Reactions of Atmospheric Ions with Selected Hydrofluorocarbons

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Selected atmospheric ions have been studied for reactivity with the hydrofluorocarbons (HFC's) CF_3CH_2F, CF_3CHFCF_3, and $CF_3CHFCHF_2$ and with $CHBrF_2$; the reactant ions chosen for study are O^+, O_2^+, O^-, O_2^-, H_3O^+, $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, NO_3^-, and $NO_3^-\cdot HNO_3$. Rate constants and product branching fractions for these ion–molecule reactions were measured using a selected ion flow tube (SIFT) instrument operated at 300 K. The ions O^+ and O^- reacted at the collisional rates, forming a number of ionic products in most cases. Most of the other reactions studied were found to be inefficient. The ions H_3O^+ and NO_3^- reacted inefficiently by association in all cases. The solvated ions $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, and $NO_3^-\cdot HNO_3$, which are representative of the abundant ionic species in the lower atmosphere, were unreactive with the compounds investigated; we conclude from this that atmospheric ion chemistry is not a significant sink for these HFC's. The observation of proton transfer from CF_3CHFCF_3 and $CF_3CHFCHF_2$ to O^- allows a lower bound to the gas-phase acidities of these HFC's to be assigned: $\Delta H_{acid}(CF_3CHFCF_3)$ and $\Delta H_{acid}(CF_3CHFCHF_2) < 1599$ kJ mol^{-1}.

Introduction

Halogenated compounds which contain one or more hydrogen atoms represent a leading class of chemicals being pursued as replacements for halocarbon refrigerants, fire suppressants, etc. The inclusion of hydrogen enables the molecule to react with hydroxyl radicals in the troposphere and lower stratosphere, thus limiting the atmospheric lifetime to years rather than decades or centuries. The lifetimes of these chemicals in the atmosphere are governed essentially by the timescale for removal by hydroxyl radical.[1–3] Most of these candidate compounds also contain no chlorine or bromine, the culprits in stratospheric ozone destruction by halocarbons. Compounds containing only hydrogen, fluorine, and carbon are termed hydrofluorocarbons (HFC's).

Ion–molecule reactions occurring in the mesosphere and lower thermosphere can have an effect on the atmospheric lifetimes of extremely long-lived chemicals such as the perfluorocarbons (PFC's),[4] which do not react with hydroxyl radicals and thus survive degradation in the lower atmosphere. For ion–molecule reactions to have an impact on HFC lifetimes would require rapid ion chemistry in the lower atmosphere which could compete with the hydroxyl reaction and other loss processes. This would require the major ions at low altitude, e.g., $NO_3^-\cdot(HNO_3)_n$ and $H_3O^+\cdot(H_2O)_n$, to be highly reactive with the HFC's. We have examined reactions of a few selected HFC's with the major atmospheric ion species. We have included in the study not only ions abundant at low altitude but those major ions from the high altitude regimes as well, both for completeness and because of fundamental interest in the chemistry. The ion chemistry of the HFC's is essentially unexplored.[5]

In this article we report rate constants and product branching fractions for reactions of three HFC's: CF_3CH_2F, CF_3CHFCF_3, and $CF_3CHFCHF_2$. The compound $CHBrF_2$ was also included in the study because of initial interest in this compound as a replacement for the fire suppressant CF_3Br. The ions chosen for study are O^+, O_2^+, O^-, O_2^-, H_3O^+, $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, NO_3^-, and $NO_3^-\cdot HNO_3$, all of which are found in the atmosphere. The oxygen ions are primary atmospheric ions and are found in the upper atmosphere. The water-derived and nitric acid-derived ions are important ions in the later stages of atmospheric ion evolution and are abundant in the lower atmosphere.[6] The experiments were performed at 300 K using a selected ion flow tube (SIFT) instrument. The technique generally enables measurements to be made under thermal conditions and in the absence of interfering ions. This is the first report of measurements of these reactions.

Experimental Section

The measurements were conducted using the SIFT instrument at Phillips Laboratory. This apparatus has been described previously;[7] the technique and generic instrumentation have been extensively reviewed.[8] Therefore, we report here only those details which are relevant to this particular study.

The ions were formed in a remote electron impact ion source from suitable precursors as follows: O^+, O_2^+, and O_2^- were produced from O_2; O^- from N_2O; H_3O^+, $H_3O^+\cdot H_2O$, and $H_3O^+\cdot(H_2O)_2$ from H_2O; NO_3^- and $NO_3^-\cdot HNO_3$ from NO_2 which contained a small impurity of HNO_3. The ion species 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 transported along the flow tube by a fast flow (~10^4 cm s^{-1}) of He buffer gas. Neutral reactant gas was added to the flow tube through one of two ring-shaped inlets. Two inlets at different axial positions are used for each rate constant measurement in order to determine the end correction which accounts for the finite mixing distance of the reactants in the flow tube;[7] this end correction is typically on the order of 10 cm. The reactant and product ions were sampled through a 0.2 mm orifice in a flat

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TABLE 1: Product Branching Fractions and Total Rate Constants for Reactions of O^+ Ions with Selected Hydrohalocarbons Measured at 300 K[a]

reaction	branching fraction	total rate constant (10^{-9} cm^3 s^{-1})
$O^+ + CHBrF_2 \rightarrow CHF^+ + BrOF$	0.44	2.9
$\rightarrow CHF_2^+ + BrO$	0.56	
$O^+ + CF_3CH_2F \rightarrow CH_2F^+ + CF_2O + F$	0.37	3.7
$\rightarrow CF_3^+ + CH_2O + F$	0.56	
$\rightarrow C_2H_2F_3^+ + OF$	0.07	
$O^+ + CF_3CHFCF_3 \rightarrow CF_3^+ + CF_2O + CHF_2$	0.38	2.6
$\rightarrow C_2HF_3^+ + CF_2O + F_2$	0.62	
$O^+ + CF_3CHFCHF_2 \rightarrow CHF_2^+ + CF_2O + CHF_2$	0.44	2.6
$\rightarrow C_2HF_3^+ + CHF_3 + O$	0.45	
$\rightarrow C_3H_2F_5^+ + OF$	0.11	

[a] Neutral products are inferred from mass balance and (limited) thermochemistry and in many cases are quite speculative (different neutral products are possible).

plate mounted on a blunt sampling cone. The ion current reaching the flat plate was recorded in the negative ion experiments in order to check for possible electron detachment reactions. 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, typically 2–3 ms, was measured directly by time-of-flight techniques.[7] Buffer and reactant gas flow rates were maintained and measured by flow controllers, and the flow tube pressure was measured with a capacitance manometer (10 Torr range; 1% accuracy). Product branching fractions were determined by recording and plotting the product ion count rates as a function of reactant neutral flow rate. The effects of secondary reactions are accounted for by extrapolating the branching fractions to zero reactant neutral flow rate. The estimated accuracy of the reported rate constants is 30% with a precision of 15%.

Ion masses were calibrated by injecting ions of known mass into the flow tube. For example, the isotopes of Xe^+ were used as calibrants for identifying $C_3H_2F_5^+$ at $m/e = 133$. This type of calibration is often not necessary in SIFT experiments,[8] but in this case the presence of hydrogen in the reactants required careful mass calibration. For ion identification tests, the downstream mass spectrometer was operated under conditions of unit mass resolution. The product branching measurements were performed under conditions of low resolution in order to minimize the effects of mass discrimination. No attempt was made to correct for mass discrimination; the accuracy of the product branching fractions is estimated to be 30%, and the branching fractions are precise to within 4 percentage points.

For the negative ion reactions, reactive electron detachment is a possible reaction pathway. This was checked in each anionic reaction by recording the current to the sampling plate as a function of added reactant neutral flow rate. If detachment occurs, a decrease is seen in the plate current because free electrons diffuse and are lost to the flow tube walls very rapidly. The fractional contribution by detachment may be quantified by comparing the initial plate current (no reactant gas added) with the plate current at completion of reaction (complete conversion of reactant ion to product ions and free electrons).[9]

While the SIFT technique usually ensures that the reactant ions are thermalized, several of the reactant ion species in the present study are notable exceptions to that rule. Under certain conditions, O_2^+ and O_2^- are known to remain somewhat vibrationally excited in the reaction region of the flow tube,[10-12] and a few percent of the O^+ may remain electronically excited.[13,14] Quenching of vibrationally excited ions has been investigated by a number of research groups,[11] and effective quenchers for O_2^+ and O_2^- have been documented.[10-12] We have performed separate experiments in which an unreactive quenching gas is added upstream of the reaction region in order to thermalize the diatomic reactant ions. Branching fractions and rate constants were measured with and without quencher added for all reactions of O_2^+ and O_2^-. For O_2^+, CO_2 was used as the quencher; for O_2^-, C_2F_6 was used. In the case of electronically excited O^+, quenching was not feasible, so we used CO as a monitor gas to follow the relative population of excited O^+ as the ion source conditions were optimized. Excited O^+ reacts rapidly with CO by charge transfer, but ground state O^+ does not.[15] Adjusting the ion source conditions allowed the percentage of excited O^+ to be reduced to 0.4% of the total O^+ signal. Since the rates of all of the present reactions with O^+ were found to be collisional,[16,17] there can be no significant error associated with this minor extent of O^+ excitation.

The reactant neutral gases were obtained commercially and were used without further purification. We requested lot purity analyses from the suppliers and received them for all compounds except CF_3CH_2F. The suppliers and purities are as follows: PCR, Inc., $CHBrF_2$ (98.8%, analyzed), CF_3CHFCF_3 (99.8%, analyzed), $CF_3CHFCHF_2$ (99.5%, analyzed); Aldrich Chemical Co., CF_3CH_2F (>99%). The He buffer gas was high purity grade (99.997%).

Results and Discussion

The results are presented in Tables 1–6. The results in the tables refer to thermalized reactant ions. For the reactions of O_2^+ with CF_3CH_2F and $CF_3CHFCHF_2$, differing results were obtained with and without a quencher gas added (see Experimental Section). These results are discussed in the text, but only those results corresponding to ground state reactants are listed in the tables. Also omitted from the tables are those very minor "product" ion species which, while detectable, were of such low abundance that they could have originated solely from impurities in the reactant neutral gas. The product ion abundance for which this would be the case can be estimated by calculating the efficiency of the particular reaction channel in question by multiplying its branching fraction by the calculated collisional rate constant.[16,17] If the channel efficiency is comparable to or less than the fractional impurity level, then that reaction channel may arise from an impurity.

The SIFT technique does not enable the detection of product neutral species. Neutral products may often be inferred unambiguously by mass balance and known reaction thermochemistry, but for many of the reactions presented here the thermochemistry is not known. Also, in many of the present reactions, several different combinations of neutral products are possible and are even chemically reasonable. Therefore, the neutral products listed in the tables are often quite speculative,

TABLE 2: Product Branching Fractions and Total Rate Constants for Reactions of O_2^+ Ions with Selected Hydrohalocarbons Measured at 300 K[g]

reaction	branching fraction	total rate constant (10^{-9} cm^3 s^{-1})
$O_2^+ + CHBrF_2 \rightarrow CHF_2^+ + Br + O_2$	0.85	2.0
$\rightarrow CHBrF_2^+ + O_2$	0.15	
$O_2^+ + CF_3CH_2F \rightarrow O_2^+{\cdot}CF_3CH_2F$[a]		≤ 0.0052[a,b]
$O_2^+ + CF_3CHFCF_3 \rightarrow$ products[c]		≤ 0.017[c]
$O_2^+ + CF_3CHFCHF_2 \rightarrow C_2HF_3^{+}$[d] $+ CHF_3 + O_2$	0.14	0.52
$\rightarrow C_3H_2F_5^{+}$[e] $+ F + O_2$	0.09	
$\rightarrow C_3HF_6^{+}$[f] $+ HO_2$	0.77	

[a] Reaction efficiency is below HFC impurity level (see text). [b] Value refers to second-order rate constant measured at 0.43 Torr. [c] $C_2F_3^+$ "product" detected but is likely to be due to an impurity in the HFC sample (see text). [d] Assumed product ion, but $m/e = 82$ also corresponds to the ion $CF_2O_2^+$. [e] Assumed product ion, but $m/e = 133$ also corresponds to the ion $C_2HF_4O_2^+$. [f] Assumed product ion, but $m/e = 151$ also corresponds to the ion $C_2F_5O_2^+$. [g] Neutral products are inferred from mass balance and (limited) thermochemistry and in many cases are quite speculative (different neutral products are possible).

TABLE 3: Product Branching Fractions and Total Rate Constants for Reactions of O^- Ions with Selected Hydrohalocarbons Measured at 300 K[a]

reaction	branching fraction	total rate constant (10^{-9} cm^3 s^{-1})
$O^- + CHBrF_2 \rightarrow F^- + HCOF + Br$	0.16	3.0
$\rightarrow Br^- + HF + FCO$	0.71	
$\rightarrow BrO^- + CHF_2$	0.11	
$\rightarrow Br^-{\cdot}HF + FCO$	0.02	
$O^- + CF_3CH_2F \rightarrow CF_3CF^- + H_2O$		4.3
$O^- + CF_3CHFCF_3 \rightarrow F^- + C_3HF_6O$	<0.02	2.6
$\rightarrow C_3HF_6O^- + F$	<0.03	
$\rightarrow C_3F_7^- + OH$	>0.95	
$O^- + CF_3CHFCHF_2 \rightarrow F^-{\cdot}OH + C_3HF_5$	0.06	2.5
$\rightarrow F^-{\cdot}HF + C_3F_4OH$	0.06	
$\rightarrow CF_3CF^- + CHF_2OH$	0.15	
$\rightarrow CF_3CFCO^- + 2HF$	0.16	
$\rightarrow C_3F_5^- + HF + OH$	0.08	
$\rightarrow C_3F_5O^- + HF + H$	0.03	
$\rightarrow C_3HF_6^- + OH$	0.27	
$\rightarrow e^- + C_3F_6 + H_2O$	0.18	

[a] Neutral products are inferred from mass balance and (limited) thermochemistry and in many cases are quite speculative (different neutral products are possible).

TABLE 4: Product Branching Fractions and Total Rate Constants for Reactions of O_2^- Ions with Selected Hydrohalocarbons Measured at 300 K[c]

reaction	branching fraction	total rate constant (10^{-9} cm^3 s^{-1})
$O_2^- + CHBrF_2 \rightarrow F^- + HF + Br + CO_2$	<0.02	1.9
$\rightarrow F^-{\cdot}HF + Br + CO_2$	0.06	
$\rightarrow Br^- + CF_2O + OH$	0.21	
$\rightarrow Br^-{\cdot}HO_2 + CF_2$	0.71	
$O_2^- + CF_3CH_2F \rightarrow O_2^-{\cdot}CF_3CH_2F$	1.0	0.13[a]
$O_2^- + CF_3CHFCF_3 \rightarrow F^- + HF + C_2F_5 + CO_2$	0.08	1.5[b]
$\rightarrow F^-{\cdot}HF + C_2F_5 + CO_2$	0.39	
$\rightarrow O_2^-{\cdot}HF + C_3F_6$	0.37	
$\rightarrow O_2^-{\cdot}CF_3CHFCF_3$	0.16	
$O_2^- + CF_3CHFCHF_2 \rightarrow O_2^-{\cdot}HF + C_3HF_5$	0.49	1.0[b]
$\rightarrow O_2^-{\cdot}CF_3CHFCHF_2$	0.51	

[a] Value refers to second-order rate constant measured at 0.43 Torr; additional values at other pressures are as follows: $k = 9.3(-11)$ at 0.29 Torr, $1.1(-10)$ at 0.35 Torr, $1.3(-10)$ at 0.53 Torr. [b] Reaction includes an association product; value refers to second-order rate constant measured at 0.43 Torr. [c] Neutral products are inferred from mass balance and (limited) thermochemistry and in many cases are quite speculative (different neutral products are possible).

based on an educated guess, and should be viewed accordingly. For this reason, discussions of reaction mechanisms are particularly speculative when the neutral product is ambiguous.

Unless otherwise noted, the reported energetics are based on ion thermochemistry found in Lias et al.[18] and neutral thermochemistry found in Slayden et al.[19] When published thermochemistry is not available, we report estimated values based on thermochemistry of analogous systems, including a description of the estimation procedures used. The estimated heats of formation used in this work are listed in Table 7.

A. Reactions of O^+. Table 1 lists the results for the O^+ ion, which reacts at the collisional rate with all four neutrals studied. In all cases the oxygen is incorporated into the various neutral products and never into the ionic products. In the reaction with $CHBrF_2$,

$$O^+ + CHBrF_2 \rightarrow CHF^+ + BrOF \qquad \Delta H = \text{? (see text)} \quad (1a)$$

$$\rightarrow CHF_2^+ + BrO \qquad \Delta H = -401 \text{ kJ mol}^{-1} \quad (1b)$$

two product channels arise, both of which involve breaking the C−Br bond, the weakest bond in $CHBrF_2$. Channel 1a violates spin conservation, as do many of the O^+ reactions reported here. However, several of the O^+ reactions have sufficiently high

TABLE 5: Rate Constants and Products for Reactions of H_3O^+, $H_3O^+{\cdot}H_2O$, and $H_3O^+{\cdot}(H_2O)_2$ Ions with Selected Hydrohalocarbons Measured at 300 K and 0.41 Torr

reaction	total rate constant (10^{-10} cm^3 s^{-1})
$H_3O^+ + CHBrF_2 \rightarrow H_3O^+{\cdot}CHBrF_2$[a]	0.15[a]
$H_3O^+{\cdot}H_2O + CHBrF_2 \rightarrow$ no reaction	<0.1
$H_3O^+{\cdot}(H_2O)_2 + CHBrF_2 \rightarrow$ no reaction	<0.1
$H_3O^+ + CF_3CH_2F \rightarrow H_3O^+{\cdot}CF_3CH_2F$	0.94
$H_3O^+{\cdot}H_2O + CF_3CH_2F \rightarrow$ no reaction	<0.1
$H_3O^+{\cdot}(H_2O)_2 + CF_3CH_2F \rightarrow$ no reaction	<0.1
$H_3O^+ + CF_3CHFCF_3 \rightarrow H_3O^+{\cdot}CF_3CHFCF_3$	0.11
$H_3O^+{\cdot}H_2O + CF_3CHFCF_3 \rightarrow$ no reaction	<0.1
$H_3O^+{\cdot}(H_2O)_2 + CF_3CHFCF_3 \rightarrow$ no reaction	<0.1
$H_3O^+ + CF_3CHFCHF_2 \rightarrow H_3O^+{\cdot}CF_3CHFCHF_2$	2.7
$H_3O^+{\cdot}H_2O + CF_3CHFCHF_2 \rightarrow$ no reaction	<0.1
$H_3O^+{\cdot}(H_2O)_2 + CF_3CHFCHF_2 \rightarrow$ no reaction	<0.1

[a] Reaction efficiency is below $CHBrF_2$ sample impurity level (see text).

TABLE 6: Rate Constants and Products for Reactions of NO_3^- and $NO_3^-{\cdot}HNO_3$ Ions with Selected Hydrohalocarbons Measured at 300 K and 0.41 Torr

reaction	total rate constant (10^{-10} cm^3 s^{-1})
$NO_3^- + CHBrF_2 \rightarrow NO_3^-{\cdot}CHBrF_2$[a]	<0.1[a]
$NO_3^-{\cdot}HNO_3 + CHBrF_2 \rightarrow$ no reaction	<0.1
$NO_3^- + CF_3CH_2F \rightarrow NO_3^-{\cdot}CF_3CH_2F$[a]	<0.1[a]
$NO_3^-{\cdot}HNO_3 + CF_3CH_2F \rightarrow$ no reaction	<0.1
$NO_3^- + CF_3CHFCF_3 \rightarrow NO_3^-{\cdot}CF_3CHFCF_3$	1.5
$NO_3^-{\cdot}HNO_3 + CF_3CHFCF_3 \rightarrow$ no reaction	<0.1
$NO_3^- + CF_3CHFCHF_2 \rightarrow NO_3^-{\cdot}CF_3CHFCHF_2$	2.3
$NO_3^-{\cdot}HNO_3 + CF_3CHFCHF_2 \rightarrow$ no reaction	<0.1

[a] Reaction efficiency below reactant neutral impurity level (see text).

TABLE 7: Estimated Heats of Formation Used in the Present Work (in kJ mol^{-1})

species	$\Delta_f H$ (kJ mol^{-1})	species	$\Delta_f H$ (kJ mol^{-1})
CF_3CF^-	<587	C_3F_4OH	−705
$CF_3CHFCHF^+$	−136	C_3F_5	−730
$CF_3CH_2CF_2^+$	−186	CF_3CFCHF	−959
$Br^-{\cdot}HO_2$	−264	n-C_3F_6OH	−1312
$C_3HF_6^+$	−291	$CF_3CHFCHF_2$	−1342
$F^-{\cdot}OH$	−307	CF_3CHFCF_3	−1573
CHF_2OH	−670		

exothermicities so as to allow bond cleavage in the neutral product and thus would not violate spin conservation. That (1a) violates spin conservation may be ameliorated by the strong spin−orbit coupling due to the heavy element Br.

The heat of formation of $CHBrF_2$ is −425 kJ mol^{-1}.[20] Assuming that BrOF is the structure of the neutral formed in (1a), a simple estimate of its heat of formation, from the assumption of thermoneutrality for the reaction HOBr + HOF → BrOF + H_2O, yields $\Delta_f H$(BrOF) = 85 kJ mol^{-1}.[21] This would lead, however, to an endothermicity of 68 kJ mol^{-1} for reaction 1a. On the basis of our observation of CHF^+ product, we conclude that the heat of formation of BrOF must be considerably lower than the above estimate of 85 kJ mol^{-1}; it must be less than or approximately equal to 17 kJ mol^{-1} for (1a) to be thermoneutral or exothermic. The above discussion would not apply if the structure of this species were actually OBrF.

The formation of the triatomic CHF^+ product ion (channel 1a) contrasts with our SIFT results for the reaction of O^+ with CF_4, in which only CF_3^+ is produced.[4] Channel 1b also violates spin conservation as written, but it is sufficiently exothermic that production of Br + O, instead of BrO, is energetically allowed and would not violate spin conservation.

The reaction with CF_3CH_2F features three product pathways.

$$O^+ + CF_3CH_2F \rightarrow CH_2F^+ + COF_2 + F \qquad \Delta H = -395\ \mathrm{kJ\ mol^{-1}} \quad (2a)$$

$$\rightarrow CF_3^+ + CH_2O + F \qquad \Delta H = -335\ \mathrm{kJ\ mol^{-1}} \quad (2b)$$

$$\rightarrow C_2H_2F_3^+ + OF \qquad \Delta H \le -52\ \mathrm{kJ\ mol^{-1}} \quad (2c)$$

For the heat of formation of CF_3^+, we use the value derived by Fisher and Armentrout,[22] 361 kJ mol^{-1}. The major product channels, 2a and 2b, both correspond to breaking the C−C bond and incorporating oxygen into the uncharged fragment, and both channels violate spin conservation. Channel 2c is simple fluoride transfer, a process commonly seen in reactions of cations with fluorinated molecules. The thermochemistry of this channel is ambiguous because the structure of the resulting cation $C_2H_2F_3^+$ is not defined. If the $C_2H_2F_3^+$ product is the least stable isomer, $CF_3CH_2^+$ (with heat of formation of 506 kJ mol^{-1}), then this reaction is exothermic by 52 kJ mol^{-1}. It is not obvious whether $CH_2FCF_2^+$ or CHF_2CHF^+ is more stable. However, whichever isomer is formed by protonation of CF_2-CHF, its heat of formation is 332 kJ mol^{-1}, so channel 2c would be exothermic by 226 kJ mol^{-1} in this case.

The chemistry of reaction 2 is essentially the same as that found for the analogous perfluorocarbon C_2F_6. In the reaction of O^+ with C_2F_6, the major product is CF_3^+ with possible minor amounts (<1%) of $C_2F_5^+$.[4]

The chemistry of O^+ with CF_3CHFCF_3 (reaction 3) contrasts with that of $CF_3CHFCHF_2$ (reaction 4).

$$O^+ + CF_3CHFCF_3 \rightarrow CF_3^+ + COF_2 + CHF_2 \qquad \Delta H = -506\ \mathrm{kJ\ mol^{-1}} \quad (3a)$$

$$\rightarrow C_2HF_3^+ + COF_2 + F_2 \qquad \Delta H = -143\ \mathrm{kJ\ mol^{-1}} \quad (3b)$$

$$O^+ + CF_3CHFCHF_2 \rightarrow CHF_2^+ + COF_2 + CHF_2 \qquad \Delta H = -487\ \mathrm{kJ\ mol^{-1}} \quad (4a)$$

$$\rightarrow C_2HF_3^+ + CHF_3 + O \qquad \Delta H = -180\ \mathrm{kJ\ mol^{-1}} \quad (4b)$$

$$\rightarrow C_3H_2F_5^+ + OF \qquad \Delta H \le -248\ \mathrm{kJ\ mol^{-1}} \quad (4c)$$

Reaction 3 proceeds by two channels, both of which involve breaking the C−C bond while forming a C−O bond in the neutral product. Reaction 4 includes the two analogous pathways as well as an additional fluoride transfer channel. It should be noted that while CF_3^+ is produced in reaction 3, it is not formed in reaction 4 despite the presence of a terminal CF_3 group. The ionization potentials of CF_3 and CHF_2 are very similar, and the CF_3−R bond strengths in CF_3CHFCF_3 and CF_3-$CHFCHF_2$ are also expected to be similar. Thus, the lack of any detectable CF_3^+ product in reaction 4 is surprising. The absence of fluoride transfer in reaction 3, while observed in reaction 4, is likewise unexpected.

There are no experimental values for the heats of formation of CF_3CHFCF_3 and $CF_3CHFCHF_2$. For CF_3CHFCF_3, we estimate a value by interpolating differences in heats of formation of similar compounds when F is substituted for CF_3; the difference in heat of formation for $CF_3CF_2CF_3$ vs CF_3CF_3 is 440 kJ mol^{-1} and that for $CF_3CH_2CF_3$ vs CF_3CH_2F is 510 kJ mol^{-1}, with an average CF_3/F difference of 475 kJ mol^{-1} for these two cases. Then, using the known heat of formation for CF_3CHF_2 of -1105 kJ mol^{-1}, substitution of CF_3 for F implies a heat of formation for CF_3CFHCF_3 of -1580 kJ mol^{-1}. Alternatively, we may derive it by interpolating CF_3/H differences using $CF_3CF_2CF_3$ vs CF_3CHF_2 (679 kJ mol^{-1}) and $CF_3CH_2CF_3$ vs CF_3CH_3 (660 kJ mol^{-1}), which yields an average CF_3/H difference of 670 kJ mol^{-1}. Imposing this difference on the substitution of CF_3 for H in CF_3CH_2F whose heat of formation is known to be -896 kJ mol^{-1}, we derive a value of -1566 kJ mol^{-1} for the heat of formation of CF_3CHFCF_3. Finally, we take the average of the two values derived by the two methods to arrive at a best estimate of -1573 ± 40 kJ mol^{-1}.

For $CF_3CHFCHF_2$, we use the heat of formation for CF_3CHFCF_3 derived above and data for other fluorinated species under the assumption of thermoneutrality for the reaction $CF_3CHFCF_3 + RCHF_2 \rightarrow CF_3CHFCHF_2 + RCF_3$ for R = CF_3, CH_2F, and CH_3. We obtain, respectively, -1334, -1368, and -1324 kJ mol^{-1} for the heat of formation of $CF_3CHFCHF_2$, with an average "best" estimate of -1342 ± 30 kJ mol^{-1}.

Reaction channel 4c appears to result from fluoride transfer; in this case the product ion would have the structure $CF_3CHFCHF^+$. The thermochemistry for this ion is formally derived from the proton affinity of CF_3CFCHF, but neither this proton affinity nor the heat of formation of CF_3CFCHF are known. The heat of formation of CF_3CFCHF is consistently estimated as -959 kJ mol^{-1} by assuming thermoneutrality for the following H/F exchange reactions: CF_3CFCF_2[23] + CHFCHF $\rightarrow$ $CF_3CFCHF + CF_2CHF$ and CF_3CHCH_2 + CHFCHF $\rightarrow$ $CF_3CFCHF + CH_2CH_2$. The differences between proton affinities of RF and RCF_3 are generally small.[24] From the experimentally determined proton affinity of CF_2CHF (707 kJ mol^{-1}) and $\Delta_fH(H^+)$ and the estimated $\Delta_fH(CF_3CFCHF)$, we derive $\Delta_fH(CF_3CHFCHF^+) = -136$ kJ mol^{-1}. There are also the isomers $CF_3CH^+CHF_2$ and $CF_3CH_2CF_2^+$, similarly derived by protonating CF_3CHCF_2; a value of -186 kJ mol^{-1} is estimated for the heat of formation of both of these isomers, leading to a minimum exothermicity of 248 kJ mol^{-1} for reaction 4c.

B. Reactions of O_2^+. Table 2 lists the results for the O_2^+ ion. The reactivity of O_2^+ with the four neutrals varies considerably.

For $CHBrF_2$, the reaction proceeds at the collisional rate by dissociative and nondissociative charge transfer.

$$O_2^+ + CHBrF_2 \rightarrow CHF_2^+ + Br + O_2 \qquad \Delta H = -17 \text{ kJ mol}^{-1} \quad (5a)$$

$$\rightarrow CHBrF_2^+ + O_2 \qquad \Delta H \sim -115 \text{ kJ mol}^{-1} \quad (5b)$$

The reaction may occur by initial charge transfer followed by either dissociation or stabilization, leading to channels 5a and 5b, respectively. If so, then this reaction would be likely to display interesting dependencies on pressure, temperature, and energy as these conditions probably have a strong influence on the product branching ratio. The 115 kJ mol^{-1} exothermicity for charge transfer (reaction 5b) is estimated by assuming a value of 10.9 eV for the ionization potential (IP) of $CHBrF_2$ based on IP's of similar molecules. The analogous PFC case, $O_2^+ + CF_4$, is unreactive at thermal energy,[4] and here, charge transfer would be endothermic. The chemistry of reaction 5 differs from that of O_2^+ with $CHClF_2$, which is slower than collisional and produces CF_2Cl^+ (74%) and CHF_2^+ (26%).[25] The nondissociative charge transfer reported here for $CHBrF_2$ was not observed in the $CHClF_2$ study[25] in spite of the fact that the C−Cl bond is stronger than the C−Br bond. If the reported CF_2Cl^+ product were in fact $CHClF_2^+$ (1 amu difference in mass), then those results would be consistent with the present data.

The reaction of O_2^+ with CF_3CH_2F proceeds exclusively by slow association.

$$O_2^+ + CF_3CH_2F \rightarrow O_2^+{\cdot}CF_3CH_2F \qquad \Delta H = ? \quad (6)$$

The bond strength for this ion−molecule cluster is not known. The corresponding PFC system ($O_2^+ + C_2F_6$) showed no association within experimental uncertainty,[4] which is not surprising since C_2F_6 has no dipole moment.

The results for reaction 6 were found to depend on whether CO_2 quenching gas was added to the reaction region (to relax vibrationally excited O_2^+; see Experimental Section). Without CO_2 added, curvature was seen in the normally linear pseudo-first-order kinetics plot of logarithm of O_2^+ signal vs added CF_3CH_2F flow rate, and an additional ionic product $C_2H_2F_3^+$ was detected. With sufficient CO_2 added to quench $O_2^+(v > 0)$ into the $v = 0$ level, based on the known rate constant for this process, both the curvature and the $C_2H_2F_3^+$ product were absent. These observations indicate that vibrationally excited O_2^+ was present and reacts faster with CF_3CH_2F than does $O_2^+(v = 0)$, producing $C_2H_2F_3^+$.

The two fluorinated propanes show quite different reactivity.

$$O_2^+ + CF_3CHFCF_3 \rightarrow \text{products} \qquad \Delta H = ? \quad (7)$$

$$O_2^+ + CF_3CHFCHF_2 \rightarrow C_2HF_3^+ + CHF_3 + O_2 \qquad \Delta H = -31 \text{ kJ mol}^{-1} \quad (8a)$$

$$\rightarrow C_3H_2F_5^+ + F + O_2 \qquad \Delta H \le -68 \text{ kJ mol}^{-1} \quad (8b)$$

$$\rightarrow C_3HF_6^+ + HO_2 \qquad \Delta H = -103 \text{ kJ mol}^{-1} \quad (8c)$$

The reaction of O_2^+ with CF_3CHFCF_3, which is slow, displayed a puzzling result. The only ionic product which was formed with an efficiency greater than the level of impurities in the CF_3CHFCF_3 was $C_2F_3^+$, a product pathway which is highly endothermic (>250 kJ mol^{-1}) for all conceivable combinations of neutral products. The most likely explanation is that the $C_2F_3^+$ product is in fact due to an impurity in the CF_3CHFCF_3 which is in higher concentration than that stated in the sample analysis. The measured rate constant for reaction 7 is reported as an upper limit ($k_7 \le 1.7 \times 10^{-11}$ cm^3 s^{-1}) since no ionic products which could be attributed to the reaction were detected. The results for reaction 7 were independent of whether or not CO_2 quenching gas was added.

The reaction of O_2^+ with $CF_3CHFCHF_2$ (reaction 8) is at least 30 times faster than reaction 7, and it proceeds by three different pathways. The fluoride transfer channel (8b) results in formation of either FO_2 or F + O_2, both of which are exothermic pathways. Reaction 8b is exothermic by at least 68 kJ mol^{-1} depending on which carbocation is produced and whether there are one or two neutral products. The main channel (77%) is hydride transfer (8c); this hydrogen probably comes from the terminal carbon since reaction 7 does not proceed by this channel. The heat of formation for the product ion $C_3HF_6^+$ (channel 8c) is estimated at −291 kJ mol^{-1} from the measured proton affinity of CF_2CHF and by noting that CF_3 substitution for F decreases proton affinities by about 38 kJ mol^{-1}.[24] Formation of separated H + O_2 in reaction 8c would be endothermic by 104 kJ mol^{-1}.

As was found for reaction 6, reaction 8 is sensitive to the vibrational level of the O_2^+. Without CO_2 quenching gas added, the measured rate constant is about 10% larger and the branching fractions are quite different, $C_2HF_3^+$ = 54%, $C_3H_2F_5^+$ = 4%, and $C_3HF_6^+$ = 42%, compared with the reported fractions 14%, 9%, and 77%, respectively, with CO_2 added.

C. Reactions of O$^-$. Table 3 lists the results for the O^- ion. All four of the neutrals react at the collisional rate with O^-, producing a variety of products in most cases.

The reaction of O^- with $CHBrF_2$ occurs mainly by halide displacement, forming Br^- (71%) and F^- (16%).

$$O^- + CHBrF_2 \rightarrow F^- + HCOF + Br \qquad \Delta H = -197\ \text{kJ mol}^{-1} \quad (9a)$$

$$\rightarrow Br^- + HF + FCO \qquad \Delta H = -344\ \text{kJ mol}^{-1} \quad (9b)$$

$$\rightarrow BrO^- + CHF_2 \qquad \Delta H = -21\ \text{kJ mol}^{-1} \quad (9c)$$

$$\rightarrow Br^-{\cdot}HF + FCO \qquad \Delta H = -415\ \text{kJ mol}^{-1} \quad (9d)$$

Additional reaction paths are bromine abstraction forming BrO^- (9c) and formation of the cluster species $Br^-{\cdot}HF$ (9d). The latter may be linked to the Br^- displacement pathway in the following sense. When the initial ion−dipole complex begins to dissociate, it may separate into $Br^-{\cdot}HF$ + FCO in which the $Br^-{\cdot}HF$ internal energy is sufficient to cause a large fraction of this species to dissociate subsequently. However, some fraction of $Br^-{\cdot}HF$ would then remain intact, leading to this interesting product. The heat of formation of BrO^- is −101 kJ mol^{-1}, derived from the measured 2.353 eV electron affinity of BrO.[26] O^- is unreactive with CF_4[27] but does react with CH_4 by hydrogen abstraction,[28] not observed in the case of $CHBrF_2$. O^- reacts rapidly with CF_3Br with similar chemistry to the $CHBrF_2$ case, producing mainly F^- and BrO^- with lesser amounts of Br^- and BrF^-.[27]

The reaction of O^- with CF_3CH_2F is an exception in the O^- set of reactions in that it proceeds by a single pathway, forming CF_3CF^- + H_2O.

$$O^- + CF_3CH_2F \rightarrow CF_3CF^- + H_2O \qquad \Delta H \le -41\ \text{kJ mol}^{-1} \quad (10)$$

Effective transfer of H_2^+ to O^- is a well-known process for a variety of organic neutral reactants.[29] The energetics of this reaction require an estimate of the unknown heat of formation of CF_3CF^-. This is accomplished by assuming (a) equal C−H bond strengths in CHF_2^- and CF_3CHF^- and (b) equal differences in the heats of formation of CHF_2^- and CF_2^- compared with CF_3CHF^- and CF_3CF^-. In so doing, we derive $\Delta_fH(CF_3CF^-) < 587$ kJ mol^{-1}, which leads to a minimum exothermicity of 41 kJ mol^{-1} for reaction 10. O^- is unreactive with the analogous PFC, C_2F_6.[4]

As in the O_2^+ reactions, the two fluorinated propanes behave quite differently from one another in reaction with O^-.

$$O^- + CF_3CHFCF_3 \rightarrow F^- + C_3HF_6O \qquad \Delta H = -96\ \text{kJ mol}^{-1} \quad (11a)$$

$$\rightarrow C_3HF_6O^- + F \qquad \Delta H = -79\ \text{kJ mol}^{-1} \quad (11b)$$

$$\rightarrow C_3F_7^- + OH \qquad \Delta H = -78\ \text{kJ mol}^{-1} \quad (11c)$$

$$O^- + CF_3CHFCHF_2 \rightarrow F^-{\cdot}OH + C_3HF_5 \qquad \Delta H \le -32\ \text{kJ mol}^{-1} \quad (12a)$$

$$\rightarrow F^-{\cdot}HF + C_3F_4OH \qquad \Delta H = -108\ \text{kJ mol}^{-1} \quad (12b)$$

$$\rightarrow CF_3CF^- + CHF_2OH \qquad \Delta H \le 23\ \text{kJ mol}^{-1} \quad (12c)$$

$$\rightarrow CF_3CFCO^- + 2HF \qquad \Delta H = -238\ \text{kJ mol}^{-1} \quad (12d)$$

$$\rightarrow C_3F_5^- + HF + OH \qquad \Delta H \sim 0 \quad (12e)$$

$$\rightarrow C_3F_5O^- + HF + H \qquad \Delta H = -139\ \text{kJ mol}^{-1} \quad (12f)$$

$$\rightarrow C_3HF_6^- + OH \qquad \Delta H = -141\ \text{kJ mol}^{-1} \quad (12g)$$

$$\rightarrow e^- + C_3F_6 + H_2O \qquad \Delta H = -160\ \text{kJ mol}^{-1} \quad (12h)$$

Reactions 11 and 12 have no ionic products in common. However, reaction 11 proceeds mainly by proton transfer, and proton transfer represents the most important pathway in reaction 12 as well (channel 12g). The occurrence of efficient proton transfer in reactions 11 and 12 indicates that the gas-phase acidities of CF_3CHFCF_3 and $CF_3CHFCHF_2$ are greater than that of OH; i.e., these HFC's have smaller enthalpies of deprotonation, ΔH_{acid}, than the 1599 kJ mol^{-1} value for $\Delta H_{acid}(OH)$. The structure of the neutral product C_3HF_6O in reaction 11a is unknown, but for the purposes of estimating the energetics of this channel we assume it is n-C_3F_6OH, formally derived from n-C_3F_7 by substituting OH for F. Using a value of 25 kJ mol^{-1} for the increase from $\Delta_fH(R-F)$ to $\Delta_fH(R-OH)$, which is typical for this type of replacement,[30] we derive $\Delta_fH(n\text{-}C_3F_6OH) = -1312$ kJ mol^{-1}, leading to an exothermicity of 96 kJ mol^{-1} for channel 11a. The branching fractions for channels 11a and 11b are given as upper limits since the uncertainty in the extrapolation to zero flow in the product branching plots includes the possibility of a zero intercept in these cases.

Reaction 12 is remarkable in that eight channels are observed. No channel is clearly dominant, with the most abundant product accounting for only about 25% of all reactions. The other channels vary from 3 to 18%. Reaction 12a forms the interesting ion FHO^-, assumed to be the hydrogen-bonded cluster species $F^-{\cdot}OH$, and the corresponding neutral C_3HF_5.

The heat of formation of the less stable C_3HF_5 isomer, CF_3CFCHF, was estimated (in the discussion of reaction 4) to be −959 kJ mol^{-1}. We estimate $\Delta_fH(F^-\cdot OH) = -307$ kJ mol^{-1} by assuming thermoneutrality for the process $F^-\cdot H_2O + OH \rightarrow F^-\cdot OH + H_2O$, leading to a minimum exothermicity of 32 kJ mol^{-1} for reaction 12a. We assume the HF_2^- product ion in channel 12b is $F^-\cdot HF$; the accompanying neutral is assumed to be either $CF_2CFCFOH$ or $CF_2C(OH)CF_2$, which should have nearly identical heats of formation due to offsetting F/OH replacements. In order to estimate $\Delta_fH(C_3F_4OH)$, we first estimate $\Delta_fH(C_3F_5) = -730$ kJ mol^{-1} from the electron affinity of C_3F_5 and from $\Delta_fH(C_3F_5^-)$. Then, from the expected 25 kJ mol^{-1} increase from $\Delta_fH(R-F)$ to $\Delta_fH(R-OH)$ discussed above,[30] we derive $\Delta_fH(C_3F_4OH) = -705$ kJ mol^{-1} and an exothermicity of 108 kJ mol^{-1} for reaction 12b. In reaction 12c, we assume that the neutral product is CHF_2OH, and using the usual 25 kJ mol^{-1} increase in heat of formation in going from CHF_3 to CHF_2OH, we derive $\Delta_fH(CHF_2OH) = -670$ kJ mol^{-1}. Combining this with the value for $\Delta_fH(CF_3CF^-)$ derived for reaction 10, we estimate a minimum exothermicity of 23 kJ mol^{-1} for reaction 12c. Reactions 12e and 12f both produce HF. Reaction 12 includes a contribution from reactive electron detachment, channel 12h; this is the only case in the present study where electron detachment was observed.

D. Reactions of O_2^-. Table 4 lists the results for the O_2^- ion, which reacts rapidly with the studied neutrals except for CF_3CH_2F which clusters slowly. Various cluster ion products were found in all cases. $CHBrF_2$ reacts with O_2^- at the collisional rate producing the cluster ion $Br^-\cdot HO_2$ as the major product; this channel is approximately thermoneutral, based on an estimated heat of formation of −264 kJ mol^{-1} for $Br^-\cdot HO_2$. This estimate was made by assuming thermoneutrality for the following ligand-switching reaction: $Br^-\cdot H_2O + HO_2 \rightarrow Br^-\cdot HO_2 + H_2O$.

$$O_2^- + CHBrF_2 \rightarrow F^- + HF + Br + CO_2 \qquad \Delta H = -336\ \text{kJ mol}^{-1} \tag{13a}$$

$$\rightarrow F^-\cdot HF + Br + CO_2 \qquad \Delta H = -498\ \text{kJ mol}^{-1} \tag{13b}$$

$$\rightarrow Br^- + COF_2 + OH \qquad \Delta H = -347\ \text{kJ mol}^{-1} \tag{13c}$$

$$\rightarrow Br^-\cdot HO_2 + CF_2 \qquad \Delta H = -2\ \text{kJ mol}^{-1} \tag{13d}$$

If the small amount of F^- tentatively identified is a true product, it is likely to arise from dissociation of a portion of the $F^-\cdot HF$ produced in reaction 13b.

The reaction of O_2^- with CF_3CH_2F proceeds exclusively by association; this bond strength is not known.

$$O_2^- + CF_3CH_2F \rightarrow O_2^-\cdot CF_3CH_2F \qquad \Delta H = ? \tag{14}$$

This reaction was studied as a function of pressure, and the second-order rate constant was found to increase with increasing pressure, with some indication of fall-off behavior. This is expected since the reaction is on the order of 10% efficient, i.e., neither close to collisional, where high-pressure kinetics is expected, nor very inefficient, where low-pressure kinetics would be favored. The results of the pressure dependence measurements are given in a footnote to Table 4.

As was found for the other ions in this study, the two fluorinated propanes behave quite differently from one another.

$$O_2^- + CF_3CHFCF_3 \rightarrow F^- + HF + C_2F_5 + CO_2 \qquad \Delta H = -193\ \text{kJ mol}^{-1} \tag{15a}$$

$$\rightarrow F^-\cdot HF + C_2F_5 + CO_2 \qquad \Delta H = -353\ \text{kJ mol}^{-1} \tag{15b}$$

$$\rightarrow O_2^-\cdot HF + C_3F_6 \qquad \Delta H = ? \tag{15c}$$

$$\rightarrow O_2^-\cdot CF_3CHFCF_3 \qquad \Delta H = ? \tag{15d}$$

$$O_2^- + CF_3CFHCF_2H \rightarrow O_2^-\cdot HF + C_3HF_5 \qquad \Delta H = ? \tag{16a}$$

$$\rightarrow O_2^-\cdot CF_3CHFCHF_2 \qquad \Delta H = ? \tag{16b}$$

Association (bond strengths unknown) as well as formation of the cluster ion $O_2^-\cdot HF$ occur for both CF_3CHFCF_3 and $CF_3CHFCHF_2$. The ion is written as $O_2^-\cdot HF$ rather than $F^-\cdot HO_2$ since the former ion is more stable. The CF_3CHFCF_3 reactant also formed two additional ionic products not seen with $CF_3CHFCHF_2$: F^- and $F^-\cdot HF$. The F^- may arise from unimolecular decomposition of the $F^-\cdot HF$ formed in reaction 15b, as discussed earlier for reaction 9. For reaction 15c to be exothermic requires a rather large cluster bond strength for $O_2^-\cdot HF$, approximately 148 kJ mol^{-1}, the energy needed for the dehydrofluorination reaction $CF_3CHFCF_3 \rightarrow CF_3CFCF_2 + HF$. This may be reconciled by the somewhat large error bars we estimate for the heat of formation of CF_3CHFCF_3, 40 kJ mol^{-1}. We also note for comparison that F^- bonds to HF with an energy of 161 kJ mol^{-1}. In channel 16a, an $O_2^-\cdot HF$ cluster bond strength of only 60 kJ mol^{-1} is required for exothermicity, based on the energetics of the dehydrofluorination $CF_3CHFCHF_2 \rightarrow CF_3CHCF_2 + HF$.

It is interesting to note that the less polar CF_3CHFCF_3 reacts more rapidly than does $CF_3CHFCHF_2$. However, association is a smaller contributor to the overall reactivity in the case of CF_3CHFCF_3, and the absolute rate constant for association is similarly smaller in this case. The larger rate constant for the overall reactivity of CF_3CHFCF_3 is likely to result from the fact that additional reaction channels are available in this case.

Both reactions 15 and 16 include significant association pathways despite the presence of several other very exothermic channels. Sometimes it is assumed that when association and bimolecular reactions compete, the reactive channel is approximately thermoneutral. This is clearly in contradiction to the present findings.

E. Reactions of H_3O^+, $H_3O^+\cdot(H_2O)$, and $H_3O^+\cdot(H_2O)_2$. Table 5 lists the results for the H_3O^+ ion and its hydrates $H_3O^+\cdot H_2O$ and $H_3O^+\cdot(H_2O)_2$. The bare H_3O^+ ion reacts exclusively by association in all cases, while its hydrates were unreactive. The H_3O^+-HFC cluster bond strengths are not known. The lack of ligand switching by the hydrates of H_3O^+ is consistent with the expectation of stronger cluster bonds for the hydrates compared with those for the $H_3O^+\cdot$HFC's.

In the case of $CHBrF_2$, the association reaction efficiency is less than the fractional impurity level in the $CHBrF_2$, but the observed product ion corresponds to the association product. We therefore feel that it is reasonable to claim that association is observed, but the caveat regarding the impurity level should be kept in mind. It is worth pointing out that the reaction of

$CF_3CHFCHF_2$ is about 25 times faster than that of CF_3CHFCF_3. While the larger dipole moment of the less symmetric $CF_3CHFCHF_2$ would be expected to lead to a larger association rate, the factor of 25 is somewhat surprising.

F. Reactions of NO_3^- and $NO_3^-{\cdot}HNO_3$. Table 6 lists the results for NO_3^- and $NO_3^-{\cdot}HNO_3$. The association product was observed in the NO_3^- reactions for all four neutrals, but for $CHBrF_2$ and CF_3CH_2F the impurity levels in the neutral samples were greater than the reaction efficiency. Thus, we report association in these cases with the caveat about impurities. The cluster bond strengths are not known. The $NO_3^-{\cdot}HNO_3$ cluster ion was unreactive with all four neutrals, as expected since this cluster is expected to be more strongly bound than the $NO_3^-{\cdot}$HFC clusters. As was found for H_3O^+, the less symmetric and thus more highly polar $CF_3CHFCHF_2$ reacts by association more rapidly than does CF_3CHFCF_3. Unlike the H_3O^+ case, on the other hand, the $CF_3CHFCHF_2$ rate is only about 50% faster.

Summary and Conclusions

The hydrofluorocarbons are found generally to be more reactive with ions than are the corresponding perfluorocarbons, as expected. The chemistry is often rich with multiple product channels, which for O^- and O_2^- include some interesting cluster ion products. In one case, the reaction of O^- with $CF_3CHFCHF_2$, eight product channels are observed. The monatomic ions O^+ and O^- are most reactive with the studied neutrals, reacting at the collisional rate within uncertainty in all cases. The less reactive ions O_2^+, O_2^-, H_3O^+, and NO_3^- react by association in many cases. The solvated ions $H_3O^+{\cdot}H_2O$, $H_3O^+{\cdot}(H_2O)_2$, and $NO_3^-{\cdot}HNO_3$, which are representative of the abundant ionic species in the lower atmosphere, are unreactive with the compounds investigated, and thus atmospheric ion chemistry is not a significant sink for these HFC's. The observation of proton transfer from CF_3CHFCF_3 and $CF_3CHFCHF_2$ to O^- allows a lower bound to the gas-phase acidities of these HFC's to be assigned: $\Delta H_{acid}(CF_3CHFCF_3)$ and $\Delta H_{acid}(CF_3CHFCHF_2) < 1599$ kJ mol^{-1}.

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References and Notes

(1) Nelson, D. D., Jr.; Zahniser, M. S.; Kolb, C. E. *Geophys. Res. Lett.* **1993**, *20*, 197.

(2) Orkin, V. L.; Khamaganov, V. G. *J. Atmos. Chem.* **1993**, *16*, 157.

(3) Schmoltner, A. M.; Talukdar, R. K.; Warren, R. F.; Mellouki, A.; Goldfarb, L.; Gierczak, T.; McKeen, S. A.; Ravishankara, A. R. *J. Phys. Chem.* **1993**, *97*, 8976.

(4) Morris, R. A.; Miller, T. M.; Viggiano, A. A.; Paulson, J. F.; Solomon, S.; Reid, G. *J. Geophys. Res.* **1995**, *100*, 1287.

(5) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. A. *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986*; Maruzen Company, Ltd.: Tokyo, 1987.

(6) Viggiano, A. A.; Arnold, F. In *Atmospheric Electrodynamics*; Volland, H., Ed.; CRC Press: Boca Raton, FL, 1995.

(7) Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F.; Giles, K.; Smith, D.; Su, T. *J. Chem. Phys.* **1990**, *93*, 1149.

(8) Smith, D.; Adams, N. G. *Adv. At. Mol. Phys.* **1988**, *24*, 1.

(9) Viggiano, A. A.; Morris, R. A.; Paulson, J. F.; Ferguson, E. E. *J. Phys. Chem.* **1990**, *94*, 7111.

(10) Bohringer, H.; Durup-Ferguson, M.; Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1983**, *79*, 4201.

(11) Ferguson, E. E. *J. Phys. Chem.* **1986**, *90*, 731.

(12) Viggiano, A. A.; Morris, R. A.; Paulson, J. F. *Int. J. Mass Spectrom. Ion Processes* **1994**, *135*, 31.

(13) Viggiano, A. A.; Morris, R. A.; Paulson, J. F. *J. Chem. Phys.* **1990**, *93*, 1483.

(14) Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F. *J. Chem. Phys.* **1990**, *93*, 1681.

(15) Glosik, J.; Rakshit, A. B.; Twiddy, N. D.; Adams, N. G.; Smith, D. *J. Phys. B: At. Mol. Phys.* **1978**, *11*, 3365.

(16) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(17) Su, T. *J. Chem. Phys.* **1988**, *89*, 5355.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*, 1.

(19) Slayden, S. W.; Liebman, J. F.; Mallard, W. G. In *The Chemistry of Functional Groups: Supplement D2. The Chemistry of the Organic Halides, Pseudohalides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, in press.

(20) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(21) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, *98*, 4773.

(22) Fisher, E. R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, R1.

(23) Papina, T. S.; Kolesov, V. P.; Gol'ovanaova, Y. G. *Russ. J. Phys. Chem.* **1988**, *61*, 1108.

(24) Liebman, J. F. In *Fluorine-Containing Molecules: Structure, Reactivity, Synthesis and Applications*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds.; VCH: New York, 1988.

(25) Raksit, A. B. *Int. J. Mass Spectrom. Ion Processes* **1986**, *69*, 45.

(26) Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 8012.

(27) Morris, R. A. *J. Chem. Phys.* **1992**, *97*, 2372.

(28) Lindinger, W.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1975**, *63*, 3238.

(29) Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611.

(30) Kunkel, D. L.; Fant, A. D.; Liebman, J. F. *J. Mol. Struct.* **1993**, *300*, 509.

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