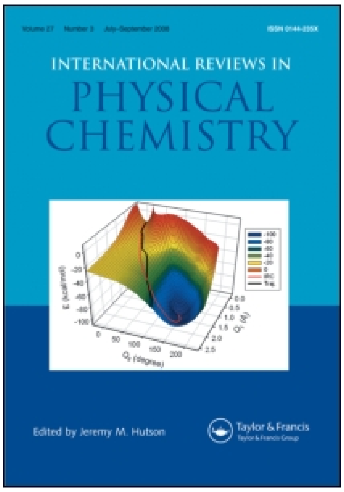

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Reactivity of gas-phase anions with fully halogenated alkanes*

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Gas-phase reactivity of negative ions with fully halogenated alkanes is reviewed, restricted to rate constant measurements under thermal conditions. Reactivity generally increases upon substitution by heavier halogens. Perfluorocarbons (PFCs) are generally unreactive with negative ions, but the highly reactive O^- anion reacts with the larger PFCs through multiple product channels. The trifluoromethyl halide series CF_3X ($X = Cl, Br, I$) has been well-studied, and the reactions tend to be fast when nondissociative electron transfer to the halocarbon would be exothermic, regardless of the actual resulting product channels. For many of the reactions of CF_3X and other perhaloalkanes, reactivity correlates with both the electron affinities and the electron attachment rates of the perhaloalkanes, though notable exceptions exist. This and other evidence suggests that many of the reactions are initiated by electron transfer to the halocarbon, which tends to explain why the reactivity of CF_3X generally increases in the order $Cl < Br < I$ for second-order reactions. The same reactivity trend in third-order association reactions is explained by the corresponding trends in CF_3X dipole moment and polarizability. The results of several studies show that negative ion reactions are not a significant removal process for halocarbons in the atmosphere.

1. Introduction

Gas-phase ion–molecule reactions have been of interest since the early days of mass spectrometry. The first quantitative study of an ion–molecule reaction was performed in 1952 (Tal'roze and Lyubimova 1952). Since that time the preponderance of the research has been concerned with reactions of positive ions; in 1965 an assessment of the status of ion chemistry contained the following statement: 'Negative-ion–molecule reactions, last reviewed by Melton (1963), continue to arouse little interest' (Henchman 1965). Nevertheless, since the 1960s, there has been increasing attention paid to negative ion chemistry. This interest was generated initially due to curiosity about radiation chemistry and the negative ion chemistry occurring in gas discharges, but the desire to understand the negative ion chemistry of the atmosphere stimulated a significant amount of research in the 1960s and 1970s. Today the field is much broader and addresses a range of questions spanning the physical sciences.

Experimental methods for studying gas-phase ion chemistry have become increasingly sophisticated since the early days when reactions were studied in relatively simple ion source experiments. Nevertheless, the available techniques still rely generally on some form of mass spectrometry to identify and quantify the reactant and product ions. Neutral products of reaction are usually not detected but often can be inferred from mass conservation and thermochemical considerations. Reaction rate constants can be measured with typical accuracies of 25 % and can be determined as

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functions of temperature, pressure, ion kinetic energy, and, in some cases, as a function of reactant internal temperature or energy level (rotational, vibrational or electronic).

Reactions between negative ions and fully halogenated alkanes have been studied for a variety of reasons ranging from fundamental scientific interest to application-oriented research and development. Basic research on this topic includes studies of reaction mechanisms, electron affinities and related thermochemistry, and reactant internal energy effects. The more applied work has focused on a variety of issues such as atmospheric chemistry, chemical effects in electron capture detectors for gas chromatographs, and plasma processing of materials.

As the number of studied reactions grows, so does the possibility that some general conclusions about the chemistry may be drawn from the data. The purpose of this article is to compile the existing reaction rate data on these reactions and to point out trends and generalities where possible. We begin by reviewing the experimental techniques in the following section. The published thermal kinetics data are then presented and discussed; reactions are organized by grouping the perhaloalkane neutral reactants as follows: table 1—perfluoroalkanes, table 2—trifluoromethyl halides, and table 3—all other perhaloalkanes studied.

Reactions of positive ions are beyond the scope of this review, as are measurements made under non-thermal conditions, e.g. beam experiments. For further information on both negative and positive ion reactions, we refer the interested reader to the reaction rate constant compilations by Ikezoe *et al.* (1987) and by Anicich (1993); the thermochemical compilation known as the 'GIANT tables' (Lias *et al.* 1988); and the 1992 issue of *Chemical Reviews* devoted to ion chemistry (volume 92; number 7). For reviews of experimental techniques in ion chemistry, an excellent collection is found in *Techniques for the Study of Ion–Molecule Reactions*, edited by Farrar and Saunders, Jr. (1988).

2. Experimental techniques

Several experimental techniques have been used in the studies reported here. Three of the techniques can be grouped into the category 'fast flow techniques', namely the flowing afterglow (FA), selected ion flow tube (SIFT), and the variable temperature—selected ion flow drift tube (VT–SIFDT). These techniques will be described together. In addition to the fast flow methods, experiments were conducted using a pulsed high pressure mass spectrometer (PHPMS) instrument and a Fourier transform ion cyclotron resonance mass spectrometer (FTICR) apparatus. While a detailed description of the experimental techniques used for these studies is well beyond the scope of this review, we will give enough details to provide a flavour of the variety of techniques that can be used to measure thermal rate constants for negative ion chemistry.

A good overview of fast flow techniques is the review by Graul and Squires (1988). The fast flow technique of simplest design is the flowing afterglow. In this method, ions and electrons are created in the upstream end of a flow tube typically 1 m in length and 3–4 cm in radius. A typical operating pressure for the flow techniques is 0·5 torr. The ion source is usually an electron impact source but can be any suitable source. Precursor gas(es) used to create the ion of interest can be added upstream or downstream of the source, depending on the particular chemistry involved. The ions are carried downstream by a fast flow of a carrier gas, frequently of the order of 10^4 cm s^{-1} of He. In approximately the middle third of the flow tube, the reactant neutral is added through an inlet. Reactant and product ions are sampled through a small hole (typically 0·2 mm diameter) in a truncated nose cone. The bulk of the gas is pumped away by a Roots-type pump. The ions are mass selected by a quadrupole mass filter and detected by a channel electron multiplier or similar device. Rate constants are calculated from the reaction time and the slope of a least squares fit of the natural logarithm of the reactant ion signal plotted versus added reactant neutral gas concentration.

A SIFT (Graul and Squires 1988) differs from a flowing afterglow only in that an external ion source is separated from the flow tube by a mass filter. Ions are created by electron impact, mass selected in a quadrupole mass filter, and injected through a Venturi inlet into a stainless steel flow tube 1 m in length. Inside the flow tube the ions are entrained in the fast flowing carrier gas which is also injected through the Venturi inlet. The ions are quickly thermalized by collisions with the buffer gas. The use of selected ion injection simplifies data acquisition in two ways: 1) ions of only a single mass are present in the flow tube in the absence of neutral reagent, and 2) the source gas(es) for ion creation are also absent from the flow tube. This leads to the situation where only one ion species and one reactant neutral gas are present in the flow tube, which simplifies the measurements. In particular, this leads to the ability to determine easily the product ion branching ratios. This is important for a number of the experiments reviewed here.

The final flow tube technique that was used in the measurements reported here is the VT–SIFDT instrument (Graul and Squires 1988, Viggiano *et al.* 1990). This instrument differs from the SIFT in two details. First, the entire reaction region can be heated or cooled to allow the temperature to be varied between liquid nitrogen temperature and about 550 K. Secondly, inside the flow tube, a concentric drift tube has been inserted. The drift tube consists of 60 stainless steel rings, electrically isolated from each other and connected by a series of resistors external to the apparatus. A dc voltage applied across the resistance chain establishes a uniform electric field inside the tube, which translationally excites the ions. The drift tube can function at any of the instrumental operating temperatures, and therefore kinetic energy dependences can be measured as a function of temperature. This in turn allows one to derive information on the internal energy dependences of the rate constants and branching ratios.

Typical accuracies of the measured overall rate constants in these flow tube instruments is ±25%, and the experimental precision is ±15% (Viggiano *et al.* 1990). The rate constant for an individual reaction channel is equal to the overall rate constant for total reaction multiplied by the product branching fraction for that channel. Therefore, the accuracy with which the branching fraction can be measured must be considered, and the uncertainty in the channel-specific rate constants is approximately ±35% with a precision of ±20% (Morris and Viggiano 1994).

A PHPMS consists of a small high pressure ($\sim$ 1–10 torr) chamber connected to a mass spectrometer (Knighton and Grimsrud 1992, Knighton *et al.* 1990). A premixed combination of the source gas, reactant gas, and a buffer, usually CH_4, is added to the chamber. A short pulse of high energy electrons of approximately 20 μs duration and about 3000 eV energy ionizes the gas mixture. This creates a mixture of ions which are rapidly thermalized by the buffer. Ions are lost both by diffusion to the walls and by reaction. Conditions are chosen so that the ion of interest reacts rapidly with the neutral of interest, while all other reactions are slow. Ion densities are kept low so that no recombination occurs. The ion concentrations are monitored by bleeding the gas mixture through a narrow slit into an evacuated chamber containing a quadrupole mass spectrometer and channeltron. The ion currents of each ion species are monitored as a function of time using a multichannel scaler. Since diffusion of the ions is an important loss process, kinetics data are obtained by recording fractional ion abundances versus time. It is assumed that all ions diffuse with the same time constant. For the experiments reported here, the primary product ion comes into equilibrium with the ion source gas, and therefore it is impossible to determine whether a product ion is solvated as a result of the primary reaction or solvated simply by clustering to the source gas.

The final experimental technique described here is the FTICR (Comisarow and Marshall 1974, Johlman *et al.* 1983, Van Orden *et al.* 1991a). In this instrument, a rectangular trapping cell resides inside an ultrahigh vacuum chamber surrounded by a magnetic field, of the order of 0·7 T, generated by an electromagnet. An electron pulse ionizes a source gas. In the experiments reviewed here, $V(CO)_6$ captures electrons of about 0·1 eV energy to produce $V(CO)_5^-$. The pulse duration is approximately 1–2 ms. In the magnetic field, the ions undergo cyclotron motion which traps the ions in two dimensions. The ion trapping in the third dimension is accomplished by a weak electric field. Extraneous ions can be ejected from the instrument by mass-selective excitation of the cyclotron motion. The ion motion caused by these fields is kept small so that the reactions are carried out under conditions close to thermal. A reactant neutral gas is added, and the ion intensities are followed as a function of time. As in the PHPMS system, fractional ion abundances are monitored, since the ions decay in time due to both reaction and diffusion. Rate constants are derived from the semilogarithmic decay of the relative ion signal versus time at a known neutral gas density. The neutral gas density is monitored by an ionization gauge and, for the experiments reported here, is in the 10^{-5} torr range. The gauge is calibrated using the well-studied reaction of O^- with N_2O. Primary product distributions are measured at short reaction time, while product distributions from secondary reactions may be determined at longer times.

3. Results

3.1. *Perfluoroalkanes*

The low reactivity of the perfluoroalkanes or perfluorocarbons (PFCs) has attracted interest in PFCs as potential replacements for CFCs and Halons since the PFCs should not contribute to stratospheric ozone destruction. Recently, however, it has been shown that PFCs have very large global warming potentials (Ravishankara *et al.* 1993), the result of a combination of their strong infrared absorption and long atmospheric lifetime due to their chemical inertness. In a subsequent study (Morris *et al.* 1995a), reactions of some PFCs with ions and electrons in the upper atmosphere were found to be significant removal processes, competing with photolysis. The largest ion effects were found for the positive ions O^+ and O_2^+. Most of the published PFC negative ion chemistry was examined as a part of the atmospheric lifetime work (Morris *et al.* 1995a, b). The published kinetics data for reactions of anions with perfluoroalkanes are listed in table 1.

The generally low reactivity of the PFCs is not surprising in view of their strong C–F bonds, their low polarizabilities, and their small or zero dipole moments; the last two factors also explain why the PFCs have low clustering rates. However, the highly reactive O^- anion does react with larger PFCs, as described below.

The smallest PFCs, CF_4 and C_2F_6, are unreactive with all of the anions studied, with the exception of NO^- which undergoes slow collisional electron detachment with CF_4. The electron detachment energy of NO^- is very small, 0·026 eV (Travers *et al.* 1989), a value essentially equal to kT at room temperature. There are available

Table 1. Product branching percentages (given in bold type) and rate constants for reactions of anions with perfluoroalkanes. For reactions with multiple literature citations, the data are listed in the chronological order of the corresponding references. Neutral products are inferred from mass balance and thermochemistry when available (not always unambiguously).

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$F^- + CF_4 \rightarrow$ no reaction		< 0·0001	*a*
$Fe^- + CF_4 \rightarrow$ no reaction		< 0·001	*a*
$FeCO^- + CF_4 \rightarrow$ no reaction		< 0·001	*a*
$H_3O^- + CF_4 \rightarrow$ no reaction		< 0·001 (at 93 K)	*b*
$NO^- + CF_4 \rightarrow e^- + NO + CF_4$		< 0·0035	*a*
$NO_2^- + CF_4 \rightarrow$ no reaction		< 0·0001	*a*
$NO_3^- + CF_4 \rightarrow$ no reaction		< 0·0001	*a*
$O^- + CF_4 \rightarrow$ no reaction		< 0·002; n.r.	*c*, *d*
$O_2^- + CF_4 \rightarrow$ no reaction		< 0·002; n.r.	*c*, *d*
$SO^- + CF_4 \rightarrow$ no reaction		< 0·001	*a*
$O^- + C_2F_6 \rightarrow$ no reaction		n.r.; < 0·003	*e*, *f*
$O_2^- + C_2F_6 \rightarrow$ no reaction		n.r.; < 0·003	*e*, *f*
$O^- + c\text{-}C_4F_8 \rightarrow F^- + C_4F_7O$	**41**	'rapid'; 1·8	*e*, *f*
$\rightarrow FCO^- + C_2F_4 + CF_3$	**6**		
$\rightarrow CF_3^- + C_3F_5O$	**4**		
$\rightarrow CF_3O^- + C_3F_5$	**3**		
$\rightarrow C_2F_3O^- + C_2F_5$	**9**		
$\rightarrow C_2F_5^- + C_2F_3O$	**3**		
$\rightarrow C_3F_5^- + CF_3O$	**3**		
$\rightarrow C_3F_5O^- + CF_3$	**2**		
$\rightarrow C_4F_7O^- + F$	**4**		
$\rightarrow e^- + C_2F_4O + C_2F_4$	**26**		
$O_2^- + c\text{-}C_4F_8 \rightarrow C_4F_8^- + O_2$		'moderate'; 0·46	*e*, *f*
$SF_6^- + C_4F_8 \rightarrow C_4F_8^- + SF_6$		< 0·01	*g*
$O^- + n\text{-}C_6F_{14} \rightarrow C_2F_5^- + C_4F_9O$	**7**	'rapid'; 1·6	*e*, *f*
$\rightarrow C_2F_5O^- + C_4F_9$	**13**		
$\rightarrow C_3F_7^- + C_3F_7O$	**7**		
$\rightarrow C_3F_7O^- + C_3F_7$	**11**		
$\rightarrow C_4F_9^- + C_2F_5O$	**1**		
$\rightarrow C_4F_9O^- + C_2F_5$	**6**		
$\rightarrow C_5F_{11}O^- + CF_3$	**2**		
$\rightarrow C_6F_{13}O^- + F$	**53**		
$O_2^- + n\text{-}C_6F_{14} \rightarrow$ products		$\leqslant$ 0·006	*f*

[a] (Morris *et al.* 1995c, 1996)
[b] (Miller *et al.* 1994b)
[c] (Morris 1992)
[d] (Mayhew *et al.* 1993)
[e] (Morris *et al.* 1995a)
[f] (Morris *et al.* 1995b)
[g] (Fehsenfeld 1971)

exothermic pathways for some of the unreactive systems, e.g. $O^- + CF_4 \rightarrow F^- + CF_3O$, but the strong C–F bond represents a likely barrier to reaction.

In contrast to the smaller PFCs, the reactions of $c\text{-}C_4F_8$ and $n\text{-}C_6F_{14}$ with O^- display a very rich chemistry with numerous reaction product channels and fast

Table 2. Product branching percentages (given in bold type) and rate constants for reactions of anions with trifluoromethyl halides. For reactions with multiple literature citations, the data are listed in the chronological order of the corresponding references. Neutral products are inferred from mass balance and thermochemistry (not always unambiguously).

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$Cl^- + CF_3Cl \rightarrow Cl^- \cdot CF_3Cl$		$< 0{\cdot}003$ (0·4 torr)	*a*
$ClF^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}005$	*a*
$ClO^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}005$	*a*
$H_3O^- + CF_3Cl \rightarrow CF_3^- + HCl + H_2O$	**80**	1·6 (141 K)	*b*
$\rightarrow OH^- \cdot CF_3Cl + H_2$	**15**		
$\rightarrow CF_3^- \cdot H_2O + HCl$	**5**		
$F^- + CF_3Cl \rightarrow F^- \cdot CF_3Cl$		$< 0{\cdot}003$ (0·4 torr)	*a*
$Fe^- + CF_3Cl \rightarrow FeCl^- + CF_3$	**70**	0·63	*c*
$\rightarrow CF_3^- + FeCl$	**15**		
$\rightarrow Cl^- + FeCF_3$	**15**		
$FeCO^- + CF_3Cl \rightarrow FeCOCl^- + CF_3$	**65**	0·21	*c*
$\rightarrow FeCl^- + CF_3CO$	**15**		
$\rightarrow CF_3^- + FeCOCl$	**10**		
$\rightarrow FeCOCF_3^- + Cl$	$\leqslant$ **10**		
$NO^- + CF_3Cl \rightarrow Cl^- + CF_3NO$	**81**	0·33	*c*
$\rightarrow ClF^- + CF_2NO$	**19**		
$NO_2^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}0001$	*c*
$NO_3^- + CF_3Cl \rightarrow NO_3^- \cdot CF_3Cl$		$< 0{\cdot}0001$ (0·43 torr)	*c*
$O^- + CF_3Cl \rightarrow F^- + CF_2O + Cl$	**64; 50**	0·86; 0·85	*a, d*
$\rightarrow Cl^- + CF_2O + F$	**19; 30**		
$\rightarrow ClO^- + CF_3$	**0** (2% at 500 K); **0**		
$\rightarrow ClF^- + CF_2O$	**17; 20**		
$O_2^- + CF_3Cl \rightarrow Cl^- + CF_3O_2$	**66;** $\leqslant$ **1**	$< 0{\cdot}004$; $\leqslant 0{\cdot}0008$	*a, d*
$\rightarrow O_2^- \cdot CF_3Cl$	**34** (0·4 torr); **99** (0·6 torr)		
$SO^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}001$	*c*
$(OC)_4ReBr^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}0001$	*e*
$(OC)_4ReCl^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}0001$	*e*
$(OC)_4MnBr^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}0001$	*e*
$(OC)_3MnBr^- + CF_3Cl \rightarrow$ no reaction		$< 0{\cdot}0001$	*e*

Table 2. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$(OC)_4MnCl^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(OC)_3MnCl^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(\eta^3\text{-}C_3H_5)Re(CO)_3^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(\eta^3\text{-}C_3H_5)Mn(CO)_3^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(OC)_5Cr^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(OC)_4Fe^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$(OC)_3Ni^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*e*
$V(CO)_5^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*f*
$(CH_3O)_2PO^- + CF_3Cl \rightarrow$ no reaction		< 0·0001	*g*
$Br^- + CF_3Br \rightarrow Br^- \cdot CF_3Br$		< 0·003 (0·4 torr)	*a*
$BrF^- + CF_3Br \rightarrow BrF^- \cdot CF_3Br$		< 0·003 (0·4 torr)	*a*
$BrO^- + CF_3Br \rightarrow BrO^- \cdot CF_3Br$		0·0099 (0·4 torr)	*a*
$F^- + CF_3Br \rightarrow Br^- + CF_4$	36	0·092	*a*, *h*
$\rightarrow F^- \cdot CF_3Br$	64 (0·4 torr)		
$Fe^- + CF_3Br \rightarrow Br^- + FeCF_3$	50	1·1	*c*
$\rightarrow FeBr^- + CF_3$	45		
$\rightarrow CF_3^- + FeBr$	$\leqslant 5$		
$FeCO^- + CF_3Br \rightarrow FeCOBr^- + CF_3$	45	0·94	*c*
$\rightarrow FeBr^- + CF_3CO$	30		
$\rightarrow CF_3^- + FeCOBr$	20		
$\rightarrow FeCOCF_3^- + Br$	$\leqslant 5$		
$O^- + CF_3Br \rightarrow F^- + CF_2O + Br$	45[a]	1·3; 1·4	*i*, *a*
$\rightarrow Br^- + CF_2O + F$	8		
$\rightarrow BrO^- + CF_3$	34		
$\rightarrow BrF^- + CF_2O$	13		
$O_2^- + CF_3Br \rightarrow Br^- + CF_3O_2$	45[a]	1·1; 1·0	*i*, *a*
$\rightarrow CF_3Br^- + O_2$	55		
$NO^- + CF_3Br \rightarrow Br^- + CF_3NO$		1·0	*c*
$NO_2^- + CF_3Br \rightarrow NO_2^- \cdot CF_3Br$		0·0005 (0·43 torr)	*c*
$NO_3^- + CF_3Br \rightarrow NO_3^- \cdot CF_3Br$		< 0·0001 (0·43 torr)	*c*
$SO^- + CF_3Br \rightarrow Br^- + CF_3SO$	98	0·066	*c*
$\rightarrow SO^- \cdot CF_3Br$	2 (0·48 torr)		

Table 2. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$(OC)_4ReBr^- + CF_3Br \rightarrow (OC)_4ReBr_2^- + CF_3$		0·11	*e*
$(OC)_4ReCl^- + CF_3Br \rightarrow (OC)_4ReClBr^- + CF_3$		0·15	*e*
$(OC)_4MnBr^- + CF_3Br \rightarrow (OC)_4MnBr_2^- + CF_3$		0·00013	*e*
$(OC)_3MnBr^- + CF_3Br \rightarrow (OC)_3MnBr_2^- + CF_3$		0·00015	*e*
$(OC)_4MnCl^- + CF_3Br \rightarrow (OC)_4MnClBr^- + CF_3$		0·00011	*e*
$(OC)_3MnCl^- + CF_3Br \rightarrow (OC)_3MnClBr^- + CF_3$		0·00013	*e*
$(OC)_5Cr^- + CF_3Br \rightarrow (OC)_5CrBr^- + CF_3$		0·21	*e*
$(OC)_4Fe^- + CF_3Br \rightarrow (OC)_4FeBr^- + CF_3$	**73**	0·0020	*e*
$\rightarrow (OC)_2FeBrCF_3^- + 2CO$	**27**		
$(OC)_3Ni^- + CF_3Br \rightarrow (OC)_3NiBr^- + CF_3$	**75**	0·46	*e*
$\rightarrow (OC)_2NiBr^- + CO + CF_3$	**25**		
$(CH_3O)_2PO^- + CF_3Br \rightarrow (CH_3O)(Br)PO_2^- + CF_3CH_3$	> **99**	'fast'	*g*
$\rightarrow Br^- + (CH_3O)_2PO + CF_3$	< **1**		
$F^- + CF_3I \rightarrow I^- + CF_4$	**10**	0·72	*a*, *h*
$\rightarrow F^- \cdot CF_3I$	**90** (0·4 torr)		
$FI^- + CF_3I \rightarrow F^- \cdot CF_3I + I$		0·94	*a*
$Fe^- + CF_3I \rightarrow I^- + FeCF_3$		1·8	*c*
$FeCO^- + CF_3I \rightarrow I^- + FeCOCF_3$	**35**	1·4	*c*
$\rightarrow FeI^- + CF_3CO$	**25**		
$\rightarrow CF_3^- + FeCOI$	**25**		
$\rightarrow FeCOI^- + CF_3$	**15**		
$I^- + CF_3I \rightarrow I^- \cdot CF_3I$		< 0·005 (0·4 torr)	*a*
$IO^- + CF_3I \rightarrow$ products		0·13	*a*
$NO^- + CF_3I \rightarrow I^- + CF_3NO$		1·9	*c*
$NO_2^- + CF_3I \rightarrow NO_2^- \cdot CF_3I$		0·063 (0·43 torr)	*c*
$NO_3^- + CF_3I \rightarrow NO_3^- \cdot CF_3I$		0·027 (0·43 torr)	*c*
$O^- + CF_3I \rightarrow F^- + CF_2O + I$	**25**^{a}	1·1; 1·9	*i*, *a*
$\rightarrow CF_3^- + IO$	**3**		
$\rightarrow IO^- + CF_3$	**62**		
$\rightarrow IF^- + CF_2O$	**6**		
$\rightarrow IOF^- + CF_2$	**4**		
$O_2^- + CF_3I \rightarrow I^- + CF_3O_2$	**88**^{a}	0·86; 1·5	*i*, *a*
$\rightarrow CF_3I^- + O_2$	**12**		
$SF_6^- + CF_3I \rightarrow SF_6^- \cdot CF_3I$		0·005	*c*

Table 2. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$SO^- + CF_3I \rightarrow I^- + CF_3SO$	**69**	1·4	*c*
$\rightarrow m/e$ 159 ± 1 amu	**12**		
$\rightarrow CF_2I^- + FSO$	**12**		
$\rightarrow CF_3I^- + SO$	**6**		
$(OC)_4ReBr^- + CF_3I \rightarrow (OC)_4ReBrI^- + CF_3$		0·48	*e*
$(OC)_4ReCl^- + CF_3I \rightarrow (OC)_4ReClI^- + CF_3$		0·39	*e*
$(OC)_4MnBr^- + CF_3I \rightarrow (OC)_4MnBrI^- + CF_3$		0·31	*e*
$(OC)_3MnBr^- + CF_3I \rightarrow (OC)_3MnBrI^- + CF_3$		0·31	*e*
$(OC)_4MnCl^- + CF_3I \rightarrow (OC)_4MnClI^- + CF_3$		0·29	*e*
$(OC)_3MnCl^- + CF_3I \rightarrow (OC)_3MnClI^- + CF_3$		0·29	*e*
$(\eta^3\text{-}C_3H_5)Mn(CO)_3^- + CF_3Cl \rightarrow (\eta^3\text{-}C_3H_5)Mn(CO)_3I^- + CF_3$		0·56	*e*
$(OC)_5Cr^- + CF_3I \rightarrow (OC)_5CrI^- + CF_3$		0·63	*e*
$(OC)_4Fe^- + CF_3I \rightarrow (OC)_4FeI^- + CF_3$	**88**	0·53	*e*
$\rightarrow (OC)_2FeICF_3^- + 2CO$	**12**		
$(OC)_3Ni^- + CF_3I \rightarrow (OC)_3NiI^- + CF_3$	**20**	0·77	*e*
$\rightarrow (OC)_2NiI^- + CO + CF_3$	**80**		
$(CH_3O)_2PO^- + CF_3I \rightarrow (CH_3O)(I)PO_2^- + CF_3CH_3$	**85**	0·64	*g*
$\rightarrow I^- + (CH_3O)_2PO + CF_3$	**9**		
$\rightarrow [(CH_3O)_2PO \cdot CF_3I]^-$	**6** (0·5 torr)		

[a] (Morris 1992)
[b] (Miller *et al.* 1994b)
[c] (Morris *et al.* 1995c, 1996)
[d] (Mayhew *et al.* 1993)
[e] (Jones *et al.* 1989)
[f] (Van Orden *et al.* 1991a)
[g] (McDonald *et al.* 1987)
[h] (Morris and Viggiano 1994)
[i] (Streit 1982a)

kinetics (Morris *et al.* 1995b). In both of these reactions, many of the product channels appear to be ordered in pairs within which they differ only by the location of the charge. For example, in the reaction of O^- with c-C_4F_8, there is a pair of product channels ($CF_3O^- + C_3F_5$) and ($C_3F_5^- + CF_3O$) where the only difference is the location of the extra electron. There are four such pairs in this reaction and three in the reaction of O^- with n-C_6F_{14}. In both reactions, it appears likely that this is the result of multiple charge exchanges in the complex before the product species fully separate. This would lead to significant probabilities for the electron ending up on either fragment within a given reaction channel. Also notable is the reactive electron detachment channel observed in the c-C_4F_8 reaction.

The ring strain in c-C_4F_8 leads to a lower stability than is typical for the PFCs, and c-C_4F_8 reacts with O_2^- by nondissociative electron transfer at a moderate rate, in similarity to the attachment of thermal electrons to c-C_4F_8, which is also moderately rapid and nondissociative (Miller *et al.* 1994a). Many of the reactions reviewed in the present paper are believed to proceed via a mechanism involving initial electron transfer to the perhaloalkane, and several investigators have found correlations between their ion–molecule results and electron attachment kinetics data, as discussed later.

3.2. *Trifluoromethyl halides*

There is a reasonably large set of kinetics data in the literature on the ion–molecule reactions of trifluoromethyl halides, CF_3X (X = Cl, Br, I). The published results for negative ion reactions with CF_3X are shown in table 2. A substantial amount of ion chemistry involving CF_3X has been performed by the present authors and co-workers at Phillips Laboratory, with emphasis on reactions of atomic ions and small molecular ions, including positive ions (Morris *et al.* 1992a–d) which are not included in this review. Another large portion of the negative ion data is from a study by Jones *et al.* (1989) which examined the reactivity of a number of transition metal complex anions with a variety of haloalkanes, including CF_3X.

In the CF_3X series there is a general trend of increasing reactivity with heavier X, i.e. as one proceeds down group VII. This trend is also seen in positive ion reactions (Morris *et al.* 1992b–d) and in neutral–neutral reactions (Bradley *et al.* 1976, Hodgins and Haines 1952, Le Bras and Combourieu 1978, Morris *et al.* 1989, Silver and De Haas 1981, Westenberg and De Haas 1977) where it can be explained simply by the decreasing C–X bond strength in the order CF_3–Cl > CF_3–Br > CF_3–I. For many of the negative ion reactions, however, there is evidence that the energetics and kinetics of electron transfer govern the reactivity by controlling the rate of electron transfer to the halocarbon in the initial phase of the reaction.

The electron affinities (EAs) of CF_3Br (0·91 eV) and CF_3I (1·57 eV) have been measured by the collisional ionization technique (Compton *et al.* 1978). While there is no experimental value for the EA of CF_3Cl (Miller 1995), theoretical calculations (using the MS Xα method) have yielded a negative EA(CF_3Cl) of $-0{\cdot}4$ eV (Preston and Kaufman 1977); however, Kühn and Illenberger (1989) have observed CF_3Cl^- following electron attachment to clusters of CF_3Cl. For the negative ions A^- tabulated here, the electron detachment energies (DEs) (or the EAs of the corresponding neutrals A) are not known for most of the transition metal complex anions but are available for most of the small anions (Miller 1995). As we have reported previously (Morris *et al.* 1995c, 1996), when the EA of CF_3X exceeds the DE of A^-, i.e. when nondissociative electron transfer (NDET) is exothermic, the reaction is usually fast (except for SF_6^- where a large geometry change is required, as discussed below). In a few of these cases, the NDET product CF_3X^- is actually observed, but in most cases, the reaction is dissociative. In the cases where the CF_3X^- product is observed, the contribution from this channel decreases with increasing exothermicity. These facts suggest that the reaction mechanism involves initial electron transfer from A^- to CF_3X. When X^- is formed as a product in what appears to be 'displacement', it may actually result from unimolecular decomposition of the internally excited CF_3X^- formed in the initial electron transfer step. The dissociation of CF_3X^- may occur either within the ion–molecule complex (with or without subsequent bonding of the CF_3 radical to A), or after the complex has dissociated, if energetics permit.

There is evidence from several studies that indicate that initial electron transfer controls the reactivity in a variety of anion–molecule systems. For the reactions of O_2^- with CF_3X and other perhalomethanes, Morris (1992) found that the rate constants correlate with both EA (perhalomethane) and the thermal electron attachment rates of the perhalomethanes. Furthermore, the branching ratios for the O_2^- reactions show less NDET product when electron transfer is more exothermic. The higher exothermicity NDET cases would be expected to lead to more dissociation because of the greater amount of internal energy in the complex. In earlier work, Jones *et al.* (1989) studied a series of reactions of 17-electron transition metal complex anions with haloalkanes and found evidence that these halogen atom transfer reactions proceed by initial electron transfer within the reaction complex. In those reactions, a halogen atom is transferred from the haloalkane to the complex anion with rates which correlate with the haloalkane rates of thermal electron attachment, while no correlation was found with C–X bond energies. These facts suggest that the mechanism does not involve direct halogen atom abstraction, but rather points to intracomplex electron transfer followed by intracomplex halide ion transfer (Jones *et al.* 1989). This investigation included both partially and fully halogenated alkanes, and the conclusions apply to the full series of haloalkanes studied, not simply to the CF_3X series. Jones *et al.* (1989) point out that the attractive ion-dipole and ion-induced dipole interactions can allow electron transfer to take place within the complex when NDET is formally endothermic.

The trend in phosphoryl anion $(CH_3O)_2PO^-$ reactivity with CF_3X, studied using a FA, suggests that electron transfer is the initial step in these reactions also (McDonald *et al.* 1987). In this study it was observed that CF_3I reacts slightly faster than does CF_3Br, and CF_3Cl does not react at all. Thus for a number of negative ions, namely NO^-, O_2^-, SO^-, the 17-electron transition metal anions, and the phosphoryl anion, it appears as though the reaction is initiated by electron transfer to the haloalkane and the overall reaction rate is controlled by this process, i.e. initial electron transfer is the rate-determining step.

These results contrast with those for the reactions of the 16-electron complex anion $V(CO)_5^-$ with chloromethanes studied by Van Orden *et al.* (1991a) in which electron transfer appears not to be operating. In this study, the rate constants were shown to correlate with the C–Cl bond strengths but not with either the chloromethane EAs or electron attachment rates. This is consistent with either a direct chlorine atom abstraction mechanism or a C–Cl bond insertion mechanism but not with initial electron transfer. Initial transfer of an electron from $V(CO)_5^-$ would leave the metal centre as a 15-electron system, whereas initial electron transfer from a 17-electron complex anion (leaving the metal centre with 16 electrons) would facilitate the transfer of a halide ion, i.e. a two electron donor, resulting in a stable 18-electron product anion.

For the association reactions of the type $A^- + CF_3X + M \rightarrow A^- \cdot CF_3X + M$, reactivity again increases for the heavier halides. In this case, the trend is explained by the increasing dipole moment and polarizability of CF_3X in the progression down group VII, which leads to stronger ion-dipole and ion-induced dipole interactions, respectively, for the heavier halides. These attractive interactions determine the cluster bond strength in the $A^- \cdot CF_3X$ adduct, which influences the association reaction rate (Bates 1979, Herbst 1980). Examples of this trend include the reactions of NO_2^- and NO_3^- with CF_3X (Morris *et al.* 1996).

Another generalization regarding energetics and reactivity is that clustering or association is observed only when $EA(CF_3X) < DE(A^-)$, i.e. only when initial electron transfer is endothermic. Furthermore, association can compete favourably with bimolecular reaction even when highly exothermic bimolecular pathways are available (Morris and Viggiano 1994), so long as nondissociative electron transfer is endothermic. For the reactions $F^- + CF_3X$, association is the dominant channel at room temperature, competing with X^- production in the case of CF_3Br and CF_3I. Morris and Viggiano (1994) measured the rate constants and branching ratios for these reactions over a wide range of experimental conditions using a variable temperature-selected ion flow drift tube instrument (VT–SIFDT). Dependences on pressure, temperature and ion translational energy were determined, along with derived dependences on the internal temperature of CF_3Br and CF_3I.

It was found for these reactions that the X^- production channel is governed by total energy, i.e. the sum of translational, vibrational and rotational energy regardless of their relative contributions. This indicates that the X^- channel behaves statistically, i.e. energy is randomized in the complex before dissociation. This is particularly interesting in light of recent evidence for non-statistical behaviour in S_N2 reactions of small ion–molecule systems (Cho *et al.* 1992, Graul and Bowers 1991, Smith 1992, Smith *et al.* 1989, Su *et al.* 1990, Van de Linde and Hase 1989, 1990a–c, Van Orden *et al.* 1991b, Viggiano *et al.* 1992).

In contrast to the X^- channel, the association channel shows a strong negative dependence on the CF_3X internal temperature compared with the weak negative dependence on translational energy. This is consistent with theoretical understanding of ion–molecule association reactions in the low pressure limit, which predicts strong effects from reactant internal energy and weak translational energy effects (Bates 1979, Herbst 1980, Viggiano 1986).

The pressure dependence measurements of the $F^- + CF_3Br$ reaction showed an interesting feature. The second-order association rate constant increases with pressure while the Br^- channel is pressure independent, i.e. shows no corresponding decrease with pressure. This lack of competition between the two channels suggests the possibility that two different intermediates are involved in the overall $F^- + CF_3Br$ reaction. The reaction of F^- with CF_3I is more efficient than the CF_3Br reaction and is at or near the high-pressure limiting regime for association. For this reason, the data are inconclusive regarding competition, but the results do suggest that the F^-/CF_3I system, like $F^- + CF_3Br$, reacts by two non-competing pathways.

Several groups have examined reactions of CF_3X species with the oxygen anions O^- and O_2^-. Streit (1982a) used a flowing afterglow (FA) instrument to study both O^- and O_2^- reacting with CF_3Br and CF_3I. The FA technique required that both reactant ions O^- and O_2^- be present in the flow tube simultaneously, which prevented assigning reaction products to a particular reactant ion, but the individual rate constants for O^- and O_2^- reactions were measured.

Table 3. Product branching percentages (given in bold type) and rate constants for reactions of anions with those perhaloalkanes not listed in tables 1 and 2. For reactions with multiple literature citations, the data are listed in the chronological order of the corresponding references. Neutral products are inferred from mass balance and thermochemistry (not always unambiguously).

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$C_{10}H_8^- + CCl_4 \rightarrow Cl^- + C_{10}H_8 + CCl_3$		0·50	*a*
$C_6H_5NO_2^- + CCl_4 \rightarrow Cl^- + C_6H_5NO_2 + CCl_3$		0·18	*a*
$o\text{-}FC_6H_4NO_2^- + CCl_4 \rightarrow Cl^- + o\text{-}FC_6H_4NO_2 + CCl_3$		0·083	*a*
$m\text{-}FC_6H_4NO_2^- + CCl_4 \rightarrow Cl^- + m\text{-}FC_6H_4NO_2 + CCl_3$		0·005	*a*
$m\text{-}CF_3C_6H_4NO_2^- + CCl_4 \rightarrow$ no reaction		< 0·001	*a*
$O^- + CCl_4 \rightarrow Cl^- +$ neutral(s)	**15**[d]	1·4; 1·0; 1·8	*b, c, d*
$\rightarrow ClO^- + CCl_3$	**45**		
$\rightarrow Cl_2^- + CCl_2O$	**5**		
$\rightarrow CCl_3^- + ClO$	**35**		
$O_2^- + CCl_4 \rightarrow Cl^- +$ neutral(s)		0·79; 1·4	*c, d*
$NO^- + CCl_4 \rightarrow Cl^- +$ neutral(s)		'fast'	*e*
$SF_6^- + CCl_4 \rightarrow$ no reaction		< 0·001	*f*
$(OC)_4ReBr^- + CCl_4 \rightarrow (OC)_4ReBrCl^- + CCl_3$	**87**	0·16	*g*
$\rightarrow (OC)_3ReBrCl^- + CO + CCl_3$	**13**		
$(OC)_4ReCl^- + CCl_4 \rightarrow (OC)_4ReCl_2^- + CCl_3$	**72**	0·17	*g*
$\rightarrow (OC)_3ReCl_2^- + CO + CCl_3$	**28**		
$(OC)_4MnBr^- + CCl_4 \rightarrow (OC)_4MnBrCl^- + CCl_3$		0·00029	*g*
$(OC)_3MnBr^- + CCl_4 \rightarrow (OC)_3MnBrCl^- + CCl_3$		0·0053	*g*
$(OC)_4MnCl^- + CCl_4 \rightarrow (OC)_4MnCl_2^- + CCl_3$		0·00049	*g*
$(OC)_3MnCl^- + CCl_4 \rightarrow (OC)_3MnCl_2^- + CCl_3$		0·0039	*g*
$(\eta^3\text{-}C_3H_5)Re(CO)_3^- + CCl_4 \rightarrow (\eta^3\text{-}C_3H_5)Re(CO)_3Cl^- + CCl_3$		0·41	*g*
$(\eta^3\text{-}C_3H_5)Mn(CO)_3^- + CCl_4 \rightarrow (\eta^3\text{-}C_3H_5)Mn(CO)_3Cl^- + CCl_3$		0·36	*g*
$(OC)_5Cr^- + CCl_4 \rightarrow (OC)_5CrCl^- + CCl_3$	**95**	0·25	*g*
$\rightarrow (OC)_4CrCl^- + CO + CCl_3$	**5**		
$(OC)_4Fe^- + CCl_4 \rightarrow (OC)_4FeCl^- + CCl_3$		0·0088	*g*
$(OC)_3Ni^- + CCl_4 \rightarrow (OC)_3NiCl^- + CCl_3$	**2**	0·61	*g*
$\rightarrow (OC)_2NiCl^- + CO + CCl_3$	**98**		
$V(CO)_5^- + CCl_4 \rightarrow V(CO)_5Cl^- + CCl_3$	**1**	0·24	*h*
$\rightarrow V(CO)_4Cl^- + CO + CCl_3$	**63**		
$\rightarrow V(CO)_3Cl^- + 2CO + CCl_3$	**36**		

Table 3. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$C_{10}H_8^- + CCl_3Br \rightarrow Br^- + C_{10}H_8 + CCl_3$		1·4	*a*
$C_6H_5NO_2^- + CCl_3Br \rightarrow Br^- + C_6H_5NO_2 + CCl_3$		0·92	*a*
o-$FC_6H_4NO_2^- + CCl_3Br \rightarrow Br^- + o$-$FC_6H_4NO_2 + CCl_3$		0·85	*a*
m-$FC_6H_4NO_2^- + CCl_3Br \rightarrow Br^- + m$-$FC_6H_4NO_2 + CCl_3$		0·59	*a*
m-$CF_3C_6H_4NO_2^- + CCl_3Br \rightarrow Br^- + m$-$CF_3C_6H_4NO_2 + CCl_3$		0·30	*a*
o-$C_6H_4(NO_2)_2^- + CCl_3Br \rightarrow Br^- + o$-$C_6H_4(NO_2)_2 + CCl_3$		0·047	*a*
p-$C_6H_4(NO_2)_2^- + CCl_3Br \rightarrow$ no reaction		< 0·001	*a*
$(OC)_4ReBr^- + CCl_3Br \rightarrow (OC)_4ReBr_2^- + CCl_3$	**51**	0·32	*g*
$\rightarrow (OC)_3ReBr_2^- + CO + CCl_3$	**36**		
$\rightarrow (OC)_4ReBrCl^- + CCl_2Br$	**13**		
$(OC)_4MnBr^- + CCl_3Br \rightarrow (OC)_4MnBr_2^- + CCl_3$		0·24	*g*
$(OC)_3MnBr^- + CCl_3Br \rightarrow (OC)_3MnBr_2^- + CCl_3$		0·32	*g*
$(OC)_4Fe^- + CCl_3Br \rightarrow (OC)_4FeBr^- + CCl_3$		0·26	*g*
$CO_3^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*i*
$CO_4^- + CCl_3F \rightarrow$ no reaction		< 0·001	*j*
$C_{10}H_8^- + CCl_3F \rightarrow Cl^- + C_{10}H_8 + CCl_2F$		0·023	*a*
$C_6H_5NO_2^- + CCl_3F \rightarrow$ no reaction		< 0·001	*a*
$O^- + CCl_3F \rightarrow Cl^- +$ neutral(s)	**35**	1·8	*d*
$\rightarrow ClO^- + CCl_2F$	**30**		
$\rightarrow Cl_2^- + COClF$	**5**		
$\rightarrow CCl_2F^- + ClO$	**30**		
$O_2^- + CCl_3F \rightarrow Cl^- +$ neutral(s)	**major; 90**	0·76; 1·3	*i*, *d*
$\rightarrow CCl_3F^- + O_2$	**minor; 10**		
$O_2^- \cdot H_2O + CCl_3F \rightarrow$ no reaction		< 0·01	*i*
$O_2^- \cdot (H_2O)_2 + CCl_3F \rightarrow$ no reaction		< 0·0001	*i*
$O_2^- \cdot (H_2O)_3 + CCl_3F \rightarrow$ no reaction		< 0·0001	*i*
$O_3^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*i*
$NO_2^- + CCl_3F \rightarrow$ no reaction		< 0·00005 (at 370 K)	*i*
$NO_3^- + CCl_3F \rightarrow$ no reaction		< 0·00002 (at 370 K)	*i*
$(OC)_4ReBr^- + CCl_3F \rightarrow (OC)_4ReBrCl^- + CCl_2F$		0·039	*g*
$(OC)_4ReCl^- + CCl_3F \rightarrow (OC)_4ReCl_2^- + CCl_2F$		0·047	*g*
$(OC)_4MnBr^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*g*

Table 3. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$(OC)_3MnBr^- + CCl_3F \rightarrow (OC)_3MnBrCl^- + CCl_2F$		0·00011	*g*
$(OC)_4MnCl^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3MnCl^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_5Cr^- + CCl_3F \rightarrow (OC)_5CrCl^- + CCl_2F$		0·11	*g*
$(OC)_4Fe^- + CCl_3F \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3Ni^- + CCl_3F \rightarrow (OC)_3NiCl^- + CCl_2F$	**13**	0·44	*g*
$\rightarrow (OC)_2NiCl^- + CO + CCl_2F$	**87**		
$C_{10}H_8^- + CBr_2F_2 \rightarrow Br^- + C_{10}H_8 + CB_rF_2$		0·82	*a*
$C_6H_5NO_2^- + CBr_2F_2 \rightarrow Br^- + C_6H_5NO_2 + CBrF_2$		0·40	*a*
o-$FC_6H_4NO_2^- + CBr_2F_2 \rightarrow Br^- +$ *o*-$FC_6H_4NO_2 + CBrF_2$		0·32	*a*
m-$FC_6H_4NO_2^- + CBr_2F_2 \rightarrow Br^- +$ *m*-$FC_6H_4NO_2 + CBrF_2$		0·047	*a*
m-$CF_3C_6H_4NO_2^- + CBr_2F_2 \rightarrow$ no reaction		< 0·001	*a*
$CO_3^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0002	*i*
$CO_4^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0004	*j*
$C_{10}H_8^- + CCl_2F_2 \rightarrow$ no reaction		< 0·001	*a*
$O^- + CCl_2F_2 \rightarrow Cl^- +$ neutral(s)	**50**	1·5	*d*
$\rightarrow ClO^- + CClF_2$	**15**		
$\rightarrow Cl_2^- + CF_2O$	**10**		
$\rightarrow Cl_2O^- + CF_2$	**25**		
$O_2^- + CCl_2F_2 \rightarrow Cl^- +$ neutral(s)	**major; 50**	0·21; 0·67	*i, g*
$\rightarrow CCl_2F_2^- + O_2$	**minor; 50**		
$O_2^- \cdot H_2O + CCl_2F_2 \rightarrow$ no reaction		< 0·01	*i*
$O_2^- \cdot (H_2O)_2 + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*i*
$O_2^- \cdot (H_2O)_3 + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*i*
$O_3^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0003	*i*
$NO_2^- + CCl_2F_2 \rightarrow$ no reaction		< 0·00004 (at 370 K)	*i*
$NO_3^- + CCl_2F_2 \rightarrow$ no reaction		< 0·00004 (at 370 K)	*i*
$(OC)_4ReBr^- + CCl_2F_2 \rightarrow (OC)_4ReBrCl^- + CClF_2$		0·00055	*g*
$(OC)_4ReCl^- + CCl_2F_2 \rightarrow (OC)_4ReCl_2^- + CClF_2$		0·00014	*g*
$(OC)_4MnBr^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3MnBr^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_4MnCl^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3MnCl^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_5Cr^- + CCl_2F_2 \rightarrow (OC)_5CrCl^- + CClF_2$		0·0052	*g*
$(OC)_4Fe^- + CCl_2F_2 \rightarrow$ no reaction		< 0·0001	*g*

Table 3. (*Cont.*)

Reaction	Branching percentage	Total rate constant (10^{-9} cm^3 s^{-1})	Ref(s)
$(OC)_3Ni^- + CCl_2F_2 \rightarrow (OC)_3NiCl^- + CClF_2$	**76**	0·18	*g*
$\rightarrow (OC)_2NiCl^- + CO + CClF_2$	**24**		
$O^- + CBrClF_2 \rightarrow$ products		0·72	*c*
$O_2^- + CBrClF_2 \rightarrow$ products		0·52	*c*
$SF_6^- + CBrClF_2 \rightarrow$ no reaction		< 0·001	*f*
$F^- + C_2F_5Br \rightarrow$ products		0·41	*c*
$O^- + C_2F_5Br \rightarrow$ products		0·72	*c*
$O_2^- + C_2F_5Br \rightarrow$ products		0·55	*c*
$SF_6^- + C_2F_5Br \rightarrow$ no reaction		< 0·001	*f*
$SF_6^- + CF_2BrCF_2Br \rightarrow$ no reaction		< 0·001	*f*
$SF_6^- + CF_2BrCFBrCl \rightarrow$ no reaction		< 0·001	*f*
$SF_6^- + CF_2ICF_2Br \rightarrow$ no reaction		< 0·001	*f*
$(OC)_4ReBr^- + CCl_2FCClF_2 \rightarrow (OC)_4ReBrCl^- + C_2Cl_2F_3$		0·041	*g*
$(OC)_4ReCl^- + CCl_2FCClF_2 \rightarrow (OC)_4ReCl_2^- + C_2Cl_2F_3$		0·042	*g*
$(OC)_4MnBr^- + CCl_2FCClF_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3MnBr^- + CCl_2FCClF_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_4MnCl^- + CCl_2FCClF_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_3MnCl^- + CCl_2FCClF_2 \rightarrow$ no reaction		< 0·0001	*g*
$(OC)_5Cr^- + CCl_2FCClF_2 \rightarrow (OC)_5CrCl^- + C_2Cl_2F_3$		0·17	*g*
$(OC)_4Fe^- + CCl_2FCClF_2 \rightarrow$ no reaction		< 0·0001	*g*

[a] Knighton and Grimsrud 1992

[b] Dotan *et al.* 1978

[c] Streit 1982a

[d] Mayhew *et al.* 1993

[e] Rinden *et al.* 1989

[f] Streit 1982b

[g] Jones *et al.* 1989

[h] Van Orden *et al.* 1991a

[i] Fehsenfeld *et al.* 1976

[j] Fehsenfeld *et al.* 1977

These reactions were investigated again using a SIFT (Morris 1992); CF_3Cl was included in the study, and product branching fractions were measured since each reactant ion could be studied separately. The O^- reactions produce F^-, X^- (except in the CF_3I case), XO^-, and XF^-, and the CF_3I reaction gives two additional products, CF_3^- and IOF^-. The O_2^- reactions form X^- for all X and, for CF_3Br and CF_3I, also generate the product of nondissociative electron transfer, CF_3X^-. Actual CF_3X^- production has been reported for these cases and for the reaction of SO^- with CF_3I (Morris *et al.* 1995c, 1996). The direct observation of CF_3X^- lends support to the initial electron transfer mechanism. The X^- produced in these reactions may in fact arise from dissociation of CF_3X^- as opposed to displacement.

Using a SIFT, Mayhew *et al.* (1993) studied the reactions of O^- and O_2^- with the series CCl_nF_{4-n} as well as with partially chlorinated methanes. The results for CF_3Cl reactions are in agreement with those of Morris (1992), as can be seen in table 2; the results for the other reactions are discussed in the next section.

An apparently anomalous result is that of Streit (1982b) on the system $SF_6^- + CF_3I$ which was found to be unreactive. Here NDET would be exothermic, yet no measurable reaction of any type was seen. The Phillips Laboratory group repeated the measurement since the result seemed curious, and only very slow clustering was observed (Morris *et al.* 1996). An ion–molecule equilibria study found that electron transfer processes involving SF_6 are slow, and the authors attributed this to large geometry changes between SF_6 and SF_6^- (Grimsrud *et al.* 1985). If electron transfer is required to initiate the reaction, then perhaps the unfavourable geometry changes involved are responsible for inhibiting reactivity in this case.

One of the more unusual CF_3X reactions is that of FI^- with CF_3I. This reaction is fast and produces $(CF_4I)^-$ which may involve hypervalent bonding by iodine, i.e a structure $(CF_3\text{–}I\text{–}F)^-$. The $(CF_4I)^-$ anion corresponds to both the intermediate complex in the bimolecular I^- 'displacement' minor channel and the third-order association major product formed in the reaction of F^- with CF_3I discussed earlier in this section. The rapidity of the association channel $F^- + CF_3I \rightarrow (CF_4I)^-$ suggests that $(CF_4I)^-$ is quite strongly bound.

3.3. *Other perhaloalkanes*

For the purposes of organizing the data, reactions with fully halogenated alkanes which are neither PFCs (table 1) nor trifluoromethyl halides (table 2) are listed in table 3, under the heading 'other perhaloalkanes'. A large fraction of the data is due to two publications: one is the 17-electron transition metal complex anion study of Jones *et al.* (1989), and the other is an investigation by Knighton and Grimsrud (1992) on reactivity of organic molecular anions. In addition, three other substantial data sets originate from the study by Mayhew *et al.* (1993) mentioned in the previous section, work by Fehsenfeld *et al.* which addressed atmospheric ion chemistry of CCl_2F_2 and CCl_3F (Fehsenfeld *et al.* 1976, 1977) and the investigations of Streit on O^-, O_2^- (Streit 1982a) and SF_6^- (Streit 1982b) reactions.

The first measurement of thermal negative ion kinetics of carbon tetrachloride was the FA study of Dotan *et al.* (1978) on the fast reaction of O^- with CCl_4. These workers were investigating atmospheric ion chemistry and used the $O^- + CCl_4$ reaction as a source of ClO^-. The reaction was studied in a flowing afterglow again several years later by Streit (1982a), who also studied $O_2^- + CCl_4$, but reliable product branching data were not available for the O^- reaction until the SIFT investigation by Mayhew *et al.* (1993), who showed that the major ionic product ClO^- is accompanied by three other anions, Cl^-, Cl_2^- and CCl_3^-. Mayhew *et al.* (1993) also studied $O_2^- + CCl_4$, which forms Cl^- exclusively. The behaviour of the O_2^- reaction with CCl_4 resembles the process of electron attachment to CCl_4, which rapidly forms Cl^- (Smith *et al.* 1984).

Similarly, the reaction of the weakly-bound anion NO^- with CCl_4 is fast and forms Cl^- as the only ionic product, as established by Rinden *et al.* (1989) using a flowing afterglow. These workers noted that high-energy alkali atom beam experiments (Dispert and Lacmann 1978) on CCl_4 had detected the production of the parent molecular anion CCl_4^- whereas the thermal energy results on both the NO^- reaction (Rinden *et al.* 1989) and electron attachment (Smith *et al.* 1984) showed no such product. It is not surprising that the NO^- reaction bears similarity to the attachment of a free electron since the extra electron in NO^- is bound by only 0·026 eV.

Carbon tetrachloride reacts with a variety of 17-electron transition metal complex anions by transfer of a chlorine atom to the reactant anion, with concomitant loss of ligands in some cases (Jones *et al.* 1989). These investigators concluded that the reactions are initiated by electron transfer, as discussed in the previous section. For the 16-electron complex anion $V(CO)_5^-$, Van Orden *et al.* (1991a) concluded that the chlorine atom transfer reaction with CCl_4 proceeds via either direct abstraction or bond insertion but not through initial electron transfer; this too is discussed in the previous section.

Knighton and Grimsrud (1992) used pulsed high-pressure mass spectrometry (PHPMS) to study the reactivity of carbon tetrachloride and seven other halomethanes with a series of organic molecular negative ions, including the parent anions of azulene, nitrobenzene, and substituted nitrobenzenes. The reactions, which yield halide (X^-) as the major ionic product, were found to decrease in rate with increasing reactant anion detachment energy. These workers concluded that the reaction occurs on a double-well potential energy surface by an electron transfer mechanism they term ‘cluster-assisted dissociative electron transfer’ (CADET). According to their CADET model, initial mutual capture of the ion A^- and neutral reactant R–X forms the first complex $[A^- \cdot RX]^*$. Then the complex passes through a transition state in which the R–X bond is being broken while an electron is transferred from A^- to X. The second complex is thus $[A \cdot X^- \cdot R]$ which can dissociate into $X^- \cdot A + R$. According to the model, a rapid equilibrium is set up between $X^- \cdot A$ and $X^- + A$, where the presence of A is due mostly to its use as the A^- precursor gas. The CADET model was found to be consistent with all of the results in the study, which determined that no detectable RX^- products were formed, while ions of the type $X^- \cdot A$ were observed in equilibrium with the major species X^-.

Fehsenfeld and co-workers examined reactions of positive and negative atmospheric ions with the CFCs CCl_2F_2 and CCl_3F and showed that atmospheric ion chemistry is not a sink for these ozone-destroying compounds (Fehsenfeld and Albritton 1977, Fehsenfeld *et al.* 1976, 1977). This is a result of the fact that the abundant negative ions in the atmosphere are formed on a very fast time scale and are extremely stable. The anions examined by these workers are $O_2^- \cdot (H_2O)_{0-3}$, O_3^-, CO_3^-, CO_4^-, NO_2^-, and NO_3^-, and of these species, only O_2^- reacts at measurable rates, as discussed below. The addition of a single H_2O to O_2^- was shown to shut off the reactions. More recently, Mayhew *et al.* (1993) studied the O_2^- and O^- reactions with these CFCs using a SIFT instrument and measured product branching ratios as well as rate constants.

The bare O_2^- anion reacts with CCl_2F_2 at a moderate rate, producing Cl^- as well as the parent molecular anion $CCl_2F_2^-$ via nondissociative charge transfer (NDET). The reaction of O_2^- with CCl_3F, whose rate constant is close to collisional, also features NDET in addition to Cl^- production. The rates of the reactions of O_2^- with CCl_3F, CCl_2F_2, $CClF_3$, CF_3Br and CF_3I correlate with both EA(halomethanes) and the halomethane electron attachment rates (Morris 1992), consistent with the initial charge transfer mechanism. Furthermore, the O_2^- results of Mayhew *et al.* (1993) show that while the CCl_3F reaction forms CCl_3F^- as only a minor (10%) product, the CCl_2F_2 reaction produces a larger fraction (50%) of the NDET product $CCl_2F_2^-$. The NDET process is nearly thermoneutral for CCl_2F_2 but is exothermic for CCl_3F, where more dissociative product Cl^- is found. This too is consistent with the initial electron transfer mechanism, since the excess energy of reaction in the CCl_3F case would be expected to lead to more dissociation. Stated differently, the complex in the CCl_3F reaction has more internal energy to dissipate, leading to a shorter complex lifetime, and therefore less time is available for stabilizing collisions with the buffer to promote the NDET channel. This trend is found in the branching ratio data for the $O_2^- + CF_3Br$ and CF_3I reactions as well, discussed in the previous section. Thus NDET products are expected to be most abundant when the reaction is close to thermoneutral. This picture becomes more complicated when other reactive channels can compete. For example, it is only slightly exothermic for the highly reactive O^- to undergo NDET with CF_3I, but five reactive channels successfully compete, and no NDET is observed (Morris 1992).

In the O^- reactions with CCl_3F, studied by Mayhew *et al.* (1993), NDET would be endothermic, and the four product channels observed are analogous to those seen for $O^- + CCl_4$. These workers found that the $O^- + CCl_2F_2$ reaction forms a new type of product not seen in the remainder of the CCl_nF_{4-n} series, namely OCl_2^-, which they attribute to nucleophilic attack by O^- on Cl.

Jones *et al.* (1989) studied reactions of transition metal complex anions with a set of perhaloalkanes, and the full data set was discussed in the previous section. In general, within the chlorofluoromethanes, the reactivity increases with chlorine substitution. Further increases in reactivity are found upon bromine substitution. The reactivities generally correlate with the thermal electron attachment rates of the perhaloalkanes in the study, suggestive of the initial electron transfer mechanism.

Streit examined the reactions of O^-, O_2^- (Streit 1982a) and SF_6^- (Streit 1982b) with a series of haloalkanes using the flowing afterglow technique. The SF_6^- reactions were studied as part of a project to determine the electron affinity of SF_6 by bracketing with compounds of known EA, and the experiments showed that SF_6^- is unreactive with all of the fully halogenated alkanes studied. An EA(SF_6) = $1{\cdot}0 \pm 0{\cdot}2$ eV was determined in that study, in close agreement with the generally accepted value of $1{\cdot}05 \pm 0{\cdot}1$ eV (Chowdhury and Kebarle 1986). O^- and O_2^- were found to be quite reactive with all of the perhaloalkanes in the study, and the author concluded that enhancing the response of electron capture detectors by adding oxygen should be 'widely applicable'. Streit (1982a) also investigated the reaction of F^- with C_2F_5Br and found it to be moderately rapid, somewhat faster than the analogous $F^- + CF_3Br$ reaction.

4. Summary

The reactivity of negative ions with fully halogenated alkanes generally increases upon substitution by heavier halogens. Perfluorocarbons (PFCs) tend to be unreactive with negative ions, but the highly reactive O^- anion reacts with the larger PFCs through multiple product channels. The trifluoromethyl halide series CF_3X (X = Cl, Br, I) has been well-studied, and the reactions tend to be fast when nondissociative electron transfer to the halocarbon would be exothermic, regardless of the actual resulting product channels. For many of the reactions of CF_3X and other perhaloalkanes, reactivity correlates with both the electron affinities and the electron attachment rates of the perhaloalkanes, though notable exceptions exist. This and other evidence suggests that many of the reactions are initiated by electron transfer to the halocarbon, which may explain why the reactivity of CF_3X generally increases in the order Cl < Br < I for second-order reactions. The same reactivity trend in third-order association reactions is explained by the corresponding trends in CF_3X dipole moment and polarizability.

Note added in proof:—Since the time of the writing of this article we have studied additional reactions of the CF_3X ($X = F$, Cl, Br, I) series (with nine anions not reported here). The results (Morris *et al.* 1996) support the conclusions in this article; one anomalous result is in the reaction of *m*-$CF_3C_6H_4CN^-$ with CF_3Br which is slow despite an apparent 0·24 eV exothermicity for NDET.

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