Reactivity of Negative Ions with Trifluoromethyl Halides

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The kinetics of reactions of selected anions (A^-) with the trifluoromethyl halides CF_3X ($X = F$, Cl, Br, I) in the gas phase were measured at 300 K. Reaction rate constants and product branching fractions were determined using a selected ion flow tube (SIFT) instrument. The chosen anions were $C_5F_5N^-$, *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$, $C_6F_5Br^-$, $C_6F_5Cl^-$, $C_6F_5CF_3^-$, $C_6F_5COCH_3^-$, Fe^-, $FeCO^-$, SF_6^-, SO^-, SO_2^-, NO^-, NO_2^-, and NO_3^-. The reactivity of these systems varies from unreactive to collisional, and a variety of reaction types was found. The results of our present and previous measurements on $A^- + CF_3X$ reactions show that, in cases where nondissociative electron transfer (NDET) is energetically allowed, the total reactivity tends to be high, approaching collisional. This suggests that reactivity in these cases is initiated and controlled by electron transfer from the anion. In addition, association reactions tend to be preempted when NDET is energetically allowed. A few exceptions to these tendencies were found and are discussed.

Introduction

We have previously reported kinetics measurements for a number of negative ions reacting with the trifluoromethyl halides CF_3X ($X = F$, Cl, Br, I).[1,2] In those studies, trends in reactivity began to emerge, but the number and variety of systems studied were quite limited. It was found that the reactivity of O_2^- with fully halogenated methanes, including CF_3X, correlates with both the electron affinities of the perhalomethanes and their rates of thermal electron attachment.[1] This was interpreted as an indication that in these cases reactivity is initiated and governed by electron transfer from the anion to the perhalomethane, i.e., that initial electron transfer is the rate-limiting step.

Substitution reactions at carbon occurring in solution via initial electron transfer were first characterized in the 1960s by Kornblum et al.[3] and by Russell and Danen.[4] Bunnett[5] named this mechanism "$S_{RN}1$" and studied its applicability to aromatic substitution. Initial electron transfer in the gas phase was proposed by McDonald et al.[6] to explain the reactivity of $(CH_3O)_2PO^-$ with CF_3X and by Jones et al.[7] to explain the reactivity of 17-electron transition-metal complex anions with a variety of haloalkanes. Knighton and Grimsrud[8] also attributed anion reactivity trends in haloalkanes to an initial electron transfer mechanism.

In order to investigate the extent of applicability of the initial electron transfer mechanism to other systems, we have studied the reactivity of the anions $C_5F_5N^-$, *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$, $C_6F_5Br^-$, $C_6F_5Cl^-$, $C_6F_5CF_3^-$, $C_6F_5COCH_3^-$, Fe^-, $FeCO^-$, SF_6^-, SO^-, SO_2^-, NO^-, NO_2^-, and NO_3^- with the trifluoromethyl halides CF_3X ($X = F$, Cl, Br, I). Rate constants and product branching fractions were measured at 300 K using a selected ion flow tube (SIFT) instrument. The results are compared with previously published measurements of other A^-/CF_3X systems performed on the same SIFT apparatus,[1,2] and some trends are apparent in the combined data.

Experimental Section

The measurements were made under thermal conditions at 300 K using the selected ion flow tube (SIFT) instrument at Phillips Laboratory. This apparatus has been described previously,[9] and the technique and generic instrumentation have been extensively reviewed.[10] Therefore, we report here only those details which are relevant to the present study.

The ions were formed in a remote electron impact ion source from precursor chemicals as follows. NO^- was formed from N_2O, Fe^- and $FeCO^-$ were formed from $Fe(CO)_5$ diluted in CO, SF_6^- was formed from an SF_6 impurity present in NF_3, SO^- and SO_2^- were formed from SO_2, NO_2^- and NO_3^- were formed from NO_2 which contained an impurity of HNO_3, and F^- was formed from CF_4. All of the organic anions were formed in the ion source from the corresponding parent neutral compounds, e.g., $C_5F_5N^-$ from C_5F_5N.

The ion of interest was mass selected in a quadrupole mass filter and injected through a Venturi aspirator inlet into a stainless steel flow tube 1 m in length. The ions were conveyed along the flow tube by a fast flow (approximately 10^4 cm s^{-1}) of He buffer gas maintained at approximately 0.4 Torr, except in the case of the NO^- reactions which were studied in an Ar carrier gas at about 0.2 Torr; the Ar carrier was used in this case because the NO^- anion is destroyed in the flow tube by thermal electron detachment in collisions with He.[11] Neutral CF_3X reactant gas was added to the flow tube, and the reactant and product ions were sampled through a 0.2 mm orifice in a flat plate mounted on a blunt sampling cone. The ion current reaching the flat plate was recorded in order to check for possible electron detachment reactions.[12] After being sampled, the ions were mass analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier.

Rate constants were determined by the standard technique of recording the pseudo-first-order attenuation of the reactant ion count rate as a function of reactant neutral flow rate. The reaction time was measured directly by time-of-flight techniques.[9] Buffer and reactant gas flow rates were maintained

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and measured with flow controllers, and the flow tube pressure was measured with a capacitance manometer. Product branching fractions were determined by recording and plotting the fractional product ion abundances as a function of reactant neutral flow rate. The effects of secondary reactions were accounted for by extrapolating the branching fractions to zero reactant neutral flow rate. The product branching measurements were performed under conditions of low resolution in order to minimize the effects of mass discrimination. The reported branching percentages have been rounded off to the nearest five percentage points, except in those cases where a very minor product percentage was determined, e.g., 2%.

Results

The experimental results are presented in Table 1. The reactions are ordered by increasing detachment energy of the anion. The NO^- reactions were carried out in Ar buffer gas[11] and all others in He. Neutral products of reaction were not detected but were inferred from mass conservation and thermochemical considerations.[13]

The reactivity of the systems studied varies from fast, i.e., collisional,[14,15] to immeasurably slow. A variety of reaction types is observed, including nondissociative electron transfer (NDET), halogen atom transfer, halide ion production, CF_3 radical transfer, and association. CF_4 does not react with any of the studied anions with the exception of a slow electron detachment “reaction” with the weakly-bound anion NO^-.

Discussion

A. Reactivity. A few general observations about reactivity are offered in this section. In Table 2 we compare not only the results of the present measurements but also the previously reported data from our laboratory on reactivity of anions with CF_3X.[1,2] The previous work involves the reactions of F^-, O^-, and O_2^- with the complete CF_3X series, as well as reactions of X^-, XO^-, and XF^- with the corresponding CF_3X compound, e.g., $IF^- + CF_3I$. The reactant anions and neutrals in Table 2 are ordered by increasing detachment energy and electron affinity, respectively.[16] Table 2 gives the measured overall reaction rate constants; cases where the nondissociative electron transfer product CF_3X^- was observed are marked with an asterisk.

i. Bimolecular Reactivity. In general, these reactions are fast (i.e., at or near the collisional limit[14,15]) when NDET is energetically allowed (exothermic or approximately thermoneutral[21]), regardless of the observed product channel(s). Actual NDET reaction products, i.e., CF_3X^-, are seen in a number of reactions with CF_3I, which has the highest electron affinity (EA) in the CF_3X series. Formation of CF_3Br^- was found in only one case, $O_2^- + CF_3Br$,[1] and no formation of CF_3Cl^- was observed in any of the reactions. (CF_3Cl^- has been observed in the gas phase from electron attachment to $(CF_3Cl)_n$ clusters[18,19] but has not been found as a product from ion−molecule reactions.)

The observation that reaction tends to be efficient in cases where NDET is energetically allowed suggests that the mechanism for these cases involves initial electron transfer from the anion to CF_3X either at long range or within the collision complex. The formation of halide ion products or other products which are fragments of CF_3X^- may then arise from subsequent dissociation of the CF_3X^- species either before or after the complex dissociates. We note that there are also cases where overall reaction is fast yet NDET is quite endothermic. Thus, while energetically-allowed NDET generally implies a fast overall reaction, endothermic NDET should not be seen as an indication that the reaction will be slow, since highly exothermic pathways may exist which do not involve electron transfer *per se*, e.g., nucleophilic attack at carbon by O^-. Jones et al.[7] have pointed out that, even in some cases where NDET is endothermic, electron transfer may occur within the collision complex, since the attractive ion−dipole and ion−induced dipole interactions supply additional energy with which to overcome the endothermicity of electron transfer. In that model, a subsequent step, halide transfer from CF_3X^-, would then take place within the collision complex, leading to the observed exothermic products.

The slow reaction of SF_6^- with CF_3I does not contradict the proposal of an initial electron transfer mechanism because SF_6^- is generally unreactive or inefficient with respect to electron transfer processes;[22] initial electron transfer from SF_6^- to CF_3I would be expected to be inhibited, which would lead to the observed low overall reactivity. Grimsrud et al.[23] have suggested that the low reactivity of SF_6^- toward electron transfer is caused by the significant geometry change required in going from SF_6^- anion to SF_6 neutral.

In addition to the $SF_6^- + CF_3I$ case, anomalous behavior is also found for the reaction of *m*-$CF_3C_6H_4CN^-$ with CF_3Br, which is slow despite an apparent 0.24 eV exothermicity for NDET. Possible explanations for this behavior include incorrect thermochemistry as well as the possibility that the geometry of this anion is significantly different from that of the parent neutral, an argument similar to that offered above for SF_6^-. An alternative explanation is that the delocalized nature of the negative charge in the reactant anion leads to the observed inefficiency of reaction. It should be noted that no NDET product CF_3X^- was observed from any of the $CF_3C_6H_4CN^-$ reactions, while all of the other organic anions studied did form some CF_3I^- in reaction with CF_3I.

We have previously shown that the rates of the reactions of O_2^- with fully halogenated methanes correlate with both the electron affinities and the electron attachment rates of the halomethanes,[1] supporting the above mechanism. Earlier, McDonald et al.[6] suggested an initial electron transfer mechanism to explain the reactivity of $(CH_3O)_2PO^-$ with CF_3X. Jones et al.[7] showed a correlation between haloalkane electron attachment rates and the rates for reactions of 17-electron transition-metal anions and concluded that the reactivity of these systems is governed by initial electron transfer. Knighton and Grimsrud[8] also concluded that initial electron transfer controls the reactivity of a series of reactions of substituted benzene anions and haloalkanes. Pan and Ridge[24,25] invoked this mechanism to explain the correlation between anion reactivity and the electron affinities of a series of organic electrophiles. Thus, a wealth of gas phase anion reactivity data support this mechanism for a variety of neutrals including CF_3X, although the mechanism does not hold for all molecules.[22]

ii. Reactivity toward Association. Another general observation is that when association occurs, it tends to occur when NDET is endothermic; however, there are many cases where NDET is endothermic yet no association is found. NDET thus appears to preempt association as do other exothermic bimolecular channels when they are operating, in most cases. The reactions of the $CF_3C_6H_4CN^-$ ions and of SF_6^- are again notable exceptions. For the reaction of SF_6^- with CF_3I, slow association is the sole reaction channel in spite of NDET being exothermic and other bimolecular channels being available. This is consistent with the initial electron transfer mechanism as follows: since initial electron transfer is inhibited, association is not preempted by electron transfer. The $CF_3C_6H_4CN^-$ ions associate with CF_3Br and CF_3I despite the apparent availability

TABLE 1: Rate Constants, Product Branching Percentages, and Reaction Efficiencies from SIFT Experiments at 300 K

reaction	branching percentage	total rate constant (10^{-9} cm^3 s^{-1})	efficiency (%)[a]
$NO^- + CF_4 \rightarrow e^- + NO + CF_4$		0.0035	0.4
$NO^- + CF_3Cl \rightarrow Cl^- + CF_3NO$	80	0.33	25
$\rightarrow ClF^- + CF_2NO$	20		
$NO^- + CF_3Br \rightarrow Br^- + CF_3NO$		1.0	71
$NO^- + CF_3I \rightarrow I^- + CF_3NO$		1.9	117
$Fe^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$Fe^- + CF_3Cl \rightarrow FeCl^- + CF_3$	70	0.63	61
$\rightarrow CF_3^- + FeCl$	15		
$\rightarrow Cl^- + FeCF_3$	15		
$Fe^- + CF_3Br \rightarrow Br^- + FeCF_3$	50	1.1	101
$\rightarrow FeBr^- + CF_3$	45		
$\rightarrow CF_3^- + FeBr$	≤5		
$Fe^- + CF_3I \rightarrow I^- + FeCF_3$		1.8	147
m-$CF_3C_6H_4CN^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
m-$CF_3C_6H_4CN^- + CF_3Cl \rightarrow CF_3C_6H_4CNCl^- + CF_3$	90	0.0010 (0.40 Torr)	0.13
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Cl$	10		
m-$CF_3C_6H_4CN^- + CF_3Br \rightarrow CF_3C_6H_4CNBr^- + CF_3$	85	0.021 (0.40 Torr)	2.7
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Br$	15		
m-$CF_3C_6H_4CN^- + CF_3I \rightarrow CF_3C_6H_4CNI^- + CF_3$	5	0.81 (0.40 Torr)	94
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3I$	95		
$C_5F_5N^- + CF_4 \rightarrow$ no reaction		<0.002	<0.4
$C_5F_5N^- + CF_3Cl \rightarrow$ no reaction		<0.002	<0.3
$C_5F_5N^- + CF_3Br \rightarrow Br^- + C_5F_5NCF_3$	90	0.12	15
$\rightarrow C_5F_5NBr^- + CF_3$	10		
$C_5F_5N^- + CF_3I \rightarrow I^- + C_5F_5NCF_3$	90	0.71	82
$\rightarrow CF_3I^- + C_5F_5N$	10		
o-$CF_3C_6H_4CN^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
o-$CF_3C_6H_4CN^- + CF_3Cl \rightarrow CF_3C_6H_4CNCl^- + CF_3$	87	0.013 (0.40 Torr)	1.7
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Cl$	11		
$\rightarrow CF_3C_6H_4CNCF_3^- + Cl$	≤2		
o-$CF_3C_6H_4CN^- + CF_3Br \rightarrow CF_3C_6H_4CNBr^- + CF_3$	90	0.34 (0.40 Torr)	43
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Br$	10		
o-$CF_3C_6H_4CN^- + CF_3I \rightarrow CF_3C_6H_4CNI^- + CF_3$	25	0.89 (0.40 Torr)	103
$\rightarrow I^- + CF_3C_6H_4CN + CF_3$	20		
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3I$	55		
p-$CF_3C_6H_4CN^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
p-$CF_3C_6H_4CN^- + CF_3Cl \rightarrow CF_3C_6H_4CNCl^- + CF_3$	91	0.0020 (0.40 Torr)	0.26
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Cl$	7		
$\rightarrow CF_3C_6H_4CNCF_3^- + Cl$	≤2		
p-$CF_3C_6H_4CN^- + CF_3Br \rightarrow CF_3C_6H_4CNBr^- + CF_3$	80	0.22 (0.40 Torr)	28
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3Br$	20		
p-$CF_3C_6H_4CN^- + CF_3I \rightarrow CF_3C_6H_4CNI^- + CF_3$	8	0.87 (0.40 Torr)	101
$\rightarrow I^- + CF_3C_6H_4CN + CF_3$	18		
$\rightarrow CF_3C_6H_4CN^- \cdot CF_3I$	74		
$C_6F_5Cl^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Cl^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Cl^- + CF_3Br \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Cl^- + CF_3I \rightarrow I^- + C_6F_5Cl + CF_3$	55	0.80	97
$\rightarrow CF_3I^- + C_6F_5Cl$	45		
$C_6F_5COCH_3^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5COCH_3^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5COCH_3^- + CF_3Br \rightarrow C_6F_5COCH_3Br^- + CF_3$	97	0.0034	0.45
$\rightarrow Br^- + C_6F_5COCH_3 + CF_3$	≤3		
$C_6F_5COCH_3^- + CF_3I \rightarrow C_6F_5COCH_3I^- + CF_3$	20	0.81	99
$\rightarrow I^- + C_6F_5COCH_3 + CF_3$	75		
$\rightarrow CF_3I^- + C_6F_5COCH_3$	5		
$SF_6^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$SF_6^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.2
$SF_6^- + CF_3Br \rightarrow$ no reaction		<0.002	<0.3
$SF_6^- + CF_3I \rightarrow SF_6^- \cdot CF_3I$		0.005 (0.40 Torr)	0.55
$C_6F_5CF_3^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5CF_3^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5CF_3^- + CF_3Br \rightarrow C_6F_5CF_3Br^- + CF_3$	50	0.0075	1.0
$\rightarrow Br^- + C_6F_5CF_3 + CF_3$	50		
$C_6F_5CF_3^- + CF_3I \rightarrow C_6F_5CF_3I^- + CF_3$	11	0.62	78
$\rightarrow I^- + C_6F_5CF_3 + CF_3$	87		
$\rightarrow CF_3I^- + C_6F_5CF_3$	2		
$SO_2^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$SO_2^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.1
$SO_2^- + CF_3Br \rightarrow SO_2Br^- + CF_3$		0.46	44
$SO_2^- + CF_3I \rightarrow I^- + CF_3SO_2$	90	1.25	105
$\rightarrow SO_2I^- + CF_3$	5		
$\rightarrow CF_3I^- + SO_2$	5		
$SO^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$SO^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.1
$SO^- + CF_3Br \rightarrow Br^- + CF_3SO$	98	0.066 (0.48 Torr)	5.6
$\rightarrow SO^- \cdot CF_3Br$	2		
$SO^- + CF_3I \rightarrow I^- + CF_3SO$	70	1.4	108
$\rightarrow m/e$ 159±1 amu	10		
$\rightarrow CF_2I^- + FSO$	10		
$\rightarrow CF_3I^- + SO$	10		
$C_6F_5Br^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Br^- + CF_3Cl \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Br^- + CF_3Br \rightarrow$ no reaction		<0.001	<0.2
$C_6F_5Br^- + CF_3I \rightarrow I^- + C_6F_5Br + CF_3$	98	0.56	71
$\rightarrow CF_3I^- + C_6F_5Br$	2		
$FeCO^- + CF_4 \rightarrow$ no reaction		<0.001	<0.2
$FeCO^- + CF_3Cl \rightarrow FeCOCl^- + CF_3$	65	0.21	23
$\rightarrow FeCl^- + CF_3CO$	15		
$\rightarrow CF_3^- + FeCOCl$	10		
$\rightarrow FeCOCF_3^- + Cl$	≤10		
$FeCO^- + CF_3Br \rightarrow FeCOBr^- + CF_3$	45	0.94	98
$\rightarrow FeBr^- + CF_3CO$	30		
$\rightarrow CF_3^- + FeCOBr$	20		
$\rightarrow FeCOCF_3^- + Br$	≤5		
$FeCO^- + CF_3I \rightarrow I^- + FeCOCF_3$	35	1.4	126
$\rightarrow FeI^- + CF_3CO$	25		
$\rightarrow CF_3^- + FeCOI$	25		
$\rightarrow FeCOI^- + CF_3$	15		
$NO_2^- + CF_4 \rightarrow$ no reaction		<0.0005	<0.1
$NO_2^- + CF_3Cl \rightarrow$ no reaction		<0.0005	<0.1
$NO_2^- + CF_3Br \rightarrow NO_2^- \cdot CF_3Br$		<0.001 (0.43 Torr)	<0.1
$NO_2^- + CF_3I \rightarrow NO_2^- \cdot CF_3I$		0.063 (0.43 Torr)	4.7
$F^- + CF_4 \rightarrow$ no reaction		<0.0005	<0.1
$NO_3^- + CF_4 \rightarrow$ no reaction		<0.0005	<0.1
$NO_3^- + CF_3Cl \rightarrow NO_3^- \cdot CF_3Cl$		<0.001 (0.43 Torr)	<0.1
$NO_3^- + CF_3Br \rightarrow NO_3^- \cdot CF_3Br$		<0.001 (0.43 Torr)	<0.1
$NO_3^- + CF_3I \rightarrow NO_3^- \cdot CF_3I$		0.027 (0.43 Torr)	2.2

[a] Calculated from the measured total rate constant divided by the collisional rate constant obtained using the parametrized trajectory method,[14,15] expressed as a percentage.

TABLE 2: Rate Constants (10^{-9} cm^3 s^{-1}) for Overall Reaction of Selected Negative Ions with CF_3X

	CF_4 (<0)[b]	CF_3Cl (>∼0)[b,c]	CF_3Br (0.91)	CF_3I (1.57)
NO^- (0.026)	0.0035	0.33	1.0	1.9
Fe^- (0.151)	nr	0.63	1.1	1.8
O_2^- (0.451)[d]	nr	<0.004	1.0*	1.5*
m-$C_8F_3H_4N^-$ (0.67)	nr	0.0010	0.021	0.81
$C_5F_5N^-$ (0.68)	nr	nr	0.12	0.71*
o-$C_8F_3H_4N^-$ (0.70)	nr	0.013	0.34	0.89
p-$C_8F_3H_4N^-$ (0.76)	nr	0.0020	0.22	0.87
$C_6F_5Cl^-$ (0.82)	nr	nr	nr	0.80*
$C_6F_5COCH_3^-$ (0.88)	nr	nr	0.0034	0.81*
SF_6^- (1.05)	nr	nr	nr	0.005
$C_6F_5CF_3^-$ (1.06)	nr	nr	0.0075	0.62*
SO_2^- (1.107)	nr	nr	0.46	1.25*
SO^- (1.125)	nr	nr	0.066	1.4*
$C_6F_5Br^-$ (1.15)	nr	nr	nr	0.56*
$FeCO^-$ (1.157)	nr	0.21	0.94	1.4
O^- (1.461)[d]	nr	0.86	1.4	1.9
NO_2^- (2.273)	nr	nr	0.0005	0.063
ClO^- (2.275)[d]		nr		
BrO^- (2.353)[d]			0.0099	
IO^- (2.378)[d]				0.13
ClF^- (2.4)[d,e]		nr		
BrF^- (∼2.5)[d,f]			<0.003	
IF^- (∼2.5)[d,f]				0.94
I^- (3.059)[d]				<0.005
Br^- (3.364)[d]			<0.003	
F^- (3.401)[d]	nr	<0.003	0.084	0.72
Cl^- (3.613)[d]		<0.003		
NO_3^- (3.937)	nr	<0.0005	<0.0005	0.027

a The notation nr denotes no evidence of reaction. An asterisk indicates observation of the nondissociative electron transfer product CF_3X^-. Values in parentheses are electron affinities of neutrals and electron binding energies of anions (both in electronvolts; ref 16 unless otherwise noted). [b] Reference 17. [c] References 18 and 19. [d] Rate constants from ref 1. [e] Reference 20. [f] Estimated.

of exothermic NDET. Here the clustering might be explained by electron transfer to CF_3X followed by association. The $CF_3C_6H_4CN^-$ ions, however, also associate with CF_3Cl for which NDET is clearly endothermic. We note that no NDET products, i.e., CF_3X^-, were observed in any of the reactions of the $CF_3C_6H_4CN^-$ ions, while all of the other organic anions studied formed some CF_3I^- from reaction with CF_3I.

Association is not observed for any of the CF_4 "reactions", and the association rates for the other CF_3X generally increase with heavier CF_3X, as expected from the increasing dipole moment and polarizability of the heavier CF_3X, both of which lead to larger cluster bond strengths.

B. Chemical Reaction Channels. *i. Halogen Atom Transfer*. A major and sometimes dominant pathway in most of the reactions of both Fe^- and $FeCO^-$ is halogen atom transfer, a channel found previously in work involving other transition metal complex anions.[7,26] The relative contribution from the halogen transfer channel diminishes with heavier CF_3X. This same trend is found in the reactions of *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$, for which halogen atom transfer dominates for CF_3Cl and CF_3Br but is a minor pathway for CF_3I, where the main channel is association. Halogen atom transfer is also observed in the reactions of $C_6F_5COCH_3^-$, $C_6F_5CF_3^-$, and SO_2^- with CF_3Br and CF_3I, with a larger contribution from CF_3Br than from CF_3I in each case. The anion $C_5F_5N^-$ is unreactive with CF_3Cl but undergoes halogen atom transfer with CF_3Br; this pathway is not seen for CF_3I. Thus, all of the results show the same trend of decreasing relative contribution from halogen atom transfer with heavier CF_3X, while the overall reactivity is increasing. The decrease in percent halogen transfer with heavier CF_3X is offset by halide formation in the cases of Fe^-, $C_6F_5COCH_3^-$, $C_6F_5CF_3^-$, and SO_2^-, by NDET for $C_5F_5N^-$, and by association for *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$. In the case of $FeCO^-$, decreasing halogen transfer with heavier CF_3X is accompanied by increases in several pathways. The decrease in the contribution by halogen atom transfer with heavier CF_3X could be the result of the increasing strength of the $C-X^-$ bond in the CF_3X^- anion. If reaction is initiated by electron transfer from A^-, forming CF_3X^- which then transfers X^- to A (the net result of which is halogen atom transfer), then the process involves breaking increasingly stronger $C-X^-$ bonds for heavier CF_3X.

ii. Halide Ion Formation. The present results show formation of halide ion X^- from CF_3X in many cases, but production of F^- is not found in any of these cases. The halide formation channel, when operating, generally increases with heavier CF_3X. In fact, some I^- is formed from CF_3I in every case except for SF_6^-, NO_2^-, and NO_3^-, which react only by association, and *m*-$CF_3C_6H_4CN^-$ which reacts by association and I atom transfer. The *o*- and *p*-$CF_3C_6H_4CN^-$ isomers both react with CF_3I to form I^- as well as the association adduct and the I atom transfer product $CF_3C_6H_4CNI^-$.

In the reactions of Fe^- with CF_3X, production of X^- increases from 15% Cl^- to 50% Br^- to 100% I^-, with the reaction rate increasing with heavier CF_3X. The rate constant for $Fe^- + CF_3I$ exceeds the collisional rate constant by 47%, which is greater than the combined uncertainties in the measured and calculated[14,15] rate constants. Because of this apparent discrepancy, we repeated the measurements and checked the calibration of the flow meters and manometer. We are confident in the measurement to within our usual absolute uncertainty of ±25%; therefore, we propose that the reaction is in fact faster than the theoretical ion−dipole capture rate. The explanation likely involves initial electron transfer at relatively long distances—distances outside of the capture radius of the ion−molecule orbiting complex. A theoretical examination of the curve crossings in this system as well as the ionic radius of Fe^- could shed light on this possibility. It should be pointed out that electron transfer at distances greater than the capture radius have been reported previously.[27,28]

iii. CF_3 Radical Transfer. Transfer of a CF_3 radical from CF_3X to the reactant anion occurs as a minor channel in the reactions of *o*- and *p*-$CF_3C_6H_4CN^-$ with CF_3Cl, where the overall reactivity is low, but not at all with the more reactive CF_3Br and CF_3I. The isomer *m*-$CF_3C_6H_4CN^-$ does not undergo CF_3 transfer with any CF_3X. Transfer of CF_3 also was observed in the cases of $FeCO^-$ with CF_3Cl and CF_3Br but not with CF_3I.

iv. Association Reactions. The ions NO_2^- and NO_3^- react with the CF_3X series only by association and only for the heavier CF_3X: measurable rates are found just for $NO_2^- + CF_3I$ and $NO_3^- + CF_3I$. At 0.43 Torr, the second-order association rate constant for $NO_2^- + CF_3I$ is more than twice the value for $NO_3^- + CF_3I$. The $NO_3^- \cdot CF_3I$ adduct has additional internal degrees of freedom and on that basis alone would be expected to display a faster rate of formation, due to the resulting longer complex lifetime. Therefore, the explanation for the difference in rates must lie in the relative cluster bond strengths for $NO_2^- \cdot CF_3I$ versus $NO_3^- \cdot CF_3I$.[29,30] These bond strengths are not available in the literature, but NO_2^- is known to bond more strongly to polar molecules than does NO_3^-.[31]

Association in competition with bimolecular channels was observed for the anions *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$ with CF_3Cl, CF_3Br, and CF_3I, and in the reaction of SO^- with CF_3Br. A pressure dependence study of these reactions might prove interesting. In our previous work on $F^- + CF_3Br$ and CF_3I,[2] we found that increasing pressure leads to larger rate constants for association but not at the expense of the rate constants for the other reaction channel, in this case halide formation, and we therefore postulated that the two pathways arise from two different intermediates.

The slow association reaction of SF_6^- with CF_3I was discussed in section A.ii.

v. Collisional Electron Detachment. Collisional electron detachment from NO^- has been the subject of several studies,[11,32-35] and the efficiency of detachment depends on the particle colliding with the NO^-. The NO^- detachment energy is only 0.026 eV,[36] essentially equal to kT at room temperature. Electron detachment from NO^- is seen in the present work in collisions with CF_4, with a modest rate constant value of 3.5×10^{-12} cm^3 s^{-1}. No *chemical* reactions, i.e., bonds broken or formed, are found for anions in collision with CF_4. Since exothermic reactive channels are available for the other CF_3X species, NO^- detachment is preempted by fast reaction. We cannot, however, rule out a very minor (∼5%) contribution by NO^- detachment in the reactive cases.

vi. Other Reaction Types. The occurrence of nondissociative electron transfer (NDET) was discussed in section A.i.

Formation of the dihalide anion ClF^- was observed in the reaction of NO^- with CF_3Cl but not with the other CF_3X and not from any other anions in the present study. In previous work on CF_3X reactions, we found production of XF^- from O^- reactant anion for X = Cl, Br, and I.[1]

CF_3^- product formation occurs in the reactions of Fe^- with CF_3Cl and CF_3Br, with decreasing percentages, respectively. CF_3^- is formed in the case of $FeCO^- + CF_3Cl$, CF_3Br, and CF_3I.

In the $FeCO^-$ reactions, formation of FeX^- is observed along with three other channels.

Transfer of F^+ is a minor pathway in the reaction of SO^- with CF_3I.

Conclusions

A wide range of reactivity is found for the systems studied. The reactions tend to be fast when nondissociative electron transfer is energetically allowed, suggesting that reactivity in these cases is determined by an initial electron transfer mechanism. Association is usually most prevalent when nondissociative electron transfer is endothermic. While the reactions of SF_6^- and of the *o*-, *m*-, and *p*-$CF_3C_6H_4CN^-$ ions do not follow these tendencies, the generally low reactivity of SF_6^- toward electron transfer is consistent with them, and the behavior of the $CF_3C_6H_4CN^-$ species may be due to similar effects.

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