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Gas-Phase Ion-Molecule Reactions of Perfluoroolefins

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The rate constants for the reactions of F^-, CF_3^-, $C_2F_5^-$, $C_3F_7^-$, and $C_4F_9^-$ with C_2F_4 and C_3F_6 have been measured in the gas phase at 295 K in a selected ion flow tube (SIFT). Most of the observed reactions involve association. F^- transfer is observed only from CF_3^-. All ions studied except $C_4F_9^-$ react with C_3F_6 with near unit efficiency. Only F^- and CF_3^- were observed to react with C_2F_4.

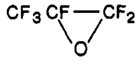
I. Introduction

Many ion-molecule reactions have been studied in hydrocarbons and a great diversity of reactions has been found.[1] Ionic reactions of perfluorocarbons provide an interesting contrast to those in hydrocarbons since the high bond strengths in perfluorocarbons make the reaction energetics quite different. Ionic reactions of some perfluoroalkanes have been studied.[2-5] Association reactions of Li^+ with CF_4, C_2F_6, and C_4F_8 have also been studied.[6] Here we report a study of the reactions of several negative ions with tetrafluoroethylene (C_2F_4) and hexafluoropropene (C_6F_6) at 295 K. C_2F_4 and C_3F_6 are industrially important monomers. (These are key monomers in most of the existing fluorocarbon products, e.g., Teflon, Viton, etc.) They are highly susceptible to nucleophilic attack especially by anionic species. However, these anionic reactions so far have been investigated only in the liquid phase.[7] It is of interest and possibly of practical importance to study the chemistry of reactions between these monomers and anions in the gas phase.

II. Experimental Section

The experiments reported here were carried out in the selected ion flow tube (SIFT) in the Geophysics Laboratory at Hanscom Air Force Base. The SIFT is similar to that described by Adams and Smith.[8] Briefly, the reactant ions are generated in an appropriate source, mass-selected, and injected into the flow tube through a venturi-type aspirator inlet, whence they are carried downstream in a stream of inert carrier gas and past the reactant-molecule inlet. The reactant ions and the product ions are detected by a mass spectrometer sampling system. An APPLE IIe computer in conjunction with an ISAAC 91A interfacing system is employed to control the experiment and to collect experimental data.

The anions generated for this study and their parent gases were F^- from SF_6, CF_3^- from HFPO



HFPO

$C_2F_5^-$ from C_3F_8 and n-C_8F_{18}, $C_3F_7^-$ from n-C_8F_{18}, and $C_4F_9^-$ from n-C_8F_{18}. C_2F_4, C_3F_6, HFPO, and n-C_8H_{18} were obtained from duPont Co., C_3F_8 was obtained from Air Products and Chemical Inc., and SF_6 was obtained from Matheson Co.

III. Results

The ion-molecule reactions observed at 295 K and their rate constants are summarized in Table I. The rate constants for association reactions shown in Table I are effective bimolecular rate constants. These reactions are believed to have reached or nearly reached saturated termolecular kinetics since the effective bimolecular rate constants remain approximately constant throughout the pressure range studied (0.3-0.5 Torr of helium pressure). The total rate coefficient for the primary ion-molecule reaction is determined from the decline of the reactant ion signal as a function of neutral gas addition. An example is given in Figure 1 for the reaction of F^- with C_3H_6. The rate constant for the secondary ion-molecule reaction 6b is determined from the distribution of primary and secondary product ions as shown in Figure 2. The method used to calculate the secondary reaction rate constant is presented below.

Let I = F^-, M = C_3F_6, P = $C_3F_7^-$, and S = $C_6F_{13}^-$. The reaction proceeds by the following steps.

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TABLE I: Reactions of Negative Ions with TFE and HFP at 295 K

		ΔH°_{rxn}, kcal/mol	rate const × 10^9 cm^3 molecule^{-1} s^{-1}		He press., Torr
			expt[a]	Langevin	
		Reactions with TFE			
(1)	$F^- + C_2F_4 \rightarrow C_2F_5^-$	−53.0	0.15	1.19	0.30–0.48
(2)	$CF_3^- + C_2F_4 \rightarrow C_2F_5^- + CF_2$	−2.10	0.34	0.74	0.41
(3)	$C_2F_5^- + C_2F_4 \rightarrow$ no reaction				0.42
(4)	$C_3F_7^- + C_2F_4 \rightarrow$ no reaction				0.41
(5)	$C_4F_9^- + C_2F_4 \rightarrow$ no reaction				0.41
		Reactions with HFP			
(6a)	$F^- + C_3F_6 \rightarrow C_3F_7^-$	−54.8	1.3	1.39	0.34–0.48
(6b)	$\xrightarrow{C_3F_6} C_6F_{13}^-$		0.6	0.64	
(7a)	$CF_3^- + C_3F_6 \rightarrow C_4F_9^-$	−70.6	0.1	0.83	0.36–0.49
(7b)	$CF_3^- + C_3F_6 \rightarrow C_3F_7^- + CF_2$	−3.9	0.9	0.83	0.45
(7c)	$\xrightarrow{C_3F_6} C_6F_{13}^-$				
(8)	$C_2F_5^- + C_3F_6 \rightarrow C_5F_{11}^-$	−63.9	0.7	0.70	0.32–0.47
(9)	$C_3F_7^- + C_3F_6 \rightarrow C_6F_{13}^-$	−48.9	0.5	0.64	0.35–0.50
(10)	$C_4F_9^- + C_3F_6 \rightarrow C_7F_{15}^-$		0.1	0.60	0.47

[a] For association reactions, the rate constants shown are effective bimolecular rate constants.

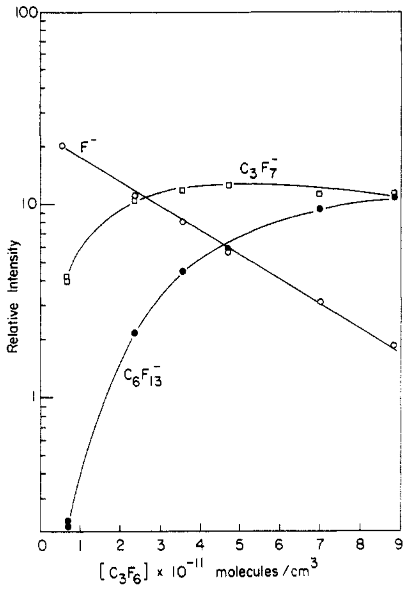


Figure 1. A plot of the relative ion intensity as a function of C_3F_6 concentration for the reaction $F^- + C_3F_6$.

$$I + M \rightarrow P \qquad k_1 \tag{3-1}$$

$$M + P \rightarrow S \qquad k_2 \tag{3-2}$$

From (3-1) and (3-2), the rate of change of [I], [P], and [S] are

$$-d[I]/dt = k_1[I][M] \tag{3-3}$$

$$d[P]/dt = k_1[I][M] - k_2[M][P] \tag{3-4}$$

$$d[S]/dt = k_2[M][P] \tag{3-5}$$

When eq 3-3 to 3-5 are solved, the ratio of the primary ionic product [P] to the secondary ionic product [S] is given by eq 3-6.

$$\frac{[P]}{[S]} = k_1\left[\frac{\exp(-k_2[M]t) - \exp(-k_1[M]t)}{k_1 - k_2 - k_1\exp(-k_2[M]t) + k_2\exp(-k_1[M]t)}\right] \tag{3-6}$$

If we know the monomer concentration *M* and the reaction time *t*, k_2 can be calculated by measuring k_1 and the ratio [P]/[S].

The thermochemical values used to calculate the heats of reaction are listed in Table II.

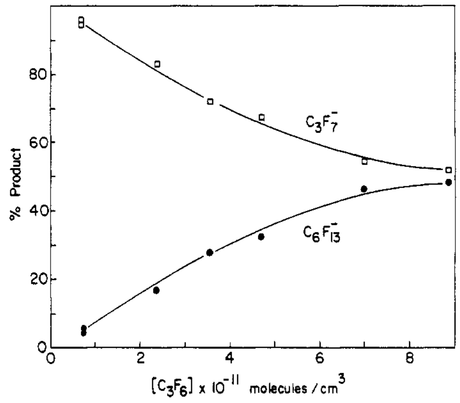


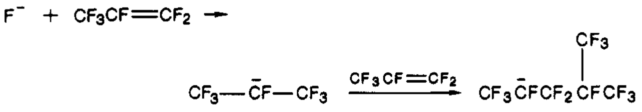
Figure 2. Distribution of product ions for the reaction $F^- + C_3F_6$.

IV. Discussion

A. Reactions of F^-, $C_2F_5^-$, $C_3F_7^-$, and $C_4F_9^-$. All reactions observed for the interactions of F^-, $C_2F_5^-$, $C_3F_7^-$, and $C_4F_9^-$ with C_2F_4 and C_3F_6 are association reactions. F^- adds readily to C_2F_4 to form $C_2F_5^-$ (reaction 1) with a rate constant of 1.5 × 10^{-10} cm^3 molecule^{-1} s^{-1}. No further addition of C_2F_4 was observed. As is expected, ion-molecule reaction rate constants are much higher than neutral-neutral reaction rate constants. The rate constants of the corresponding free-radical reaction,[16] $F^\bullet + C_2F_4 = C_2F_5$ is 4 × 10^{-11} cm^3 molecule^{-1} s^{-1}. F^- also adds to C_3F_6 rapidly to form $C_3F_7^-$ which subsequently adds to another C_3F_6 molecule to form $C_6F_{13}^-$ (reaction 6). These reactions are believed to involve addition rather than cluster formation. That is, chemical bond formation occurs:

$$F^- + CF_2{=\!=}CF_2 \rightarrow CF_3{-}\bar{C}F_2$$

and



$$F^- + CF_3CF{=\!=}CF_2 \rightarrow CF_3{-}\bar{C}F{-}CF_3 \xrightarrow{CF_3CF{=}CF_2} CF_3\bar{C}FCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}FCF_3$$

There are several factors that lead to this conclusion.

(1) The association reactions are very fast with the effective two-body rate constants approaching the collision rate coefficient. Association reactions that proceed at or near the collision rate at room temperature generally imply large bond strengths. Examples of this include association reactions involving WF_6[17] and assocations of CH_3^+ to a variety of neutrals to form protonated

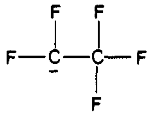
TABLE II: Enthalpies of Formation of Fluorocarbon Species at 298 K

species	ΔH°_f, kcal/mol	ref
CF_2	-46.4	9
C_2F_4	-155.0	10
C_3F_6	-266.2	11
F^-	-59.9	12
CF_3^-	-157.2	13
$C_2F_5^-$	-267.9	14
$C_3F_7^-$	-380.9	15
$C_4F_9^-$	-494.0	15
$C_5F_{11}^-$	-598.0	15
$C_6F_{13}^-$	-696.0	15

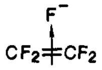
CH_3NH_2, CH_3CN, and CH_3OH.[18] In these examples the rate constants are fast and the bond strengths large.

(2) When $C_3F_7^-$ ions are generated from C_8F_{18} in the ion source and injected into the flow tube, they react at essentially the same rate with C_3F_6 as do $C_3F_7^-$ ions produced in the reaction of F^- with C_3F_6. They also form the same products. This suggests that both reactant ions have the same structure. $C_3F_7^-$ ions generated from C_8F_{18} can be expected to be a stable chemical species. One therefore assumes that $C_3F_7^-$ ions generated in the reaction of F^- with C_3F_6 are stable as well. Similarly, both $C_2F_5^-$ produced in the reaction F^- with C_2F_4 and $C_2F_5^-$ produced in the ion source from either C_3F_8 or C_8F_{18} do not react with C_2F_4 (see reactions 1 and 3). Again this suggests that these ions have the same stable structure.

(3) An ab initio molecular orbital calculation[11] shows that $C_2F_5^-$ and $C_3F_7^-$ are stable ions. Another ab initio molecular orbital calculation[19] of the $C_2F_5^-$ ion shows that the structure



is more stable than the π complex structure



(4) $C_2F_5^-$ and $C_3F_7^-$ do not associate with C_2F_4 but associate with C_3F_6 at close to the collision rate. If only cluster bond formation were present, one would expect that these ions would associate with both these similar species, although with different rate constants. The fact that they associate rapidly with one and not the other indicates that chemical bond formation is not possible in the C_2F_4 reactions. In the C_3F_6 reactions a chemical bond is formed with a large bond strength (compared to ligand bond strengths). This accounts for the large association rate constants in the C_3F_6 reactions.

B. Reactions of CF_3^-. CF_3^- reacts with C_2F_4 via F^- transfer to form $C_2F_5^-$ and CF_2 with a reaction efficiency of ~50% (reaction 2). Association of CF_3^- with C_2F_4 was not observed. CF_3^- reacts with C_3F_6 with near unit efficiency. Approximately 90% of the reaction follows the F^- transfer channel to form $C_3F_7^-$, while 10% of the reaction proceeds by association (reaction 7a). $C_6F_{13}^-$ was also observed in the reaction of CF_3^- and C_3F_6. This is the product of the subsequent addition reaction of the $C_3F_7^-$ ion [formed by reaction 7b] with C_3F_6 (reaction 7c).

C. Reactions with Mixed Gases. An experiment was performed in which F^- ions were injected from the ion source into the flow tube with a 1:1 mixture of C_2F_4 and C_3F_6. $C_2F_5^-$, $C_3F_7^-$, $C_5F_{11}^-$, and $C_6F_{13}^-$ product ions were observed. This is consistent with the above observations.

V. Conclusion

In contrast to negative ion–molecule reactions in olefin systems, where proton-transfer processes are abundant,[20] most of the reactions observed in this study for negative ion–perfluoroolefin systems are association reactions. These reactions give an efficient means of producing medium-size perfluorinated alkane negative ions. C_3F_6 is more reactive than C_2F_4. All ions, except $C_4F_9^-$, studied in this report react with C_3F_6 with a total effective bimolecular reaction rate constant near the collision rate constant. F^- and CF_3^- have less than 50% reaction efficiency toward C_2F_4. Reactions of $C_2F_5^-$, $C_3F_7^-$, and $C_4F_9^-$ with C_2F_4 were not observed.

Registry No. F^-, 16984-48-8; CF_3^-, 54128-17-5; $CF_3CF_2^-$, 35476-45-0; $CF_3CF^-CF_3$, 35556-60-6; $CF_3(CF_2)_3^-$, 108292-11-1; $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CFCF_3$, 116-15-4.

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