A Kinetic and Product Study of the Cl + HO2 Reaction

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Absolute rate data and product branching ratios for the reactions Cl + HO2 → HCl + O2 (k1a) and Cl + HO2 → OH + ClO (k1b) have been measured from 226 to 336 K at a total pressure of 1 Torr of helium using the discharge flow resonance fluorescence technique coupled with infrared diode laser spectroscopy. For kinetic measurements, pseudo-first-order conditions were used with both reagents in excess in separate experiments. HO2 was produced by two methods: through the termolecular reaction of H atoms with O2 and also by the reaction of F atoms with H2O2. Cl atoms were produced by a microwave discharge of Cl2 in He. HO2 radicals were detected as ClO. Under pseudo-first-order conditions with Cl

\[ \Delta H = -(54.4 \pm 0.8) \text{ kcal mol}^{-1} \] (1a)

\[ \Delta H = (0.9 \pm 0.8) \text{ kcal mol}^{-1} \] (1b)

Above 40 km, reaction 1a is thought to produce HCl in significant quantities compared with the reactions of Cl with methane and of OH with ClO, the major sources of HCl at these altitudes. The fraction of Cl that is converted through reaction 1b to ClO, however, has not been well determined by previous work. Several earlier studies have been performed to better understand the kinetics of reaction 1. These studies consist of measurements of the total rate coefficient, k1, and of the minor channel rate coefficient, k1b, by relative rate (indirect) methods,1-4 via fits to a complex mechanism,5,6 or through absolute measurements.7-9 The relative rate studies used the techniques of discharge-flow coupled with mass spectrometric detection12/laser magnetic resonance3 or flash photolysis coupled with UV absorption spectroscopy.4 The studies involving complex mechanisms used flash photolysis coupled with UV absorption spectroscopy.5,6 These studies obtained values for k1 which range from (1.9-6.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. There are three previous absolute determinations of the kinetics of reaction 1. The earliest, by Lee and Howard,7 was undertaken using a discharge-flow technique coupled with laser magnetic resonance detection of HO2, OH, and ClO. Chlorine atom concentrations were determined by titration with O3 and were subsequently detected as ClO. Under pseudo-first-order conditions with Cl

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as the excess reagent, they reported a temperature-independent value for $k_1 = (4.2 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ from 250 to 420 K. A later study by Dobis and Benson$^8$ used a very low-pressure reactor (VLPR) coupled with mass spectrometric detection to determine $k_1$. They obtained $k_1 = (4.45 \pm 0.06) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ also independent of temperature in the range $T = 243–368$ K. The most recent and the most complete study of the reaction of Cl with HO$_2$ by Riffault et al.$^5$ used a discharge-flow technique combined with mass spectrometric detection. They followed the pseudo-first-order kinetics of Cl consumption in excess HO$_2$ and of HO$_2$ consumption in excess Cl to determine a weakly negative temperature dependence for $k_1$. Considering the experimental uncertainty, they quote a temperature-independent value for $k_1$ of $(4.4 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ from 230 to 360 K.

Despite the apparent agreement for the value of $k_1$ between previous studies, the fraction of the reaction that proceeds through channel 1b is not well established. Burrows et al.$^3$ looked for the production of OH radicals in an attempt to determine the branching ratio $k_{1b}/k_1$. OH radicals were not observed, which led the authors to publish an upper limit of $k_{1b} \leq 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, which yielded a small branching fraction for $k_{1b}/k_1(298\text{K}) \leq 0.008$. Dobis and Benson$^9$ also reported a small value for $k_{1b}/k_1 = (0.05 \pm 0.03)$ over the temperature range 243–368 K. Lee and Howard$^7$ observed the production of both OH and ClO from reaction 1b and reported an expression for $k_{1b}/k_1 = (1.09 \pm 0.06) \exp[–(478 \pm 17)/T]$, which gave $k_{1b}/k_1(298\text{K}) = 0.22$. Similarly, Cattell and Cox$^6$ reported $k_1 = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ and $k_{1b} = 9.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, which gave rise to a value for $k_{1b}/k_1(308\text{K}) = 0.18$. Finally, Riffault et al.$^9$ observed the time evolution of OH and ClO formed in reaction 1b and subsequently fitted these profiles by varying the input parameters, $k_1$ and $k_{1b}/k_1$. The best fit to the data was obtained for a value of $k_{1b}/k_1(298\text{K}) = (0.22 \pm 0.01)$. The available data for the branching fraction $k_{1b}/k_1$ range between 0 and 0.22 at 298 K and it is clear that further study of this quantity is required. Apart from its importance to stratospheric modeling, an accurate determination of $k_{1b}$ would be useful for the calculation of the enthalpy of formation of HO$_2$. By coupling the experimentally determined Arrhenius expression for reaction 1b with the Arrhenius expression for reaction 2a,

$$\text{OH} + \text{ClO} \rightarrow \text{Cl} + \text{HO}_2 \quad (2a)$$

$$\rightarrow \text{HCl} + \text{O}_2 \quad (2b)$$

we can obtain a value for the reaction enthalpy, $\Delta H_r$, by using the van’t Hoff equation. The enthalpy of formation of HO$_2$, $\Delta H_f(298\text{K})$, can be subsequently determined using Hess’ law.$^{10}$ Current evaluations$^{11,12}$ of the available data for reaction 1 used in stratospheric modeling are either based upon the results of Lee and Howard$^7$ alone$^{11}$ over the temperature range 250 to 420 K or upon the results of Lee and Howard$^7$ and Riffault et al.$^5$ together$^{12}$ over the temperature range 230 to 420 K. The former evaluation recommends a temperature-independent value for $k_1$ of $(4.2 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, the latter adopts a value of $4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$.

The present study, using a discharge-flow, resonance-fluorescence technique coupled with tunable diode laser absorption for HCl detection, has been undertaken to provide kinetic and product data for reaction 1. Specifically, kinetic data have been recorded by monitoring the kinetics of both Cl and HO$_2$ at temperatures ranging from 226 to 336 K. Product data have been taken by measuring HCl produced by reaction 1a and OH produced by reaction 1b under conditions of excess Cl at temperatures also ranging from 226 to 336 K.

**Experimental Section**

The flow system used in the present study is essentially that described in a recent paper in detail.$^{13}$

**Reactor.** The main reaction vessel was constructed from Pyrex and has an internal diameter of 5.04 cm and is 62 cm in length. The downstream end of the vessel was connected to an octagonal stainless steel resonance fluorescence cell. The gas pressure was measured via a 10 Torr capacitance manometer that was attached to the system between the resonance fluorescence cell and the reactor. At the upstream end of the reactor were connections to either a fixed HO$_2$ source and a moveable Cl inlet, or a moveable HO$_2$ source and a fixed Cl inlet depending upon the desired configuration. These sources are described in more detail below. The inner surface of the reaction vessel and the inner and outer surfaces of the moveable inlet were coated with halocarbon wax (Series 15-00, Halocarbon Corp.) to minimize heterogeneous radical loss. The carrier gas used in all experiments was helium, at a total flow rate of approximately 2300 to 2800 sccm (std atm cm$^3$ min$^{-1}$), which allowed total flow velocities ranging from 1400 to 2100 cm s$^{-1}$. Measurements were made at temperatures ranging from 226 to 336 K. The flow system was evacuated by a 38 L s$^{-1}$ rotary pump and a throttling valve was used to maintain the pressure at approximately 1 Torr. Temperatures in the reaction zone were maintained to within ±2 K using a temperature-controlled bath (Neslab, ULT-80DD or RTE-100) that circulated a given fluid (methanol or water) through the external jacket of the reactor. Two thermocouples (Type E, chromel–constantan) were used to monitor the fluid temperature inside the jacket, one at either end of the reaction vessel.

**HO$_2$ Source.** HO$_2$ was generated by one of two methods during the course of this study. The first method, to produce a low concentration of HO$_2$ radicals ($\leq 5 \times 10^{10}$ molecules cm$^{-3}$) for experiments in excess Cl atoms, utilized the reaction

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (3)$$

with M being He, the carrier gas. H atoms were produced in a 2.45 GHz discharge (60 W) of a dilute mixture of H$_2$/He in a quartz tube and were subsequently further diluted with a larger flow of He through the discharge. Total flow rates of He through the discharge were approximately 1700 sccm. The output of the discharge was mixed with a flow of approximately 550 sccm of O$_2$ in a region coated with halocarbon wax to prevent radical losses. This flow corresponded to concentrations of O$_2$ in the flow tube in the range $(6–8) \times 10^{15}$ molecules cm$^{-3}$. This region, 19 cm long with an internal cross-section of 2.5 cm$^2$, was attached to a sideport upstream of the main reactor and was maintained at a pressure of approximately 20 Torr to drive the three-body formation of HO$_2$ through reaction 3. Flow velocities in this pre-reactor were calculated to be of the order of 620 cm s$^{-1}$ giving a residence time of approximately 31 ms. Using $k_1 = 5.8 \times 10^{-32}$ cm$^6$ molecule$^{-2}$ s$^{-1}$,$^{11}$ we calculate that the H + O$_2$ reaction was sufficiently fast to prevent any H atoms from entering the main reaction vessel. By this method, HO$_2$ concentrations in the flow tube could be produced in the range $(0.3–7.0) \times 10^{10}$ molecules cm$^{-3}$.

The second method, to produce a high concentration of HO$_2$ radicals (up to $4 \times 10^{12}$ molecules cm$^{-3}$) for experiments in excess HO$_2$, utilized the reaction
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\[ F + H_2O_2 \rightarrow HF + HO_2 \]  (4)

\[ k_d(300K) = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]

F atoms were generated using a 2.45 GHz discharge (20 W) of a dilute mixture of F2/He in an alumina tube to improve the F2 dissociation efficiency. The F atoms were subsequently flowed into a moveable inlet at the upstream end of the reaction vessel through an inner injector. H2O2 was contained in a temperature-controlled vessel held at 291 K to prevent H2O2 condensation further downstream and a small flow of He was bubbled through the H2O2 to carry some of the vapor into the outer injector of the moveable inlet. The pressure in the temperature-controlled vessel was kept at approximately 6 Torr. The relative position of the inner injector, which had an internal cross-section of 0.2 cm², could be altered such that it was possible to vary the reaction time between F + H2O2 to ensure that no F atoms entered the main reactor. The moveable inlet itself was 180 cm long with an internal cross-section of 1.3 cm². The total flow through the moveable inlet was approximately 900 sccm such that flow velocities ranging from 3900 to 5400 cm s⁻¹ within the inlet were routinely used. All surfaces within the inlet were coated with halocarbon wax. H2O2 was purified prior to use by pumping and also by bubbling He through it to remove most of the H2O impurity. The H2O2 purity was estimated to be approximately 96 wt % based on earlier measurements under the same experimental conditions.

**HO2 Detection.** HO2 was not directly detected in these experiments. Instead, HO2 was first converted to OH by adding a large excess of NO (approximately 2 x 10¹⁴ molecules cm⁻³) to the flow approximately 3 ms upstream from the resonance cell via the reaction

\[ HO_2 + NO \rightarrow OH + NO_2 \]  (5)

\[ k_5(298K) = 8.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]

NO was purified prior to use by passing it through a molecular sieve held at 195 K to remove any potential NO2 impurity. The OH radicals generated by this titration were subsequently detected by resonance fluorescence. A quartz resonance lamp operated at a microwave power of 60 W was used to excite the OH fluorescence. A stream of helium saturated with water vapor was flowed through the lamp at a pressure of approximately 1.1 Torr. The light was baffled and collimated prior to entering the main reactor in a fixed side port. A flow of a known composition of NO was introduced together with an internal cross-section of 1.3 cm². The total flow of NO was 180 cm long with an internal cross-section of 1.3 cm². The total flow through the moveable inlet was approximately 900 sccm such that flow velocities ranging from 3900 to 5400 cm s⁻¹ within the inlet were routinely used. All surfaces within the moveable inlet were coated with halocarbon wax. H2O2 was purified prior to use by pumping and also by bubbling He through it to remove most of the H2O impurity. The H2O2 purity was estimated to be approximately 96 wt % based on earlier measurements under the same experimental conditions.

**OH Detection.** Product OH radicals generated by channel 1b were detected in an identical fashion to HO2 radicals, without the need for initial chemical conversion.

**OH Calibration.** To accurately determine HO2 concentrations, it was necessary to know the absolute OH concentrations generated by titration with NO. As such, a calibration of the OH resonance fluorescence lamp was performed on a daily basis to determine its detection sensitivity. The system was calibrated by forming specific amounts of OH radicals from the reaction of a known flow of NO2 and an excess of H atoms

\[ H + NO_2 \rightarrow OH + NO \]  (11)

\[ k_{11}(298K) = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]

H atoms were generated as described above, upstream of the main reactor in a fixed side port. A flow of a known composition of NO2 in helium was added to the main flow through the moveable inlet. The OH signal intensity was recorded and then averaged over 5 or 10 iterations. During the experimental runs, background fluorescence signals were recorded with the NO flow through the fixed inlet switched off. During the conversion of HO2 to OH, some radical loss was expected to occur mainly through the reaction

\[ OH + H_2O_2 \rightarrow H_2O + O_2 \]  (6)

\[ k_6(298K) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]

\[ OH + OH \rightarrow H_2O + O \]  (7)

\[ k_7(298K) = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]

\[ OH + wall \rightarrow products \]  (8)

\[ k_8 = \text{experimentally determined} \]

\[ OH + NO + He \rightarrow HONO + He \]  (9)

\[ k_9(298K) = 7.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ (ref 11)} \]

To estimate the magnitude of radical loss, the HO2 to OH conversion was simulated with computer models. These losses were calculated to be within the range of 2 to 30% and were found to be approximately 8% on average. The conversion losses were subsequently incorporated into the HO2 concentration measurements. Concentrations of HO2 when used as the excess reagent were calculated from the average observed OH fluorescence intensities at the minimum and maximum reaction times of each experimental run. These concentrations differed by up to approximately 8% due to the heterogeneous loss of HO2 in addition to its gas-phase self-reaction

\[ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \]  (10)

\[ k_{10}(298K) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 11)} \]
corresponded to OH concentrations ranging from 1 × 10⁸ to 4 × 10¹⁸ molecule cm⁻³. Typical background signals were near 250 cts s⁻¹, and for the 50 s counting times used, a minimum detectable OH concentration of 1 × 10⁸ molecule cm⁻³ at a signal-to-noise ratio of unity could be observed.

**OH and HO₂ Wall Losses.** OH radicals were generated as a product of the minor channel of the Cl + HO₂ reaction. Consequently, it was important to determine the heterogeneous losses of OH to correct the OH product concentrations if necessary. OH radicals were also produced as a method for HO₂ detection as described above. The losses of OH radicals on the walls of the main reactor were measured by generating OH radicals at the tip of the moveable inlet via the reaction of H atoms with an excess of NO₂ (reaction 1) at different reaction times. Thus a plot of the log of the intensity of the OH fluorescence signal versus reaction time yielded the pseudo-first-order loss rate for OH at the temperature of measurement. The measurements were repeated at all temperatures used during the course of the experiments and are presented in Table 1. These values contain a correction for the diffusional loss of OH radicals.

HO₂ wall losses prior to conversion to OH also needed to be considered. These loss rates were not measured directly, but were taken to be the intercepts of the second-order plots of the loss of HO₂ radicals in the presence of excess Cl. The measured wall loss rates after corrections for the diffusional loss of HO₂ have been made are presented in Table 1.

**Cl Source.** Cl atoms were generated in both sets of experiments using a 2.45 GHz discharge at 60 W of a dilute mixture of Cl₂/He in a Suprasil quartz tube, either in the moveable inlet or in the fixed side port depending on the experimental method used. The walls of the tube were coated with phosphoric acid immediately downstream of the discharge to minimize the loss of Cl through heterogeneous recombination. Dissociation efficiencies were found to be on the order of 15% for typical Cl atom concentrations ranging from 2 × 10¹⁰ to 3 × 10¹² molecule cm⁻³.

**Cl Detection.** Relative intensities of atomic chlorine emission were observed in the resonance fluorescence cell downstream from the temperature-controlled portion of the flow system. Atomic chlorine fluorescence was excited by radiation from a 60 W microwave discharge in a resonance lamp. A mixture of approximately 0.13% Cl₂ in He was passed through the lamp at a total pressure of approximately 1.5 Torr. Light emitted from the lamp was collimated using a series of concentric baffles, before entering the resonance cell. Fluorescence was emitted from the atomic chlorine within the illuminated portion of the cell on-resonance with the exciting radiation, mainly in the (4s³p)⁴P₃/₂ → (3p)⁴P₃/₂ transition at 137.96 nm. The fluorescence was observed perpendicular to the incident radiation using a channel photomultiplier (CPM) (Perkin-Elmer 1911P) which was sensitive to light between 120 and 200 nm. Immediately in front of the CPM, a 1 mm thick BaF₂ window was used as a cut-on filter to eliminate possible interference from oxygen and hydrogen atom emission. It was thought that this might potentially result from impurities in some of the gas flows. A second series of baffles was used in front of this window and Wood’s horns were placed opposite the lamp and CPM to reduce further the detection of scattered light. The CPM output signal was passed to a photon counting system (Stanford Research Systems SR400) where typically signals were integrated for 10 s and averaged over 5 iterations. During the experimental runs, background fluorescence signals were recorded with the Cl₂ flow through the fixed inlet switched off.

**Cl Calibration.** To accurately determine Cl atom concentrations, in particular for experiments where Cl atoms were used as the excess reagent, it was important to calibrate the chlorine atom concentrations on a daily basis. The sensitivity of the detection system to Cl atom concentrations in the flow cell was determined by generating a known concentration of Cl atoms via the reaction of excess F atoms with Cl₂.

\[
F + Cl₂ → Cl + FCl
\]  

F atoms were produced in a microwave discharge of a 0.5% mixture of F₂ in helium in a fixed port upstream of the main reactor. An uncoated 1 cm i.d. alumina tube was used in the microwave source, which was operated at 20 W. Typical flow rates through the discharge were on the order of 600 sccm. Background signals which consisted of scattered light and light from secondary sources of Cl atoms were determined by simply turning off the Cl₂ flow through the microwave discharge. Calibrations were performed under similar flow conditions to those used in the experiments. It was discovered that when O₂ was added to the system for the generation of HO₂ radicals by reaction 3, the sensitivity to Cl was reduced by a significant amount probably due to absorption of lamp light. As such, all calibrations for experiments of this type were performed with the same concentration of O₂ present. Typical detection sensitivities were found to be in the region of 2 × 10⁻⁶ cts s⁻¹/atoms cm⁻³ with background signals at about 5000 cts s⁻¹ for Cl atom concentrations less than approximately 2 × 10¹¹ atoms cm⁻³. For a 50 s counting time, this was equivalent to a minimum detectable Cl atom concentration of 7 × 10⁸ atoms cm⁻³ at a signal-to-noise ratio of unity. For higher concentrations, such as when the experiments were performed in excess Cl, the Cl atom sensitivity was found to be nonlinear. Consequently a polynomial function was fitted to the measured chlorine atom intensities obtained during these calibrations. These calibrations were performed at the same temperatures and pressures as the experiments themselves although no temperature dependence of the Cl atom signals was observed.

**Chlorine Atom Wall Loss.** Chlorine atoms were added to the flow both through a fixed port and via a moveable inlet during the course of the experiments so it was necessary to take into consideration chlorine atom wall losses. It was also necessary to determine the magnitude of these wall losses to calculate the axial and radial diffusion corrections described below. Wall loss measurements were conducted under the same experimental conditions of flow velocities, temperatures, and pressures as the main Cl + HO₂ experiments, although no HO₂ was added to the flows. In these experiments, Cl atoms were generated in the moveable inlet of the flow system via the microwave discharge of a similarly dilute mixture of Cl₂ in He as used for the production of Cl atoms during the course of the experiments. The Cl atoms were then added at different points along the flow tube and the fluorescence intensity was recorded.
using the same averaging procedures as described earlier. The resultant semilog plots of fluorescence intensity versus reaction time clearly showed that heterogeneous reactions were first order with respect to loss of Cl. A linear least-squares fit to the slope was then used to determine the rate coefficient for Cl atom wall loss at that temperature. The procedure was then repeated at all of the temperatures used. The measured values, after corrections for diffusional loss have been applied, are listed in Table 1.

**HCl Detection.** HCl produced in channel 1a of the Cl + HO2 reaction was monitored using a long path infrared absorption technique. A tunable diode laser (TDL) (Laser Components model DH5) mounted in a liquid nitrogen cooled dewar (Laser Photonics model L5736) produced light at approximately 3.4 μm such that it was coincident with the fundamental vibration—rotation band of HCl. The laser temperature, current, and modulation amplitude were set by a TDL controller (Laser Photonics model L5830). The laser used for this study was typically operated at approximately 84 K with currents ranging between 290 and 330 mA to produce an output at 2944.9 cm⁻¹. This wavelength coincided with the R(2) line of H35Cl and was chosen due to it being the maximum of the Boltzmann distribution at room temperature. The infrared output signals were monitored using an indium antimonide detector with a built in preamplifier (Kolmar Technologies model KISDP-1-J1) that was cooled to 77 K prior to use. To avoid the occurrence of potential multiple absorptions, it was necessary to verify that the laser was operating at a single discrete wavelength (single mode). The cw laser output was modulated at 1100 Hz using a mechanical chopper (EG&G model 197) before being separated into its component wavelengths via a 0.5 m focal length monochromator (Acton model SP500). The output of the monochromator was subsequently detected using a second indium antimonide detector (Infrared Associates model HCT-100) before being demodulated at the reference frequency with a lock-in amplifier (Stanford Research Systems model SR810). A digital-to-analogue (D/A) data acquisition card (Keithley model DAS-16G) connected to a PC allowed the lock-in output to be displayed and stored. During the experiments themselves, the laser was frequency modulated by applying a small amplitude modulation to the laser current. Typically, a 1.4 mA amplitude variation was superimposed on the main current at a frequency of 12.5 kHz. The D/A card was used to scan the laser current across the selected spectral range at a combined resolution for the D/A card and laser controller of 0.0244 mA bit⁻¹. The tuning rate of the laser was 0.068 cm⁻¹ mA⁻¹, which gave a spectral step size of 1.7 × 10⁻³ cm⁻¹ bit⁻¹. The laser beam was passed into a Herriott cell15.16 that was coaxial with the gas flow and downstream of the resonance fluorescence cell. This cell comprised two convergent, spherical gold-coated mirrors 7.6 cm in diameter with a focal length of 45.7 cm. The mirrors were located at a separation of 84.6 cm, which gave rise to a path length of 35.5 m for the 42 passes between the mirrors. Upon exiting the Herriott cell, the attenuated laser beam was collected by the detector—preamplifier and subsequently demodulated at the first harmonic frequency, 2f at 25 kHz by a lock-in amplifier (Stanford Research Systems model SR830). The resultant second derivative absorption signal was then processed by the D/A card before being displayed and stored on a PC. An example of a HCl signal obtained during the course of the experiments is shown in Figure 1. The amplitude of the central positive peak was used as a measure of the HCl concentration.

**HCl Calibration.** To accurately determine HCl product concentrations, it was important to calibrate the HCl detection sensitivity for each experiment undertaken, especially as the sensitivity was known to be dependent upon the laser operating conditions, the path length, and the optical alignment which could vary from experiment to experiment. The HCl detection sensitivity was determined by flowing a known concentration of HCl through the Herriott cell under similar conditions of pressure and temperature to those used during the experiments. A mixture of a known composition of HCl in He stored in a 5 L Pyrex flask was flowed into the cell upstream of the main reactor using a stainless steel flow meter, the flow being controlled by a Teflon needle valve. During the calibration experiment, the flow meter was initially set by adjusting the needle valve to obtain the required throughput and then the flow meter was bypassed to prevent any HCl losses on its metal interior. All flow lines downstream of this point were constructed from either Pyrex or Teflon to minimize any further heterogeneous loss of HCl. The flow rates were recorded before and after the calibration to measure the average flow rate. The needle valve was then adjusted and the procedure repeated to obtain several measurements of the HCl signal at different known flow rates. A subsequent plot of the HCl concentration determined from the flow against the absorption signal yielded a straight line with the sensitivity, S_{HCl}, as the gradient. An example of a calibration plot is given in Figure 2. The signal was seen to be linear up to [HCl] ≈ 1 × 10⁻¹² molecule cm⁻³ and S_{HCl} was found to range between 2 × 10⁻¹¹ and 1 × 10⁻¹⁰ mV cm³ molecule⁻¹. At the minimum sensitivity and at

![Figure 1. HCl absorption signal of the R(2) line at 2944.91 cm⁻¹. The amplitude of the positive peak is taken as a measure of the signal strength.](image1)

![Figure 2. Calibration plot of HCl signal versus [HCl].](image2)
a signal-to-noise of unity, a detection limit of $1 \times 10^6$ molecule cm$^{-3}$ could be obtained. In a previous study, the HCl calibrations were checked for possible losses through simultaneous absorption measurements of CH$_4$ and HCl. These two methods showed no significant discrepancies in the measured HCl concentrations using a similar experimental setup to the current study. Furthermore, experiments in which flows of HCl were passed through the moveable inlet into the main reactor showed no change in the observed HCl absorption while varying the position of the inlet at all temperatures under investigation. As such, no additional checks on the heterogeneous loss of HCl were thought to be necessary.

**Calibrations.** The mass flow controllers and meters used during the course of the experiments were calibrated for the particular gas mixture to be flowed using a pressure drop/rise at constant volume method. Factory calibrated capacitance manometers were used to calibrate the pressure gauges on the system. The thermocouples used to monitor the cell temperature were calibrated at 273 and 195 K using ice/water and CO$_2$ (s)/ethanol mixtures, respectively. The internal temperature of the flow tube was measured at several positions using a thermocouple probe in place of the usual moveable inlet. At room temperature (296 K) and above, the probe temperature was within 0.1 K of the jacket thermocouple temperatures. At low temperatures the probe temperature and jacket thermocouple temperatures were within 1 K, the probe thermocouple reading the lower of the two. The reported temperatures are those measured using the probe thermocouple.

**Corrections.** The observed pseudo-first-order rate coefficients were corrected for axial and radial diffusion. The diffusion coefficients for atomic chlorine in He, OH in He, and HO$_2$ in He were given by $0.0237 \times T^{0.75}$, $0.1447 \times T^{1.5}$, and $0.0332 \times T^{1.5}$ Torr cm$^2$ s$^{-1}$, respectively. These gave rise to corrections to the rate coefficients of between 4.1% and 9.4%. No corrections were made for the viscous pressure drop between the reaction zone and the pressure measurement port because earlier observations using the present reactor showed that the corrections were less than 0.5%.

**Reagents.** High-purity chemicals were used to minimize the introduction of impurities into the flow. Research grade He (99.9999%) was further purified prior to use by flowing through a molecular sieve (Linde 3A) trap held at 77 K. Furthermore, research grade O$_2$ (99.9999%), research grade Cl$_2$ (99.9999%), research grade H$_2$ (99.9999%), ULSI grade HCl (99.9999%), CP grade NO (99%) which was further purified prior to use by flowing through a molecular sieve (Linde 3A) trap held at 195 K, 0.5% and 1% mixtures of F$_2$ in He, H$_2$O$_2$ (90%) which was further purified by pumping prior to use, and NO$_2$ which was prepared from NO by adding excess O$_2$ were all used during the course of the experiments.

### Kinetic Results

**Excess Cl.** Cl atom concentrations used were in the range of $3 \times 10^{11}$ to $3 \times 10^{12}$ molecule cm$^{-3}$ with initial HO$_2$ concentrations ranging from $1 \times 10^{10}$ to $5 \times 10^{10}$ molecule cm$^{-3}$. Initial stoichiometric ratios ranged from 6 to 300. O$_2$ concentrations were between $6 \times 10^{15}$ and $8 \times 10^{15}$ molecule cm$^{-3}$. Measurements were made at temperatures ranging from 226 to 336 K and at an approximate total pressure of 1 Torr of helium.

#### Data Analysis.** Under the conditions described above, the loss of HO$_2$ radicals was well described by a pseudo-first-order decay profile. When Cl was added to the system, not only did we observe the loss of HO$_2$ but we also observed the production of OH simultaneously due to the conversion of HO$_2$ to OH via reaction 1b. After integration of the relevant kinetic equations, it can be written that

$$[\text{HO}_2] + [\text{OH}] = [\text{HO}_2]_0 \left(1 - k_{1a}[\text{Cl}]t\right) + k_{1b}/k_1 - (k_{1b}/k_1) \exp[-k_1[\text{Cl}]t] \quad (13)$$

For small values of $t$, the expansion of $e^t = 1 + x$. Consequently, we can simplify this expression to give

$$[\text{HO}_2] + [\text{OH}] = [\text{HO}_2]_0(1 - k_{1a}[\text{Cl}]t) \quad (14)$$

As $\ln(1 - k_{1a}[\text{Cl}]t) \approx -k_{1a}[\text{Cl}]t$ for $k_{1a}[\text{Cl}]t < 1$, it can be written that

$$\ln([\text{HO}_2] + [\text{OH}]) = \ln([\text{HO}_2]_0) - k_{1a}[\text{Cl}]t \quad (15)$$

Furthermore, as the OH resonance fluorescence signal, $I_{OH}$, varied linearly with [OH], i.e., $[\text{OH}] = S_{OH}I_{OH}$. and HO$_2$ was detected as OH and since [Cl] was in excess, it could be written that

$$\ln(I_{\text{HO}_2} + I_{\text{OH}}) = -k_{1a}t + \ln(I_{\text{HO}_2}^0) \quad (16)$$

where $k_{1a} = k_{1a}[\text{Cl}]$. Values of $k_{1a}$ were determined from the slopes of $\ln(I_{\text{HO}_2} + I_{\text{OH}})$ against reaction length ($l$) plots by linear least-squares analysis. Under plug flow conditions, the reaction time was subsequently calculated by the relationship $t = lv$, where $v$ represents the flow velocity. Typical reaction lengths used varied from 5 to 26 cm giving rise to reaction times of between 3 and 18 ms. A summary of the measured rate coefficients is given in Table 2 and the data obtained at the two extremes of measurement, 336 and 226 K, are presented in Figure 3.

An Arrhenius plot of the data is shown in Figure 4 as ◆ and yields the following expression

$$k_{1a} = (1.6 \pm 0.2) \times 10^{-11} \exp[(249 \pm 34)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (17)$$

for 226 $\leq T \leq 336$ K. The measurement errors are obtained from an unweighted linear least-squares analysis and are cited at the level of a single standard deviation.

**Excess HO$_2$.** Concentrations of HO$_2$ were in the range of $4 \times 10^{11}$ to $4 \times 10^{12}$ molecule cm$^{-3}$ with initial Cl atom concentrations ranging from $2 \times 10^{10}$ to $5 \times 10^{10}$ molecule cm$^{-3}$. Initial stoichiometric ratios ranged from 6 to 150. H$_2$O$_2$ concentrations were between $8 \times 10^{15}$ and $1.1 \times 10^{13}$ molecule cm$^{-3}$. Measurements were made at temperatures ranging from 246 to 296 K and at an approximate total pressure of 1 Torr of helium.

### Table 2: Measured Values for $k_{1a}$

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>no. of measurements</th>
<th>$[\text{Cl}]/10^{12}$ molecule cm$^{-3}$</th>
<th>$k_{1a}/10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>336</td>
<td>15</td>
<td>0.3–2.1</td>
<td>3.6 ± 0.2$^{a,e}$</td>
</tr>
<tr>
<td>316</td>
<td>17</td>
<td>0.4–2.2</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>296</td>
<td>16</td>
<td>0.5–2.7</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>276</td>
<td>16</td>
<td>0.6–3.3</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>256</td>
<td>15</td>
<td>0.6–3.3</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>236</td>
<td>14</td>
<td>0.3–2.0</td>
<td>4.7 ± 0.1</td>
</tr>
<tr>
<td>226</td>
<td>14</td>
<td>0.3–1.4</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ Corrected for axial and radial diffusion. $^e$ Errors are cited at the level of a single standard deviation. $^c$ From plots of $k_{1a}[\text{Cl}]$ versus [Cl].
yields the following expression for 246 ≤ T ≤ 296 K. The measurement errors are obtained from an unweighted linear least-squares analysis and are cited at the level of a single standard deviation. Experiments were limited to temperatures greater than 246 K due to the difficulty of producing HO2 in excess. As this expression exhibits only a weakly negative temperature dependence, we report a temperature-independent value for \( k_1 \) and \( k_{1b} \) at the temperatures where the experimental values coincide (256, 276, and 296 K). This results in

\[
k_{1b} = (7.7 \pm 0.8) \times 10^{-11} \exp[(-708 \pm 29)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

(21)

This expression is valid over the range 256 ≤ T ≤ 296 K and is plotted in Figure 4 as a line alongside the previously determined values for \( k_{1b} \).

**Product Results**

**OH Yields.** To obtain the OH product yield from reaction 1b it was necessary to measure the amount of OH produced for a given amount of HO2 reacted. We can write the rate of HO2 loss and the rate of OH production as

\[
d[\text{HO}_2]/dt = k_1[\text{HO}_2][\text{Cl}]
\]

(22)

\[
d[\text{OH}]/dt = k_{1b}[\text{HO}_2][\text{Cl}]
\]

(23)

Integrating and combining these equations from time zero to time \( t \) gives

\[
[\text{OH}] = k_{1b}k_1[\text{HO}_2]_0(1 - \exp[-k_1[\text{Cl}]/t])
\]

(24)

As \( k_1[\text{Cl}]/t \) becomes large, it can be written that

\[
[\text{OH}]_p/[\text{HO}_2]_0 = k_{1b}/k_1
\]

(25)

Furthermore, as \([\text{OH}] = S_{\text{OH}}I_{\text{OH}}(\text{HO}_2) \) and \([\text{HO}_2] = S_{\text{HO}_2}I_{\text{HO}_2}\), we can write

\[
I_{\text{OH}}(\text{HO}_2) = k_{1b}/k_1
\]

(26)

\([\text{OH}]_p \) represents the amount of OH produced for a consumption of HO2 approaching 100%. \( I_{\text{OH}} \) represents the corresponding OH resonance fluorescence signal, \([\text{HO}_2]_p \) and \( I_{\text{HO}_2}\), are the initial HO2 concentration and the initial HO2 (detected as OH) resonance fluorescence signal, respectively. The OH product measurements were performed under the conditions of Cl in excess over HO2 with Cl atom concentrations ranging from 9.0 × 10^{11} to 1.3 × 10^{13} molecule cm^{-3}. HO2 was generated via reaction 3 in all of the product measurements reported in this study. HO2 concentrations were varied by changing the flow rate of H2 into the HO2 pre-reactor and ranged from 1.0 × 10^{10} to 1.5 × 10^{11} molecule cm^{-3}. A 4% mixture of H2 in He was flowed into the system in the range of 0.15–2.2 sccm. During the product experiments, an initial measurement of \( I_{\text{OH}} \) with NO flowing but in the absence of Cl. Subsequently, Cl was added to the system through the moveable inlet at a reaction length of approximately 34 cm, which corresponded to reaction times ranging from 16 to 22 ms. The NO flow was then turned off and the signal due to product OH, \( I_{\text{OH}}\text{imp} \), was recorded. The experiment was then repeated at several H2 flows

\[
[\text{Cl}]/10^{12} \text{ molecule cm}^{-3}
\]

\[
\text{TABLE 3: Measured Values for } k_1^a
\]

<table>
<thead>
<tr>
<th>T/K</th>
<th>no. of measurements</th>
<th>[HO2]/10^{12} molecule cm^{-3}</th>
<th>( k_1/10^{11} ) cm3 molecule^{-1} s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>26</td>
<td>0.4–4.1</td>
<td>4.3 ± 0.1^e</td>
</tr>
<tr>
<td>276</td>
<td>10</td>
<td>0.4–3.8</td>
<td>4.4 ± 0.3</td>
</tr>
<tr>
<td>256</td>
<td>14</td>
<td>0.4–2.4</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>246</td>
<td>15</td>
<td>0.4–2.3</td>
<td>4.6 ± 0.2</td>
</tr>
</tbody>
</table>

^a Corrected for axial and radial diffusion. ^b Errors are cited at the level of a single standard deviation. ^c From plots of \( k_1[^{13} \text{C}] \) versus [Cl].

![Figure 3](image-url) Plots of pseudo-first-order rate coefficient, \( k_1[^{13} \text{C}] \) versus [Cl]. All of the data have been corrected for axial and radial diffusion and for HO2 conversion losses. Lines are linear least-squares fits to the data. Temperatures are given alongside each plot.

**Data Analysis.** Under the conditions described above, the loss of Cl atoms was well described by a pseudo-first-order decay profile. When HO2 was added to the system, the loss of Cl could be written as

\[
-d[\text{Cl}]/dt = k_1[\text{HO}_2][\text{Cl}]+k_{1\text{CL}}[\text{Cl}]
\]

(18)

Here \( k_{1\text{CL}} \) represents the pseudo-first-order loss of Cl atoms in the absence of HO2. This was thought to be due to heterogeneous reactions and also some secondary gas-phase reactions may have contributed. As the Cl resonance fluorescence signal, \( I_{\text{Cl}} \), varied linearly with [Cl] at the low concentrations used in these experiments, i.e., \([\text{Cl}] = S_{\text{Cl}}I_{\text{Cl}} \) and [HO2] was in excess, it could be written that

\[
-d\ln[I_{\text{Cl}}]/dt = k_1'+k_{1\text{CL}}
\]

(19)

where \( k_1' = k_1[\text{HO}_2] \). Values of \( k_1' + k_{1\text{CL}} \) were determined from the slopes of \( \ln(I_{\text{Cl}}) \) against reaction length (l) plots by linear least-squares analysis. Under plug flow conditions, the reaction time was subsequently calculated by the relationship \( t = l/v \), where \( v \) represents the flow velocity. Typical reaction lengths used varied from 5 to 34 cm giving rise to reaction times of between 3 and 22 ms. A summary of the measured rate coefficients is given in Table 3 and the data obtained at the two extremes of measurement, 296 and 246 K, are presented in Figure 5.

An Arrhenius plot of the data is shown in Figure 4 as a line and yields the following expression

\[
k_1 = (2.8 \pm 0.1) \times 10^{-11} \exp[(123 \pm 15)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

(20)
to vary $[\text{HO}_2]$.

A plot of $I_{\text{OH}}$ versus $I_{\text{HO}_2\text{O}_2}$ gave rise to a straight line from which a linear least-squares analysis yielded the product branching ratio from the gradient. A plot of $I_{\text{OH}}$ versus $I_{\text{HO}_2\text{O}_2}$ at the two extremes of temperature measurement, 226 and 336 K, is shown in Figure 6.

The measured values for the branching ratio $k_{1a}/k_1$ are presented in Table 4 and have been corrected for losses incurred during the conversion of HO$_2$ to OH via reaction 5. These values are plotted in Figure 7 alongside the previously determined values for the OH product yield.

**HCl Yields.** To measure the branching ratio, $k_{1a}/k_1$, it was necessary to measure the HCl product yield for a given amount of HO$_2$ reacted. The rates of loss of HO$_2$ and formation of HCl are shown below.

$$-\frac{d[\text{HO}_2]}{dt} = k_1[\text{HO}_2][\text{Cl}]$$  \hspace{1cm} (22)

$$\frac{d[\text{HCl}]}{dt} = k_{1a}[\text{HO}_2][\text{Cl}]$$  \hspace{1cm} (27)

In a manner analogous to that for the OH product yields, at large $k_1[\text{Cl}]$, it can be written that

$$[\text{HCl}]_{\infty}/[\text{HO}_2]_0 = k_{1a}/k_1$$  \hspace{1cm} (28)

As before, $[\text{HCl}]_{\infty}$ represents the amount of HCl produced for a consumption of HO$_2$ approaching 100% and $[\text{HO}_2]_0$ represents the initial HO$_2$ concentration. Initial reactant concentrations were identical with those used in the OH product experiments. Unlike the OH product yield measurements, however, which used the same technique for both OH and HO$_2$ detection (as HO$_2$ was converted to OH), it was necessary to calculate actual concentrations for a quantitative measurement of the HCl product yield. As such, calibrations of the OH intensity and the HCl intensity, as described in earlier sections of this paper, were performed alongside the experiments themselves. During these experiments, an initial measurement of $I_{\text{HO}_2\text{O}_2}$ was made with NO on but in the absence of Cl. Subsequently, Cl was added to the system through the moveable inlet at a reaction length of approximately 34 cm, which corresponded to reaction times ranging from 110 to 114 ms at the midpoint of the Herriott cell where HCl was monitored. The NO flow was turned off, and the absorption due to product HCl and background HCl, $I_{\text{HCl}}$, was recorded. The H$_2$ microwave discharge was then switched off, and the absorption due to background HCl alone, $I_{\text{HCl},\text{bkd}}$, was recorded. Background HCl was predominantly produced through the reaction of Cl with hydrocarbon wax coating the inside surfaces of the reactor. The relative sizes of these absorptions, which varied between 5 ± $I_{\text{HCl}}/I_{\text{HCl},\text{bkd}}$ ≤ 30 were dependent upon $[\text{HO}_2]_0$ with small values of $[\text{HO}_2]_0$ leading to small values for the above ratio. The experiment was then repeated at several H$_2$ flows to vary $[\text{HO}_2]_0$. Measurements of the HO$_2$ sensitivity,
$S_{\text{HO}_2} \equiv S_{\text{OH}}$, and the HCl sensitivity, $S_{\text{HCl}}$, were then taken to convert the measured intensities to absolute concentrations. A plot of $[\text{HCl}]_\infty$ versus $[\text{HO}_2]_0$ then gave rise to a straight line from which a linear least-squares analysis yielded the product branching ratio $k_1a/k_1$ from the gradient of the slope. A plot of $[\text{HCl}]_\infty$ versus $[\text{HO}_2]_0$ at the two extremes of temperature measurement, 236 and 296 K, is shown in Figure 8. The measured values for the branching ratio $k_1a/k_1$ are presented in Table 5 and have been corrected for HO$_2$ wall losses in addition to the losses incurred during the conversion of HO$_2$ to OH via reaction 5. No HCl wall losses were observed at any of the temperatures used in this study. These values are also plotted in Figure 9. It should be noted that the previously determined yields for $k_1a/k_1$ are simply subtractions of the previously determined values for $k_1b/k_1$, i.e. $(1 - k_1b/k_1)$.

**TABLE 5: HCl Yields from Product Measurements**

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>no. of measurements</th>
<th>HCl yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>20</td>
<td>72.4 ± 2.0$^c$</td>
</tr>
<tr>
<td>276</td>
<td>13</td>
<td>77.1 ± 2.3</td>
</tr>
<tr>
<td>256</td>
<td>22</td>
<td>81.5 ± 2.1</td>
</tr>
<tr>
<td>236</td>
<td>27</td>
<td>97.7 ± 3.2</td>
</tr>
</tbody>
</table>

$^a$ Corrected for HO$_2$ → OH conversion losses and for HO$_2$ wall losses. $^b$ Errors are cited at the level of a single standard deviation. $^c$ From plots of $[\text{HCl}]_\infty$ versus $[\text{HO}_2]_0$. The size of the corrections depended on $[\text{HO}_2]_0$ and varied from $[\text{HCl}]_\infty$ versus $[\text{HO}_2]_0$ at the two extremes of temperature measurement, 236 and 296 K, is shown in Figure 8.

The measured values for the branching ratio $k_1a/k_1$ are presented in Table 5 and have been corrected for HO$_2$ wall losses in addition to the losses incurred during the conversion of HO$_2$ to OH via reaction 5. No HCl wall losses were observed at any of the temperatures used in this study. These values are also plotted in Figure 9. It should be noted that the previously determined yields for $k_1a/k_1$ are simply subtractions of the previously determined values for $k_1b/k_1$, i.e. $(1 - k_1b/k_1)$.

**Discussion**

**Numerical Modeling and Secondary Chemistry.** Computer models were used to check for losses incurred during the NO + HO$_2$ reaction for the conversion of HO$_2$ to OH and also to check for possible interference from secondary reactions in the kinetic and product studies. The simulations were carried out using the CHEMRXN program, which has been validated versus a standard differential integrator and a stochastic algorithm.$^{18}$ The rate coefficients used in the models were taken from the NASA-JPL Chemical Kinetics Data Evaluation,$^{11}$ the IUPAC Gas Kinetics Data Evaluation,$^{12}$ and the NIST Chemical Kinetics Database.$^{19}$

Models were used to test for losses of OH and HO$_2$ during the HO$_2$ + NO reaction. Concentrations of initial HO$_2$ were in the range $1 \times 10^{10}$ to $6 \times 10^{12}$ molecules cm$^{-3}$; this covered the concentration range used in the experiments. NO was added at a concentration of $2 \times 10^{14}$ molecules cm$^{-3}$ and the model was run for 3 ms to simulate the actual laboratory runs. The [OH] calculated at 3 ms was plotted versus [HO$_2$]$_0$; this plot was then parametrized and used to correct the experimental data.

$^*$ Corrected for HO$_2$ → OH conversion losses and for HO$_2$ wall losses. $^b$ Errors are cited at the level of a single standard deviation. $^c$ From plots of $[\text{HCl}]_\infty$ versus $[\text{HO}_2]_0$.
plotted in Figure 10 for runs at 298 K. The effect of secondary to 5.0 atoms and excess HO\textsubscript{2} at 298 and 236 K. The concentrations values; the average correction was about 8%.

2% at the lowest concentrations to about 30% at the highest concentrations with excess Cl present and [HO\textsubscript{2}] without Cl in the system. No corrections for wall losses of OH or HO\textsubscript{2} were made. However, HO\textsubscript{2} concentrations were corrected for losses incurred during the conversion to OH with excess NO. The model yield was then calculated from the ratio of [OH] to [HO\textsubscript{2}]. The effect of secondary chemistry on the OH yield at 236 K is plotted in Figure 11. The effect ranges from 2.5% to 8% and no corrections were made to the observed OH yields.

In the case of HCl product, the model was run to long reaction times simulating detection in the Herriott cell downstream of the main reaction zone. The model yield was then obtained from the calculated [HCl] at long reaction times and [HO\textsubscript{2}] at the resonance cell. No corrections were made to [HCl] but the [HO\textsubscript{2}] was corrected as above for losses due to the conversion to OH by excess NO and for wall losses. The results at 236 K are presented in Figure 11 although calculations were also performed at 298 K. The effects of secondary chemistry predicted by the model range from 1.5% to 6.5% over the range of concentrations and temperatures used in the experiments and no corrections were made to the observed HCl yields.

**Comparison with Earlier Kinetic Work.** The previously determined values for the total rate coefficient, $k_1$, of the Cl + HO\textsubscript{2} reaction are summarized in Table 6. Lee and Demore,\textsuperscript{1} Poulet et al,\textsuperscript{2} and Burrows et al.\textsuperscript{3} used mass spectrometric detection\textsuperscript{1,2} or laser magnetic resonance detection\textsuperscript{3} of HO\textsubscript{2} generated by the reaction

$$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2 \quad (29)$$

in low-pressure discharge-flow systems. They measured the rate of loss of HO\textsubscript{2} through reaction 1 relative to reaction 29. Cox\textsuperscript{4} measured the rate of loss of HO\textsubscript{2} produced in reaction 3 relative to reaction 30

$$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \quad (30)$$

It can be seen that although there is scatter in the measurements, the quoted errors in the measurements means that there is reasonable agreement between the values for $k_1$ derived by previous studies and the value obtained here. It should be noted that these indirectly determined numbers have been updated to reflect the currently recommended data\textsuperscript{11} for reactions 29 and 30. Cox and Derwem\textsuperscript{5} and Cattell and Cox\textsuperscript{6} used the flash photolysis technique coupled with UV absorption of mixtures of Cl\textsubscript{2}−H\textsubscript{2}−O\textsubscript{2} and Cl\textsubscript{2}−H\textsubscript{2}−O\textsubscript{2}−N\textsubscript{2}, respectively. The UV absorptions of Cl\textsubscript{2} and of both HO\textsubscript{2} and ClO\textsubscript{6} were monitored and the corresponding concentrations were fit to a complex mechanism where the rate coefficient values for reaction 1 or reactions 1a and 1b separately were allowed to vary until a best fit was obtained. The values for $k_1$ obtained by Cattell and Cox\textsuperscript{6} are in good agreement with this study although the earlier work by Cox and Derwent\textsuperscript{5} is certainly outside the range of our error limits. Lee and Howard,\textsuperscript{2} Dobis and Benson,\textsuperscript{8} and Riffault et al.\textsuperscript{9} all undertook direct measurements of $k_1$. It can be seen that all three studies are in excellent agreement with each other and with the work presented here, especially as these studies were performed using a range of methods and detection techniques. The study by Lee and Howard\textsuperscript{2} operated in the regime of [Cl] $\gg$ [HO\textsubscript{2}] monitoring the decay of HO\textsubscript{2}. They determined a weakly negative temperature dependence for $k_1 = (3.87 \pm 0.54) \times 10^{-11}$ exp[(25 ± 42)/T] cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. Riffault et al.\textsuperscript{9} measured $k_1$ under
the conditions of both [Cl] $\gg$ [HO$_2$] and [HO$_2$] $\gg$ [Cl] and also calculated a weakly negative temperature dependence for $k_1 = (3.8 \pm 0.6) \times 10^{-11}$ exp(40 + 90)/T cm$^3$ molecule$^{-1}$ s$^{-1}$. Considering the experimental uncertainties, both sets of authors quote the temperature-independent values for $k_1$ listed in Table 6. In a manner similar to both Lee and Howard and Riffault et al. we obtain a weakly negative temperature dependence for $k_1 = (2.8 \pm 0.1) \times 10^{-11}$ exp(123 + 15)/T under the conditions of [HO$_2$] $\gg$ [Cl] and therefore quote a temperature-independent value of $k_1 = (4.5 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the range 246–296 K. This value agrees well with current evaluations of the available data for $k_1$.

Table 7 reports all of the previously determined data for the two individual reaction channels 1a and 1b. Under the conditions of [Cl] $\gg$ [HO$_2$] we observed the decay of HO$_2$ radicals via conversion to OH initially. Consequently, we also monitored the formation of product OH radicals simultaneously and an analysis of the relevant rate expressions led to the conclusion that we only measured $k_{1a}$ by this method. It should be noted that although Lee and Howard and Riffault et al. we obtain a weakly negative temperature dependence for $k_1 = (2.8 \pm 0.1) \times 10^{-11}$ exp(123 + 15)/T under the conditions of [HO$_2$] $\gg$ [Cl] and therefore quote a temperature-independent value of $k_1 = (4.5 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the range 246–296 K. This value agrees well with current evaluations of the available data for $k_1$.

**Figure 10.** (a) Calculated percentage differences in modeled $k_{1a}$ (out/in) at 298 K with excess Cl. (b) Calculated percentage differences in modeled $k_1$ (out/in) at 298 K with excess HO$_2$. Percentages reflect the differences between output/input pseudo-first-order rate coefficients.

**Figure 11.** (a) Calculated percentage differences between output and input modeled OH yield at 236 K. (b) Calculated percentage differences between output and input modeled HCl yield at 236 K. Calculations performed in excess Cl.

**TABLE 6: Summary of Data for the Rate Coefficient for the Reaction Cl$^+$ + HO$_2$ $\rightarrow$ Products, $k_1$**

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/Torr</th>
<th>$k_1/10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>technique</th>
<th>method</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1–2</td>
<td>$1.9_{-1.2}^{+2.8}$</td>
<td>DF-MS</td>
<td>RR</td>
<td>Leu and Demore$^1$</td>
</tr>
<tr>
<td>298</td>
<td>0.24–0.36</td>
<td>6.8 $\pm$ 2.5$^a$</td>
<td>DF-MS</td>
<td>RR</td>
<td>Poulet et al.$^2$</td>
</tr>
<tr>
<td>298</td>
<td>$\sim$2</td>
<td>4.4 $\pm$ 1.5$^a$</td>
<td>DF-LMR</td>
<td>RR</td>
<td>Burrows et al.$^3$</td>
</tr>
<tr>
<td>274–338</td>
<td>760</td>
<td>6.0 $\pm$ 3.0$^a$</td>
<td>FP-UV</td>
<td>RR</td>
<td>Cox$^4$</td>
</tr>
<tr>
<td>306</td>
<td>760</td>
<td>2.5 $\pm$ 1.0$^a$</td>
<td>FP-UV</td>
<td>CM</td>
<td>Cox and Derwent$^5$</td>
</tr>
<tr>
<td>308</td>
<td>50–760</td>
<td>$4.4_{-2.2}^{+4.4}$</td>
<td>FP-UV</td>
<td>CM</td>
<td>Cattell and Cox$^6$</td>
</tr>
<tr>
<td>250–414</td>
<td>0.9–1.5</td>
<td>4.2 $\pm$ 0.7$^a$</td>
<td>DF-LMR</td>
<td>ABS</td>
<td>Lee and Howard$^7$</td>
</tr>
<tr>
<td>243–368</td>
<td>$\sim$0.001</td>
<td>4.45 $\pm$ 0.06$^r$</td>
<td>VLPR-MS</td>
<td>ABS</td>
<td>Dobis and Benson$^8$</td>
</tr>
<tr>
<td>230–360</td>
<td>$\sim$1</td>
<td>4.4 $\pm$ 0.6$^r$</td>
<td>DF-MS</td>
<td>ABS</td>
<td>Riffault et al.$^9$</td>
</tr>
<tr>
<td>256–296</td>
<td>$\sim$1</td>
<td>4.5 $\pm$ 0.4$^b$</td>
<td>DF–RF</td>
<td>ABS</td>
<td>This Work</td>
</tr>
<tr>
<td>250–420</td>
<td>4.3</td>
<td>4.2 $\pm$ 0.2$^b$</td>
<td>EVAL</td>
<td>EVAL</td>
<td>Sander et al.$^{11}$</td>
</tr>
<tr>
<td>230–420</td>
<td>4.3</td>
<td></td>
<td>EVAL</td>
<td>EVAL</td>
<td>Atkinson et al.$^{12}$</td>
</tr>
</tbody>
</table>

$^a$ Errors are cited at the level quoted by these authors. $^b$ Errors are cited at the level of a single standard deviation. RR = relative rate, CM = complex mechanism, ABS = absolute method, and EVAL = evaluation.
also operated under the conditions of [Cl] ≫ [HO2], they observed HO2 loss and OH product formation as separate processes. The solution of the relevant rate equations for their systems produces the result that the total rate coefficient, k1, was measured by this method. The values for k1 of Riffault et al. quoted in Table 6 are therefore based on data obtained with both [Cl] ≫ [HO2] and [HO2] ≫ [Cl]. To date, the current study represents the only direct measurement of $k_{1a} = (1.6 ± 0.2) \times 10^{-11} \exp[(249 ± 34)/T]$ for 226 ≤ T ≤ 336 K although the current NASA panel recommendation11 provides an estimate of the Arrhenius parameters for this channel based on a knowledge of the Arrhenius parameters for k1 and k1b provided by Lee and Howard.7 The agreement between these estimated values and our direct measurement of the same parameters is good although the recommended Ea/R value falls outside our error limits. We determine that $k_{1a}(296 K) = (3.6 ± 0.1) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which compares reasonably well with the current evaluations11,12 also listed in Table 7 although both recommend slightly lower values at room temperature.

Previous measurements of the kinetics of channel 1b fall into two categories. The first category of measurements3,8 conclude that reaction 1b has only a small role in the overall kinetics of reaction 1. Burrows et al.3 were unable to observe any OH product formation during their experiments, which led them to report an upper limit for $k_{1b}(298 K) < 3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Similarly, using a VLPR technique coupled with MS detection, Dobis and Benson8 measured $k_{1b}(298 K) = (2.2 ± 1.4) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ although no temperature dependence could be obtained due to the large scatter in the experimental data.

In contrast, the second category of measurements6,7,9 conclude that the endothermic channel 1b plays a more significant role in the partitioning of reaction 1. Cattell and Cox6 obtained $k_{1b}(308 K) = (9.4_{-4.7}^{+9.4}) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ using a complex fitting procedure of the measured data from their UV photolytic system. Lee and Howard7 detected both OH and ClO products in separate experiments to measure the branching fraction $k_{1b}/k_1$. A linear least-squares fit to the data subsequently yielded the relative Arrhenius expression $k_{1b}/k_1 = (1.09 ± 0.06) \exp[(478 ± 17)/T]$. Arrhenius parameters for reaction 1b were inferred by combining the observed branching ratios with their measured values of $k_1$. Riffault et al.9 also detected both OH and ClO products but from the initial reactants Cl atoms and H2O2. HO2 radicals were generated through reaction 29 and the changes in concentrations of Cl, ClO, OH, and HO2 were observed with time. The resultant experimental profiles were fitted by allowing only the variation of two parameters: $k_1$ and the branching fraction $k_{1b}/k_1$. The best fit to the data was obtained with $k_1 = (4.0 ± 0.2) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{1b}/k_1(298 K) = 0.22 ± 0.01$. The procedure was repeated at a range of temperatures to yield the Arrhenius expression $k_{1b}(T) = (8.6 ± 3.2) \exp[−(660 ± 100)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In the current study, we have not directly measured $k_{1b}$ by kinetic methods, but in a manner analogous to that used by Lee and Howard, we can infer values for $k_{1b}$ from a subtraction of the respective $k_1$ and $k_{1a}$ data. An Arrhenius fit to the three data points where values overlap (from $k_1$ to $k_{1a}$ at 256, 276, and 296 K) gives $k_{1b}(7.7 ± 0.8) \times 10^{-11} \exp[−(708 ± 29)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for 256 ≤ T ≤ 296 K and $k_{1b}(296 K) = (71 ± 1.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The derived Arrhenius parameters from this study are close to those previously determined by Lee and Howard and by Riffault et al. and show a similar significant positive temperature dependence for $k_{1b}$ although these earlier studies lie outside our error limits. Furthermore, our room-temperature value is in good general agreement with the values of Cattell and Cox, Lee and Howard, and Riffault et al. by giving a much larger significance to reaction 1b compared to the determinations by Burrows et al. and Dobis and Benson.

As a further examination of the Cl + HO2 chemical system, we also studied the temperature dependence of the product formation channels in experiments separate from those already mentioned above. In these experiments, the concentrations of HCl and OH formed in reactions 1a and 1b respectively were measured as a function of the initial HO2 concentration over a range of temperatures. The derived relative Arrhenius expressions for the branching ratios $k_{1a}/k_1$ and $k_{1b}/k_1$ are

$$k_{1a}/k_1 = (3.4 ± 0.2) \times 10^{-11} \exp[(222 ± 17)/T] \quad (256 ≤ T ≤ 296 K) \quad (31)$$

$$k_{1b}/k_1 = (2.4 ± 0.3) \exp[−(733 ± 41)/T] \quad (226 ≤ T ≤ 336 K) \quad (32)$$

Although data were obtained at 236 K for the ratio $k_{1a}/k_1$ as shown in Figure 9, these data points have been excluded from the dataset used in the calculation of expression 31. It is apparent that at this temperature there may have been a heterogeneous source of HCl unaccounted for by the normal HCl background subtraction method.

These expressions can be converted to absolute numbers using the temperature-independent value of $k_1 = (4.5 ± 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ determined in this study by kinetic methods. The derived Arrhenius expressions and room temperature rate coefficients are shown in Table 8 and displayed graphically in Figure 4 as ▲ and ● for $k_{1a}$ and $k_{1b}$, respectively.

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TABLE 7: Summary of Data for the Rate Coefficients $k_{1a}$ and $k_{1b}$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$k_{1a}$/cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>$k_{1b}$/cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$&lt;3 \times 10^{-13}$</td>
<td>$&lt;3 \times 10^{-13}$</td>
<td>Burrows et al.3</td>
</tr>
<tr>
<td>308</td>
<td>$(9.4_{-4.7}^{+9.4}) \times 10^{-12}$</td>
<td>$(9.4_{-4.7}^{+9.4}) \times 10^{-12}$</td>
<td>Cattell and Cox6</td>
</tr>
<tr>
<td>250–414</td>
<td>$1.8 \times 10^{-11} \exp(170/T)$</td>
<td>$4.1 \times 10^{-11} \exp(-450/T)$</td>
<td>Lee and Howard7</td>
</tr>
<tr>
<td>243–368</td>
<td>$(2.2 ± 1.4) \times 10^{-12}$</td>
<td>$(9.1 ± 1.3) \times 10^{-12}$</td>
<td>Dobis and Benson8</td>
</tr>
<tr>
<td>230–360</td>
<td>$6.6 \times 10^{-11} \exp(-660/T)$</td>
<td>$(9.4 ± 1.9) \times 10^{-12}$</td>
<td>Riffault et al.9</td>
</tr>
<tr>
<td>226–336</td>
<td>$1.6 \times 10^{-11} \exp(249/T)$</td>
<td>$7.7 \times 10^{-11} \exp(-708/T)$</td>
<td>this work (kinetic)</td>
</tr>
<tr>
<td>250–420</td>
<td>$(3.6 ± 0.1) \times 10^{-11}$ (T = 296 K)</td>
<td>$(7.1 ± 1.7) \times 10^{-12}$</td>
<td>Sander et al.10</td>
</tr>
<tr>
<td>230–420</td>
<td>$3.2 \times 10^{-11}$ (T = 298 K)</td>
<td>$4.1 \times 10^{-11} \exp(-450/T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3.4 \times 10^{-11}$ (T = 298 K)</td>
<td>$6.3 \times 10^{-11} \exp(-570/T)$</td>
<td>Atkinson et al.11</td>
</tr>
</tbody>
</table>

*$^a$ Errors are cited at the level quoted by these authors. $^b$ Errors are cited at the level of a single standard deviation. $^c$ Room temperature (296 K) values are the actual experimental numbers and are not derived from the fit.
TABLE 8: Arrhenius Parameters and Rate Coefficients Derived from Product Data

<table>
<thead>
<tr>
<th>T/K</th>
<th>$k_1$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$</th>
<th>$k_2$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>256−296</td>
<td>$(1.5 \pm 0.1) \times 10^{-11}\exp[(222 \pm 17)/T]$</td>
<td>$(10.6 \pm 1.5) \times 10^{-11}\exp[(-733 \pm 41)/T]$</td>
</tr>
<tr>
<td>226−336</td>
<td>$(3.2 \pm 0.1) \times 10^{-11}\exp[(-T = 296)/T]$</td>
<td>$(8.5 \pm 0.1) \times 10^{-12}\exp[(-T = 296)/T]$</td>
</tr>
</tbody>
</table>

*Errors are cited at the level of a single standard deviation. Room temperature (296 K) values are the actual experimental numbers and are not derived from the fit.

The parameters for $k_{1a}$ and $k_{1b}$ listed in Tables 7 and 8 obtained in this study by independent kinetic and product experiments are in good agreement, especially with respect to the values derived for $k_{1a}$. This is particularly notable as different experimental techniques were used for the kinetic and product experiments. The kinetic measurements for $k_{1a}$ utilized resonance fluorescence of the loss of HO$_2$ reagent whereas the product measurements used long path IR absorption for the detection of HCl product. There seems to be a discrepancy, however, between the derived preexponential factors from kinetic and product experiments for $k_{1b}$ although the activation energies compare favorably. This discrepancy translates to values of $k_{1b}$(298K) = 7.2 × 10$^{-11}$ and 9.1 × 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from the fits for kinetic and product determinations, respectively, a difference of approximately 20%. At 256 K this difference becomes approximately 30% from the fits. This discrepancy, although significant, is still indicative of a greater contribution by channel 1b to the overall loss of HO$_2$ through reaction 1 than determined by Burrows et al.$^3$ and Dobis and Benson.$^8$

The separate datasets from kinetic and product experiments can be combined to derive two final Arrhenius expressions for $k_{1a}$ and $k_{1b}$:

$$k_{1a} = (1.4 \pm 0.3) \times 10^{-11}\exp[(269 \pm 58)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (33)$$

$$k_{1b} = (12.7 \pm 4.1) \times 10^{-11}\exp[(-801 \pm 94)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (34)$$

These expressions are both reported for the temperature range 226 ≤ T ≤ 336 K.

In addition to the derived kinetic equations, we can also calculate thermochemical parameters due to the reversibility of reaction 1b:

$$\text{Cl} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{ClO} \quad (1b, 2a)$$

The enthalpy of reaction, $\Delta H_r$, can be calculated by using the van’t Hoff equation, $-RT\ln K_{eq} = \Delta H_r - T\Delta S_r$, and by plotting $\ln(K_{eq})$ against 1/T. Using $k_{1b} = (12.7 \pm 4.1) \times 10^{-11}\exp[-(801 \pm 94)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from this study and $k_{2a} = (7.2 \pm 2.2) \times 10^{-12}\exp[(333 \pm 70)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from the study by Wang and Keyser$^{20}$ we obtain $\Delta H_r = (2.3 \pm 0.3)$ kcal mol$^{-1}$. This also yields a value for the reaction entropy $\Delta S_r$ of (5.7 ± 2.5) cal mol$^{-1}$ deg$^{-1}$. Using the known heats of formation for OH, ClO, and Cl of 8.9, 24.3, and 29.0 kcal mol$^{-1}$, respectively,$^11$ and the enthalpy of reaction derived above, we can calculate the heat of formation of HO$_2$: $\Delta H_f(298K)(\text{HO}_2) = (1.9 \pm 0.3)$ kcal mol$^{-1}$. The current NASA panel recommendation$^{11}$ of $\Delta H_f(298K)(\text{HO}_2) = (3.3 \pm 0.8)$ kcal mol$^{-1}$ is somewhat higher than the currently determined value although the error limits overlap. The currently determined value is also lower than that recommended by IUPAC$^{12}$ of $\Delta H_f(298K)(\text{HO}_2) = 3.5$ kcal mol$^{-1}$.

The mechanism of reaction 1 has been the subject of some debate. It was postulated in an early theoretical study by Weissman et al.$^{21}$ that the large value and negative temperature dependence of the rate coefficient for reaction 1a seemed to be inconsistent with the reaction proceeding through a simple hydrogen abstraction mechanism. Their suggestion, which was subsequently supported by Phillips and Quelch,$^{22}$ was that the reaction could proceed through a stabilized intermediate of the form

$$\text{Cl} + \text{HO}_2 \rightleftharpoons [\text{HOOC}--\text{Cl}] \rightleftharpoons [\text{HOCl}]$$ (35)
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References and Notes