always in conjunction with one another. Therefore, since a line-fitting process to obtain the best values for k_{17} and k_{18} independently leads to rather arbitrary values, the definition of a composite rate constant appears more practical as well as more exact, $k_{17} + 0.356k_{18} = 1.22 \times 10^7$ M^{-1} s^{-1}. This composite rate constant was calculated by using the aforementioned values for k_8, k_{19}, X, and Y and the experimentally determined values for k_{obsd} in the pH range 2–7. Although k_{17} and k_{18} can be varied, the relationship $k_{17} + 0.356 = 1.22 \times 10^7$ M^{-1} s^{-1} was found to be very exact.

Using these rate constants, k_8, $k_{17} + 0.356k_{18}$, and k_{19}, one can calculate a k_{obsd} vs. pH curve (see Figure 1), in good agreement with the experimental values.

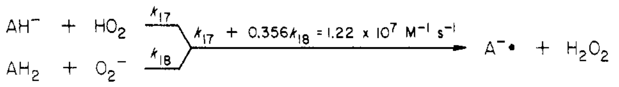
As discussed previously, the reaction between AH_2/AH^- and HO_2/O_2^- (reactions 8, 17, and 18) was measured under steady-state conditions. If, however, the AH_2/AH^- concentration is increased substantially, all of the HO_2/O_2^- is consumed in reaction with AH_2/AH^- (reactions 8, 17, and 18) and the $A^-\cdot$ that is formed subsequently disappears by reactions 14–16. Since the molar absorbance of $A^-\cdot$ is well established (ϵ_{360nm} = 3300 M^{-1} cm^{-1} (ref 21)), the quantity of $A^-\cdot$ that is formed can be measured. It was found that at pH 6–7 (0.5 M AH_2/AH^-, 5×10^{-6} M O_2^-/HO_2) the formation of $A^-\cdot$ was quantitative while at pH 8.5–9.5 (at pH 9.5 O_2^- was added anaerobically in order to eliminate the formation of $A^-\cdot$ by an autooxidation process) no $A^-\cdot$ was observed. These experiments indicate that, although reactions 8, 17, and 18 lead to the formation of $A^-\cdot$, reaction 19, the reaction between AH^- and O_2^-, does not yield $A^-\cdot$.

As discussed previously, a further probe of reaction 19 involved mixing equimolar amounts of AH^- and O_2^- at pH 8.6. Since the ratio of O_2^- to AH^- consumed was 2:1, the product of reaction 19 either reacts rapidly with another O_2^- radical or disproportionates in a manner similar to $A^-\cdot$ (reactions 14–16). The possibility that AH^- reacts with O_2^- in a single two-electron step as suggested previously[11] cannot be ruled out at this point. Unfortunately, none of these possibilities for reaction 19, can, at present, be either verified or eliminated.

Conclusion

The presented results indicate that the oxidation of AH_2/AH^- by HO_2/O_2^- proceeds with the following rates:

$$AH_2 + HO_2 \xrightarrow{k_8 = 1.6 \times 10^4\ M^{-1}\ s^{-1}} A^-\cdot + H_2O_2 + H^+$$



$$AH^- + O_2^- \xrightarrow{k_{19} = 5 \times 10^4\ M^{-1}\ s^{-1}} \text{product}$$

In addition, the radical–radical reactions between $A^-\cdot$ and HO_2/O_2^- proceed by the following rates:

$$A^-\cdot + HO_2 \xrightarrow{k_9 = 5 \times 10^9\ M^{-1}\ s^{-1}} A + HO_2^-$$

$$A^-\cdot + O_2^- \xrightarrow[H_2O]{k_{11} = 2.6 \times 10^8\ M^{-1}\ s^{-1}} A + HO_2^- + OH^-$$

Acknowledgment. We thank Dr. H. A. Schwarz for many stimulating discussions on the present work and Mr. D. A. Comstock for excellent technical assistance. This research was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported in part by its Office of Basic Energy Sciences.

Registry No. AH_2, 50-81-7; AH^-, 299-36-5; HO_2, 3170-83-0; O_2^-, 11062-77-4; $A^-\cdot$, 34481-26-0.

Kinetics of the Reaction of Chlorine Atoms with Vinyl Bromide and Its Use for Measuring Chlorine-Atom Concentrations

Jong-Yoon Park, Irene R. Slagle, and David Gutman*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616 *(Received: October 27, 1982)*

The reaction of chlorine atoms with vinyl bromide, $Cl + C_2H_3Br \rightarrow C_2H_3Cl + Br$, has been tested as a titration reaction for chlorine atoms in gas-phase fast-flow reactors using both continuous and pulsed atom sources. The vinyl chloride produced by this reaction was determined by using photoionization mass spectrometry and was found to be an accurate measure of the in situ chlorine-atom concentration down to 5×10^{10} atoms cm^{-3}. The reaction is rapid and stoichiometric and involves the use of easily handled substances. It is particularly well suited for use with photoionization mass spectrometer detectors because of the low ionization potentials and high photoionization cross sections of both vinyl bromide and vinyl chloride. The rate constant of this reaction was measured at 298 K and determined to be 1.43 (±0.29) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

Introduction

The rapid reactions of chlorine atoms with organic molecules have been found to be useful sources of polyatomic free radicals in many chemical kinetic studies. In most investigations it has not been necessary to accurately know the concentration of either the chlorine atoms or the free radicals which were produced. These studies include ones conducted under photostationary-state conditions, where relative rates have been measured and mechanisms established, and others in which the reaction of the free radical of interest could be isolated for quantitative study under pseudo-first-order conditions. Examples of the first kind of such studies include the many smog-chamber experiments, particularly by Niki and co-workers,[1,2] which

---

(1) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1974**, *45*, 567; **1978**, *55*, 289; **1978**, *57*, 596; **1978**, *59*, 78; **1979**, *61*, 100; **1980**, *73*, 43; **1980**, *75*, 533.

(2) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1980**, *84*, 14; **1981**, *85*, 877; **1982**, *86*, 3825–9; *Int. J. Chem. Kinet.* **1980**, *12*, 100, 915.

0022-3654/83/2087-1812$01.50/0

have provided a wealth of detailed knowledge of the reactions of a large number of the polyatomic free radicals which are important in tropospheric smog cycles.[3] Recently studies of the second type have been reported by Sander and Watson,[4] Plumb and Ryan,[5] and also Slagle and Park from our laboratory.[6,7]

We have begun to study recombination reactions of polyatomic free radicals which are generated by Cl-atom reactions. Following the rapid production of the polyatomic free radicals of interest in a tubular reactor, their concentration profiles are recorded by using time-resolved photoionization mass spectrometry (PIMS). In these experiments the initial free-radical concentrations must be established and are determined from the measured concentration of the chlorine atoms which produced them. Although several excellent methods have already been established to measure in situ chlorine-atom concentrations using various diagnostic probes,[8] none is particularly well suited for studies employing PIMS detection of reactants and products. The PIMS ionizing radiation is provided by intense atomic resonance lamps with ionizing energies up to 11.6 eV.[9,10] High sensitivity and maximum accuracy are, however, obtained only with those lamps which provide radiation below 10.6 eV. Of the currently tested Cl-atom titration procedures, two require detection of species with ionization potentials (IPs) above this value: measurement of Cl_2 depletion following passage through a microwave discharge,[5a,11,12] and determination of Br_2 consumed by the Cl + Br_2 reaction.[12,13] The widely used measurement of NO production from the Cl + NOCl reaction as a Cl-atom titration procedure involves the detection of a species with a suitably low IP,[14] but NO has a relatively low photoionization cross section which makes it difficult to measure low chlorine-atom concentrations.

For the reasons mentioned above, we have searched for a different Cl-atom titration reaction, one which would be as quantitative as the established ones, but which would be more suitable for use in studies employing PIMS detectors. We sought a rapid stoichiometric titration reaction involving an easily handled gas which produces a stable product and whose yield could be easily measured even at low concentrations with our detection method. Ready access and ease of handling of this product were also considered important due to the need to use the gas often for mass spectrometer sensitivity measurements. The reaction which we have found most convenient is

$$\mathrm{Cl} + \mathrm{C_2H_3Br} \rightarrow \mathrm{C_2H_3Cl} + \mathrm{Br} \qquad \Delta H = -13\ \mathrm{kcal/mol} \tag{1}$$

Under low-pressure flow-reactor conditions, this reaction proceeds without any observable side reactions which would prevent equating measured vinyl chloride yield with the initial chlorine-atom concentration. Alternate reactive routes such as

$$\mathrm{Cl} + \mathrm{C_2H_3Br} \rightarrow \mathrm{C_2H_2Br} + \mathrm{HCl} \qquad \Delta H = 5\ \mathrm{kcal/mol} \tag{2}$$

$$\mathrm{Cl} + \mathrm{C_2H_3Br} \rightarrow \mathrm{C_2H_2BrCl} + \mathrm{H} \qquad \Delta H = 27\ \mathrm{kcal/mol} \tag{3}$$

$$\mathrm{Cl} + \mathrm{C_2H_3Br} \rightarrow \mathrm{C_2H_3} + \mathrm{BrCl} \qquad \Delta H = 25\ \mathrm{kcal/mol} \tag{4}$$

are endothermic and do not proceed to a measurable extent under our experimental conditions.[15] The excited C_2H_3BrCl adduct formed in the initial phase of reaction 1 has an extremely short lifetime (<3 ps) and is not stabilized by collisions at subatmospheric pressures.[16]

In view of the increasing use of PIMS detection methods in studies of gas-phase reactions,[5,17-21] we are reporting the procedure that we have developed to use reaction 1 as a quantitative titration reaction for chlorine atom. The method should be applicable in a wide variety of experimental arrangements.

We have also measured the rate constant of this reaction at ambient temperature. The results of this second study are also included here. Although there is now considerable knowledge available regarding the molecular dynamics of the Cl + C_2H_3Br reaction from both angle-resolved molecular beam and chemiluminescence studies,[16,22,23] the thermal rate constant of this reaction has not yet been reported.

Experimental Section

The experiments which were performed to test the suitability of reaction 1 as a Cl-atom titration reaction involved the use of two different flow reactor systems and the use of both pulsed and continuous sources of Cl atoms. The rate constant of this reaction was measured by using the continuous Cl-atom source.

Experiments were performed over a range of low pressures (0.7–2.1 torr), at moderate flow velocities (5–20 m s^{-1}), and always in high dilution in an inert carrier gas (He or Ar).

The carrier gases He (99.995%) and Ar (99.998%) were obtained from Linde and used without further purification except as mentioned below. Most of the reactant gases were obtained from Matheson: Cl_2 (99.5%), C_2H_3Br (99.5%), C_2H_3Cl (99.9%), and CH_3OCH_3 (99.9%). The C_6F_5Cl (99%) was obtained from PCR Chemical Co. Each of these compounds was purified by condensation followed by fractional distillation, the middle third being retained for the experiments.

---

(3) (a) Cox, R. A.; Tyndall, G. S. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 153–63. (b) Bahta, A.; Simonaitis, R.; Heicklen, J. *J. Phys. Chem.* **1982**, *86*, 1849–53.

(4) Sander, S. P.; Watson, R. T. *J. Phys. Chem.* **1980**, *84*, 1664–74.

(5) (a) Plumb, I. C.; Ryan, K. R. *Int. J. Chem. Kinet.* **1981**, *13*, 1011–28. (b) Plumb, I. C.; Ryan, K. R.; Steven, J. R.; Mulcahy, M. F. R. *Ibid.* **1982**, *14*, 183–94.

(6) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1982**, *104*, 4741–8.

(7) Park, J. Y.; Gutman, D. *J. Phys. Chem.*, in press.

(8) Clyne, M. A. A.; Nip, W. S. In "Reactive Intermediates in the Gas Phase"; Setser, D. W., Ed.; Academic Press: New York, 1979; Chapter 1.

(9) Kanofsky, J. R.; Lucas, D.; Gutman, D. *Symp. (Int.) Combust., [Proc.]* **1973**, *14*, 285.

(10) Kanofsky, J. R.; Lucas, D.; Pruss, F.; Gutman, D. *J. Phys. Chem.* **1974**, *78*, 311.

(11) Leu, M. T.; DeMore, W. B. *Chem. Phys. Lett.* **1976**, *41*, 121–4.

(12) Ray, G. W.; Keyser, L. F.; Watson, R. T. *J. Phys. Chem.* **1980**, *84*, 1674–81.

(13) Clyne, M. A. A.; Smith, D. J. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 263–79.

(14) Clyne, M. A. A.; Cruse, H. W.; Watson, R. T. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 153–68.

(15) Enthalpies of reaction calculated by using enthalpies of formation in: (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6* (Suppl. 1), 1. (b) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976. It was assumed that the C–H bond strengths in C_2H_3Br are the same as in C_2H_4 and that the C–Cl bond strength in C_2H_2BrCl is the same as in C_2H_3Cl.

(16) Buss, R. J.; Coggiola, M. J.; Lee, Y. T. *Faraday Discuss. Chem. Soc.* **1979**, *67*, 162–72.

(17) Lenhardt, T. M.; McDade, C. E.; Bayes, K. D. *J. Chem. Phys.* **1980**, *72*, 304–10.

(18) Washida, N. *J. Chem. Phys.* **1980**, *73*, 1665.

(19) Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 5430.

(20) Herron, J. T.; Huie, R. E. *Int. J. Chem. Kinet.* **1978**, *10*, 1019.

(21) Bierman, H. W.; Harris, G. W.; Pitts, J. N. *J. Phys. Chem.* **1982**, *86*, 2958–64.

(22) Cheung, J. T.; McDonald, J. D.; Herschbach, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 7889–91.

(23) Durana, J. F.; McDonald, J. D. *J. Chem. Phys.* **1976**, *64*, 2518–27.

Mechanism and Titration Experiments Using a Continuous Cl-Atom Source. A conventional fast-flow reactor with a movable concentric inlet tube was used to verify the stoichiometry of reaction 1 and to measure its rate constant. The important dimensions are essentially the same as those of a similar one described by Niki, Daby, and Weinstock.[24] Details of our system including those dealing with the coating of the reactor walls with phosphoric acid, the gas sampling from the end of the reactor tube, the photoionization mass spectrometer detection methods, and the data reduction procedures have been described previously.[7,25] The experiments involved searching for possible primary and secondary products of the Cl + C_2H_3Br reaction, comparing measurements of vinyl bromide loss due to reaction with Cl atoms with vinyl chloride formation, and comparing Cl-atom concentration measurements using both the Cl_2 depletion and C_2H_3Cl formation methods.

Chlorine atoms were generated upstream by passing a Cl_2–He (or Ar) gas mixture through a microwave discharge. The extent of dissociation varied from 9% to 27%, the higher values being obtained in experiments using the lower Cl_2 concentrations. Care was taken to remove trace impurities from the inert carrier gases. They were passed through a liquid-nitrogen-cooled trap just prior to the addition of Cl_2 and the subsequent passage of the mixture through the discharge. Tests for the presence of H and O atoms produced by the microwave discharge when only the carrier gas was used indicated negligible amounts present compared to the Cl-atom concentrations when Cl_2 was present.

Search for Primary and Secondary Products of the C_2H_3Br Reaction. Series of experiments were performed to detect the possible primary and secondary products which could be formed under our experimental conditions. Both Ar- (11.6 eV) and H-atom (10.2 eV) resonance lamps were used in the search. The only significant products detected were C_2H_3Cl and Br. At long reaction times small amounts of Br_2 were also detected. In spite of the use of lengthy ion counting times, the following products were not detected at all: C_2H_4, C_2H_3, C_2H_2, HBr, C_2H_2ClBr, and C_2H_3ClBr.

Comparison of C_2H_3Br Consumption with C_2H_3Cl Formation. When reaction 1 is used for titration purposes, C_2H_3Br is added in large excess over the ambient Cl-atom concentration in order to complete the titration rapidly and to suppress secondary reactions which might scavenge some of the chlorine atoms. It is presumed that the reaction is stoichiometric, namely, that the ratio $-\Delta[C_2H_3Cl]/\Delta[C_2H_3Br] = 1$ exactly. This presumption cannot be tested with C_2H_3Br in large excess. We have however performed experiments to determine the reaction stoichiometry with $[C_2H_3Br]_0/[Cl]_0 = 2.6$. Measurements were made of C_2H_3Br, C_2H_3Cl, and Br ion signals at 11 positions of the movable inlet tube. The ion signals of vinyl bromide and vinyl chloride were calibrated by using known flows of the two gases. The ion signal profiles and the measured values of the stoichiometry ratio are shown in Figure 1.

Comparison of Cl-Atom Determination Methods. Cl_2 Depletion vs. C_2H_3Cl Formation. In order to establish that the measurement of vinyl chloride yield by reaction 1 is as quantitative a procedure for measuring absolute Cl-atom concentrations in flow reactors as another already well-established one, we have conducted a thorough comparison of the Cl_2-depletion method, which has been used extensively and tested frequently,[5a,11,12] with our procedure. Experiments were performed over a wide range of Cl-atom concentrations (6×10^{10}–1.5×10^{13} atoms cm^{-3}), total gas pressures, flow velocities, concentrations of Cl_2 and C_2H_3Br, and using two different carrier gases.

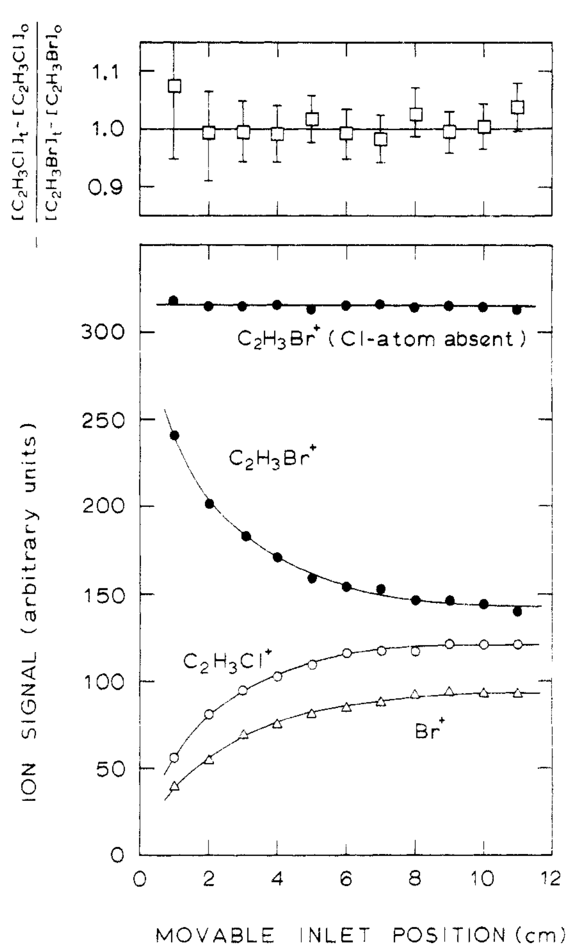


Figure 1. Measured ion signal profiles of species in source C_6F_5Cl) $C_2H_3Br \rightarrow C_2H_3Cl + Br$ reaction and cumulative stoichiometry ratio. Conditions of experiment: $P = 1.88$ torr (He diluent), $v = 13.2$ m s^{-1}, $[Cl] = 3.2 \times 10^{12}$ atoms cm^{-3}, $[C_2H_3Br]_0/[Cl]_0 = 2.6$, $T = 298$ K. Standard deviation of the net ion signals (signal minus background) is near the size of the symbols used to plot the data. The standard deviation of the calculated stoichiometry ratios are shown as error bars.

Under each set of experimental conditions, the Cl-atom concentration was first measured by the Cl_2-depletion method with vinyl bromide being admitted through the movable inlet tube positioned 5 cm from the sampling point. This procedure assures chlorine-atom removal at the same position in the flow reactor where they will be measured by using the vinyl chloride formation method and eliminates any possible Cl-atom recombination back to Cl_2 between the titration and sampling points. Failure to conduct comparisons under these conditions can result in Cl_2-depletion measurements yielding systematically lower Cl concentration values than those obtained by titrations upstream from the sampling point.[5a,12] The measured fractional loss of Cl_2 combined with the measured Cl_2 flow rate yielded the absolute Cl-atom concentration from the relationship $-2\Delta[Cl_2] = [Cl]$.

The determination of Cl-atom concentrations using reaction 1 involves simply measuring the vinyl chloride yield resulting from the titration reaction while vinyl bromide is flowing down the movable inlet tube (which is again positioned 5 cm from the sampling orifice). Vinyl bromide concentrations sufficiently high to assure complete reaction

---

(24) Niki, H.; Daby, E. E.; Weinstock, B. *Symp. (Int.) Combust., [Proc.]* **1973**, *12*, 277–88.

(25) Slagle, I. R.; Pruss, F. J.; Gutman, D. *Int. J. Chem. Kinet.* **1974**, *6*, 111–23.

TABLE I: Chlorine-Atom Concentration Measurements by the Cl_2-Depletion and C_2H_3Cl-Formation Methods at 300 ± 1 K

carrier gas	P, torr	v, m s^{-1}	10^{-12} × $[Cl_2]_0$, molecules cm^{-3}	10^{-13} × $[C_2H_3Br]$, molecules cm^{-3}	(-2×10^{-12}) × $\Delta[Cl_2]$, molecules cm^{-3}	10^{-12} × $\Delta[C_2H_3Cl]$, molecules cm^{-3}	$-\Delta[C_2H_3Cl]/(2\Delta[Cl_2])$
He	1.39	11.56	0.351	8.63	0.0656	0.0660	1.01
He	1.39	11.56	0.890	8.63	0.160	0.147	0.92
He	1.64	15.06	0.655	4.93	0.197	0.197	1.00
Ar	1.44	8.56	1.24	11.2	0.422	0.413	0.98
He	1.69	14.61	2.60	5.13	0.656	0.622	0.95
Ar	1.39	9.16	1.76	11.1	0.618	0.657	1.06
He	1.76	13.95	6.00	5.04	1.52	1.25	0.82
He	1.64	15.10	6.16	4.92	1.75	1.55	0.89
He	1.63	15.13	9.19	1.68	1.93	1.86	0.96
Ar	1.40	8.80	9.99	12.6	3.60	3.55	0.99
Ar	1.39	9.18	26.2	13.4	8.66	8.53	0.98
Ar	1.85	11.22	19.5	9.18	10.5	10.6	1.01
Ar	1.40	8.80	49.8	12.6	15.4	16.4	1.06
							av = 0.97 ± 0.07 (1σ)

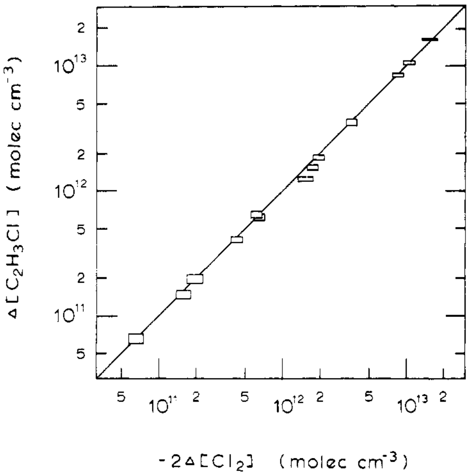


Figure 2. Plot of vinyl chloride formation vs. Cl_2 depletion. Conditions of experiments are given in Table I. Dimensions of the boxes used to plot the data indicate the calculated standard deviations of the two measured variables under each set of conditions (based on at least 10 measurements of each of these quantities made under each set of conditions). The line drawn on the plot represents equivalence of two measurements.

(>99%) within 3 cm of the mixing point are always used ($1.5 \times 10^{13} - 13 \times 10^{13}$ molecules cm^{-3}). Vinyl bromide was in greater than 100-fold excess over the ambient Cl-atom concentration in the experiments conducted at very low atom concentrations and about in 5-fold excess in the titration experiment conducted at the highest Cl-atom concentration measured. The sensitivity of the mass spectrometer for detecting C_2H_3Cl is determined immediately after or during such an experiment using known flows of vinyl chloride added to the system down the same tube. We have found it very convenient to flow both C_2H_3Br and C_2H_3Cl down the center tube at the same time and to perform the titration and calibration in a single experiment.[26] Under these conditions the C_2H_3Cl ion signal with the Cl-atom source turned on is the sum of that due to the titration reaction and the calibration gas present and that with the discharge turned off due only to the calibration gas.

The results of this extensive comparison of titration methods are presented in Table I and plotted in Figure 2.

TABLE II: Conditions and Results of Experiments To Measure the Extent of C_6F_5Cl Decomposition and C_2H_3Cl Formation Using a Pulsed Cl-Atom Source[a]

10^{-14} × $[C_2H_3Br]$, molecules cm^{-3}	10^{-13} × $[C_6F_5Cl]_0$, molecules cm^{-3}	$10^{-12}\Delta$-$[C_6F_5Cl]$, molecules cm^{-3}	$10^{-12}\Delta$-$[C_2H_3Cl]$, molecules cm^{-3}	$-\Delta[C_2H_3Cl]/\Delta[C_6F_5Cl]$
1.56	3.31	4.05	3.81	0.94
1.56	3.28	3.29	3.38	1.03
1.56	1.44	1.97	1.99	1.01
1.56	0.645	0.814	0.756	0.93
16.0	3.33	3.38	3.60	1.07
				av = 1.00 ± 0.06 (1σ)

[a] The total pressure in all experiments is 0.7 torr (helium). The fluence of the photolyzing light (984.38 cm^{-1}) is approximately 2.8 J cm^{-2}.

Stoichiometry Experiments Using a Pulsed Source of Cl Atoms. We have conducted a shorter set of experiments to determine whether reaction 1 could also be used to titrate chlorine atoms produced by a pulsed source, the CO_2-laser-induced multiple-photon dissociation of C_6F_5Cl. These experiments involve the use of a second flow reactor with side-on sampling of gas into the ion source of a similar photoionization mass spectrometer. The 0.044-cm-diameter sampling orifice is located 35 cm from the NaCl window at the end of the flow tube through which the laser light is admitted. The pulsed laser photolysis method and additional details of the apparatus and experimental procedures have already been published.[6,27]

The experiment consisted of flowing a gas mixture of C_6F_5Cl and C_2H_3Br highly diluted in helium through the flow reactor and monitoring the absolute extent of decomposition of the Cl-atom source and the amount of vinyl chloride produced. In all the experiments the C_2H_3Br concentrations were kept high to assure rapid titration. C_6F_5Cl was chosen as the Cl-atom source for these experiments because its decomposition/pulse under the mild laser fluences used in this study is relatively high and therefore accurately measurable.

The results are interpreted by using the assumption that the observed loss of C_6F_5Cl is a quantitative measure of the Cl atoms produced by the photolysis process:

$$C_6F_5Cl + nh\nu \rightarrow C_6F_5 + Cl \qquad (5)$$

Measurement of the fraction of the C_6F_5Cl decomposed (typically 15% in each laser pulse) combined with the measured flow rates of all gases in the system yielded the

---

[26] In these experiments flows of C_2H_3Cl are used which produce concentrations comparable to the in situ Cl-atom concentrations. The measured vinyl chloride yield from reaction 1 is independent of an initial presence or absence of C_2H_3Cl, indicating that negligible reaction occurs between Cl atoms and C_2H_3Cl.

[27] Slagle, I. R.; Yamada, F.; Gutman D. *J. Am. Chem. Soc.* **1981**, *103*, 149–53.

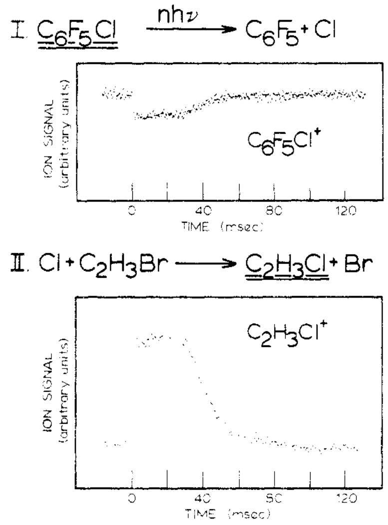


Figure 3. Temporal ion signal profiles of pulsed Cl-atom source (C_6F_5Cl) and of C_2H_3Cl produced by the titration reaction. Conditions of the experiment are given in the first line of Table II. Flat portions of ion signal profiles after laser pulse ($t = 0$) are approximately 30 ms in duration. Ion signals return to original base lines due to eventual mixing of photolyzed gas with fresh test gas.

Cl-atom concentration following photolysis. The measured amount of C_2H_3Cl which is produced essentially immediately after the laser pulse (within 1 ms) yields the titrated value of the same Cl-atom concentration.

Typical recorded ion signal profiles of C_6F_5Cl and C_2H_3Cl are shown in Figure 3, and the experimental conditions of each experiment are given in Table II. Photolysis yields ($-\Delta[C_6F_5Cl]$) and amounts of vinyl chloride formed by reaction 1 ($\Delta[C_2H_3Cl]$) were obtained from the differences between base-line ion signals and the constant ion signal which persists for about 30 ms after photolysis. The ion signals return to their original base lines due to the replacement of the photolyzed gas at the sampling point by fresh gas flowing down the tubular reactor.

A second search for alternate products of the Cl + C_2H_3Br reaction was not conducted with the pulsed source of chlorine atoms. Secondary photolysis of C_6F_5 produced by reaction 5 occurs to some extent during the laser pulse in these experiments producing fluorine atoms.[28] The rapid F-atom reaction with vinyl bromide which follows photolysis does not interfere with the process under study (it cannot produce vinyl chloride) but does produce other intermediates which could not be uniquely assigned to either the Cl- or the F-atom reaction with C_2H_3Br.

Measurement of the Rate Constant of the Cl + C_2H_3Br Reaction. The rate constant of reaction 1 was measured at 298 K in experiments conducted under pseudo-first-order conditions (Cl in excess) using the microwave discharge to generate the chlorine atoms. Basic experimental procedures to measure rate constants with this apparatus and under these conditions have been already reported.[7] In the eight experiments performed, several variables were changed including total pressure, flow velocity, and reactant concentrations. The $[Cl]/[C_2H_3Br]_0$ ratio was never less than 15. The exponential decay constant obtained from the measured C_2H_3Br ion signal profiles, k^{app} (see Figure 4), were corrected for axial diffusion as before to obtain pseudo-first-order rate constants, k', for reaction 1. The second-order rate constant was obtained from the slope of the line through the data in the plot of k' vs. [Cl] (see Figure 5).[7,29] The Cl-atom concentrations were measured as outlined above with C_2H_3Br in large excess.

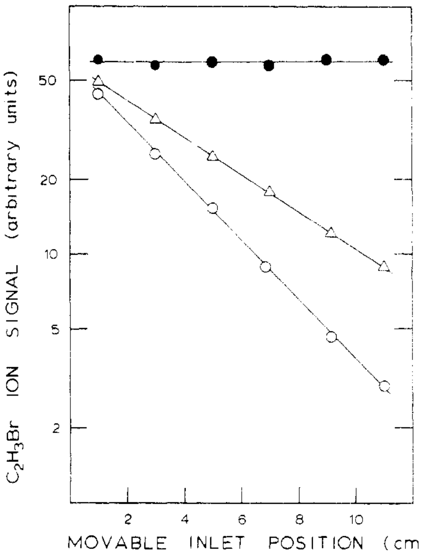


Figure 4. Semilog plot of $C_2H_3Br^+$ ion signal as a function of the position of the C_2H_3Br inlet from the sampling orifice. Condition of experiments: $P = 2.1$ torr; $v = 11.9$ m s^{-1}; $T = 297$ K; [Cl] = 2.53×10^{12} (○), 1.57×10^{12} (△), none (●). Units of concentrations are molecules cm^{-3}. Standard deviations of the net ion signals are less than the height of the symbols used to plot the data except for the two lowest ion signals shown (for which the standard deviations are about twice the symbol height).

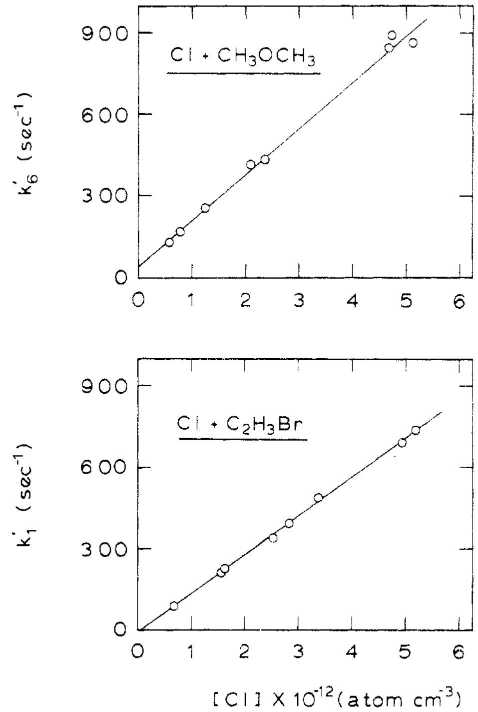


Figure 5. Plot of measured diffusion-corrected pseudo-first-order rate constants for the two Cl-atom reactions studied as a function of the Cl-atom concentration in each experiment. Lines through the data obtained from a linear regression analysis of the data. The second-order rate constants, k_1 and k_6, obtained from the slopes of these lines and the intercepts of these lines with the ordinate are given in Table III.

To verify that all procedures used to measure the rate constants of reaction 1 were as quantitative as presumed, a second Cl-atom reaction rate constant was also measured

---

(28) Slagle, I. R.; Gutman, D. *J. Phys. Chem.*, following article in this issue.

(29) Diffusion coefficients for reactants in helium were calculated from Leonard-Jones (6–12) potentials. Potential parameters for CH_3OCH_3 and C_2H_3Br (taken to be the same as those of C_2H_5Cl) were obtained from: Fristrom, R. M.; Westenberg, A. A. "Flame Structure"; McGraw-Hill: New York, 1965; Chapter 12.

TABLE III: Conditions and Results of Experiments To Measure Rate Constants of Cl-Atom Reactions at 298 ± 3 K

P, torr	v, m s^{-1}	$10^{-10}[RX]_0$, molecules cm^{-3}	$10^{-12}[Cl_2]$, molecules cm^{-3}	$10^{-12}[Cl]$, molecules cm^{-3}	k',[a,b] s^{-1}
		CH_3OCH_3 + Cl			
0.71	20.43	6.00	5.43	1.24	264 ± 8
0.70	20.54	15.0	15.6	4.73	890 ± 16
1.41	11.86	4.00	3.37	0.570	127 ± 7
1.37	18.69	10.3	6.18	2.36	430 ± 35
1.38	18.54	12.8	15.0	4.68	846 ± 21
1.38	18.54	24.3	15.0	5.13	864 ± 10
2.09	12.23	4.97	3.43	0.775	164 ± 3
2.06	12.21	8.92	7.53	2.10	414 ± 18
		k_6 = 1.70 (±0.06) × 10^{-10}, Intercept = 40 (±19)[b]			
		C_2H_3Br + Cl			
0.70	21.05	15.1	12.4	3.37	486 ± 13
0.70	21.62	25.2	20.8	4.94	689 ± 18
0.70	21.62	14.3	20.8	5.19	732 ± 20
1.38	18.03	3.77	3.32	0.679	87 ± 9
1.37	11.15	8.40	9.95	1.63	225 ± 7
1.38	10.96	14.0	15.6	2.83	393 ± 10
2.10	11.89	10.4	9.64	1.57	210 ± 2
2.10	11.89	10.4	13.9	2.53	337 ± 6
		k_1 = 1.43 (±0.02) × 10^{-10}, Intercept = −12 (±7)[b]			

[a] k' is the axial diffusion-corrected first-order rate constant. Correction was made from $k' = k^{app}(1 + k^{app}D/v^2)$, where k^{app} = the observed first-order rate constant, D = the binary diffusion coefficient, and v = flow velocity. Error limits are standard deviations of slopes of lines through data (as in Figure 4). [b] Error limits are standard deviations of the straight-line parameters in the lines through the data in Figure 5 from which k's were obtained. Actual estimated error limits of k's are ±20%.

in the same manner, one for a reaction which has already been carefully investigated by another method:

$$Cl + CH_3OCH_3 \rightarrow HCl + CH_2OCH_3 \qquad (6)$$

The results of these two studies are given in Table III.

Results and Discussion

Titration of Cl Atoms Using the Cl + C_2H_3Br Reaction. The several sets of experiments which were peformed to test the use of reaction 1 as a Cl-atom titration reaction all indicate that it is well suited for this purpose. The reaction is rapid, stoichiometric, and free of interfering secondary reactions and involves the use of a stable, readily available titrant.

In the experiments which were performed with the continuous source of Cl atoms in which C_2H_3Br depletion and C_2H_3Cl formation were simultaneously measured during the course of the Cl + C_2H_3Br reaction, the cumulative ratio of these two dynamic variables, $-([C_2H_3Cl]_t - [C_2H_3Cl]_0)/([C_2H_3Br]_t - [C_2H_3Br]_0)$, did not vary during the titration reaction (see Figure 1). The average value of this stoichiometry ratio, measured at 11 positions of the movable inlet (40–100% reaction), is 1.01. The value of this ratio, which could be measured accurately when reaction was near completion, indicates that even under conditions not normally well suited for eliminating interference from secondary reactions (the C_2H_3Br added was not in great excess over the ambient Cl atoms present) the conversion is quantitative within the accuracy limits of the measurement (±5%). The observation that the formation/depletion ratio is unity under conditions which are less favorable for suppressing secondary reactions than those used in titration experiments assures that this ratio is also one when C_2H_3Br is present in large excess.

The results given in Table II indicate that reaction 1 may also be used to quantitatively measure Cl-atom yields of photolysis processes. The measured value of the apparent stoichiometry ratio ($-\Delta[C_2H_3Cl]/\Delta[C_6F_5Cl]$) using the pulsed source of chlorine atoms is 1.00 ± 0.06. Essentially the same equivalence ratio was obtained in each experiment. The variables which were changed include C_2H_3Br (a 10-fold range) and C_6H_5Cl (a 3-fold range). It was found however that C_2H_3Br had to be present in significant excess over C_6F_5Cl, the Cl-atom source, in order to channel all the chlorine atoms through reaction 1. For $[C_2H_3Br]/[C_6F_5Cl]$ ratios less than 5, Cl atoms were also lost by other processes. In typical experiments in which we used reaction 1 to measure Cl-atom yields, the vinyl bromide to C_6F_5Cl concentration ratios used were 10 or greater. Vinyl bromide does absorb the 984-cm^{-1} photolysis radiation used in these experiments. However, at the mild fluences used (~3 J cm^{-2}), we observed no decomposition of the titrant.

In the comparison run between the Cl_2-depletion method and the use of reaction 1 to measure Cl-atom concentrations, we have found that both yield the same results over the full range of conditions studied (see Table I). The small differences which were obtained between the two measurement techniques under each set of conditions were not systematic in nature and were well within our estimated precision limits for determining Cl-atom concentrations by either method (±10% by the Cl_2-depletion procedure and ±5% by the C_2H_3Cl-formation method).

The PIMS detection sensitivity for C_2H_3Cl is about 5 times greater than that for detecting NO, and C_2H_3Cl is effectively cryopumped by the cold trap on the mass spectrometer vacuum chamber diffusion pump while NO is not. These factors make it possible to measure Cl-atom concentrations with our PIMS detector using reaction 1 down to 5 × 10^{10} atoms cm^{-3} (with an uncertainty less than ±10%), which is about a factor of 10 lower than the smallest Cl-atom concentration which we could have determined with our detection method by measuring NO yields from the Cl + NOCl → Cl_2 + NO titration reaction.

Measurement of the Cl + C_2H_3Br Rate Constant. The first set of rate constant measurements, those of k_6 which were performed to further test the quantitative procedures used in these studies, yielded results which are in complete agreement with those reported by Michael and co-workers.[30] This latter study employed another dynamic detection method (resonance fluorescence detection of Cl atoms) and their experiments were conducted under reaction conditions substantially different from those used in our study (CH_3OCH_3 in large excess). The results of our investigation (eight experiments in which several reaction variables were varied; see Table III) yielded an average value for k_6 = 1.70 (±0.06) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Michael et al. obtained a value of 1.80 (±0.09) × 10^{-10} at 300 K.

Eight measurements were made of k_1 again varying concentrations and flow conditions over wide ranges (see Table III). The results of these studies, all conducted at 298 (±3) K, yield a value of k_1 = 1.43 (±0.02) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

The estimated accuracy of both of these rate constant determinations is ±20%. The error limits reported above with the rate constants reflect the precision of the measurements and are the standard deviations of the slopes of the lines which were fitted through the data points in Figure 5.

There are no prior reported values of the rate constant of reaction 1 but estimates have been reported.[22,31]

---

(30) Michael, J. V.; Nava, D. F.; Payne, W. A.; Stief, L. J. *J. Chem. Phys.* **1979**, *70*, 3652–6.

(31) Lee, F. S. C.; Rowland, F. S. *J. Phys. Chem.* **1977**, *81*, 86–7.

Cheung, McDonald, and Herschbach, who studied four Cl + bromoalkene reactions in molecular beams including reaction 1, reported that they are rapid and have large cross sections, estimated to be in the range 20–35 A^2.[22] Our value of k_1 is equivalent to a thermally averaged cross section of 29 A^2.

Final Comments

The results of this study indicate that chlorine-atom concentrations can be quantitatively measured by using the rapid titration reaction, $Cl + C_2H_3Br \rightarrow C_2H_3Cl + Br$. This reaction should be useful in a wide variety of situations where absolute Cl-atom concentrations must be established, including use in studies of Cl-atom reactions themselves and in investigations where chlorine atoms are used to produce known concentrations of polyatomic free radicals. Absolute chlorine-atom yields from photolysis processes can also be measured by using this reaction. The apparent absence of any rapid secondary processes under our experimental conditions indicates that this reaction may also be used as a convenient and quantitative source of bromine atoms for a variety of purposes.

Acknowledgment. The research using the continuous Cl-atom source was supported by the National Science Foundation under Grant CHE-80-06573. The experiments involving the pulsed Cl-atom source were supported by the Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-78ER14593. Special thanks are extended to Paul F. Sawyer, who developed the data acquisition system used in these experiments.

Registry No. C_6F_5Cl, 344-07-0; C_2H_3Cl, 75-01-4; Cl, 22537-15-1; C_2H_3Br, 593-60-2; CH_3OCH_3, 115-10-6.

Extent of the Displacement Route in the Reactions of Fluorine Atoms with Ethylene, Vinyl Chloride, and Vinyl Bromide

Irene R. Slagle and David Gutman*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616 (Received: November 16, 1982)

The chemical branching of three fluorine-atom reactions, those with C_2H_4, C_2H_3Cl, and C_2H_3Br, was studied in real-time experiments using a tubular reactor coupled to a photoionization mass spectrometer. The fluorine atoms were generated by the CO_2-laser-induced secondary photolysis of C_6F_5Cl which also appears to produce tetrafluorobenzyne ($c\text{-}C_6F_4$). The measured fractional extents that the three reactions studied proceed by a displacement route at 295 K (to yield $C_2H_3F + X$) are 0.65 (±0.06), 0.72 (±0.14), and 0.72 (±0.14) for C_2H_4, C_2H_3Cl, and C_2H_3Br, respectively.

Introduction

The reactions of fluorine atoms with olefins and other unsaturated organic molecules have been shown to proceed via two distinct routes, either by direct H-atom abstraction to form HF or through the formation of an energy-rich intermediate complex which subsequently decomposes more or less as expected presuming internal energy randomization and statistical (RRKM) behavior.[1,2] The many angle- and energy-resolved molecular beam studies of these reactions (by Lee and co-workers[3]) and the investigations of the infrared chemiluminescence of the products which they produce (by the research groups of McDonald,[4] Setser,[5] and others[6,7]) have provided a large amount of knowledge regarding the detailed molecular dynamics of both of these routes for a large number of F-atom reactions of this type.

Considerably less information is available, however, on the absolute chemical branching (rate constant ratios) between the two reactive routes of these F-atom reactions. Moehlmann and McDonald[4c] have determined several abstraction/substitution cross-section ratios based on comparisons of the integrated infrared chemiluminescence from the products of both routes. The accuracy of these determinations is not certain due to a need to assume populations of the $v = 0$ state of HF and the difficulty of determining absolute Einstein coefficients for polyatomic molecules. Interesting trends were observed. The presence of more abstractable hydrogens (e.g., due to the presence of CH_3 groups) did not necessarily increase the relative importance of the abstraction route. On the other hand, polarization of the π system appears to enhance the likelihood of addition relative to direct abstraction. Williams and Rowland reacted moderated ^{18}F atoms (produced by the $^{19}F(n,2n)^{18}F$ nuclear reaction) with C_2H_2 and C_2H_4 and determined the importance of the substitution reaction under thermal conditions (ambient temperatures) from an

---

(1) Smith, I. W. M. "Kinetics and dynamics of elementary gas reactions"; Butterworths: London, 1980; Chapter 7.

(2) Bogan, D.; Setser, D. W. In "Fluorine-Containing Free Radicals"; Root, J. W., Ed.; American Chemical Society Washington DC, 1978; *ACS Symp. Ser.* No. 66, pp 237–80.

(3) (a) Parson, J. M.; Lee, Y. T. *J. Chem. Phys.* **1972**, *56*, 4658–66. (b) Parson, J. M.; Shobatake, K.; Lee, Y. T.; Rice, S. A. *Ibid.* **1973**, *59*, 1402–15. (c) Shobatake, K.; Parson, J. M.; Lee, Y. T.; Rice, S. A. *Ibid.* **1973**, *59*, 1416–26, 1427–34. (d) Shobatake, K.; Lee, Y. T.; Rice, S. A. *Ibid.* **1973**, *59*, 1435–48, 6104–11. (e) Parson, J. M.; Shobatake, K.; Lee, Y. T.; Rice, S. A. *Faraday Discuss. Chem. Soc.* **1973**, *55*, 344–55. (f) Farrar, J. M.; Lee, Y. T. *J. Chem. Phys.* **1976**, *65*, 1414–26. (g) Buss, R. J.; Coggiola, M. J.; Lee, Y. T. *Faraday Discuss. Chem. Soc.* **1979**, *67*, 162–72.

(4) (a) Moehlmann, J. G.; Gleaves, J. T.; Hudgens, J. W.; McDonald, J. D. *J. Chem. Phys.* **1974**, *60*, 4790–9. (b) Moehlmann, J. G.; McDonald, J. D. *Ibid.* **1975**, *62*, 3052–60. (c) Moehlmann, J. G.; McDonald, J. D. *Ibid.* **1975**, *62*, 3061–5. (d) Moss, M. G.; Ensminger, M. D.; Stewart, G. M.; Mordaunt, D.; McDonald, J. D. *Ibid.* **1980**, *73*, 1256–64.

(5) Bogan, D. J.; Setser, D. W. *J. Chem. Phys.* **1976**, *64*, 586–602.

(6) Donaldson, D. J.; Watson, D. G.; Sloan, J. *J. Chem. Phys.* **1982**, *68*, 95–107.

(7) Vasil'ev, G. K.; Ivanov, V. B.; Makarov, E. F.; Ryabenko, A. Y.; Talrose, V. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1975**, *3*, 537–43.

0022-3654/83/2087-1818$01.50/0