AIP | The Journal of Chemical Physics

Studies of reactions of importance in the stratosphere. III. Rate constant and products of the reaction between ClO and HO2 radicals at 298 K

Thomas J. Leck, JacE L. Cook, and John W. Birks

Citation: The Journal of Chemical Physics **72**, 2364 (1980); doi: 10.1063/1.439484
View online: http://dx.doi.org/10.1063/1.439484
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/72/4?ver=pdfcov
Published by the AIP Publishing

Studies of reactions of importance in the stratosphere. III. Rate constant and products of the reaction between ClO and HO_2 radicals at 298 K

Thomas J. Leck,[a] Jac-E L. Cook, and John W. Birks

Department of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado 80309

(Received 4 October 1979; accepted 29 October 1979)

The rate constant for the radical–radical reaction $\mathrm{ClO} + \mathrm{HO_2} \xrightarrow{k_1} \mathrm{HOCl} + \mathrm{O_2}$ was measured at 298 K by the discharge flow technique using mass spectrometry for detection of the HOCl product at $m/e = 52$. The ClO radical was generated by reacting ozone with chlorine atoms produced in a microwave discharge, and the concentration of ClO determined by measuring the decrease in ion current due to Cl_2^+ at $m/e = 70$ upon activation of the discharge. This method was found to be in agreement with a nitric oxide titration of ClO and with the stochiometric conversion of ClO to NO_2 by reaction with a large excess of NO followed by absolute calibration for NO_2 at $m/e = 46$. Two reactions were used to generate the hydroperoxyl radical: (1) $\mathrm{H} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M}$, and (2) $\mathrm{Cl} + \mathrm{H_2O_2} \rightarrow \mathrm{HCl} + \mathrm{HO_2}$. The rate constant k_1 was found to be independent of pressure over the range 2–6 Torr, the result being $k_1 = (4.5 \pm 0.9) \times 10^{-12}\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, where the error includes our estimate of the maximum possible systematic error. An upper limit of 2% for the branching ratio to the alternative products of this reaction, $\mathrm{HCl} + \mathrm{O_3}$, was established by attempting to detect ozone as a reaction product. For these measurements the reactions $\mathrm{Cl} + \mathrm{ClOCl} \rightarrow \mathrm{Cl_2} + \mathrm{ClO}$ and $\mathrm{Cl} + \mathrm{OClO} \rightarrow 2\mathrm{ClO}$ were used to generate the ClO radical in the absence of ozone. No other reaction products could be identified in the mass spectrum.

I. INTRODUCTION

Two measurements by the discharge flow technique of the rate constant for the reaction between HO_2 and ClO radicals have recently been reported.[1,2] Reimann and Kaufman[1] studied the reaction at ambient temperature by following the loss of HO_2 in the presence of a large excess of ClO. In that study the HO_2 radical was stochiometrically converted to OH by reaction with a large excess of NO near the end of the flow reactor and the OH concentration monitored by resonance fluorescence. The HO_2 and ClO radicals were directly detected by the laser magnetic resonance technique in a temperature dependent study covering the range 235–393 K by Stimpfle, Perry, and Howard.[2] Neither of these techniques allowed the determination of the products of the reaction. We have identified HOCl as a major product of this reaction by the discharge flow method with mass spectrometry for detection, and have measured the rate constant for the reaction between HO_2 and ClO radicals based on appearance of HOCl in the mass spectrum.[3] This technique also allows the direct detection of the ClO radical as well as other species in the reaction mixture such as Cl_2, O_3, OClO, ClOCl, H_2, O_2, H_2O_2, and H_2O. The concentration of the HO_2 radical may be determined in the absence of ClO by reaction with a large excess of NO and detection of NO_2.

Possible products of the reaction of ClO with HO_2 include

$$\mathrm{ClO} + \mathrm{HO_2} \xrightarrow{k_1} \left\{ \begin{array}{lr} \rightarrow \mathrm{HOCl} + \mathrm{O_2},\ \Delta H = -43\ \mathrm{kcal\ mol^{-1}}, & \text{(1a)} \\ \rightarrow \mathrm{HCl} + \mathrm{O_3}\ ,\ \Delta H = -12\ \mathrm{kcal\ mol^{-1}}, & \text{(1b)} \\ \rightarrow \mathrm{HClO} + \mathrm{O_2}, & \text{(1c)} \\ \xrightarrow{M} \mathrm{HOOClO\ or\ HOOOCl}\ . & \text{(1d)} \end{array} \right.$$

The effect of Reaction (1) on ozone concentrations in the stratosphere is highly dependent on the reaction products and the subsequent fate of those products. There are at least two possible exothermic reaction channels, Reactions (1a) and (1b). Based on recent measurements of the absorption cross sections for HOCl by Molina and Molina[4] and Jaffe and DeMore,[5] and as discussed by Stimpfle *et al.*,[2] HOCl is probably photolyzed in the stratosphere with a lifetime of less than 2×10^3 s. The effect of HOCl on ozone chemistry is then dependent on the possible photolysis products:

$$\mathrm{HOCl} + h\nu \left\{ \begin{array}{lr} \rightarrow \mathrm{HCl} + \mathrm{O}\quad (\lambda < 508\ \mathrm{nm})\ , & \text{(2a)} \\ \rightarrow \mathrm{OH} + \mathrm{Cl}\quad (\lambda < 503\ \mathrm{nm})\ , & \text{(2b)} \\ \rightarrow \mathrm{ClO} + \mathrm{H}\quad (\lambda < 301\ \mathrm{nm})\ . & \text{(2c)} \end{array} \right.$$

The effect of the direct formation of HCl by Reaction (1b) is the same as for the formation of HCl by Reaction (2a). Both reactions reduce ozone depletion estimates by partitioning a greater fraction of the total chlorine in the stratosphere in the form HCl which does not participate in odd oxygen depletion cycles. Model calculations by Sze indicate that even if a few percent of ultimate products of Reaction (1) are HCl, then estimates of ozone depletion due to continued release of chlorofluoromethanes will be significantly lowered.[6] On the other hand, the effect of Reaction (2b) is an increase in ozone depletion estimates because it leads to an additional cycle whose net effect is to destroy ozone:

$$\mathrm{ClO} + \mathrm{HO_2} \rightarrow \mathrm{HOCl} + \mathrm{O_2}\ , \qquad \text{(1a)}$$

---

[a] This work was performed as partial fulfillment of the requirements for the Ph.D. degree in the Department of Chemistry, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Ill. 61801.

2364 J. Chem. Phys. 72(4), 15 Feb. 1980 0021-9606/80/042364-10$01.00

$$HOCl + h\nu \rightarrow OH + Cl \ , \tag{2b}$$

$$Cl + O_3 \rightarrow ClO + O_2 \ , \tag{3}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \ ; \tag{4}$$

$$\text{Net: } 2O_3 \rightarrow 3O_2 \ .$$

Since the principal fate of H atoms in the atmosphere is to attach to O_2 to form the HO_2 radical, the effect of Reaction (2c) is simply to reverse Reaction (1a) and thus has no effect on ozone depletion estimates.

One must also consider the possibility that the products of Reaction (1) are those of (1c). In our experiments we cannot distinguish between the geometrical isomers HOCl and HClO. Although HOCl is a well known species, HClO has apparently never been identified. Reaction (1c) is exothermic even if HClO has a heat of formation as much as 43 kcal mol^{-1} above that of HOCl. Furthermore, any HClO formed in the atmosphere is likely to provide an additional path to HCl either by reaction with O_2 or O_3 or by photolysis:

$$HClO + O_2 \rightarrow HCl + O_3 \ , \tag{5}$$

$$HClO + O_3 \rightarrow HCl + 2O_2 \ , \tag{6}$$

$$HClO + h\nu \rightarrow HCl + O \ . \tag{7}$$

The species HClO is stable with respect to cleavage of the HCl–O bond provided that its ΔH_f^{298} is less than +37.5 kcal mol^{-1}, compared to $\Delta H_f^{298} = -18.7$ kcal mol^{-1} for HOCl.

The formation of the possible adducts HOOClO and HOOOCl given by Reaction (1d) must also be considered. The observation that k_1 is independent of pressure over the 2–6 Torr pressure range by ourselves and other investigators[1,2] is good evidence that these species are not significant reaction products. The negative activation energy observed by Stimpfle *et al.*[2] implicates these species as excited short-lived intermediates decomposing to the products (1a) or (1b). It is conceivable that these species could be collisionally stabilized in higher pressure experiments or in the stratosphere.

II. EXPERIMENTAL

A. Reagents

The suppliers and purities of gases used in experiments described here are summarized in Table I. Ozone was produced by electrical discharge through oxygen and collected on silica gel as described previously.[7] Nitrogen dioxide was reacted with oxygen to remove nitric oxide impurity by repeated freezing and thawing of NO_2 in the presence of oxygen. The process was repeated until the original bright blue solid had changed to a pure white amorphous solid which upon sublimation formed colorless crystals. The nitrogen dioxide impurity in nitric oxide was removed by flowing the gas through a column of Ascarite. Removal of NO_2 was verified by mass spectral analysis in the flow system. Ninety percent hydrogen peroxide was obtained from F.M.C. Corporation, the balance being water. Chlorine dioxide (OClO) was prepared by reacting chlorine gas with sodium chlorite powder in the presence of oxygen, followed by vacuum distillation. The result was bright red crystals of high purity. Dichlorine monoxide (ClOCl) was prepared by reacting chlorine gas with mercuric oxide powder followed by vacuum distillation. The brown liquid at −78 °C typically contained ~10% chlorine as demonstrated by mass spectral analysis, but this chlorine does not interfere with the experiments described here.

TABLE I. Summary of suppliers and purities of gases used.

Gas	Source	Grade and purity
He	Air Products	U.P.C. (99.997%)
O_2	Air Products	U.P.C. (99.994%)
H_2/He	Scientific Gas Products	U.H.P. (0.1389% H_2 in He)
NO	Air Products	C.P. (99%)
NO_2	Air Products	C.P. (99.5%)
Cl_2	Linde	Research (99.99%)

B. Discharge flow apparatus

The discharge flow technique was used to study the reaction between ClO and HO_2. Since both ClO and HO_2 are labile species the fixed inlet system of previous studies could not be used. Instead, a modified apparatus having several fixed inlets and one moveable inlet as shown in Fig. 1 was constructed. The moveable inlet has five 1 mm i.d. radially directed orifices for injection of one of the reactants at various positions along the 2.5 cm i.d. reaction tube. For studies of Reaction (1), the HO_2 radical was introduced through the moveable inlet and chlorine atoms and ozone were introduced at fixed inlets near the beginning of the reaction tube to form the ClO radical as shown in the diagram. An additional fixed inlet was used to introduce additional He so as to vary the total pressure. To determine HO_2 radical concentrations, nitric oxide was introduced at the fixed inlet near the end of the reaction tube as described below. Reaction time was varied by translating the moveable inlet horizontally along an optical rail. The reaction time is given by the distance from the moveable inlet to the first sampling orifice divided by the linear velocity of the carrier gas. The average linear velocity is determined by the pumping speed of the pump, conductance of the flow system, and temperature of the reaction tube. At 298 K the linear velocity was determined to be 12.04 m/s by introducing known flow rates of He and measuring the resulting pressures in the flow tube. Within experimental error the linear velocity was found to be independent of total pressure in the flow tube (or alternatively, independent of flow rates of gases into the flow tube) for the pressure range 0.1 to 6.0 Torr and to vary inversely with absolute temperature of the flow tube. Pressures were found to be additive, i.e., a flow rate which results in 0.100 Torr when there are no other gases flowing into the reaction tube will result in a 0.100 Torr pressure rise when the total pressure is already 5.000 Torr due to the flow of other gases. Pressures were measured near the end of the reaction tube as shown in Fig. 1 using a 0–100 Torr mks Baratron capacitance manometer (Model 170M). Before any ki-

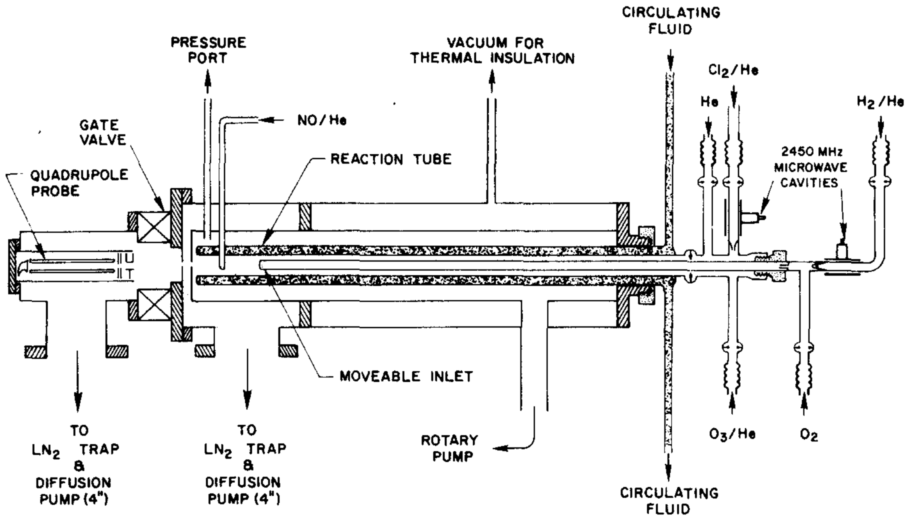

FIG. 1. Schematic diagram of the discharge flow apparatus with mass spectrometry for detection.

netic experiments were performed, the pressure was measured within the reaction tube at various positions along its length using a pressure measuring probe in place of the sliding inlet. These measurements were made for a wide range of flow conditions and correlated with the pressure measured at the fixed pressure port of Fig. 1. These results allowed us to make single pressure measurements during kinetic experiments. In agreement with the Poiseuille equation, the pressure drop across the reaction tube was typically 0.001 Torr/cm at 2.5 Torr average pressure.

The capacitance manometer was also used to prepare gas mixtures of known compositions. These mixtures were prepared in 22 l Pyrex bulbs. The pressure of the minor ingredient was measured using the capacitance manometer, and the total pressure was brought to 760 Torr as indicated by a Matheson bourdon tube gauge. This gauge was calibrated against the capacitance manometer by expansion of He between two accurately known volumes. Thus, all flow velocities and all concentrations in the flow tube are ultimately referenced to the factory-calibrated Baratron manometer.

The flow through the reaction tube is established by a 500 l/min Welch Model 1397 rotary vacuum pump. Reactants and products are sampled via a 0.7 mm orifice into a differential pumping chamber followed by a 2.8 mm orifice into the chamber containing a UTI 100C-02 quadrupole mass spectrometer. Reactants and products are ionized by electron impact, focused and accelerated along the axis of the quadrupole rods where they are selected according to mass-to-charge ratio, and then detected by the current produced upon impact with a Cu–Be electron multiplier. The two vacuum chambers are pumped by Varian VHS-4 diffusion pumping stacks having a nominal pumping speed for He at the top of the stack of 470 l/s. These stacks contain liquid nitrogen traps to separate the chambers from the diffusion pumps and provide additional pumping speed for condensable species. To minimize background peaks in the mass spectrum both pumps are charged with polyphenol ether diffusion pump oil (Santovac 5). The chamber containing the mass spectrometer is also pumped by a Varian titanium sublimation pump (Mini Ti-Ball). This chamber can be isolated by a gate valve from the remaining system, and is occasionally isolated and baked to reduce background. The ultimate low pressure achievable in the mass spectrometer chamber is 10^{-8} Torr. A pressure of 1 Torr in the reaction tube results in a pressure of 7×10^{-7} Torr in the chamber containing the mass spectrometer. This low pressure avoids nonlinearities due to space charging of the ion optics. Typical detection limits for a variety of molecules of atmospheric interest are in the range 2×10^9 to 2×10^{10} molecules cm^{-3} in the reaction tube. Thus, detection limits within the mass spectrometer chamber are in the range 2×10^3 to 2×10^4 molecules cm^{-3}.

Temperature regulation is achieved by circulating either chilled methanol or heated water from a thermostated bath through a jacket surrounding the reaction tube. The liquid is injected at the extreme end of the liquid jacket and forced to return by a spiral motion. The temperature in the gas stream was measured at the extreme temperature of 200 K using a temperature probe in place of the sliding inlet and found to vary by less than 1 °K over the entire 90 cm length of reaction tube used in these studies. Also, the temperature of the thermostated bath differed from the gas temperature in the reaction tube by only 2.5° at 200 K.

C. Generation of ClO radicals and measurement of concentrations

For the reaction rate constant measurements ClO radicals were generated by the reaction

$$Cl + O_3 \rightarrow ClO + O_2 \ , \qquad (8)$$

the Cl atoms being produced by a 2450 MHz microwave discharge of Cl_2 dilute in He. The minimum excess O_3 concentration used was 1.0×10^{14} molecules cm^{-3}. The rate constant at 298 K for Reaction (8) is 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1},[8–12] so that the reaction is 99.99% complete in 7.7 ms. There are 20 ms of reaction time prior to mixing with the HO_2 radicals from the moveable inlet when this inlet is fully extended (90 cm from the first sampling orifice). Concentrations of ClO in the range

1×10^{12} to 1×10^{14} molecules cm^{-3} were generated in this manner.

To determine the ClO concentration, the fractional amount of Cl_2 dissociated by the microwave discharge was first found by measuring the ion current at $m/e = 70$ for both the chlorine discharge on and the chlorine discharge off. The fraction of chlorine dissociated varied from 0.05 to 0.70 depending on the microwave power, chlorine concentration, total pressure and freshness of the phosphoric acid coating on the discharge tube. The ClO concentration was calculated from the fraction of Cl_2 dissociated, the pressure rise due to the flow of the chlorine mixture into the flow tube, the temperature, and the known composition of the Cl_2/He mixture. We found this method of determining ClO concentrations preferable to calibrating for the ion current of ClO^+ at $m/e = 51$ because of its simplicity (eliminates day to day calibrations for ClO) and because the method is independent of the total pressure in the flow tube as well as any changes in the sensitivity of the detector (the gain of the electron multiplier is degraded by an average of 2% per day). The method requires linearity of the detector to Cl_2 over a dynamic range of not much more than a factor of 2. The basic assumption of this method of ClO determination is that chlorine is present only as the two species Cl_2 and ClO. Any other chlorine containing species formed in the discharge or along the reaction tube would result in an overestimate of the ClO concentration and an underestimate of k_1.

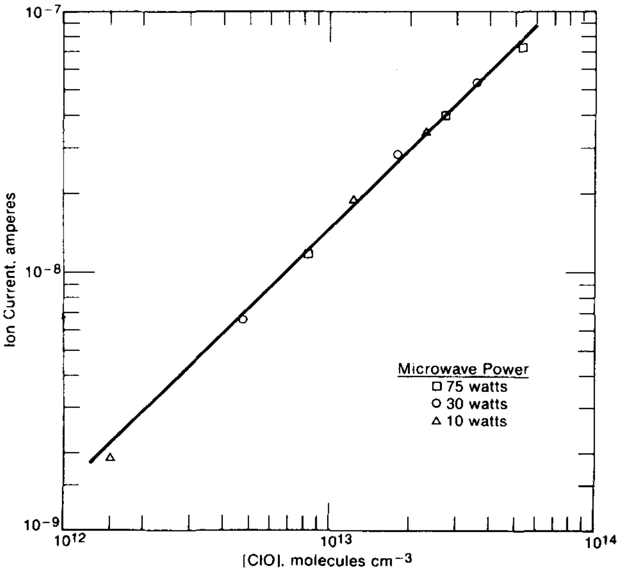

FIG. 2. Log-log plot of ClO^+ ion current vs ClO concentration as measured by the Cl_2 dissociation method. At a given microwave power, the ClO concentration was varied by varying the Cl_2 flow rate through the discharge, the total pressure being held constant.

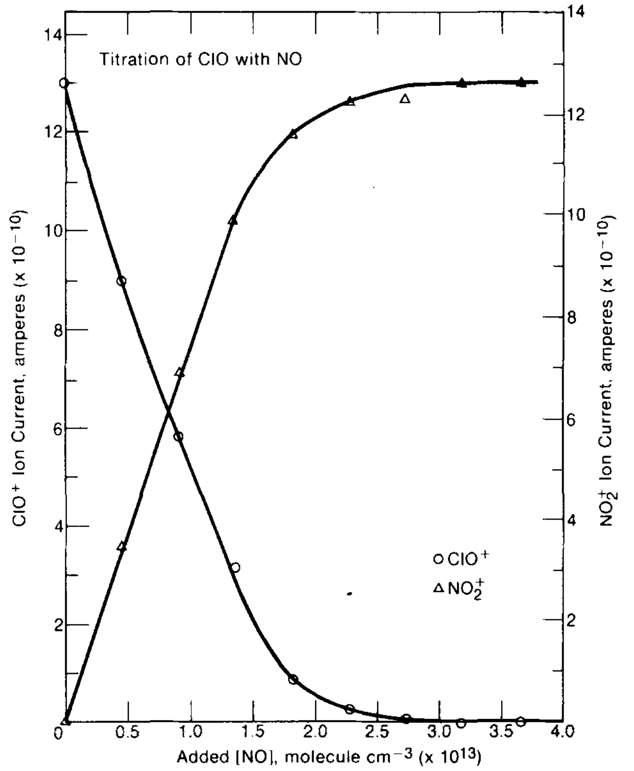

FIG. 3. Typical result for the titration of ClO with NO. Note that the two curves are normalized with ClO^+ ion current given on the left and NO_2^+ ion current on the right. The initial slopes of these curves give the sensitivity of the detector to ClO. The limiting ion current due to NO_2^+ provides an additional check of the sensitivity to ClO upon absolute calibration for NO_2.

Figure 2 is a plot of ClO^+ ion current at $m/e = 51$ vs ClO concentration as measured by the dissociation method. The ClO concentration was varied by varying the flow rate of the Cl_2/He mixture through the discharge and by varying the microwave power, the total pressure being held constant at 3.0 Torr by addition of He through a fixed inlet (see Fig. 1). The plot is seen to be linear over the range 10^{12} to 10^{14} molecules cm^{-3} of ClO, the concentration range used in rate constant measurements described here. As a critical check of the fractional dissociation technique for ClO concentration measurement, we compared the sensitivity of the ClO^+ ion current as determined by three methods: (i) based on fractional dissociation of Cl_2, (ii) a nitric oxide titration of ClO, and (iii) stoichiometric conversion of ClO to NO_2 followed by an absolute calibration for NO_2. Figure 3 shows a typical titration of ClO with NO by monitoring both the decrease in ClO^+ ion current at $m/e = 51$ and the increase in NO_2^+ ion current at $m/e = 46$. The titration reaction is

$$NO + ClO \rightarrow NO_2 + Cl \ . \qquad (9)$$

For these titrations initial chlorine atoms were in excess over ozone by a factor of 2. This was achieved by first adding a large excess of O_3, followed by reducing the O_3 flow rate until the ClO ion current was reduced by a factor of 2. Nitric oxide (0.14% in He) was added at the 40 cm reaction distance in small increments (0.1 Torr pressure rises) through the moveable inlet, the total pressure being held constant by an additional flow of helium. The sensitivity to ClO, S_{ClO}, is given by the negative of the initial slope of the ClO^+ ion current vs added nitric oxide concentration plot. Curvature in the titration is due to incomplete reaction once the ClO concentration is decreased below 8×10^{12}, the rate constant for Reaction (9) being 1.8×10^{-11} cm^3 molecule^{-1} s^{-1}.[8,13] When the titration curves for loss of ClO and appearance of NO_2 are normalized, they cross at 0.5 and sum to 1.0 within experimental error for all added concentrations of NO, thus verifying the stoichiometry of the titration reaction. The NO_2^+ ion current after complete reaction (large excess of NO added) was also used to calculate S_{ClO} by absolutely calibrating the ion current at $m/e = 46$ for NO_2^+, the concentrations of NO_2 being based on pressure measurements. These two methods of calibrating the ClO^+ ion current were both found to always agree to within ten percent with the fractional chlorine dissociation method in which ozone is in large excess over Cl.

Reaction (9) was also used to determine whether ClO radicals decay along the length of the reaction tube. Again, chlorine atoms were generated in a factor of two excess over the initial ozone concentration. A large excess of nitric oxide was added through the moveable inlet so as to stoichiometrically convert ClO to NO_2. The NO_2^+ ion current was then monitored for various positions of the moveable inlet. In this way it was found that there is less than a 1% decay of the ClO radical along the length of the reaction tube.

In experiments in which we attempted to detect O_3 as a reaction product the ClO radical was generated by reaction of chlorine atoms with chlorine dioxide or dichlorine monoxide,

$$Cl + OClO \rightarrow 2\,ClO\ , \tag{10}$$

$$Cl + ClOCl \rightarrow Cl_2 + ClO\ . \tag{11}$$

For these sources the ClO concentration is conveniently determined from the change in the OClO concentration as measured at $m/e = 67$ or from the change in the ClOCl concentration as measured at $m/e = 86$.

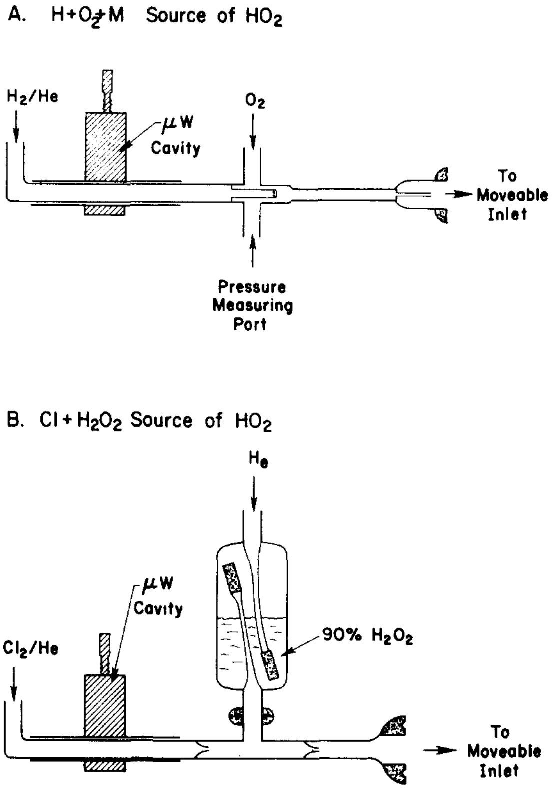

FIG. 4. Schematic diagrams of the $H + O_2 + M$ source of HO_2 (upper) and the $Cl + H_2O_2$ source of HO_2 (lower).

D. Generation of HO_2 radicals and measurement of concentrations

Two sources of the HO_2 radical were used for rate constant measurements and product analysis. One source employed the reaction

$$Cl + H_2O_2 \rightarrow HCl + HO_2\ . \tag{12}$$

A flow of ~1 STP cm^3 s^{-1} of a 0.01% mixture of Cl_2 in He and an additional flow of ~9 STP cm^3 s^{-1} of He passed through a microwave discharge and mixed with a flow of ~2 STP cm^3 s^{-1} of He saturated with the vapor of 90% H_2O_2. A diagram of the source is provided in Fig. 4. The reaction

$$Cl + HO_2 \rightarrow HCl + O_2 \tag{13}$$

tends to limit the quantity of HO_2 produced, but does not otherwise interfere. The concentration of H_2O_2 was in the range $(1-3)\times10^{15}$ molecules cm^{-3} and the rate constant for Reaction (12) is 4.7×10^{-13} cm^3 molecule^{-1} $\times$ s^{-1}.[8,14,15] Thus, this reaction is 99.99% complete in the 20 ms residence time within the moveable inlet. This source generates a small quantity of HOCl as seen in the mass spectrum when the HO_2 generator is modulated by switching the microwave discharge on and off. A likely source is the reaction

$$Cl + H_2O_2 \rightarrow HOCl + OH\ . \tag{14}$$

This quantity of HOCl is typically 3% of the concentration of HO_2 generated. It is independent of reaction distance and ClO concentration, and thus does not affect the measurement of k_1. The fate of OH generated by Reaction (14) or from any other source is simply to generate more HO_2:

$$OH + H_2O_2 \rightarrow H_2O + HO_2\ . \tag{15}$$

The rate constant for Reaction (15) is 8.1×10^{-13} cm^3 $\times$ molecule^{-1} s^{-1}.[8,16,17] The $Cl + H_2O_2$ source allowed us to generate typical concentrations of HO_2 of 5×10^{11} molecules cm^{-3}.

Another source used to generate the HO_2 radical is the reaction

$$H + O_2 + M \rightarrow HO_2 + M\ , \tag{16}$$

$k_{16} = 5.5\times10^{-32}$ cm^6 molecule^{-1} s^{-1}.[8,18] This source is similar to that used by Stimpfle, Perry, and Howard.[2] A diagram of this source is also shown in Fig. 4. Hydrogen atoms were generated by 2450 MHz discharge of a 0.7 STP cm^3 s^{-1} flow of a 0.14% mixture of H_2 in He. These hydrogen atoms were mixed downstream with a flow of 4.7 STP cm^3 s^{-1} of O_2 in a region maintained at 40 Torr total pressure by a constriction formed by a 4 cm length of a 1.5 mm i.d. capillary tube. The ratio of O_2 to H must be high in order to prevent complications from the reaction

$$H + HO_2 \rightarrow 2\,OH \tag{17}$$

for which $k_{17} = 4.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.[8,19] The concentration of HO_2 in the flow tube was typically found to be 5×10^{10} molecules cm^{-3}. This corresponds to 2.5×10^{12} molecules cm^{-3} in the high pressure (40 Torr) region of the source. Based on the rate constants k_{16} and k_{17} and the O_2 concentration in the source, the maximum fraction of hydrogen atoms that produce OH is expected to be 1.4×10^{-3}, resulting in a flow tube concentration of OH of 7.0×10^{7} molecules cm^{-3} which cannot significantly alter the flow tube concentrations of either HO_2 or ClO. As an added precaution that OH not interfere in these studies, the moveable inlet was not coated with phosphoric acid. Because of the very large heterogeneous rate constant for loss of OH on uncoated silica surfaces, this assured that no significant amount of OH exit the moveable inlet regardless of its mechanism of production.

The HO_2 produced by these sources could not be directly detected because of the large background peaks at $m/e=33$ for both sources. For the $Cl+H_2O_2$ source there is a large peak at $m/e=33$ due to the fragmentation of H_2O_2 to HO_2^+ in the ion source. For the $H+O_2+M$ source, $m/e=33$ is significantly overlapped by the very large $^{16}O\,^{16}O^+$ peak and $^{16}O\,^{17}O^+$ makes a direct contribution. In order to determine the concentration of HO_2 we used the reaction

$$HO_2+NO\rightarrow OH+NO_2 \qquad (18)$$

for which $k_{18}=7.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (Refs. 8 and 20) to stoichiometrically convert HO_2 to NO_2. The NO_2 was detected as ion current at $m/e=46$. Nitric oxide was added in large excess at a port near the end of the reaction tube as shown in Fig. 1. The NO_2^+ ion current was absolutely calibrated by flowing standard mixtures of NO_2 dilute in He. Reaction (18) is also the reaction used by Reimann and Kaufman[1] who detected HO_2 indirectly by resonance fluorescence of OH. Because of the fast reaction of NO with ClO, Reaction (9), it was not possible for us to follow the loss of HO_2 in analogous fashion. Reaction (18) could only be used to determine the concentration of HO_2 in the absence of the ClO reactant. Furthermore, Reaction (18) could not be used to directly determine the concentration of HO_2 produced by the $Cl+H_2O_2$ source because of the catalytic cycle which produces additional NO_2:

$$HO_2+NO\rightarrow OH+NO_2\ , \qquad (18)$$

$$OH+H_2O_2\rightarrow HO_2+H_2O\ , \qquad (15)$$

$$\text{Net:}\ NO+H_2O_2\rightarrow NO_2+H_2O\ .$$

However, Reaction (18) could be used to determine the absolute HO_2 concentration when the $H+O_2+M$ source was used, and Reaction (18) was also useful for both sources in verifying that HO_2 does not decay along the length of the reaction tube in the absence of ClO. To determine the concentration of HO_2 produced by the $Cl+H_2O_2$ source, the concentration of HO_2 produced by the $H+O_2+M$ source was first determined by use of Reaction (18). A large excess ($\sim5\times10^{13}$ molecules cm^{-3}) of ClO was then used to force Reaction (1) to completion ($k^I\sim225$ s^{-1}) and the ion current due to HOCl at $m/e=52$ measured for both the $H+O_2+M$ source and the $Cl+H_2O_2$ source. Using the $Cl+H_2O_2$ source concentrations of HO_2 as large as 5×10^{11} molecules cm^{-3} could be generated before decay due to the reaction

$$HO_2+HO_2\rightarrow H_2O_2+O_2 \qquad (19)$$

became significant.

In the reaction rate constant measurements pseudo-first-order conditions were used with ClO in at least a 20 : 1 excess over HO_2. The concentration of HO_2 does not enter into the calculation of the rate constant from the data, and is only required to be certain that the approximation of first order kinetics is valid. For this reason HO_2 concentrations were not measured for each experimental run.

III. RESULTS

A. Rate constant for the reaction of ClO with HO_2 based on appearance of ion current at $m/e=52$

In order to measure k_1 two concentrations of the ClO radical were generated. A small concentration, $[\mathrm{ClO}]_S$, in the range 1×10^{12} to 9×10^{12} molecules cm^{-3} resulted in an exponential decay of HO_2 along the length of the reaction tube and a corresponding increase in the concentration of HOCl (and/or HClO; when we write HOCl in this section we imply no distinction between the two geometrical isomers) which is detected as ion current at $m/e=52$. A second, much larger concentration of ClO, $[\mathrm{ClO}]_L$, was used to force Reaction (1) to greater than 99% completion. For both the small and large ClO concentrations, the modulation in ion current due to switching on and off the microwave power to the HO_2 generator was measured. The rate constant k_1 is then given by

$$k_1=\frac{\bar{v}}{l\,[\mathrm{ClO}]_S}\ln\left(\frac{[\mathrm{HOCl}]_L}{[\mathrm{HOCl}]_L-[\mathrm{HOCl}]_S}\right)\ , \qquad (20)$$

where $[\mathrm{HOCl}]_L$ is proportional to the modulation of ion current at $m/e=52$ when $[\mathrm{ClO}]_L$ is used and $[\mathrm{HOCl}]_S$ is proportional to the modulation of ion current at $m/e=52$ when $[\mathrm{ClO}]_S$ is used. The cancellation of the proportionality constant allows k_1 to be determined without absolutely calibrating for HOCl. These measurements were made at five or more reaction distances l, and the least squares slope of a plot of $\ln\{[\mathrm{HOCl}]_L/([\mathrm{HOCl}]_S)\}$ vs l was divided by $[\mathrm{ClO}]_S$ and multiplied by the linear velocity $\bar{v}$ to give k_1.

The high and low ClO concentrations were measured at each reaction distance by extinguishing the ClO discharge while noting the change in ion current due to Cl_2 at $m/e=70$. Observation of $[\mathrm{HOCl}]_L$ at each distance verified that the initial concentration of HO_2 did not change over the course of individual experiments. The value of $[\mathrm{ClO}]_L$ was varied from 1.3×10^{13} to 1.1×10^{14} molecules cm^{-3}. The lowest value of $[\mathrm{ClO}]_L$ required the full reaction distance of 90 cm to obtain complete reaction of HO_2, and thus a value for $[\mathrm{HOCl}]_L$. As can be seen in Table II, the observed reaction rate constant did not vary with $[\mathrm{ClO}]_L$. The total time to obtain the data at five reaction distances was about 15 min.

It is important to recognize that this method produces k_1, the total reaction rate constant independent of prod-

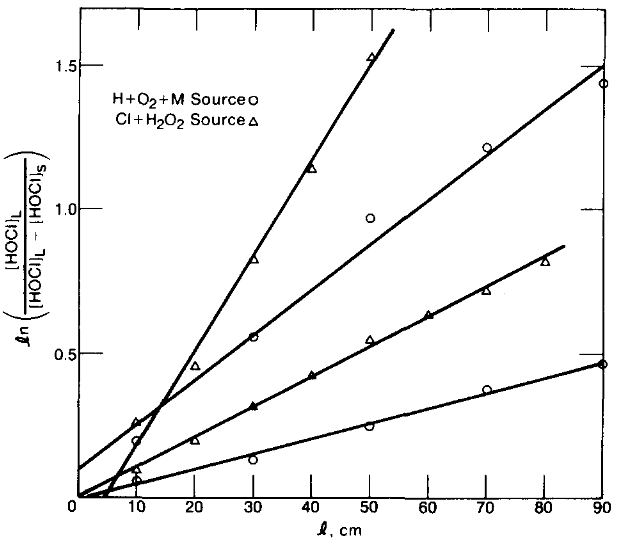

FIG. 5. Typical kinetic plots for both the Cl + H_2O_2, and H + O_2 + M sources of HO_2 for $[ClO]_S = 1.25\times10^{12}$, 3.39×10^{12}, 4.68×10^{12}, and 9.06×10^{12} molecules cm^{-3} in order of increasing slope; $\bar{v} = 1204$ cm s^{-1}.

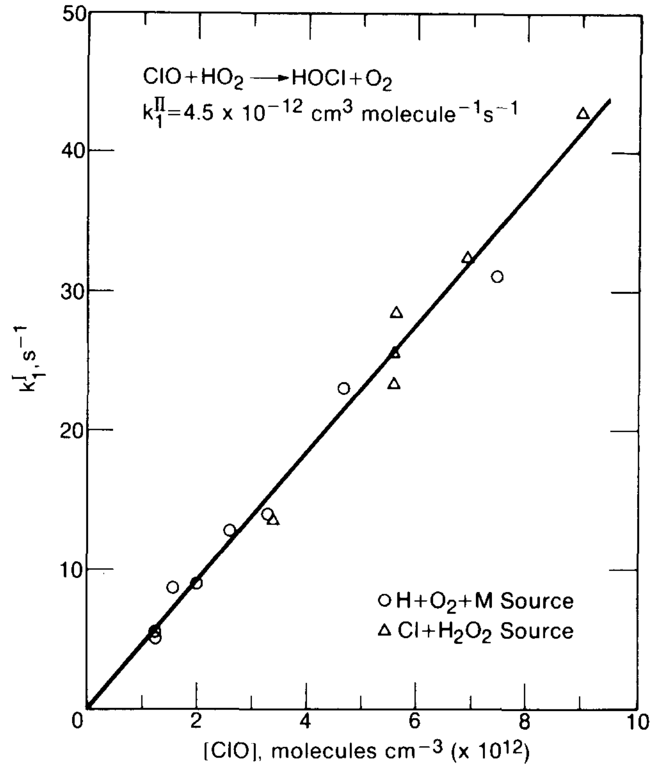

FIG. 6. Plot of the first order rate constant k_1^I vs $[ClO]_S$ for all of the data.

ucts, and not k_{1a} or $k_{1a} + k_{1c}$. In terms of the initial HO_2 concentration, $[HO_2]_0$, we have the relationships

$$[HOCl]_S = f\{[HO_2]_0 - [HO_2]_0 \exp(-k_1[ClO]_S\, l/\bar{v})\} , \quad (21)$$

$$[HOCl]_L = f[HO_2]_0 , \quad (22)$$

where

$$f = (k_{1a} + k_{1c})/(k_{1a} + k_{1b} + k_{1c} + k_{1d}) , \quad (23)$$

i.e., f is the branching ratio to HOCl and HClO. The branching ratio is eliminated upon combination of Eqs. (21) and (22) to produce Eq. (20). Thus, any product of Reaction (1) could be monitored by this method to determine the total reaction rate constant k_1.

Typical plots of $\ln\{[HOCl]_L/([HOCl]_L - [HOCl]_S)\}$ vs l for both the Cl + H_2O_2 and the H + O_2 + M sources are shown in Fig. 5 for a range of values of $[ClO]_S$. The results of 14 measurements of k_1 at 298 K are summarized in Table II. The average values obtained for k_1 are 4.63×10^{-12} and 4.52×10^{-12} cm^3 molecule^{-1} s^{-1} based on eight measurements using the H + O_2 + M source and six measurements using the Cl + H_2O_2 source, respectively. Figure 6 is a plot of the first order rate constant versus $[ClO]_S$ for both sources. The intercept of the plot is 0.1 s^{-1} which is not significantly different from zero, and the slope of the plot gives $k_1 = 4.53\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. We conclude that $k_1 = (4.5 \pm 0.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} where the error includes 5% for the precision of the data and 15% as our estimate of the maximum possible systematic error. That k_1 is

TABLE II. Results of measurements of k_1 at 298 K.

HO_2 source	$[ClO]_S$ ($\times10^{12}$) (molecules cm^{-3})	$[ClO]_L$ (molecules cm^{-3})	P (Torr)	k_1 ($\times10^{-12}$)^a (cm^3 molecule^{-1} s^{-1})
H + O_2 + M	1.57	2.70×10^{13}	3.0	5.60
	1.25	1.61×10^{13}	3.0	4.40
	1.24	1.53×10^{13}	5.0	4.21
	3.31	2.10×10^{13}	4.0	4.23
	7.50	8.64×10^{13}	3.0	4.13
	1.99	1.33×10^{13}	6.0	4.58
	2.60	1.50×10^{13}	4.0	4.91
	4.68	2.14×10^{13}	2.0	4.98
Cl + H_2O_2	5.64	1.06×10^{14}	3.0	5.04
	5.59	6.50×10^{13}	3.0	4.54
	5.58	6.03×10^{13}	4.0	4.16
	3.39	1.03×10^{14}	5.0	3.99
	9.06	3.28×10^{13}	5.0	4.71
	6.95	2.98×10^{13}	6.0	4.65

[a] $\bar{k}_1 = (4.58 \pm 0.26)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at the 95% confidence interval.

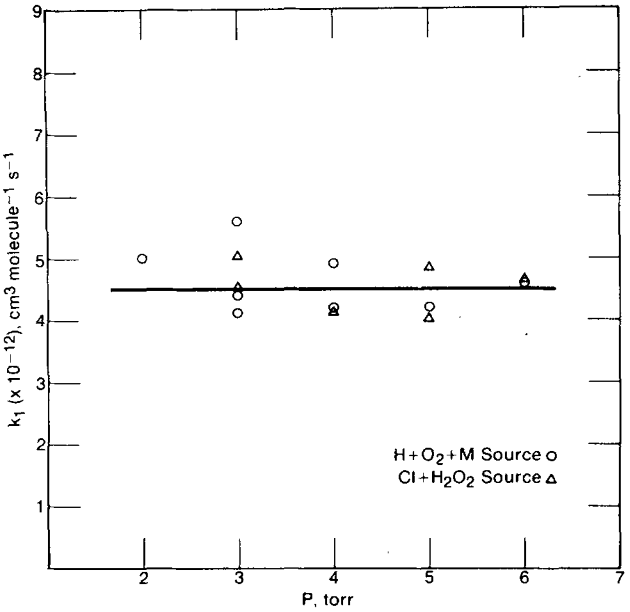

FIG. 7. Second order rate constant k_1 plotted against total pressure in the reaction tube. The line is drawn at $k_1 = 4.5 \times 10^{-12}$ for reference only and is not a least squares line.

independent of pressure over the range 2–6 Torr is shown in Fig. 7.

B. Attempts to detect other products of Reaction (1)

No significant modulation in ion current could be detected for the species HCl, O_3, $HClO_3$, $HClO_2$, or ClO_2 when the HO_2 generator was switched on and off. Modulation of ion current at $m/e = 36$ would be expected for channels (1b) and (1c). The $H + O_2 + M$ source was used to attempt to detect ion current due to HCl^+ since the $Cl + H_2O_2$ source produces HCl directly. A large $m/e = 36$ background which is always present when chlorine containing compounds are admitted to the system (e.g., see Fig. 1 of Ref. 21) limits our ability to detect changes at this mass. From these experiments we can only conclude that HCl^+ ion current due to products of Reaction (1) is less than 10% of the ion current due to $HOCl^+$.

In order to place an upper limit on the branching ratio for channel (1b) we attempted to detect O_3 at $m/e = 48$. For these experiments we reacted Cl atoms with ClOCl and OClO to generate ClO [Reactions (10) and (11)] as previously described. No O_3 could be detected when using either the Cl + ClOCl or the Cl + OClO sources of ClO with the $H + O_2 + M$ source of HO_2 or by combining the Cl + ClOCl source of ClO with the $Cl + H_2O_2$ source of HO_2. To set a quantitative upper limit to the branching ratio to the products $HCl + O_3$, it was necessary to determine the relative sensitivities of the instrument to O_3 and HOCl. This was done in two steps. First, the relative sensitivities to NO_2 and O_3 were found by reacting NO with O_3,

$$NO + O_3 \rightarrow NO_2 + O_2 , \qquad (24)$$

as in a previous study.[7] The decrease in O_3 is accompanied by a stoichiometric increase in NO_2. Figure 8 presents results of a typical run in which O_3 and NO_2 were monitored as a function of reaction distance. Five measurements of the rate constant for Reaction (24) produced the result $k_{24} = 1.72 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} in excellent agreement with our previous measurement of 1.73×10^{-14} cm^3 molecule^{-1} s^{-1} using a different apparatus having a fixed inlet system. The ratio of sensitivities S_{O_3}/S_{NO_2} was found to be 1.25. To determine the relative sensitivities to NO_2 and HOCl, a large excess of NO (5×10^{13} molecules cm^{-3}) followed by a large excess of ClO (5×10^{13} molecules cm^{-3}) were separately added to the same flow of HO_2. The modulation of NO_2^+ and $HOCl^+$ ion currents were monitored, respectively. From these experiments the ratio of sensitivities S_{NO_2}/S_{HOCl} was found to be 0.58. The ratio of sensitivities S_{O_3}/S_{HOCl} is then given by

$$\frac{S_{O_3}}{S_{HOCl}} = \frac{S_{O_3}}{S_{NO_2}} \cdot \frac{S_{NO_2}}{S_{HOCl}} = 0.73 . \qquad (25)$$

Figure 9 shows the modulation of $HOCl^+$ ion current and O_3^+ ion current when the $Cl + H_2O_2$ source of HO_2 is used in combination with the Cl + ClOCl source of ClO. Based on this data and Eq. (25), we conclude that no more than 2% of the products of Reaction (1) lead to O_3 formation, i.e., $k_{1b} < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

IV. DISCUSSION

Our result for k_1 at 298 K of 4.5×10^{-12} cm^3 molecule^{-1} $\times$ s^{-1} is in good agreement with those of Reimann *et al.*[1] and Stimpfle *et al.*[2] who obtained values of 3.8×10^{-12} and 6.3×10^{-12}, respectively. Our value of 4.5×10^{-12} represents a significant change from our preliminary

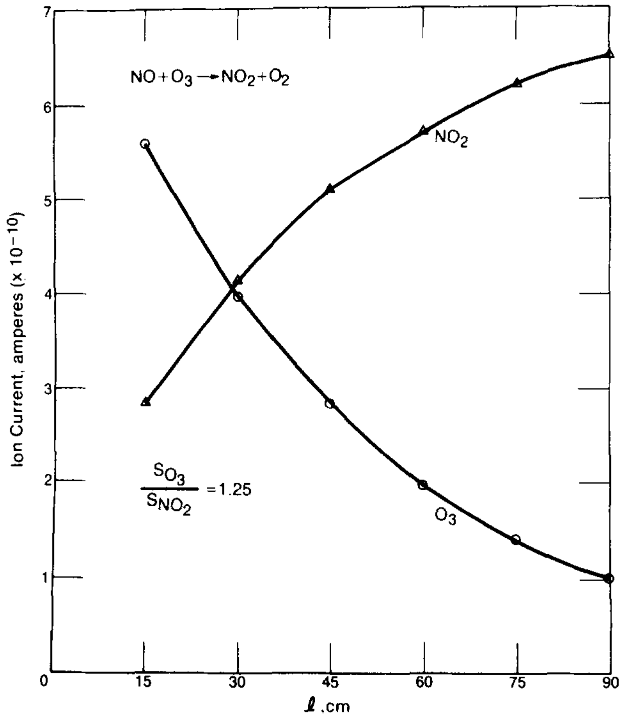

FIG. 8. Typical results monitoring the loss of O_3 and appearance of NO_2 for the reaction between NO and O_3. From these data the rate constant can be determined as well as the ratio of sensitivities of the detector to O_3 and NO_2.

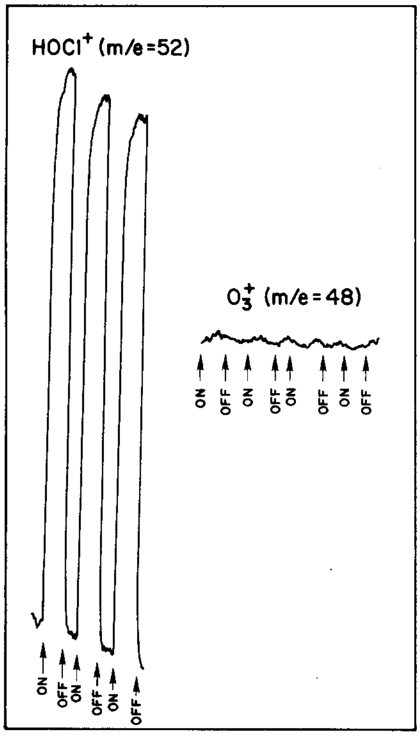

FIG. 9. Comparison of the modulation of $HOCl^+$ ion current with that due to O_3^+. From these data the branching ratio for channel (1b) is established to be less than 0.02.

result reported[3] as 3.1×10^{-12}. The lower value of k_1 was obtained using the $Cl+H_2O_2$ source under conditions for which the flow rate of gas through the moveable inlet was somewhat greater than that entering the flow tube directly. Under these conditions the reaction time is poorly defined due to back-flushing (or stagnation) of the HO_2. The plot of $\ln\{[HOCl]_L/([HOCl]_L-[HOCl]_S)\}$ versus reaction distance tends to be curved with a positive intercept. Addition of He directly to the flow tube (outside the moveable inlet) tends to linearize the plot and shift the intercept to zero. Increasing the flow rate beyond the point where the flow rates through the reaction tube and moveable inlet are equal has no effect on the slope of the plot and thus no effect on the measured rate constant. Back-flushing of a reactant can seriously affect the rate constant when determined by monitoring a product (as described here) for flow conditions that have little or no effect on the rate constant when a reactant is being monitored. If, for example, a small amount of HO_2 is lost due to reaction with ClO at a point behind the initial point of injection, the effective $[HO_2]_0$ is changed, but the measured rate constant based on decay of HO_2 is unaltered since the same amount of initial loss of HO_2 occurs at every inlet position (i.e., $[HO_2]_0$ is reduced by the same amount at every inlet position). However, if the HOCl product is being monitored, then the amount of HOCl produced by the back-flushed HO_2 increases $[HOCl]_S$ but not $[HOCl]_L$ since $[HOCl]_L$ represents total conversion of HO_2 anyway. This results in a curved plot of $\ln\{[HOCl]_L/([HOCl]_L-[HOCl]_S)\}$ versus reaction distance as described above.

Stimpfle *et al.*[2] attempted to use the reaction

$$F+H_2O_2\rightarrow HF+HO_2 \tag{26}$$

as a source of HO_2 in their study of Reaction (1). They found the decay of HO_2 to be unexpectedly small with HO_2 reaching a steady state after ~40 ms of reaction time. They postulated that this is a result of an HO_2 production mechanism

$$ClO+H_2O_2\rightarrow HOCl+HO_2\ . \tag{27}$$

Reaction (27) prevented them from measuring k_1 using the $F+H_2O_2$ source. Reaction (27) does not interfere with our measurement of k_1 when we use our $Cl+H_2O_2$ source, however, since we observe the modulation of the HOCl product by the HO_2 source. Any HOCl formed directly by Reaction (27) or from the HO_2 produced in Reaction (27) is present both when the HO_2 generator is on and when the HO_2 generator is off, and thus makes no contribution to the observed HOCl modulation for either the high or low ClO concentration. The background at $m/e=52$ did increase with increasing reaction distance (the H_2O_2 entered through the moveable inlet) and increased with increasing ClO, being much higher for the high ClO concentration; both observations being consistent with a significant rate for Reaction (27).

The method employed here of measuring a reaction rate constant based on the relative amounts of product formed for two concentrations of the excess reactant is somewhat unusual for flow tube kinetic studies. We have demonstrated that this technique can be used to measure the total reaction rate constant with precision (~5%) as good as that achievable by the commonly used method of monitoring the loss of a reactant.

As pointed out by Stimpfle *et al.*[2] the negative temperature dependence which they observed for Reaction (1) cannot be due to a third order reaction between ClO and HO_2 since the reaction rate is independent of pressure and since an unreasonably large value of the third order rate constant of ~10^{-28} $cm^6\,molecule^{-2}\,s^{-1}$ would be required. This rules out channel (1*d*). Stimpfle, *et al.*[2] also found that the temperature dependence of the rate constant was best described by one part having a negative activation energy and one part having a positive activation energy. They suggest that the negative temperature dependence is due to a reaction involving a short-lived complex and that the positive temperature dependence is due to a direct hydrogen abstraction reaction. The hydrogen abstraction reaction could produce $HOCl+O_2$ or $HClO+O_2$ depending upon which end of the ClO molecule is attacked [channels (1a) and (1c) respectively]. The short-lived intermediate could be either $\dot{H}\dot{O}\dot{O}\dot{C}l\dot{O}$ or $\dot{H}\dot{O}\dot{O}\dot{O}\dot{C}l$, subsequently decomposing to $HOCl+O_2$ or $HCl+O_3$, respectively [channels (1a) and (1b)]. Our inability to detect significant amounts of HCl or O_3 as reaction products rules out channel (1b). We would also expect to detect ion current due to HCl^+ if HClO is a product since fragmentation of HClO in the electron impact ion source is likely. Although we cannot place an upper limit on the amount of HClO produced, it appears that the major products of Reaction (1) are certainly $HOCl+O_2$ [channel (1a)]. This set of products could be produced by two mechanisms, one involving a direct hydrogen abstraction reaction and another involving the intermediate complex $\dot{\mathrm{H}}\dot{\mathrm{O}}\dot{\mathrm{O}}\dot{\mathrm{C}}\dot{\mathrm{l}}\dot{\mathrm{O}}$, resulting in the unusual temperature behavior observed by Stimpfle *et al.*[2] It is still very important to determine an upper limit to the amount of HClO produced by channel (1c), however, since a branching ratio of only a few percent could significantly affect ozone depletion calculations.[6] An *ab initio* calculation by Hirsch *et al.* places the heat of formation of HClO at ~60 kcal mol^{-1} above that of HOCl.[22] If this calculation is correct channel (1c) can be ignored since this channel is then endothermic by ~17 kcal mol^{-1}.

Our studies of the temperature dependence of this reaction will be reported in a subsequent article.

ACKNOWLEDGMENTS

We thank Rick Stimpfle, Bob Perry, and Carl Howard for helpful discussions concerning this work, for providing us with a preprint of their article, and for sharing with us their design of the $H + O_2 + M$ source. This work was supported by the Chemical Manufacturers Association's Technical Panel on Fluorocarbon Research.

---

[1] B. Reimann and F. Kaufman, J. Chem. Phys. 69, 2925 (1978).

[2] R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. 71, 5183 (1979). Preliminary results were reported at the Fourth Biennial Rocky Mountain Reginal Meeting of the American Chemical Society, June 5–7, 1978 (unpublished).

[3] J. W. Birks, T. J. Leck, and B. Shoemaker, Fourth Biennial Rocky Mountain Regional Meeting of the American Chemical Society, June 5–7, 1978 (unpublished).

[4] L. T. Molina and M. J. Molina, J. Phys. Chem. 82, 2410 (1978).

[5] S. Jaffe and W. B. DeMore (unpublished work) quoted in S. S. Prasad, R. L. Jaffe, R. C. Whitten, and R. P. Turco, Planet. Space Sci. 26, 1017 (1978).

[6] N. D. Sze (private communication).

[7] J. W. Birks, B. Shoemaker, T. J. Leck, and D. M. Hinton, J. Chem. Phys. 65, 5181 (1976).

[8] All rate constants quoted are those recommended by the NASA Panel on Kinetic and Photochemical Data, W. B. DeMore, Chairman; JPL Publication No. 79-27.

[9] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. II 72, 838 (1976).

[10] M. J. Kurylo and W. Braun, Chem. Phys. Lett. 37, 232 (1976).

[11] R. T. Watson, G. Machado, S. Fisher, and D. D. Davis, J. Chem. Phys. 65, 2126 (1976).

[12] M. S. Zahniser, F. Kaufman, and J. G. Anderson, Chem. Phys. Lett. 37, 226 (1976).

[13] M. S. Zahniser and F. Kaufman, J. Chem. Phys. 66, 3673 (1977).

[14] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. 41, 121 (1976).

[15] G. Poulet, G. LeBras, and J. Combourieu, J. Chem. Phys. 69, 767 (1978).

[16] W. Hack, K. Hoyermann, and H. Wagner, Int. J. Chem. Kinet. Symp. 1, 329 (1975).

[17] N. R. Greiner, J. Phys. Chem. 51, 5049 (1969).

[18] M. J. Kurylo, J. Phys. Chem. 76, 3518 (1972).

[19] W. Hack, A. W. Preuss, and H. G. Wagner, Ber. Bunsenges. Phys. Chem. 83, 212 (1979).

[20] C. J. Howard and K. M. Evenson, Geophys. Res. Lett. 4, 437 (1977).

[21] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. 66, 4591 (1977).

[22] G. Hirsch, P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. Lett. 52, 442 (1977).