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.

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

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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- 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-workers³) 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 ¹⁸F 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

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analysis of the yields of the ultimate stable ¹⁸F-containing compounds which were formed.⁸ The results obtained by Williams and Rowland on the $F + C_2H_4$ reaction are in essential agreement with those obtained by Moehlmann and McDonald. The addition process in this reaction occurs about twice as frequently as does abstraction.

We have recently been using the reactions of Cl and F atoms with a substituted olefin, C_2H_3Br , to quantitatively measure the Cl- and F-atom yields of infrared multiplephoton-induced decompositions (IRMPD) of halogencontaining organic molecules.⁹ Absolute yields of C₂H₃Cl and C_2H_3F , produced when the precursor molecule (e.g., C_6F_5Cl) is photolyzed in the presence of C_2H_3Br , are compared to the extent of precursor molecule decomposition in each laser pulse. These halogen-atom "titration" reactions are

$$Cl + C_2 H_3 Br \rightarrow Br + C_2 H_3 Cl$$
(1)

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_3 \mathbf{B} \mathbf{r} \rightarrow \mathbf{B} \mathbf{r} + \mathbf{C}_2 \mathbf{H}_3 \mathbf{F} \tag{2}$$

The vinyl chloride yield may be equated directly to the amount of chlorine atoms produced by the photolysis process because the $Cl + C_2H_3Br$ reaction proceeds exclusively, under most conditions, by reaction 1.9,10 However, accurate knowledge of the product branching between reactions 3 and 4 is needed to use the measured C_2H_3F yields to determine the extent to which these same photolysis processes yield fluorine atoms.

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_3 \mathbf{X} \to \mathbf{H} \mathbf{F} + \mathbf{C}_2 \mathbf{H}_2 \mathbf{X} \tag{3}$$

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_3 \mathbf{X} \to \mathbf{X} + \mathbf{C}_2 \mathbf{H}_3 \mathbf{F} \tag{4}$$

Because of the uncertain accuracy of the chemical branching ratios which are currently available for F-atom reactions with C_2H_3X compounds, we have remeasured those of three (X = H, Cl, or Br). The method used is different from those employed previously and involves the use of time-resolved photoionization mass spectrometry. The results of this study, which are reported here, provide new quantitative information on the chemical branching in this important class of reactions which complements the detailed information which is already available on the molecular dynamics of the individual routes.

Experimental Section

Two sets of experiments were performed. The first involved comparing the yields of C_2H_3F , produced by the displacement route of each of the three reactions, in a group of experiments in which the same initial fluorineatom concentration was used. These experiments vielded the relative importance of reaction 4 among the three reactions studied.

The source of the fluorine atoms was the IRMPD of C_6F_5Cl which yields chlorine atoms in a primary photolysis step and fluorine atoms in a secondary photolysis process:

$$C_6 F_5 Cl + nh\nu \to C_6 F_5 + Cl \tag{5}$$

$$C_6 F_5 + mh\nu \to C_6 F_4 + F \tag{6}$$

The secondary process occurs to an extent of about 58% under the conditions of our experiments (see below). Measurements were made by using an excess of an inert carrier gas (~95% He; less than 0.1% C_6F_5Cl), to assure negligible physical heating by the photolysis process, and with enough C_2H_3X present ($C_2H_3X/C_6F_5Cl > 20$) to assure complete scavenging of the halogen atoms by C_2H_3X .

The second group of experiments was performed to measure the absolute extent to which the $F + C_2H_4$ proceeds by reaction 4. The combined results of these and the preceding experiments yielded the desired chemical branching ratios of all three reactions studied. In the latter experiments, C_2H_4 was not in large excess over the initial fluorine-atom concentration, and both the C_2H_4 depletion and C_2H_3F production caused by reaction 4 were repeatedly measured. These data could be used to obtain an absolute chemical branching ratio for this reaction, because the chlorine atoms produced by the same photolysis process which produced the fluorine atoms did not react with C_2H_4 to any measurable extent under our experimental conditions. Hence, the total C_2H_4 depletion could be associated with the $F + C_2H_4$ reaction. Chlorine atoms did however react rapidly with the other C₂H₃X compounds studied. Strong C₂H₃Cl⁺ product ion signals were recorded when C_2H_3Br was used as the halogen-atom scavenger,¹⁰ but none was detected when C_2H_4 was used for the same purpose.

The pulsed-laser photolysis method and details of the apparatus and experimental procedures have been published.^{11,12} Briefly, light from a Lumonics 103-2 CO₂ TEA laser is first mildly concentrated by a 5-m focal length spherical mirror and then directed down the length of a 0.95-cm i.d. Pyrex flow reactor. Gas is sampled continuously from a 0.044-cm diameter hole in the side of the tubular reactor and analyzed in real-time experiments using photoionization mass spectrometry (PIMS). In this study, radiation at 984.38 cm⁻¹ was used to decompose C_6F_5Cl using fluences close to 3 J cm⁻². Ion signal profiles of C_6F_5Cl yielded the extent of decomposition of the halogen-atom precursor during each laser pulse and those of the C_2H_3F produced by reaction 4 when the three C₂H₃X compounds were alternately metered into the system yielded the relative chemical branching ratios. Before and after each experiment a known flow of the gas being monitored was metered into the system and its ion signal recorded to maintain accurate calibration of the mass spectrometer sensitivity. Representative temporal ion signal profiles of C₆F₅Cl⁺ and C₂H₃Cl⁺ recorded under comparable conditions have already been published.⁹ Those of $C_2H_4^+$ and $C_2H_3F^+$ were similar in appearance and quality.

The C_2H_3X compounds were obtained from Matheson, purified by freeze-pump-thaw cycles, and then fractionally distilled with the middle third of the sample being retained for these experiments. Mass spectrometric analysis of the purified gases indicated greater than 99% purity. C_6F_5Cl was obtained from PCR Chemical Co. and purified in a similar manner.

Photoionization was done with the H-atom resonance lamp (10.2 eV) to detect all species except C_2H_4 and C_2H_3F for which the Ar lamp was used (11.6-11.8 eV).

Results and Discussion

Photolysis of C_6F_5Cl . We have already reported that the IRMPD of C_6F_5Cl yields only C_6F_5 and Cl in the primary step.⁹ Measured C_6F_5Cl depletion caused by photolysis exactly equals the Cl-atom yield (as determined by measuring the C_2H_3Cl produced when C_2H_2Br is present in large excess). As part of the present study we have also studied details of the secondary photolysis process.

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First a search was conducted to identify possible secondary photolysis products by looking for product ion signals ($C_iF_jCl_k^+$; i = 1-6, j = 1-5, and k = 0 or 1) at all the mass numbers which correspond to possible products. Searches were conducted with both 10.2- and 11.6-eV ionizing energy. In these experiments the total pressure was 0.7 torr and the only other gas present was the inert carrier gas (99.95% He). The laser fluence was again near 3 J cm⁻², the fluence used to measure the chemical branching ratios.

The only significant apparent secondary product ion signal detected was $C_6F_4^+$. The temporal behavior of this ion signal was that of a stable product; i.e., it remained constant after its sudden appearance during the laser pulse. Its apparent stability was not affected by the presence of common free-radical scavengers: NO₂, O₂, or C₂H₃Br. This product could be detected with the H-atom resonance lamp, indicating that its ionization potential is under 10.2 eV. No CF_2^+ ion signals were recorded, indicating the absence of $\overline{C}F_2$, a known tertiary photolysis product of C_6F_5X compounds.¹³ The failure to detect ion signals from other possible secondary or tertiary photolysis products does not necessarily indicate their absence. Their ionization potentials are mostly unknown and may be above 11.6 eV, the highest ionizing energy available with our PIMS. In addition their parent ions may be unstable.

The principal secondary photolysis product detected is most probably tetrafluorobenzyne formed by reaction 6 when the primary product, C_6F_5 , loses a fluorine atom to form this quasi-stable cyclic compound. Tetrafluorobenzyne is a well-recognized intermediate in fluoroorganic chemistry,¹⁴ but it has not been isolated or previously detected. The high yield of fluorine atoms, under the conditions of these experiments (see below), supports the suggestion that the major secondary photolysis process involves the simple loss of a fluorine atom.

A set of experiments was performed to determine whether a reduction of the laser fluence significantly reduces secondary photolysis. C_6F_5Cl was photolyzed with C_2H_3Br also present in the system and relative yields of C_2H_3Cl and C_2H_3F (produced by reactions 1 and 2) were measured. As the fluence was reduced from 3 to about 0.5 J cm⁻², the extent of decomposition of C_6F_5Cl fell from 18 to ~1%, and the relative importance of the secondary photolysis process decreased from ~58% of the primary step to below 10% (C_2H_3F was not detected at all at the lowest fluence used in these experiments). The primary photolysis product, C_6F_5 , was never detected. The reason for this is not known. Possible explanations were given above.

In summary, these experiments indicate that the photolysis of C_6F_5Cl at 3 J cm⁻² proceeds by simple chlorine-atom loss in the primary step followed by a secondary photolysis process which substantially decomposes (~ 58%) the primary product, C_6F_5 , into fluorine atoms and a stable product (C_6F_4). The latter is probably tetrafluorobenzyne. Minor amounts of additional secondary or tertiary photolysis processes may also occur.

Relative Branching Ratios for Three $F + C_2H_3X$ Reactions. The results of the extensive set of experiments which were performed to measure the relative importance of reaction 4 among the three $F + C_2H_3X$ reactions studied are given in Table I. These experiments involved repeated measurement of the absolute amount of C_2H_3F formed by

TABLE I: Conditions and Results of Experiments To Measure the Relative Branching Ratios of Three F + C_2H_3X Reactions at 295 (±3) K

10 ⁻¹³ ×	10 ⁻¹⁴ ×	10 ⁻¹²	10 ⁻¹² Δ-	$-\Delta [C_2H_3F]/$
$[C_6F_5Cl]_0^a$	$[C_2H_3X]_0^a$	$[C_6F_5Cl]^a$	$[C_2H_3F]^a$	$\Delta \left[C_{6}F_{5}Cl \right]$
		$F + C_{2}H_{4}$		
3.0	7.3	4.2 7	1.6	0.38
3.0	7.3	5.1	1.9	0.37
3.0	7.4	4.4	1.9	0.43
3.0	7.4	4.5	2.0	0.44
3.2	7.1	4.7	1.8	0.38
3.2	7.1	5.0	1.5	0.30
			av =	$0.38 (\pm 0.05)^{b}$
		$F + C_{1}H_{3}C$	21	
2.9	7.0	4.8	2.1	0.44
3.0	9.2	4.6	2.0	0.43
3.0	9.2	4.9	2.2	0.45
3.2	7.0	4.9	1.9	0.39
			av =	$0.43 (\pm 0.03)^{b}$
		$F + C_{2}H_{3}E$	B r	
2.9	6.8	4.1	1.8	0.44
3.0	7.0	4.6	1.6	0.35
3.0	7.0	5.1	1.5	0.29
3.0	7.1	4.4	2.3	0.52
3.0	7.1	4.5	2.1	0.47
3.2	7.0	5.0	2.0	0.40
			av =	$0.41 \ (\pm 0.08)^{b}$

^{*a*} Units: molecules cm⁻³. ^{*b*} Standard deviation of mean value.

reaction 4 when each of the three C_2H_3X compounds was alternately added to the basic reactant gas mixture containing the F-atom source (0.1% C_6H_5Cl in He at a total pressure of 0.7 torr, subjected to CO_2 laser photolysis at 3 J cm^{-2}). The C₂H₃X concentrations used were all nearly the same and were about a factor of 10 times higher than was needed to completely scavenge all the fluorine atoms produced by the photolysis process. The laser fluence and F-atom precursor concentrations were kept as constant as possible throughout this set of experiments to assure uniform conditions, including initial F-atom concentrations, in all the experiments. The results are reported both as absolute C_2H_3F yields and as the ratio of the C_2H_3F yield to the amount of C_6F_5Cl which decomposed in the individual experiments. This ratio normalizes the C_2H_3F yields for the small C₆F₅Cl concentration differences in each experiment and (to first order) for the small differences in average laser fluence in each experiment.

Since each C_2H_3X compound used reacted with all the fluorine atoms generated by the photolysis process, the normalized yields in Table I establish the relative fractional extents ($Fr(C_2H_3X)$) to which each F-atom reaction studied proceeds by the addition route:

$$Fr(C_2H_3X) = k_4(C_2H_3X) / \{k_3(C_2H_3X) + k_4(C_2H_3X)\}$$

When one takes the normalized yield of the $F + C_2H_4$ reaction to be 1.0 and scales the other two measured yields to maintain proportionality, the ratios of these fractions are

 $Fr(C_2H_4):Fr(C_2H_3Cl):Fr(C_2H_3Br) = 1.0:1.1:1.1$

The accuracy of $Fr(C_2H_3Cl)$ and $Fr(C_2H_3Br)$ relative to $Fr(C_2H_4)$ is estimated to be $\pm 15\%$.

Absolute Branching Ratio of the $F + C_2H_4$ Reaction. Since the Cl + C_2H_4 reaction proceeds to a negligible extent under the conditions of our experiments, measurements of both the C_2H_4 depletion and the C_2H_3F formation in these experiments determine $Fr(C_2H_4)$ directly:

$$Fr(C_2H_4) = -\Delta[C_2H_3F] / \Delta[C_2H_4] = k_4(C_2H_4) / \{k_3(C_2H_4) + k_4(C_2H_4)\}$$

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TABLE II: Conditions and Results of Experiments To Determine the Absolute Branching Ratio of the F + C_2H_4 Reaction at 295 (±3) K

$\frac{10^{-13} \times}{[C_6 F_5 Cl]_0^a}$	$-10^{-12}\Delta - [C_6F_5Cl]^a$	$10^{-13} \times [C_2H_4]_0^a$	$-10^{-11}\Delta - [C_2H_4]^a$	$10^{-11}\Delta - [C_2H_3F]^a$	$\frac{-\Delta \left[C_2 H_3 F \right]}{\Delta \left[C_2 H_4 \right]}$	
1.2	1.9	3.4	4.6	3.3	0.72	
2.6	3.5	1.6	5.9	3.6	0.61	
2.6	3.6	6.5	11	7.0	0.64	
2.8	4.5	1.3	4.8	3.2	0.67	
2.9	4.1	3.4	10	6.5	0.65	
2.9	4.4	4.2	12	6.9	0.58	
5.8	10	3.4	17	11	0.65	
					$av = 0.65 (\pm 0.04)^b$	

^a Units: molecules cm⁻³. ^b Standard deviation of mean value.

TABLE III: Branching Ratios for C_2H_3F Formation in $F + C_2H_3X$ Reactions at 295 (±3) K

	C ₂ H ₄	C ₂ H ₃ Cl	C_2H_3Br
this study	0.65	0.72	0.72
ref 4c ^a	0.75	0.80	0.67
ref 8	0.65		

^a Branching ratios based on k_4/k_3 reported by authors to one significant figure.

Seven experiments were performed to determine $Fr(C_2H_4)$. All experiments were run at a total pressure of 0.7 torr and again using a laser fluence of 3 J cm⁻² which yielded a high (~15%) extent of dissociation of C_6F_5Cl during each laser pulse. The concentrations of both C_6F_5Cl and C_2H_4 were varied in these experiments. The conditions of each experiment and the results obtained are given in Table II.

The seven measured values of $Fr(C_2H_4)$ have an average value of 0.65 ($1\sigma = \pm 0.04$). The results are independent of the two concentrations which were changed between experiments. Because C_2H_4 cannot be in large excess over the initial F-atom concentration in these experiments, not all the fluorine atoms produced by the photolysis process react with C_2H_4 . In principle this fact should not affect the outcome of the experiments. The fact that the measured values of $Fr(C_2H_4)$ are independent of $[C_2H_4]$ indicates that the results are indeed independent of the fraction of fluorine atoms which react with C_2H_4 .

The measured value of $Fr(C_2H_4)$ may be combined with the relative values of the three fractional branching ratios obtained in the first set of experiments to obtain Fr-(C₂H₃Cl) and Fr(C₂H₃Br). These numbers are given in Table III together with the measured values obtained by others for these same branching ratios. The agreements with the results of Moehlmann and McDonald,^{4c} whose results were reported with only one significant figure, is good, which suggests that the presumptions which they required to relate chemiluminescent emission intensities of the reaction products to the rate constants of the routes which produced them were valid. The agreement with Williams and Rowland's branching ratio for the $F + C_2H_4$ reaction is excellent.⁸

The estimated accuracy of the values of $Fr(C_2H_3X)$ determined in this study are $\pm 10\%$ for $Fr(C_2H_4)$ and $\pm 20\%$ for the other two branching fractions which were obtained more indirectly.

Since these determinations have narrower error limits than those reported previously, these branching fractions may be used with more confidence in experiments which require quantitative knowledge of these variables. For example, the measured value of $Fr(C_2H_4)$ was used to determine the extent of secondary photolysis of C_6F_5Cl quoted earlier in this paper (58%). The data which were needed to determine it are all given in Table I. They include the absolute C₂H₃F yields as well as C₆F₅Cl depletions resulting from the photolysis of C_6F_5Cl in the presence of a sufficient excess of C_2H_4 to react with all the fluorine atoms which were produced during the laser pulse. The calculation presumes that fluorine atoms are generated only by the secondary photolysis process, reaction 6. The accuracy of the determination is $\pm 10\%$. In the future C_2H_3F yields measured under similar conditions will be used to study F-atom production in other CO₂-laser-induced decompositions of fluorine-atom-containing organic compounds.

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Registry No. C_2H_4 , 74-85-1; C_2H_3Cl , 75-01-4; C_2H_3Br , 593-60-2; C_6F_5Cl , 344-07-0; $(c-C_6F_4)$, 5488-71-1; H_2 , 1333-74-0; atomic fluorine, 14762-94-8.