Measuring Gas-Phase Chlorine Atom Concentrations: Rate Constants for Cl + HN_3, CF_3I, and C_2F_5I

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A convenient method is reported for the measurement of gas-phase Cl atom concentrations in the $10^{11}-10^{13}$ atoms cm^{-3} range in a flow reactor. The titration reaction with vinyl bromide is used to measure the absolute Cl atom concentration, and the relative Cl atom concentration is monitored by the HCl(v) infrared emission intensity produced by the reaction of Cl atoms with hydrogen sulfide. A microwave discharge through dilute flows of Cl_2, CCl_4, $CFCl_3$, and CF_2Cl_2 in Ar were characterized as sources of Cl atoms in the flow reactor. The elementary rate constants for reaction of Cl atoms with HN_3, CF_3I, and C_2F_5I were measured as (1.1 ± 0.3) × 10^{-12}, (5.1 ± 1.5) × 10^{-13}, and (3.9 ± 0.8) × 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, at 300 K. These rate constants were obtained after adjustment of the apparent rate constants for secondary reactions.

I. Introduction

Large NCl($a^1\Delta$) and NF($a^1\Delta$) concentrations can be chemically generated in the gas phase using the F/Cl/HN_3 reaction scheme.[1] In this system, reactions 1−3 are used to make NCl($a^1\Delta$,$b^1\Sigma^+$) and NF($a^1\Delta$,$b^1\Sigma^+$) at room temperature in a flow reactor.

$$F + HN_3 \rightarrow HF + N_3 \tag{1}$$

$$F + N_3 \rightarrow NF(a^1\Delta,b^1\Sigma^+,X^3\Sigma^-) + N_2 \tag{2}$$

$$Cl + N_3 \rightarrow NCl(a^1\Delta,b^1\Sigma^+,X^3\Sigma^-) + N_2 \tag{3}$$

The rate constants[2] for reactions 1 and 2 are accepted as (1.1 ± 0.2) × 10^{-10} and (5 ± 2) × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively, at 300 K. The rate constant and product branching fractions for reaction 3 are still subjects of study.[1,3] To understand the competitive reactions for N_3, the concentrations of F and Cl atoms must be measured.[3] Reaction 4,

$$Cl + HN_3 \rightarrow HCl + N_3 \tag{4}$$

with a reported rate constant[4] of (8.9 ± 1.0) × 10^{-13} cm^3 molecule^{-1} s^{-1}, also needs to be included in analysis of the kinetics of a F/Cl/HN_3 reaction system. This rate constant needs to be confirmed, and k_3 needs to be established. As part of our program[3a] to characterize the generation and removal reactions of NCl($a^1\Delta$), we needed a convenient and reliable way to measure Cl atom concentrations in the flow reactor. Many other Cl atom reaction systems also would benefit from the availability of a convenient method for measurement of the absolute and relative Cl atom concentrations.

The measurement of Cl atom densities in gas-phase flow reactors has been accomplished by a number of techniques, including atomic resonance fluorescence and absorption,[5] electron paramagnetic resonance,[6] mass spectrometry,[7] and the Cl_2-afterglow[8] emission intensity. A sensitive method for measuring absolute concentrations in flow reactors is chemical titration with monitoring of the Cl(^2P_J) concentration by resonance fluorescence. However, measurement of the Cl atom emission intensity, which is in the vacuum-ultraviolet, requires special equipment. The most common alternative for a [Cl] monitor is the Cl_2-afterglow intensity,[8] but this technique has two problems: the Cl_2(B−X) emission intensity in the 600−700 nm region is weak, and it is overlapped by the nitrogen first-positive bands, which are commonly observed as a background emission from many discharge systems. Observation of the Cl_2-afterglow intensity is only reliable for rather high Cl atom concentrations of $10^{14.5}$ molecules cm^{-3} at room temperature.[9,10]

Two Cl atom titration reactions have been used. The first, developed initially by Clyne et al.,[5] uses reaction 5 to remove Cl atoms.

$$Cl + ClNO \rightarrow Cl_2 + NO \tag{5}$$

Unfortunately, nitrosyl chloride is unstable, and it is often necessary to synthesize ClNO, since commercial sources usually contain appreciable amounts of Cl_2, NO, and NO_2 impurities. An alternative titrant is vinyl bromide,[7] with a room-temperature rate constant of 1.4 × 10^{-10} cm^3 molecule^{-1} s^{-1}.

$$Cl + C_2H_3Br \rightarrow C_2H_3Cl + Br \tag{6}$$

The secondary reaction

$$Cl + C_2H_3Cl \rightarrow C_2H_3Cl_2^* \tag{7}$$

has a bimolecular rate constant[11] of 1.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} at atmospheric pressure, because the addition product, $C_2H_3Cl_2$*, can be collisionally stabilized. Experiments examining the pressure dependence[12] of reaction 7 show that $C_2H_3Cl_2$* dissociates to Cl + C_2H_3Cl, and the effective bimolecular rate constant[13] is ∼(2−3) × 10^{-12} cm^3 molecule^{-1} s^{-1} at 2 Torr. This rate constant is sufficiently small that the secondary step does not remove an appreciable amount of Cl atoms in a flow reactor at <2 Torr. Thus, the stoichiometry for reaction 6 is one Cl atom removed for each C_2H_3Br molecule reacted.

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We used the reaction with vinyl bromide to titrate the Cl atom concentration with observation of the relative [Cl] by the HCl infrared chemiluminescence produced by reaction 8.

$$Cl + H_2S \rightarrow HCl(v{=}0,1) + SH \qquad (8)$$

The rate constant for reaction 8[14] is 5.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and the reaction is thermochemically restricted to HCl(v = 0 and 1).[15] The HCl(1−0) signal is first-order in [Cl], and the relative intensity serves as a measure of [Cl] as the [C_2H_3Br] is added during the titration. Linear extrapolation of the HCl(1−0) emission intensity to zero on a plot of intensity vs [C_2H_3Br] gives $[Cl]_0$, since reaction 6 goes to completion and has 1:1 stoichiometry. The infrared emission intensity from reaction 8 could be observed with an InSb detector for $[Cl] \geq 3 \times 10^{11}$ cm^{-3} in our experiments.

In this paper the method described above is demonstrated for measuring Cl atom concentration in our flow reactor. We then used it to calibrate the reaction time in the flow reactor by observing the Cl + HBr reaction, which has a known rate constant.[16] Next the rate constants for Cl atom removal by HN_3, CF_3I, and C_2F_5I were measured. We also show that a microwave discharge through dilute flows of Cl_2, CCl_4, $CFCl_3$, and CF_2Cl_2 in Ar are suitable sources for Cl atoms in a flow reactor.

II. Experimental Methods

(i) Description of the Flow Reactor. The 0.5 m long, 4.0 cm i.d., Pyrex flow reactor used in this study has been used extensively for infrared chemiluminescence experiments, and it has been described elsewhere.[17] Although the reactor walls were not coated, the loss of Cl atoms by recombination at the wall was not serious. Measurement of the fractional dissociation in a halocarbon wax coated reactor[18] by observation of the reduction of Cl_2 when the discharge was turned on gave approximately the same results as the titration reaction used here in the uncoated reactor.[18] The reactor was pumped by a Stokes mechanical pump, and the flow velocity was ~2750 cm s^{-1} at 2.0 Torr. The Ar carrier gas was purified by passage through no fewer than three molecular sieve filled traps cooled to 195 K. The Cl atom precursors and all other reagents were degassed by freeze−pump−thaw cycles before being diluted with Ar and stored in 12 L bulbs. Dilute mixtures of Cl_2 (Matheson), CF_2Cl_2 (PCR or Matheson), $CFCl_3$ (MG Industries), and CCl_4 (Aldrich) in Ar were passed through a microwave discharge to generate a flow of Cl atoms. The microwave power was coupled to the discharge with an Evenson type cavity, and the power (~20 W) was adjusted for maximum Cl atom concentration. The alumina discharge tube was inserted into the reactor through an aluminum flange. In other applications we have used a quartz discharge tube. Vinyl bromide (Matheson) was added via a separate tube to the bulk flow; the C_2H_3Br inlet tube terminated just downstream of the point where the Cl atoms entered the reactor. Controlled flows of H_2S (Matheson) were added 30 cm downstream of the Cl and C_2H_3Br inlets. The HCl(1−0) emission was observed through a NaCl window placed 3 cm downstream of the H_2S inlet. The Ar and Cl atom precursor flow rates were controlled by needle valves and monitored continuously by calibrated Hastings mass flow meters. The flow rates of the dilute C_2H_3Br and H_2S mixtures were also controlled by needle valves, but their flow rates were measured by diverting the flows to a vessel of known volume and measuring the rate of pressure rise.

A calibration of the reaction time was made using a reference reaction with rate constant k_R for removal of Cl atoms. For pseudo-first-order reaction conditions with fixed-point observation, a plot of ln I(HCl) vs [reagent] has a slope equal to the product of $k_R\Delta t$. Dividing the slope by k_R gives an experimental value for Δt. For the initial test, we selected C_2F_5I as the reference reaction. However, the value for the rate constant in the literature[19] gave a reaction time that was ~3 times longer than the plug flow prediction. Therefore, we selected the more thoroughly studied HBr reaction[16] as the reference. The experimental value for Δt using HBr as the reference reagent was 20% smaller than the plug flow predictions at 2 Torr pressure. For the positions of the inlets in this reactor, the reaction times are 18 and 0.6 ms from the C_2H_3Br and H_2S inlets to the NaCl observation window, respectively.

Hydrogen azide is not commercially available, since it is shock sensitive and decomposes if stored for long periods of time (3−4 weeks). It was synthesized by the reaction of stearic acid (Aldrich) with NaN_3 (Aldrich) and stored as a 10% Ar mixture in a 10 L reservoir. The reaction mixture, which usually consisted of 3 g of NaN_3 and 30 g of $C_{17}H_{35}COOH$, was evacuated and then heated to ~100 °C for 3−4 h or until the HN_3 pressure reached ~40 Torr in a 20 L bulb. The HN_3 was then diluted by Ar. The purity was periodically checked by mass spectrometry. The major peaks in the mass spectrum were at $m/z = 40$ and 43, corresponding to Ar and HN_3, respectively. Evidence of CO_2($m/z = 44$), a frequent impurity from this synthetic method, was also observed; however, the CO_2 impurity was less than 10% (of the HN_3) and, in fact, probably came mainly from the added Ar. The CF_3I and C_2F_5I were purchased from PCR.

(ii) Detection Methods. Two different infrared detection systems were used. In the initial experiments to establish the titration method, we used a Biorad FTS-60 spectrometer with an InSb detector, which gave resolved vibrational−rotational HCl spectra.[15,17] The band center of the $v = 1 \rightarrow 0$ emission is at 2886 cm^{-1}, and the Einstein emission coefficient[20] is 40 s^{-1}. For better sensitivity, a band-pass filter for 3125−2500 cm^{-1} (Perkin-Elmer) was used to block the background thermal radiation. The emission was collected by a 7.5 cm focal length lens and focused into the spectrometer.

The FT spectrometer, which was equipped with a liquid nitrogen cooled InSb detector (Infrared Associates, $D^* = 2.165 \times 10^{11}$ cm $Hz^{0.5}$ W^{-1}), was operated at 2 cm^{-1} resolution. Despite the HCl band-pass filter, the experimental HCl spectra were superimposed on a weak 300 K thermal background. To correct for this thermal emission, a background spectrum was collected with no reagents present and subtracted from the HCl signal; the only feature remaining after subtraction of the background spectrum was the HCl(1−0) band. The spectrometer was scanned 256 times (~3 min), and the I(HCl) signal was taken as the intensity of the strongest line in the HCl(1−0) band. After the method was proven, the detection system was simplified for general use with other flow reactors by using an isolated InSb detector with the same collecting lens and band-pass filter. The InSb detector in the stand-alone system was identical with the one in the spectrometer. A mechanical light chopper (EG&G Model 196) operated at 50 Hz was placed between the detector and the 7.5 cm focal length quartz lens. The current produced by the detector was converted to a voltage by a homemade preamplifier. The modulated output of the preamplifier was processed by a lock-in amplifier set for a 1 s time constant (Princeton Applied Research, Model HR-8), monitored on a digital electrometer (Keithley Model 614) and recorded on a personal computer. The thermal background was subtracted by adjusting the dc offset of the lock-in amplifier,

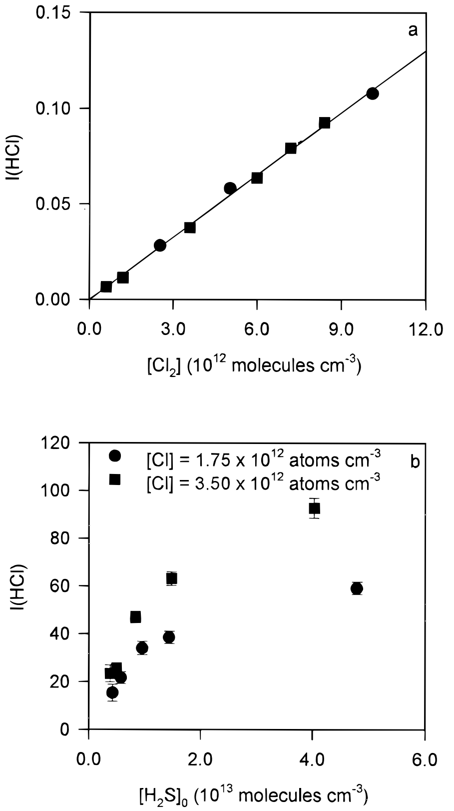

Figure 1. Plots of I(HCl) as a function of [H_2S] and [Cl]. The FTIR spectrometer was used to measure I(HCl). The data points in panel a indicated by the circles were obtained by titration. In panel b, CF_2Cl_2 was the Cl source and the stand-alone InSb detector was used to measure I(HCl). The Cl atom concentrations were determined by titration.

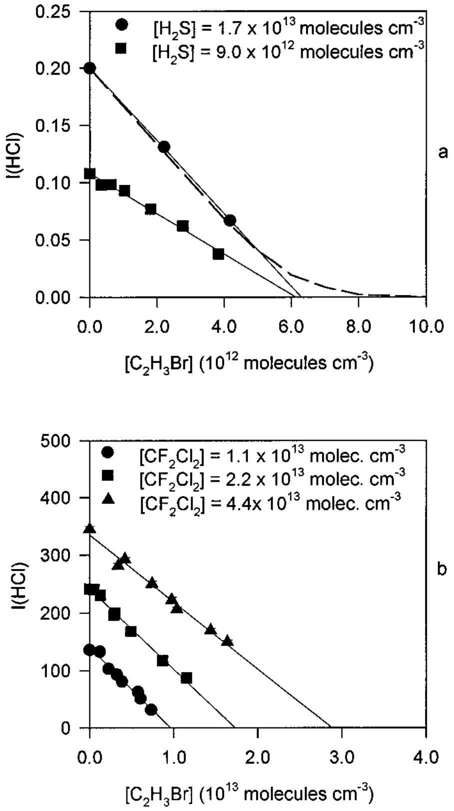

Figure 2. Sample Cl atom titration plots: (a) Two titrations on different days for the same [Cl_2], but with [H_2S] = 1.7 × 10^{13} or 9.0 × 10^{12} molecules cm^{-3}; the [Cl] was (6.2 ± 0.1) × 10^{12} atoms cm^{-3} for both experiments; I(HCl) was measured with the FTIR spectrometer. (b) Three titrations for CF_2Cl_2 as the Cl atom source with [H_2S] = 6.5 × 10^{12} molecules cm^{-3}; the I(HCl) was measured by the stand-alone InSb detector.

and the I(HCl) data were acquired with a 20 s average of the signal. With optical and electronic filtering, signal-to-noise ratios of 100:1 or better were routinely attained for [H_2S] = 1.0 × 10^{13} molecules cm^{-3}.

The most significant advantages of the stand-alone detector over the FT spectrometer are portability and ease of use. When using the interferometer to collect the data, at least 3 min was required to collect a spectrum, and about a half hour was needed to complete a Cl atom titration. The signal from the InSb detector can be monitored continuously, and a titration can be performed in a few minutes. On the other hand, the resolved spectrum from the FT spectrometer can be very helpful for some experiments.

III. Experimental Results

(i) Experiments with the FT Spectrometer To Establish the Titration Method. Because the reaction time for the Cl + H_2S reaction is short (0.6 ms), the [HCl] follows the differential rate law, and I(HCl) is first-order in [H_2S] and [Cl], e.g. $I(\mathrm{HCl}) \propto k_8[\mathrm{H_2S}][\mathrm{Cl}]\Delta t$. Figure 1a demonstrates that I(HCl) is proportional to [Cl], for [H_2S] = 9 × 10^{12} molecules cm^{-3}. The I(HCl) is also proportional to [H_2S] for fixed [Cl] as shown in Figure 1b. For sufficiently large [H_2S], the I(HCl) reaches a plateau because some Cl atoms are removed, and the differential rate law no longer holds. However, even in this high [H_2S] region, the I(HCl) still scales with [Cl]. Although nearly any H_2S concentration except [H_2S] ≪ [Cl] can be used to generate the I(HCl) signals, the best choice is $[\mathrm{H_2S}] \approx 5[\mathrm{Cl}]_0$. Checks should be made to maintain a constant H_2S flow during a Cl atom titration or any other relative Cl atom concentration measurement.

The HCl(1−0) emission intensity increased linearly with the Cl_2 (10% mixture) flow rate through the discharge over the 6.0 × 10^{11}−1.0 × 10^{13} molecules cm^{-3} range for [H_2S] = 9.0 × 10^{12} (see Figure 1a). The linear fit to the data extrapolates through the origin, indicating that $I(\mathrm{HCl}) \propto [\mathrm{Cl_2}]$ for the whole range of [Cl_2]; i.e., the fractional dissociation of Cl_2 was constant. This point was confirmed by titration measurements of [Cl] over this range of [Cl_2]. For the other Cl atom precursors, the linearity of I_0(HCl) vs [Cl source] fails for higher flows, which implies that the effective dissociation efficiency depends on the concentration of the precursor.

The utility of the vinyl bromide titration reaction has been shown previously[7] using mass spectrometry as the measure of [Cl], and we describe the titration method only briefly here. The I(HCl) is monitored vs added [C_2H_3Br] for constant [H_2S], Δt, and [Cl atom precursor]. The [Cl] value is given by the linearly extrapolated I(HCl) = 0 intercept on the [C_2H_3Br] axis. The reaction time for reaction 6 was 8 ms, so [Cl] will be 80% removed for $[\mathrm{Cl}]_0 = [\mathrm{C_2H_3Br}]_0 \geq 3 \times 10^{12}$ molecules cm^{-3}. Two sample titrations using Cl_2 as the precursor are shown in Figure 2a. The titrations were performed on different days with [H_2S] = 1.7 × 10^{13} or 0.9 × 10^{13} molecules cm^{-3}, but for the same [Cl_2] = 1.0 × 10^{13} molecules cm^{-3}. The I(HCl) signal, which was recorded with the FT spectrometer, decreases linearly with added vinyl bromide, and a smooth extrapolation to zero I(HCl) gives $[\mathrm{Cl}]_0$. The broken line in Figure 2a represents the calculated Cl atoms remaining at the detector for $[\mathrm{Cl}]_0$ = 6.2 × 10^{12} atoms cm^{-3}. The agreement between the experimental data and the theoretical line shows that the linear extrapolation from the data for $[C_2H_3Br] \leq 0.8[Cl]_0$ is valid. The titrations in Figure 2a both extrapolate to $(6.2 \pm 0.1) \times 10^{12}$ cm^{-3}, and the same fractional dissociation of Cl_2 was obtained in both experiments. Three additional Cl atom titrations are shown in Figure 2b for CF_2Cl_2 as the Cl atom source. For these experiments, the *I*(HCl) was recorded with the stand-alone detector and $[H_2S] = 6.5 \times 10^{12}$ molecules cm^{-3}. The zero intensity intercepts give $[Cl]_0 = 0.95 \times 10^{13}$, 1.7×10^{13}, and 2.9×10^{13} atoms cm^{-3} for $[CF_2Cl_2] = 0.52 \times 10^{13}$, 1.1×10^{13}, and 2.2×10^{13} molecules cm^{-3}, respectively. The titration plots in Figure 2 show that we can calibrate the *I*(HCl) signal vs known $[Cl]_0$ using titrations with vinyl bromide to establish the absolute Cl atom concentration scale.

Attempts to titrate Cl atoms for $[Cl_2] < 3 \times 10^{12}$ molecules cm^{-3} gave unreliable results, because reaction 6 does not go to completion in the fixed 8 ms reaction time for low [Cl]. It would be possible to increase Δt by decreasing the pumping speed and complete the titration. However, this is unnecessary after preparation of a calibration curve of *I*(HCl) vs [Cl]. The lowest [Cl] that can be measured is limited by the sensitivity of the detector for *I*(HCl). The smallest reliable signal for the FT spectrometer was $[Cl] = 3.3 \times 10^{11}$ atoms cm^{-3}. The smallest signal detected using the stand-alone detector with the phase-lock amplifier set for a 1 s time constant was $[Cl] = 6.0 \times 10^{11}$ atoms cm^{-3}. In principle, the stand-alone detector should be more sensitive, and even smaller [Cl] could be detected with better optics and by increasing the time constant and sensitivity of the lock-in amplifier, but we did not attempt such measurements.

(ii) Microwave Discharges of Cl_2, CCl_4, CCl_3F, and CCl_2F_2 as Cl Atom Sources. In many chemical systems, the presence of Cl_2 is undesirable, and an alternative precursor to molecular chlorine as a source of Cl atoms is needed. This is the case for the F/Cl/HN_3 reaction scheme, because the reaction rate of NCl($a^1\Delta$) with Cl_2 causes complications. The CF_2Cl_2, $CFCl_3$, and CCl_4 molecules have all been used in this laboratory as possible Cl atom sources.[3a,21] These molecules, however, are not without problems of their own. Experiments with the FT spectrometer, but without the HCl band-pass filter, showed that Cl and F atoms are both generated when CF_2Cl_2 and $CFCl_3$ (to a much smaller degree) are passed through a microwave discharge. The Cl and F atoms react with H_2S to form HCl and HF, respectively. On the basis of the relative HCl and HF infrared emission intensities, the nascent vibrational distributions, the HX formation rate constants, and the Einstein *A* coefficients,[20] we estimate that the [Cl]:[F] ratio from the discharge through CF_2Cl_2 was ~14:1. Only a trace of HF emission was observed when $CFCl_3$ was passed through the discharge, so the F atom concentration generated from $CFCl_3$ was negligible. The HF(v) contribution to the infrared emission signal detected by the stand-alone InSb detector is effectively eliminated by the HCl band-pass filter, and a small concentration of F atoms can be tolerated in the measurement of the Cl atom concentrations. Another disadvantage for $CFCl_3$, and more seriously for CCl_4, is the development of a black residue in the discharge tube after a few hours of use. This residue suggests the formation of carbon and possibly Cl_2 from the discharge. In any case, the residue can be removed easily by flowing O_2 through the discharge tube with the discharge operating. One should always be on guard for other reactive species when passing polyatomic molecules through microwave discharges. Indeed, we have evidence[21] that $CFCl_3$ gives some species other than Cl atoms when concentrations of $\geq 1 \times 10^{13}$ molecules cm^{-3} of $CFCl_3$ were used for NCl(a) and NF(a) quenching experiments.

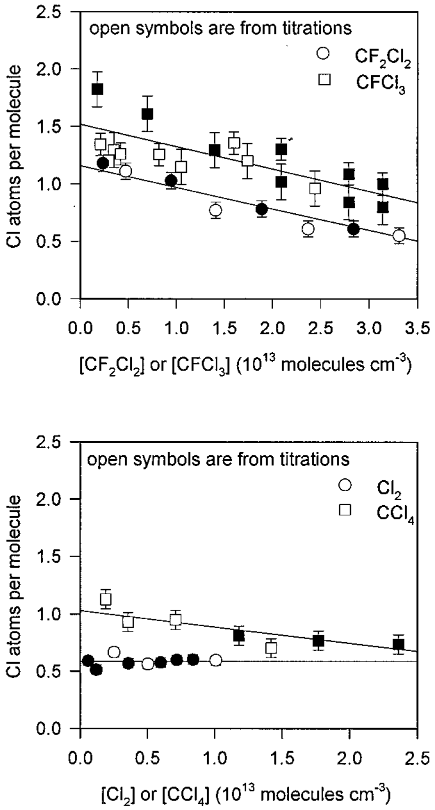

Figure 3. Dissociation efficiency for Cl_2, CF_2Cl_2, $CFCl_3$, and CCl_4 vs precursor concentration. The number of Cl atoms produced per molecule of Cl_2 is 0.6 for the $[Cl_2]$ range studied. The apparent dissociation efficiency for the chlorofluoromethanes decreases linearly, with the same apparent slope for increasing precursor concentration. The highest number of Cl atoms per precursor molecule is 1.5, 1.1, and 1.0 for CF_2Cl_2, $CFCl_3$, and CCl_4, respectively.

The Cl atom titration method worked very well with all the precursor molecules for measurement of the Cl atom concentration, as shown by the plots in Figure 2b. The average number of Cl atoms per precursor molecule is plotted vs the precursor concentration in Figure 3. After calibration of the *I*(HCl) by titration, the [Cl] was determined from the relative *I*(HCl). The fractional dissociation of Cl_2 is low, but constant, at ~30%; i.e., each Cl_2 molecule gives 0.6 atom up to $[Cl_2] = 1 \times 10^{13}$ cm^{-3}. We have obtained a similar result in a different flow reactor.[18] The concentration range for CF_2Cl_2, $CFCl_3$, and CCl_4 was extended to 3×10^{13} molecules cm^{-3}, and the dissociation efficiency decreases for higher concentrations. The low concentration limit corresponds to 1.5, 1.2, and 1.0 Cl atoms per CF_2Cl_2, $CFCl_3$, and CCl_4 molecule, respectively. Perhaps fortuitously, the apparent reduction in dissociation efficiency with increased precursor concentration was the same for all three molecules. The number of Cl atoms obtained per $CFCl_3$ molecule seemed less reproducible than for the other precursors; however, two separate experiments with $CFCl_3$ gave the same qualitative result.

Using dilute mixtures in Ar (Cl_2, 10% or 5%; CF_2Cl_2, 30%; $CFCl_3$, 20%; CCl_4, 15%), we measured the dependence of the Cl atom production on microwave power using the titration by C_2H_3Br to establish the absolute Cl atom concentration. The highest fractional dissociation in all cases was for the lowest microwave power for which the discharge was stable, ~20 W. For higher power, the F atom concentrations increased with CF_2-

Cl_2 and $CFCl_3$, and the rate of deposition of the solid residue increased for $CFCl_3$ and CCl_4.

A note of precaution should be reserved for use of the fluorochloromethanes as Cl atom sources. The cofragment from dissociation is likely to be halomethyl or halocarbene radicals. The former have recombination rates with Cl atoms, as well as with themselves. The Cl + CF_3 recombination rate constant at 300 K can be estimated[22] as ~1 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 1 Torr. If $[Cl] = [CF_3] = 1 \times 10^{13}$ cm^{-3}, then one-half of the Cl atoms could be lost by recombination in 0.01 s. The recombination rate constants for Cl + $CFCl_2$ and CCl_3 will be similar.[22] The decline in the apparent dissociation efficiency shown in Figure 3 could be a consequence of these recombination reactions. A microwave discharge in CF_4 is commonly used as a source of F atoms.[2,3,21] However, that source gives 2F per CF_4 molecule in the 1 × 10^{13} molecules cm^{-3} range, and recombination seems not to be a problem, because the rate constant for F + CF_2 is less than for F + CF_3.[23]

(iii) Measurement of Cl Atom Removal Rate Constants. The measurement of reliable rate constants for Cl atom removal in a flow reactor depends on knowing the reaction time. Experiments with HBr demonstrated that, in fact, the plug-flow reaction time was approximately correct.

$$\mathrm{Cl} + \mathrm{HBr} \rightarrow \mathrm{HCl}(v) + \mathrm{Br} \tag{9}$$

Reaction 9 has a room-temperature rate constant[16] of (1.05 ± 0.1) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and it produces vibrationally excited HCl (the nascent distribution[15] is $v = 0{:}1{:}2 = 33{:}50{:}17$) and some vibrationally excited molecules survive to the IR detection zone. Therefore, the observed IR signal from the Cl + H_2S reaction must be adjusted for the background emission from reaction 9. The I(HCl) with the flow of H_2S turned off was subtracted from the total I(HCl) signal obtained from H_2S plus reaction 9.

The rate constants for removal of Cl atoms by HN_3, C_2F_5I, and CF_3I were measured by direct comparison to the HBr reaction, and, in fact, we did not use the reaction time. Pseudo-first-order conditions were used for all reagents, so the integrated rate law simplifies to eq 10 with Δt fixed for the HBr reaction.

$$I(\mathrm{HCl})/I_0(\mathrm{HCl}) \propto [\mathrm{Cl}]/[\mathrm{Cl}]_0 = \exp[-(k_{\mathrm{HBr}}[\mathrm{reagent}]\Delta t)] \tag{10}$$

The slopes of the pseudo-first-order plots for reaction with HN_3 and CF_3I (see Figure 4 for representative plots), relative to the slope for HBr, were used to calculate the overall rate constant (see eq 11 for CF_3I).

$$k_{\mathrm{CF_3I}} = \frac{\mathrm{slope}(\mathrm{CF_3I})}{\mathrm{slope}(\mathrm{HBr})} k_{\mathrm{HBr}} \tag{11}$$

The comparison between HBr and C_2F_5I is shown in Figure 5. Several experiments for each reagent were performed, and $[Cl]_0$ and Δt were both varied. In addition, two different Cl atom precursors, CF_2Cl_2 and $CFCl_3$, were used. No systematic difference in rate constants was noted between the two Cl atom sources. We did not use Cl_2 as the Cl atom source, because the reaction of CF_3 with Cl_2 would regenerate Cl atoms. The data give linear plots, and the slopes were reproducible. The total Cl atom removal rate constants for HN_3, CF_3I, and C_2F_5I are summarized in Table 1.

The removal of Cl atoms from secondary reactions must be considered for HN_3, CF_3I, and C_2F_5I, before the apparent rate constants can be converted to elementary rate constants. The rate constant for Cl + N_3 is still uncertain,[1,3,18] but it is larger than 2 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and each HN_3 molecule will remove two Cl atoms. With this assumption, our rate constant for HN_3 agrees with the previously published value, although those previous measurements were somewhat indirect.[4] The importance of the secondary reaction for CF_3I is more difficult to ascertain. The rate constants for Cl + ICl[24] and for Cl + CF_3 (at 1 Torr)[22] are 0.8 × 10^{-11} and ~1 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. Numerical integration of the rate equations suggests that *each* secondary reaction consumes about 0.5 Cl atom per molecule of CF_3I that reacts. Thus, the apparent rate constant was divided by a factor of 2 to estimate the primary rate constant.

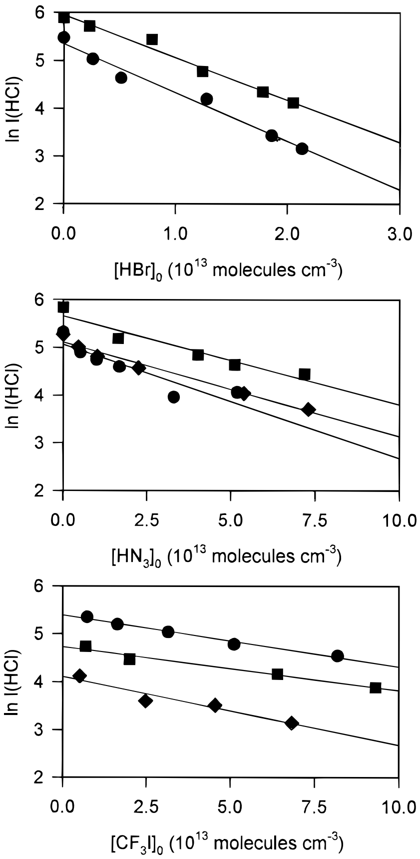

Figure 4. Pseudo-first-order plots of Cl atom concentration vs reagent concentration. In all cases $[H_2S]$ was ~1 × 10^{13} cm^{-3}, the reactor pressure was 2 Torr, and Δt was 11 ms. (a) The slopes (cm^3 $molecule^{-1}$) and Cl atom concentrations (atoms cm^{-3}) for the HBr reaction are as follows: (●) [Cl] = 2.3 × 10^{12}, slope = 1.0 × 10^{-13}; (■) [Cl] = 8.8 × 10^{12}, slope = 8.9 × 10^{-14}. (b) For the Cl + HN_3 reaction: (●) [Cl] = 3.1 × 10^{12}, slope = 1.9 × 10^{-14}; (■) [Cl] = 6.2 × 10^{12}, slope = 1.9 × 10^{-14}; (◆) [Cl] = 1.2 × 10^{13}, slope = 2.0 × 10^{-14}. (c) For the Cl + CF_3I reaction: (●) [Cl] = 8.8 × 10^{12}, slope = 1.1 × 10^{-14}; (■) [Cl] = 5.2 × 10^{12}, slope = 9.2 × 10^{-15}; (◆) [Cl] = 2.3 × 10^{12}, slope = 1.4 × 10^{-14}.

The Cl + C_2F_5 recombination reaction probably is close to its high-pressure limit at 1 Torr, and this reaction will remove a second Cl atom. We ran a numerical simulation of the Cl + C_2F_5I system that included Cl + ICl and Cl + C_2F_5, with rate constants of 0.8 × 10^{-11} and 1.0 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} to estimate the stoichiometry. The results indicate that each C_2F_5I molecule that reacts removes about 2.5 Cl atoms, and the apparent rate constant was divided by 2.5 to estimate the primary rate constant.

Our rate constants for CF_3I and C_2F_5I are both larger than the measurements of Ahonkhai and Whittle.[19] In their study, mixtures of Cl_2 + C_2F_5I (or CF_3I) + CH_4 were photolyzed,

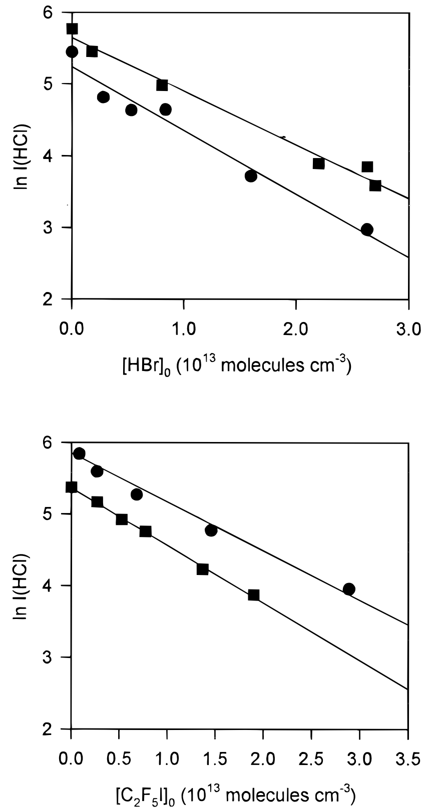

Figure 5. Pseudo-first-order plot of Cl atom concentration vs C_2F_5I concentration. The reaction pressure was 2 Torr, $[H_2S] = 1 \times 10^{13}$ cm^{-3}, and $\Delta t = 11$ ms. (a) The slope (cm^3 molecule^{-1}) and $[Cl]_0$ (atoms cm^{-3}) for the HBr experiments are as follows: (●) $[Cl]_0 = 6.2 \times 10^{12}$, slope $= 8.9 \times 10^{-14}$; (■) $[Cl]_0 = 1.2 \times 10^{13}$, slope $= 7.5 \times 10^{-14}$. (b) For Cl + C_2F_5I: (●) $[Cl] = 6.2 \times 10^{12}$, slope $= 6.9 \times 10^{-14}$; (■) $[Cl]_0 = 1.2 \times 10^{13}$, slope $= 8.0 \times 10^{-14}$.

TABLE 1: Cl Atom Removal Constants

	rate constant[a]		
reagent	apparent value	elementary step	literature
HN_3	2.2 ± 0.6	1.1 ± 0.3	0.89 ± 0.10[b]
CF_3I	1.0 ± 0.3	0.50 ± 0.15	0.17 ± 0.14[c]
C_2F_5I	9.8 ± 2.0	3.9 ± 0.8	1.5 ± 1.2[c]

[a] In units of 10^{-12} cm^3 molecules^{-1} s^{-1}; the uncertainties are the standard deviation from six experiments for each reaction. See text for justification for corrections for secondary reactions. [b] Reference 4. [c] Reference 19.

and the removal of Cl atoms was monitored by end product analysis using gas chromatography. The ratio of CH_3Cl to C_2F_5Cl generated by reaction 12

$$CH_3 \text{ (or } C_2F_5) + Cl_2 \rightarrow CH_3Cl \text{ (or } C_2F_5Cl) + Cl \quad (12)$$

was related to the competition between Cl + CH_4 and Cl + C_2F_5I to obtain the rate constant. Although our measurement is more direct, we have not eliminated the secondary reactions. We loaded several C_2F_5I samples taking care to remove any I_2 or other impurities, but the same apparent rate always was obtained. Our rate constant values for CF_3I and C_2F_5I probably are upper limits to the true elementary rate constant, because of the uncertainty associated with the treatment of the secondary reactions.

IV. Conclusions

A successful titration reaction requires a large rate constant, known stoichiometry, and chemical stability of the titrant. Since reaction 6 is ~5 times faster than the Cl + ClNO reaction, vinyl bromide is inherently more sensitive as a titrant than nitrosyl chloride. In addition, vinyl bromide is stable at room temperature, not corrosive, and commercially available in high purity. On the basis of these considerations, we recommend C_2H_3Br for the titration of gas-phase Cl atom densities of $\geq 3 \times 10^{12}$ atoms cm^{-3} in a flow reactor. While this laboratory has little experience in generating or measuring Cl atom concentrations above 1×10^{14} atoms cm^{-3}, we do not expect any complications in extending reaction 6 to higher Cl atom concentrations. It is important to note, however, that the stoichiometry of Cl removal by vinyl bromide will change if the pressure in the reactor is too high, due to the increasing importance of the Cl + C_2H_3Cl secondary reaction.

In addition to testing the C_2H_3Br titration reaction, we have also demonstrated the use of HCl(1−0) emission intensity as a monitor of the relative [Cl] using a Fourier transform infrared spectrometer or a stand-alone InSb detector with a band-pass filter. High-sensitivity IR detectors for the HCl(1−0) spectral region are commercially available, and in many instances the observation of IR emission is more easily implemented than the two-photon laser-induced fluorescence on the vacuum-ultraviolet atomic resonance fluorescence or absorption techniques. If H_2S is not chemically compatible with other reagents in the flow reactor, other H atom donors with low bond energies, such as HI or SiH_4, could be substituted. After calibration of the HCl infrared emission intensity by titration to establish the absolute [Cl], the Cl atom concentrations ($\geq 3 \times 10^{11}$ atoms cm^{-3}) could be measured from the relative infrared emission intensities.

The Cl atom concentration from a microwave discharge through four precursor molecules diluted in Ar have been characterized. Under our conditions, Cl_2, CF_2Cl_2, $CFCl_3$, and CCl_4 are all satisfactory sources of Cl atoms in a flow reactor. However, CF_2Cl_2 gives Cl and F atoms in a 14:1 ratio, while $CFCl_3$ and CCl_4 both generate carbon deposits inside the discharge tube. The F atoms and the deposits are minimized by operation of the discharge at low power. The possibility for loss of Cl atoms from recombination reactions with CF_2Cl, $CFCl_2$, and CCl_3 radicals should be remembered. Such loss processes will become important for higher Ar pressures and longer reaction times.

The Cl atom removal rate constants for HN_3, CF_3I, and C_2F_5I have been measured at 300 K, relative to a reference reaction, Cl + HBr. After allowance for secondary reactions, the elementary rate constants were assigned as $(1.1 \pm 0.3) \times 10^{-12}$, $(0.51 \pm 0.15) \times 10^{-12}$, and $(3.9 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. The quoted statistical uncertainties do not include the uncertainties introduced by the corrections for secondary reactions. In other work[21] we have demonstrated that the major product from the Cl + HN_3 reaction is HCl + N_3. Although the rate is relatively slow at room temperature, the reaction could be a chemical source of N_3 at higher temperature.

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paper reports the branching ratio for HNF formation in reaction 1 as $0.03^{+0.02}_{-0.01}$.

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