = (4.1 \pm 0.8)$$

 $\times 10^{-11} \exp[-(450 \pm 60)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ (V)

To a first approximation, by assuming that reaction (7) is very rapid compared to reaction (1), it can be shown that

 k_1 (corrected) = k_1 (measured)

$$\times \left[1 - \left\{\frac{k_{\underline{1}\underline{b}}}{k_{\underline{7}}} \times 1 - \left(\frac{k_{\underline{1}\underline{b}}}{k_{\underline{1}}}\right)\right\}\right]^{-1} , \quad (VI)$$

where $k_{1} = k_{1a} + k_{1b}$ and $k_{1} = k_{1a} + k_{1b}$. However, we employed a rigorous iterative procedure where each value of measured $[OH]_0/[OH]$ (at various values of d and [ClO]) was corrected by using Eqs. (III) and (I). These corrections were made by assuming that k_{ib} is zero. The justification for this assumption is twofold: for reaction (1) to have a significant (i.e., >10%) branching ratio to yield HCl is not very likely since the reaction has to proceed via a four-centered complex and (b) if $k_{1b} \neq 0$, then it is very easy to correct our data accordingly. [For example, using Eq. (VI)]. It was found that the difference between using Eq. (VI) vs the iterative procedure is minimal. As expected, the concentration of Cl atoms had no effect as long as it was much greater than that of ClO. In Figs. 2-4, the corrected points are shown as separate lines. The bimolecular rate coefficient obtained using the corrected points are shown as separate lines. The bimolecular rate coefficient obtained using the corrected data is also tabulated in Table I. The corrections for individual data points ranged from ~ 5% to ~ 30%, while the value of k_1 changed by ~13% at 248 K and ~30% at 335 K. The larger cor-

TABLE I. Rate coefficients for the reaction of OH with ClO as a function of temperature. The corrected values in the last column were obtained as described in the text.

104001011 (1)	Corrected for reaction (7) $k \times 10^{12} \text{ cm}^3$ molecule ⁻¹ s ^{-1 a}
Temperature $k \times 10^{12} \text{ cm}^3$ (K)molecule ⁻¹ s ^{-1 a}	
10.9±2.5	12.3 ± 2.6
10.6 ± 2.0	12.7 ± 2.3
8.7 ± 1.6	10.5 ± 2.1
9.3 ± 2.0	12.0 ± 2.5
8.6 ± 1.2	11.0 ± 2.0
	$\frac{k \times 10^{12} \text{ cm}^3}{\text{molecule}^{-1} s^{-1} a}$ 10.9 ± 2.5 10.6 ± 2.0 8.7 ± 1.6 9.3 ± 2.0 8.6 ± 1.2

^aOverall estimated error which includes 2σ statistical error.

J. Chem. Phys., Vol. 78, No. 3, 1 February 1983

and

rections at higher temperatures are due to the increasing values of k_{7b}/k_7 with temperature. As seen from Table I, the corrected data show a negligible temperature dependence and indicate that the temperature dependence seen in the uncorrected data is due to the variation of k_{7b}/k_7 with temperature. A fit of the corrected data to an Arrhenius expression yields

 $k_1 = (9.2 \pm 6.5)$

 $\times 10^{-12} \exp[(66 \pm 200)/T] \mathrm{cm}^3 \mathrm{molecule}^{-1} \mathrm{s}^{-1}$.

We prefer to quote an unweighted average temperature independent value of $(11.7\pm3.3)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ for k_1 over the range 248–335 K. The quoted errors completely bracket the range of errors shown in Table I.

A short justification of the chemical system that was chosen to study this reaction is in order. First, in the absence of a direct method for ClO monitoring in our laboratory, it is prudent to use the $Cl + O_3$ reaction to produce ClO since its concentration could be accurately calculated. Second, the presence of excess Cl atoms was needed not only for complete conversion of O_3 to ClO but also to ensure that ClOO formed by the reaction between ClO radicals would be quickly converted to ClO via ClOO + Cl reaction. Third, it seemed most appropriate to convert the very reactive product of reaction (1) HO_2 into a stable species.

A comparison of our uncorrected value of k_1 , (9.3 ± 2.0)×10⁻¹² cm³ molecule⁻¹ s⁻¹ with that of Leu and Lin,¹ (9.1 \pm 1.3)×10⁻¹² cm³ molecule⁻¹ s⁻¹ shows excellent agreement. Leu and Lin¹ did not correct their values of k_1 to take into account the effect of reaction (7b) since, at the time of their measurement, it was generally believed that the Cl + HO₂ reaction yielded only HCl + O₂. Like the present investigation, Leu and Lin used excess Cl atoms in their kinetics experiments and the above described correction procedure is applicable to their measurement also. Therefore, it is clear that the agreement between the two studies is good.

Using the currently recommended value of 5.0×10^{-12} cm³ molecule⁻¹ s⁻¹ for the rate coefficient for the reaction

$$ClO + HO_2 - HOCl + O_2$$
(8)

and the branching ratio data obtained by Leu and Lin,¹ we recalculated k_{1a}/k to be greater than 60% at 298 K. Reaction (1b) which requires a four-centered reaction mechanism is unlikely to be competitive with the fast reaction rate measured for the overall process and therefore k_{1b}/k_1 is likely to be much less than 40%. However, a definitive determination of k_{1b}/k_1 is still needed for stratospheric modeling purposes.

Assuming $k_{1b} = 0$, we can use our measured value of k_1 in conjunction with the value of k_{7b} determined by Lee and Howard⁷ to calculate the equilibrium constant K at 298 K to be 0.76 for the reaction

$$Cl + HO_2 = OH + ClO$$

This equilibrium constant yields a value of 3.1 kcal/mol for $\Delta H_{f298\,\mathrm{K}}^{\circ}$ (HO₂), which is lower than 3.3 kcal/mol obtained using the uncorrected value of Leu and Lin, and overlaps with the upper limit of the value (2.5±0.6 kcal/mmol) measured by Howard.¹⁰

Reaction (1) can have the maximum impact on stratospheric chemistry at an altitude where the product of [CIO] and [OH] is the maximum, i.e., ~40 km. Even at this altitude, reaction (1) can contribute at most ~ 3% towards converting OH to HO₂ while the majority of the conversion proceeds through the OH + O₃ - HO₂ + O₂ reaction. Hence, only if k_{1b}/k_1 is significant can reaction (1) have a large impact on stratospheric chemistry.

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- ¹M. T. Leu and C. L. Lin, Geophys. Res. Lett. 6, 425 (1979).
- ²NASA Panel for Data Evaluation, *Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling*, Evaluation #4, Jet Propulsion Laboratory Publication 81-3 (1981).
- ³M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **41**, 121 (1976).
- ⁴G. Poulet, G. LeBras, and J. Combourieu, J. Chem. Phys. **69**, 767 (1978).
- ⁵J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Proc. R. Soc. London, Ser. A **368** 463 (1980).
- ⁶R. A. Cox, Int. J. Chem. Kinet. 12, 649 (1980).
- ⁷Y. P. Lee and C. J. Howard, J. Chem. Phys. 77, 756 (1982).
- ⁸R. T. Watson, J. Phys. Chem. Ref. Data 6, 871 (1977).
- ⁹P. H. Wine, A. R. Ravishankara, D. L. Philen, D. D. Davis, and R. T. Watson, Chem. Phys. Lett. 50, 101 (1977).
- ¹⁰C. J. Howard, J. Am. Chem. Soc. 102, 6937 (1980).