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Studies of reactions of importance in the stratosphere. IV. Rate constant for the reaction $CI+HOCI\rightarrow HCI+CIO$ over the temperature range 243–365 K

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The title reaction was studied over the temperature range 243-365 K using the discharge flow technique with mass spectrometry for detection. The rate constant was measured by detecting the loss of HOCl in the presence of a large excess of chlorine atoms. The resulting temperature dependent rate constant is given by $k = (3.0 \pm 0.5) \times 10^{-12} \exp[-(130 \pm 60)/T] \text{ cm}^3$ molecule⁻¹ s⁻¹, where the stated errors include our estimate of the maximum possible systematic error. This reaction becomes a significant pathway to HCl in the stratosphere when the total ClX exceeds 10 ppbv. Upper limits for rate constants for the reactions HOCl + NO-products and HOCl + O₃-products at 300 K were established to be 1.0×10^{-17} and 4.0×10^{-16} cm³ molecule⁻¹ s⁻¹, respectively.

I. INTRODUCTION

Recent studies of the reaction

$$HO_2 + CIO \rightarrow HOC1 + O_2 \tag{1}$$

have shown that the species HOCl is readily formed in the stratosphere.¹⁻³ The rate constants measured by Reimann and Kaufman,¹ Stimpfle, Perry, and Howard,² and Leck, Cook, and Birks³ are $(3.8\pm0.5)\times10^{-12}$, (6.3 ± 1.0) $\times10^{-12}$, and $(4.5\pm0.9)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K, respectively. The temperature dependence work of Stimpfle *et al.*² demonstrated an enhanced reaction rate at lower temperatures, suggesting that the rate constant is as high as 1.5×10^{-11} at 220 K. It is necessary to determine the subsequent chemistry of hypochlorous acid in the stratosphere because of its potential effect on ozone depletion estimates.

Photolysis appears to be the principal means of destruction of HOCl in the stratosphere. Ultraviolet absorption spectra have recently been reported by Molina and Molina⁴ and by Knauth, Alberti, and Clausen.⁵ These spectra are in excellent agreement in the wavelength region 330-370 nm, where HOCl and Cl_2O exhibit near isosbestic behavior, and are in good agreement throughout the wavelength region 200-460 nm when the Molina and Molina data are corrected using the preferred value of 0.082 for the equilibrium constant for the reaction

$$Cl_2O + H_2O \neq 2 HOCl$$
 (2)

at 298 K.⁵ In the past there has been some controversy with regard to the absorption maximum near 310 nm. In early work of Timmons⁶ and Hisatsune⁷ this absorption maximum was absent, in agreement with theoretical predictions.^{8,9} The presence of an absorption maximum near 310 nm has been substantiated in recent laser photolysis experiments of Molina, Ishiwata, and Molina.¹⁰ In those experiments, HOCl was photolyzed using a microsecond laser pulse which served both as a photolytic source and as an excitation source for detection of fluorescence of OH radicals. They conclude that HOCl will

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photodissociate rapidly in the stratosphere and thus will not serve as a significant reservoir for ClX in the stratosphere. Reaction (1) does lead to an additional catalytic cycle for destruction of ozone, as previously discussed.^{2,3}

Although the HOCl molecule is not itself a chlorine reservoir, we have investigated the possibility that HOCl serves as an additional pathway to HCl via the reaction

$$HOC1 + C1 - HC1 + C1O \quad . \tag{3}$$

HCl is an important temporary sink for ClX in the stratosphere. We report here the first measurement of the rate constant and temperature dependence for Reaction (3) and compare the rate of this reaction in the stratosphere with other sources of HCl.

II. EXPERIMENTAL

A. Reagents

The suppliers and purities of gases are the same as those of the previous study.³ Dichlorine monoxide was prepared as previously described.³ Hypochlorous acid was prepared by equilibrating 0.2 Torr of Cl₂O with 18 Torr of H₂O in a 22-l silica bulb for 1 h or longer. The bulb was subsequently pressurized to 760 Torr with helium. Assuming a value of 0.08 for the equilibrium constant for Reaction (2), 30% of the original Cl₂O remains unreacted. The presence of this Cl₂O did not interfere with the measurement of k_3 since the rate constant was measured under pseudo-first-order conditions by detecting the loss of HOCl in a large excess of chlorine atoms. Ozone was produced by electrical discharge in oxygen and stored on silica gel as described previously.¹¹ For titration of Cl atoms, ozone was desorbed into a 22-l silica bulb. The composition of the O_3/O_2 mixture was determined by decomposing a small volume of the gas with a Tesla discharge and measuring the pressure change with a Baratron capacitance manometer. A typical gas mixture contained 90% ozone by volume. Once the composition of the gas was determined, the silica bulb was pressurized to 760 Torr with helium.

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TABLE I.	Summary	of	experimental	data.
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Temperature (K)	Number of measurements	Pressure (Torr)	Flow tube diameter (cm)	Flow velocity (cm s ⁻¹)	Nitric oxide	[Cl] range (molecules cm ⁺³)	k_3 (cm ³ molecule ⁻¹ s ⁻¹) ^a
243	6	2.0	2.6	1085	_	$(0.85-2.19) \times 10^{13}$	$(1, 77 \pm 0, 24) \times 10^{-12}$
243	4	2.0	2.6	1085	+	$(1, 32-2, 41) \times 10^{13}$	$(1, 75 \pm 0, 20) \times 10^{-12}$
						All data at 243 K:	$(1.76 \pm 0.21) \times 10^{-12}$
258	3	2.0	2, 6	1152	-	$(1, 46-2, 03) \times 10^{13}$	$(1,79\pm0,08)\times10^{-12}$
258	2	2.0	2.6	1152	+	$(1.08-2.29) \times 10^{13}$	$(1.84 \pm 0.04) \times 10^{-12}$
						All data at 258 K:	$(1.81 \pm 0.07) \times 10^{-12}$
300	10	2.0	2,6	1340	_	$(0, 51-2, 89) \times 10^{13}$	$(1, 92 \pm 0, 18) \times 10^{-12}$
300	7	2.0	2.6	1340	+	$(0, 43 - 2, 75) \times 10^{13}$	$(2.16 \pm 0.16) \times 10^{-12}$
300	1	3.0	2.6	1340	_	1.90×10^{13}	1.88×10^{-12}
300	1	4.0	2.6	1340	-	1.72×10^{13}	1.83×10^{-12}
300	1	5.0	2.6	1340	-	0.89×10^{13}	1.90 \times 10 ⁻¹²
300	12	2.0	4.6	454	-	$(0.58 - 1.62) \times 10^{13}$	$(1.75 \pm 0.16) \times 10^{-12}$
						All data at 300 K:	$(1, 90 \pm 0, 22) \times 10^{-12}$
365	6	2.0	2.6	1630	_	$(1, 17-2, 55) \times 10^{13}$	$(2, 18 \pm 0, 22) \times 10^{-12}$
365	9	2.0	2.6	1630	+	$(0, 79 - 3, 08) \times 10^{13}$	$(2.08 \pm 0.16) \times 10^{-12}$
						All data at 365 K:	$(2, 12 \pm 0, 18) \times 10^{-12}$

^aError limits are one standard deviation.

B. Rate constant measurements

The rate constant for Reaction (3) was determined using the discharge flow method with mass spectrometry for detection. A detailed description of this apparatus is given in a previous article.³ The gas mixture containing HOCl was introduced through a fixed inlet on the flow tube. Chlorine atoms were produced by microwave discharge of a dilute mixture of molecular chlorine in helium and introduced through the movable inlet. Pseudo-first-order conditions were established with at least a 20-fold excess of Cl over HOC1. The species HOCl was detected at m/e = 52, the ion current being measured both for the discharge on (Cl atoms present) and the discharge off (no Cl atoms). The ion current due to molecular chlorine at m/e = 70 was simultaneously measured, and the concentration of chlorine atoms determined from the fraction of chlorine dissociated. Titrations with ozone verified the fractional dissociation method of determining the chlorine atom concentrations. Both the appearance of CIO at m/e = 51 and breakthrough of O_3 observed at m/e = 48 gave end points that agreed to within 5% of that calculated from the fraction of Cl₂ dissociated.

The flow tube, discharge region, and movable inlet were coated with phosphoric acid to prevent the heterogeneous recombination of chlorine atoms. Since chlorine atoms were admitted through the movable inlet, it was possible to determine wall loss of Cl in each kinetic run. Any data for which there was greater than a 10% decay of Cl along the full length of the flow tube $(k_w^{\rm I} > 1.6 {\rm s}^{-1})$ were discarded.

Due to the very fast reaction

 $Cl + Cl_2O \rightarrow 2ClO$

 $k_4 = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{Ref. 12})$

all Cl_2O from the $Cl_2O/H_2O/HOCl$ mixture is rapidly converted to ClO radicals in the flow reactor. We con-

sidered the possibility that the ClO radical produced in both Reactions (3) and (4) would contribute to the ion current at m/e = 52 by attaching H⁺ in the ion source of the mass spectrometer, thus resulting in a systematic error. For this reason, approximately half of the experiments were performed in the presence of nitric oxide [NO] $\approx 5 \times 10^{13}$ molecules cm⁻³. The rapid reaction

ClO + NO → Cl + NO₂ ,

$$k_{\rm r} = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{Refs. } 13-15)$$
(5)

returns all ClO to chlorine atoms, thus eliminating the possibility of this error and guaranteeing first-order kinetics.

The rate constant k_3 is given by

$$k_3 = (\overline{v}/l[\text{Cl}])\ln(\text{HOCl}]_0/[\text{HOCl}]) , \qquad (6)$$

where \overline{v} is the average linear velocity of gas in the flow tube, l is the distance from the point of mixing of the reactants to the first sampling orifice into the mass spectrometer, [Cl] is the chlorine atom concentration, [HOCl]₀ is the HOCl concentration with the discharge off, and [HOCl] is the HOCl concentration when the discharge is ignited. Because of the cancelation of proportionality constants, absolute calibration for HOCl is not required, and the value of k_3 reported here is independent of the equilibrium constant K_2 . Corrections for axial diffusion were applied to the data, but were only significant for the larger flow tube data, and in no case exceeded 5%. Corrections for deviation from plug flow (insufficient axial diffusion) were not required.

III. RESULTS

The measurements of k_3 based on linear regression of $\overline{v}[C1]^{-1}[\ln([HOC1]_0/[HOC1])]$ on *l* are summarized in Table I. Sixty-two measurements of k_3 were made at four temperatures in the range 243-365 K. The addition of nitric oxide had no significant effect on the measured

(4)



FIG. 1. Typical kinetic plots for individual measurements of k_3 at 300 K: Δ , [Cl] = 4.31×10¹² cm⁻³, [NO] = 5.0×10¹³ cm⁻³; **a**, [Cl] = 1.11×10¹³ cm⁻³, NO absent; **b**, [Cl] = 2.29×10¹³ cm⁻³, [NO] = 5.0×10¹³ cm⁻³.

rate constant, the average value of k_3 being slightly higher at 258 and 300 K in the presence of NO, but slightly lower at 243 and 365 K. The rate constant was found to be independent of pressure in the range 2-5 Torr at 300 K. Most of the data were obtained using a 2.6 cm i.d. flow tube. However, 12 measurements were made at 300 K using a 4.6 cm i.d. flow tube. The average value of k_3 obtained using the larger flow tube was lower by ~9%, but since the means differ by only 1 σ , we do not conclude that there is a significant heterogeneous component to the reaction.

Typical plots of $\ln([HOC1]_0/[HOC1])$ vs *l* at 300 K are provided in Fig. 1. Figure 2 is a plot of the first-order rate k_3^{I} vs chlorine atom concentration for all data at 300 K. The slope of the least squares line is 1.90 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, in exact agreement with the average value of k_3^{II} , and the intercept is -0.056 s⁻¹.

Linear regression of $\ln k_3$ on T^{-1} results in the expression

i

$$k_3 = (3.0 \pm 0.3) \times 10^{-12} \exp[-(130 \pm 30)/T]$$
, (7)

where the errors are one standard deviation. In consideration of all possible systematic errors, we enlarge the uncertainties by an additional 7%, so that

$$k_3 = (3.0 \pm 0.5) \times 10^{-12} \exp[-(130 \pm 60)/T]$$
 (8)

To be certain that HOCl does not react with either nitric oxide or ozone, we established upper limits for these reactions by introducing these species in large concentrations through the movable inlet. We were interested in the reaction with nitric oxide since many of the measurements of k_3 were performed in its presence. The channel leading to $HC1 + NO_2$, although exothermic, would not be expected to occur as a homogeneous gas phase reaction because of the extensive rearrangement of bonds required. We were interested in the reaction of HOC1 with O_3 as a possible route to chlorous acid HOC10 in the stratosphere.

We observed no detectable change in the ion current for HOCl in the presence of a large excess of nitric oxide ($[NO] = 1.1 \times 10^{16}$ molecules cm⁻³) over a reaction time of 165 ms. Based on this result, we place a conservative upper limit on the reaction

$$HOC1 + NO - products$$
 (9)

of 1.0×10^{-17} cm³ molecule⁻¹ s⁻¹. Similarly, for a concentration of ozone of 8.4×10^{14} molecules cm⁻³ we could detect no change in the HOCl signal over a reaction time of 165 ms. We conclude that the rate constant for the reaction

$$HOCl + O_3 - products$$
 (10)

is less than 4.0×10^{-16} cm³ molecule⁻¹ s⁻¹. Both upper limits were determined at 300 K. For neither Reaction (9) nor (10) could any products be detected in the mass spectrum. In particular, the possible product HOClO could not be detected at m/e = 68.

IV. DISCUSSION

In order to play a significant role in stratospheric chemistry, Reaction (3) must compete with the reaction

$$Cl + CH_4 - HCl + CH_3 , \qquad (11)$$

which is the major pathway to HCl. Figure 3 compares



FIG. 2. Plot of first-order rate constant $k_3^{\rm I}$ vs chlorine atom concentration for all data at 300 K: 0, 2.6 cm i.d. flow tube, NO absent; D, 2.6 cm i.d. flow tube, [NO] = 5.0×10¹³ cm⁻³; Δ , 4.6 cm i.d. flow tube, NO absent.



FIG. 3. Rates of formation of HCl in the stratosphere due to reaction of Cl with CH_4 and with HOCl according to the 1D model of Sze.

the rates of reactions (3) and (11) as a function of altitude in the stratosphere for the 1D model of Sze, ¹⁶ incorporating our results for Reaction (3). This model uses the HOCl absorption coefficients of Molina and Molina. For Reaction (1), the temperature-dependent results of Stimpfle, Perry, and Howard² are scaled to the average of the three determinations¹⁻³ at 298 K. The significance of Reaction (3) is highly dependent on the total CIX mixing ratio in the atmosphere, since the rate of Reaction (3) increases approximately as the square of ClX, whereas that of Reaction (11) increases more slowly than the first power of ClX. The latter is due to the fact that at high CIX concentrations reaction with chlorine atoms becomes a significant loss process for methane. For a model having 2.2 ppbv of CIX, Reaction (3) accounts for less than 3% of the total formation rate of HCl. At 12.1 ppbv ClX, Reaction (3) accounts for $\sim 25\%$ of the HCl formation rate.

The background concentration of ClX in the stratosphere is still uncertain. The July 1977 measurement of ClO by Anderson *et al.*¹⁷ reached levels as high as 7 ppbv near 40 km for this single species, but numerous measurements since that time have not reproduced such high levels, the median peak ClO concentration being ~1 ppbv.¹⁸ Measurements of individual source compounds such as CH₃Cl, CCl₄, CH₃CCl₃, HCl, CFCl₃, and CF₂Cl₂ sum to approximately 2.2 ppbv total ClX. Continued release of CFCl₃ and CF₂Cl₂ at their 1977 release rates is expected to result in an increase in total ClX to 7–9 ppbv at steady state. Reaction (3) has a negligible effect on ozone depletion calculations for this scenario.¹⁶

The 12.1 ppbv calculation of Fig. 3 corresponds to approximately twice the present release rates for F-11 and F-12. The ozone column perturbations are -26% and -30% for this calculation with and without inclusion of Reaction (3), respectively. We conclude that Reaction (3) must be included in models of the stratosphere when total ClX exceeds 10 ppbv. This would occur if the back-ground level of ClX were found to be much higher than 2.2 ppbv or if fluorocarbons were released at rates much above the 1977 level.

Although releases of F-11 and F-12 have been approximately constant since 1973, the recent National Academy

of Sciences report¹⁹ considers a scenario (scenario D) in which there is a 7% per annum growth of F-11 and F-12 release between the years 1980 and 2000, followed by a continuing constant release rate at the year 2000 level beyond that date. This results in a total C1X of ~ 20 ppbv and an ozone perturbation of -56.7% at steady state. Inclusion of our results for Reaction (3) would significantly lower this figure for ozone depletion. Reaction (3) would be expected to play a significant role in the more realistic scenario of continued fluorocarbon release at 1977 levels if the background level of C1X were found to be significantly higher than 2.2 ppbv or if the photolysis rate of HOC1 were found to be much slower than is presently accepted.

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- ¹B. Reimann and F. Kaufman, J. Chem. Phys. **69**, 2925 (1978).
 ²R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. **71**, 5183 (1979).
- ³T. J. Leck, J. L. Cook, and J. W. Birks, J. Chem. Phys. 72, 2364 (1980).
- ⁴L. T. Molina and M. J. Molina, J. Phys. Chem. 82, 2410 (1978).
- ⁵H. D. Knauth, H. Alberti, and H. Clausen, J. Phys. Chem. 83, 1604 (1979).
- ⁶R. B. Timmons, report to the Manufacturing Chemists Association, 1977; unpublished results cited in Ref. 5.
- ⁷J. C. Hisatsune, report to the Manufacturing Chemists Association, 1978; unpublished results cited in Ref. 5.
- ⁸G. Hirsch, P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. Lett. **52**, 442 (1977).
- ⁹R. L. Jaffe and S. R. Langhoff, J. Chem. Phys. 68, 1638 (1978).
- ¹⁰M. J. Molina, T. Ishiwata, and L. T. Molina, J. Phys. Chem. 84, 821 (1980).
- ¹¹J. W. Birks, B. Shoemaker, T. J. Leck, and D. M. Hinton, J. Chem. Phys. **65**, 5181 (1976).
- ¹²G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. 84, 1674 (1980).

- ¹³M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 70, 2250 (1974).
- ¹⁴M. T. Leu and W. B. DeMore, J. Phys. Chem. 82, 2049 (1978).
- ¹⁵M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).
- ¹⁶N. D. Sze (private communication).

- ¹⁷J. G. Anderson, J. J. Margitan, and D. H. Stedman, Science 198, 501 (1977).
- ¹⁸J. G. Anderson, H. J. Grassl, R. E. Shetter, and J. J. Margitan, J. Geophys. Res. 85, 2869 (1980).
- ¹⁹"Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport," Report of the National Academy of Sciences, Washington, D.C., 1979.