

## Reactions of Atmospheric Ions with Selected Hydrofluorocarbons

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Selected atmospheric ions have been studied for reactivity with the hydrofluorocarbons (HFC's)  $\text{CF}_3\text{CH}_2\text{F}$ ,  $\text{CF}_3\text{CHF}_2$ , and  $\text{CF}_3\text{CHF}_2$  and with  $\text{CHBrF}_2$ ; the reactant ions chosen for study are  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ ,  $\text{NO}_3^-$ , and  $\text{NO}_3^-\cdot\text{HNO}_3$ . 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  $\text{O}^+$  and  $\text{O}^-$  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  $\text{H}_3\text{O}^+$  and  $\text{NO}_3^-$  reacted inefficiently by association in all cases. The solvated ions  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ , and  $\text{NO}_3^-\cdot\text{HNO}_3$ , 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  $\text{CF}_3\text{CHF}_2$  and  $\text{CF}_3\text{CHF}_2$  to  $\text{O}^-$  allows a lower bound to the gas-phase acidities of these HFC's to be assigned:  $\Delta H_{\text{acid}}(\text{CF}_3\text{CHF}_2) < 1599$  kJ mol<sup>-1</sup>.

### 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.<sup>1–3</sup> 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),<sup>4</sup> 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.,  $\text{NO}_3^-\cdot(\text{HNO}_3)_n$  and  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n$ , 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.<sup>5</sup>

In this article we report rate constants and product branching fractions for reactions of three HFC's:  $\text{CF}_3\text{CH}_2\text{F}$ ,  $\text{CF}_3\text{CHF}_2$ , and  $\text{CF}_3\text{CHF}_2$ . The compound  $\text{CHBrF}_2$  was also included

in the study because of initial interest in this compound as a replacement for the fire suppressant  $\text{CF}_3\text{Br}$ . The ions chosen for study are  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ ,  $\text{NO}_3^-$ , and  $\text{NO}_3^-\cdot\text{HNO}_3$ , 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.<sup>6</sup> 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;<sup>7</sup> the technique and generic instrumentation have been extensively reviewed.<sup>8</sup> 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:  $\text{O}^+$ ,  $\text{O}_2^+$ , and  $\text{O}_2^-$  were produced from  $\text{O}_2$ ;  $\text{O}^-$  from  $\text{N}_2\text{O}$ ;  $\text{H}_3\text{O}^+$ ,  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ , and  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$  from  $\text{H}_2\text{O}$ ;  $\text{NO}_3^-$  and  $\text{NO}_3^-\cdot\text{HNO}_3$  from  $\text{NO}_2$  which contained a small impurity of  $\text{HNO}_3$ . 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 ( $\sim 10^4$  cm s<sup>-1</sup>) 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;<sup>7</sup> 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<sup>+</sup> Ions with Selected Hydrohalocarbons Measured at 300 K<sup>a</sup>**

reaction	branching fraction	total rate constant (10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup> )
O <sup>+</sup> + CHBrF <sub>2</sub> → CHF <sup>+</sup> + BrOF	0.44	2.9
→ CHF <sub>2</sub> <sup>+</sup> + BrO	0.56	
O <sup>+</sup> + CF <sub>3</sub> CH <sub>2</sub> F → CH <sub>2</sub> F <sup>+</sup> + CF <sub>2</sub> O + F	0.37	3.7
→ CF <sub>3</sub> <sup>+</sup> + CH <sub>2</sub> O + F	0.56	
→ C <sub>2</sub> H <sub>2</sub> F <sub>3</sub> <sup>+</sup> + OF	0.07	
O <sup>+</sup> + CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub> → CF <sub>3</sub> <sup>+</sup> + CF <sub>2</sub> O + CHF <sub>2</sub>	0.38	2.6
→ C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> + CF <sub>2</sub> O + F <sub>2</sub>	0.62	
O <sup>+</sup> + CF <sub>3</sub> CHF <sub>2</sub> CF <sub>2</sub> → CHF <sub>2</sub> <sup>+</sup> + CF <sub>2</sub> O + CHF <sub>2</sub>	0.44	2.6
→ C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> + CHF <sub>3</sub> + O	0.45	
→ C <sub>3</sub> H <sub>2</sub> F <sub>5</sub> <sup>+</sup> + OF	0.11	

<sup>a</sup> 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.<sup>7</sup> 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<sup>+</sup> were used as calibrants for identifying C<sub>3</sub>H<sub>2</sub>F<sub>5</sub><sup>+</sup> at *m/e* = 133. This type of calibration is often not necessary in SIFT experiments,<sup>8</sup> 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).<sup>9</sup>

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<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> are known to remain somewhat vibrationally excited in the reaction region of the flow tube,<sup>10–12</sup> and a few percent of the O<sup>+</sup> may remain electronically excited.<sup>13,14</sup> Quenching of vibrationally excited ions has been investigated by a number of research groups,<sup>11</sup> and effective

quenchers for O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> have been documented.<sup>10–12</sup> 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<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup>. For O<sub>2</sub><sup>+</sup>, CO<sub>2</sub> was used as the quencher; for O<sub>2</sub><sup>-</sup>, C<sub>2</sub>F<sub>6</sub> was used. In the case of electronically excited O<sup>+</sup>, quenching was not feasible, so we used CO as a monitor gas to follow the relative population of excited O<sup>+</sup> as the ion source conditions were optimized. Excited O<sup>+</sup> reacts rapidly with CO by charge transfer, but ground state O<sup>+</sup> does not.<sup>15</sup> Adjusting the ion source conditions allowed the percentage of excited O<sup>+</sup> to be reduced to 0.4% of the total O<sup>+</sup> signal. Since the rates of all of the present reactions with O<sup>+</sup> were found to be collisional,<sup>16,17</sup> there can be no significant error associated with this minor extent of O<sup>+</sup> 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<sub>3</sub>CH<sub>2</sub>F. The suppliers and purities are as follows: PCR, Inc., CHBrF<sub>2</sub> (98.8%, analyzed), CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub> (99.8%, analyzed), CF<sub>3</sub>CHF<sub>2</sub>CF<sub>2</sub> (99.5%, analyzed); Aldrich Chemical Co., CF<sub>3</sub>CH<sub>2</sub>F (>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<sub>2</sub><sup>+</sup> with CF<sub>3</sub>CH<sub>2</sub>F and CF<sub>3</sub>CHF<sub>2</sub>CF<sub>2</sub>, 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.<sup>16,17</sup> 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<sub>2</sub><sup>+</sup> Ions with Selected Hydrohalocarbons Measured at 300 K<sup>g</sup>**

reaction	branching fraction	total rate constant (10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup> )
O <sub>2</sub> <sup>+</sup> + CHBrF <sub>2</sub> → CHF <sub>2</sub> <sup>+</sup> + Br + O <sub>2</sub>	0.85	2.0
→ CHBrF <sub>2</sub> <sup>+</sup> + O <sub>2</sub>	0.15	
O <sub>2</sub> <sup>+</sup> + CF <sub>3</sub> CH <sub>2</sub> F → O <sub>2</sub> <sup>+</sup> ·CF <sub>3</sub> CH <sub>2</sub> F <sup>a</sup>		≤0.0052 <sup>a,b</sup>
O <sub>2</sub> <sup>+</sup> + CF <sub>3</sub> CHF <sub>2</sub> → products <sup>c</sup>		≤0.017 <sup>c</sup>
O <sub>2</sub> <sup>+</sup> + CF <sub>3</sub> CHFCH <sub>2</sub> F → C <sub>2</sub> HF <sub>3</sub> <sup>d</sup> + CHF <sub>3</sub> + O <sub>2</sub>	0.14	0.52
→ C <sub>3</sub> H <sub>2</sub> F <sub>5</sub> <sup>e</sup> + F + O <sub>2</sub>	0.09	
→ C <sub>3</sub> HF <sub>6</sub> <sup>f</sup> + HO <sub>2</sub>	0.77	

<sup>a</sup> Reaction efficiency is below HFC impurity level (see text). <sup>b</sup> Value refers to second-order rate constant measured at 0.43 Torr. <sup>c</sup> C<sub>2</sub>F<sub>3</sub><sup>+</sup> "product" detected but is likely to be due to an impurity in the HFC sample (see text). <sup>d</sup> Assumed product ion, but *m/e* = 82 also corresponds to the ion CF<sub>2</sub>O<sub>2</sub><sup>+</sup>. <sup>e</sup> Assumed product ion, but *m/e* = 133 also corresponds to the ion C<sub>2</sub>HF<sub>4</sub>O<sub>2</sub><sup>+</sup>. <sup>f</sup> Assumed product ion, but *m/e* = 151 also corresponds to the ion C<sub>2</sub>F<sub>5</sub>O<sub>2</sub><sup>+</sup>. <sup>g</sup> 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<sup>-</sup> Ions with Selected Hydrohalocarbons Measured at 300 K<sup>a</sup>**

reaction	branching fraction	total rate constant (10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup> )
O <sup>-</sup> + CHBrF <sub>2</sub> → F <sup>-</sup> + HCOF + Br	0.16	3.0
→ Br <sup>-</sup> + HF + FCO	0.71	
→ BrO <sup>-</sup> + CHF <sub>2</sub>	0.11	
→ Br <sup>-</sup> ·HF + FCO	0.02	
O <sup>-</sup> + CF <sub>3</sub> CH <sub>2</sub> F → CF <sub>3</sub> CF <sup>-</sup> + H <sub>2</sub> O		4.3
O <sup>-</sup> + CF <sub>3</sub> CHF <sub>2</sub> → F <sup>-</sup> + C <sub>3</sub> HF <sub>6</sub> O	<0.02	2.6
→ C <sub>3</sub> HF <sub>6</sub> O <sup>-</sup> + F	<0.03	
→ C <sub>3</sub> F <sub>7</sub> <sup>-</sup> + OH	>0.95	
O <sup>-</sup> + CF <sub>3</sub> CHFCH <sub>2</sub> F → F <sup>-</sup> ·OH + C <sub>3</sub> HF <sub>5</sub>	0.06	2.5
→ F <sup>-</sup> ·HF + C <sub>3</sub> F <sub>4</sub> OH	0.06	
→ CF <sub>3</sub> CF <sup>-</sup> + CHF <sub>2</sub> OH	0.15	
→ CF <sub>3</sub> CF <sub>2</sub> O <sup>-</sup> + 2HF	0.16	
→ C <sub>3</sub> F <sub>5</sub> <sup>-</sup> + HF + OH	0.08	
→ C <sub>3</sub> F <sub>2</sub> O <sup>-</sup> + HF + H	0.03	
→ C <sub>3</sub> HF <sub>6</sub> <sup>-</sup> + OH	0.27	
→ e <sup>-</sup> + C <sub>3</sub> F <sub>6</sub> + H <sub>2</sub> O	0.18	

<sup>a</sup> 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<sub>2</sub><sup>-</sup> Ions with Selected Hydrohalocarbons Measured at 300 K<sup>c</sup>**

reaction	branching fraction	total rate constant (10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup> )
O <sub>2</sub> <sup>-</sup> + CHBrF <sub>2</sub> → F <sup>-</sup> + HF + Br + CO <sub>2</sub>	<0.02	1.9
→ F <sup>-</sup> ·HF + Br + CO <sub>2</sub>	0.06	
→ Br <sup>-</sup> + CF <sub>2</sub> O + OH	0.21	
→ Br <sup>-</sup> ·HO <sub>2</sub> + CF <sub>2</sub>	0.71	
O <sub>2</sub> <sup>-</sup> + CF <sub>3</sub> CH <sub>2</sub> F → O <sub>2</sub> <sup>-</sup> ·CF <sub>3</sub> CH <sub>2</sub> F	1.0	0.13 <sup>a</sup>
O <sub>2</sub> <sup>-</sup> + CF <sub>3</sub> CHF <sub>2</sub> → F <sup>-</sup> + HF + C <sub>2</sub> F <sub>5</sub> + CO <sub>2</sub>	0.08	1.5 <sup>b</sup>
→ F <sup>-</sup> ·HF + C <sub>2</sub> F <sub>5</sub> + CO <sub>2</sub>	0.39	
→ O <sub>2</sub> <sup>-</sup> ·HF + C <sub>3</sub> F <sub>6</sub>	0.37	
→ O <sub>2</sub> <sup>-</sup> ·CF <sub>3</sub> CHF <sub>2</sub>	0.16	
O <sub>2</sub> <sup>-</sup> + CF <sub>3</sub> CHFCH <sub>2</sub> F → O <sub>2</sub> <sup>-</sup> ·HF + C <sub>3</sub> HF <sub>5</sub>	0.49	1.0 <sup>b</sup>
→ O <sub>2</sub> <sup>-</sup> ·CF <sub>3</sub> CHFCH <sub>2</sub> F	0.51	

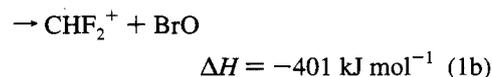
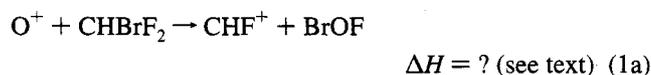
<sup>a</sup> Value refers to second-order rate constant measured at 0.43 Torr; additional values at other pressures are as follows: *k* = 9.3(-11) at 0.29 Torr, 1.1(-10) at 0.35 Torr, 1.3(-10) at 0.53 Torr. <sup>b</sup> Reaction includes an association product; value refers to second-order rate constant measured at 0.43 Torr. <sup>c</sup> 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.<sup>18</sup> and neutral thermochemistry found in Slayden et al.<sup>19</sup> 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<sup>+</sup>.** Table 1 lists the results for the O<sup>+</sup> 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<sub>2</sub>,



two product channels arise, both of which involve breaking the C-Br bond, the weakest bond in CHBrF<sub>2</sub>. Channel 1a violates spin conservation, as do many of the O<sup>+</sup> reactions reported here. However, several of the O<sup>+</sup> reactions have sufficiently high

**TABLE 5: Rate Constants and Products for Reactions of  $\text{H}_3\text{O}^+$ ,  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ , and  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$  Ions with Selected Hydrohalocarbons Measured at 300 K and 0.41 Torr**

reaction	total rate constant ( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ )
$\text{H}_3\text{O}^+ + \text{CHBrF}_2 \rightarrow \text{H}_3\text{O}^+\cdot\text{CHBrF}_2^a$	0.15 <sup>a</sup>
$\text{H}_3\text{O}^+\cdot\text{H}_2\text{O} + \text{CHBrF}_2 \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 + \text{CHBrF}_2 \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+ + \text{CF}_3\text{CH}_2\text{F} \rightarrow \text{H}_3\text{O}^+\cdot\text{CF}_3\text{CH}_2\text{F}$	0.94
$\text{H}_3\text{O}^+\cdot\text{H}_2\text{O} + \text{CF}_3\text{CH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 + \text{CF}_3\text{CH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+ + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow \text{H}_3\text{O}^+\cdot\text{CF}_3\text{CHFCH}_2\text{F}$	0.11
$\text{H}_3\text{O}^+\cdot\text{H}_2\text{O} + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+ + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow \text{H}_3\text{O}^+\cdot\text{CF}_3\text{CHFCH}_2\text{F}$	2.7
$\text{H}_3\text{O}^+\cdot\text{H}_2\text{O} + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1

<sup>a</sup> Reaction efficiency is below  $\text{CHBrF}_2$  sample impurity level (see text).

**TABLE 6: Rate Constants and Products for Reactions of  $\text{NO}_3^-$  and  $\text{NO}_3^-\cdot\text{HNO}_3$  Ions with Selected Hydrohalocarbons Measured at 300 K and 0.41 Torr**

reaction	total rate constant ( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ )
$\text{NO}_3^- + \text{CHBrF}_2 \rightarrow \text{NO}_3^-\cdot\text{CHBrF}_2^a$	<0.1 <sup>a</sup>
$\text{NO}_3^-\cdot\text{HNO}_3 + \text{CHBrF}_2 \rightarrow$ no reaction	<0.1
$\text{NO}_3^- + \text{CF}_3\text{CH}_2\text{F} \rightarrow \text{NO}_3^-\cdot\text{CF}_3\text{CH}_2\text{F}^a$	<0.1 <sup>a</sup>
$\text{NO}_3^-\cdot\text{HNO}_3 + \text{CF}_3\text{CH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{NO}_3^- + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow \text{NO}_3^-\cdot\text{CF}_3\text{CHFCH}_2\text{F}$	1.5
$\text{NO}_3^-\cdot\text{HNO}_3 + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1
$\text{NO}_3^- + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow \text{NO}_3^-\cdot\text{CF}_3\text{CHFCH}_2\text{F}$	2.3
$\text{NO}_3^-\cdot\text{HNO}_3 + \text{CF}_3\text{CHFCH}_2\text{F} \rightarrow$ no reaction	<0.1

<sup>a</sup> Reaction efficiency below reactant neutral impurity level (see text).

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

species	$\Delta_f H$ ( $\text{kJ mol}^{-1}$ )	species	$\Delta_f H$ ( $\text{kJ mol}^{-1}$ )
$\text{CF}_3\text{CF}^-$	<587	$\text{C}_3\text{F}_4\text{OH}$	-705
$\text{CF}_3\text{CHFCHF}^+$	-136	$\text{C}_3\text{F}_5$	-730
$\text{CF}_3\text{CH}_2\text{CF}_2^+$	-186	$\text{CF}_3\text{CFCHF}$	-959
$\text{Br}^-\cdot\text{HO}_2$	-264	<i>n</i> - $\text{C}_3\text{F}_6\text{OH}$	-1312
$\text{C}_3\text{HF}_6^+$	-291	$\text{CF}_3\text{CHFCHF}_2$	-1342
$\text{F}^-\cdot\text{OH}$	-307	$\text{CF}_3\text{CHFCH}_2\text{F}$	-1573
$\text{CHF}_2\text{OH}$	-670		

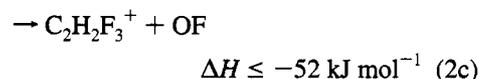
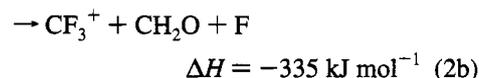
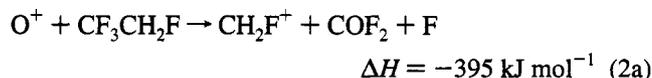
exothermicities so as to allow bond cleavage in the neutral product and thus would not violate spin conservation. That (1a) violates spin conservation may be ameliorated by the strong spin-orbit coupling due to the heavy element Br.

The heat of formation of  $\text{CHBrF}_2$  is  $-425 \text{ kJ mol}^{-1}$ .<sup>20</sup> Assuming that  $\text{BrOF}$  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  $\text{HOBr} + \text{HOF} \rightarrow \text{BrOF} + \text{H}_2\text{O}$ , yields  $\Delta_f H(\text{BrOF}) = 85 \text{ kJ mol}^{-1}$ .<sup>21</sup> This would lead, however, to an endothermicity of  $68 \text{ kJ mol}^{-1}$  for reaction 1a. On the basis of our observation of  $\text{CHF}^+$  product, we conclude that the heat of formation of  $\text{BrOF}$  must be considerably lower than the above estimate of  $85 \text{ kJ mol}^{-1}$ ; it must be less than or approximately equal to  $17 \text{ kJ mol}^{-1}$  for (1a) to be thermoneutral or exothermic. The above discussion would not apply if the structure of this species were actually  $\text{OBrF}$ .

The formation of the triatomic  $\text{CHF}^+$  product ion (channel 1a) contrasts with our SIFT results for the reaction of  $\text{O}^+$  with  $\text{CF}_4$ , in which only  $\text{CF}_3^+$  is produced.<sup>4</sup> Channel 1b also violates spin conservation as written, but it is sufficiently exothermic

that production of  $\text{Br} + \text{O}$ , instead of  $\text{BrO}$ , is energetically allowed and would not violate spin conservation.

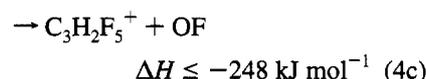
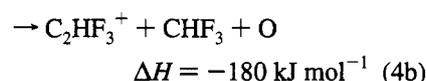
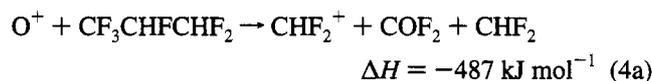
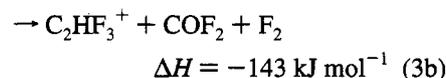
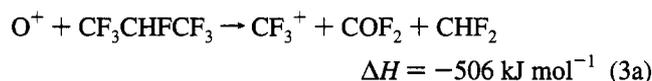
The reaction with  $\text{CF}_3\text{CH}_2\text{F}$  features three product pathways.



For the heat of formation of  $\text{CF}_3^+$ , we use the value derived by Fisher and Armentrout,<sup>22</sup>  $361 \text{ kJ mol}^{-1}$ . 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  $\text{C}_2\text{H}_2\text{F}_3^+$  is not defined. If the  $\text{C}_2\text{H}_2\text{F}_3^+$  product is the least stable isomer,  $\text{CF}_3\text{CH}_2^+$  (with heat of formation of  $506 \text{ kJ mol}^{-1}$ ), then this reaction is exothermic by  $52 \text{ kJ mol}^{-1}$ . It is not obvious whether  $\text{CH}_2\text{FCF}_2^+$  or  $\text{CHF}_2\text{CHF}^+$  is more stable. However, whichever isomer is formed by protonation of  $\text{CF}_2\text{-CHF}$ , its heat of formation is  $332 \text{ kJ mol}^{-1}$ , so channel 2c would be exothermic by  $226 \text{ kJ mol}^{-1}$  in this case.

The chemistry of reaction 2 is essentially the same as that found for the analogous perfluorocarbon  $\text{C}_2\text{F}_6$ . In the reaction of  $\text{O}^+$  with  $\text{C}_2\text{F}_6$ , the major product is  $\text{CF}_3^+$  with possible minor amounts (<1%) of  $\text{C}_2\text{F}_5^+$ .<sup>4</sup>

The chemistry of  $\text{O}^+$  with  $\text{CF}_3\text{CHFCH}_2\text{F}$  (reaction 3) contrasts with that of  $\text{CF}_3\text{CHFCH}_2\text{F}$  (reaction 4).



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  $\text{CF}_3^+$  is produced in reaction 3, it is not formed in reaction 4 despite the presence of a terminal  $\text{CF}_3$  group. The ionization potentials of  $\text{CF}_3$  and  $\text{CHF}_2$  are very similar, and the  $\text{CF}_3$ -R bond strengths in  $\text{CF}_3\text{CHFCH}_2\text{F}$  and  $\text{CF}_3\text{-CHFCH}_2\text{F}$  are also expected to be similar. Thus, the lack of any detectable  $\text{CF}_3^+$  product in reaction 4 is surprising. The absence of fluoride transfer in reaction 3, while observed in reaction 4, is likewise unexpected.

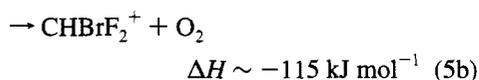
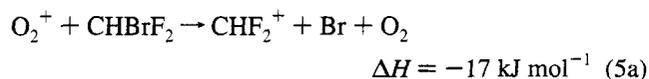
There are no experimental values for the heats of formation of  $\text{CF}_3\text{CHF}_2$  and  $\text{CF}_3\text{CHFCH}_2$ . For  $\text{CF}_3\text{CHF}_2$ , we estimate a value by interpolating differences in heats of formation of similar compounds when F is substituted for  $\text{CF}_3$ ; the difference in heat of formation for  $\text{CF}_3\text{CF}_2\text{CF}_3$  vs  $\text{CF}_3\text{CF}_3$  is  $440 \text{ kJ mol}^{-1}$  and that for  $\text{CF}_3\text{CH}_2\text{CF}_3$  vs  $\text{CF}_3\text{CH}_2\text{F}$  is  $510 \text{ kJ mol}^{-1}$ , with an average  $\text{CF}_3/\text{F}$  difference of  $475 \text{ kJ mol}^{-1}$  for these two cases. Then, using the known heat of formation for  $\text{CF}_3\text{CHF}_2$  of  $-1105 \text{ kJ mol}^{-1}$ , substitution of  $\text{CF}_3$  for F implies a heat of formation for  $\text{CF}_3\text{CFHCF}_3$  of  $-1580 \text{ kJ mol}^{-1}$ . Alternatively, we may derive it by interpolating  $\text{CF}_3/\text{H}$  differences using  $\text{CF}_3\text{CF}_2\text{CF}_3$  vs  $\text{CF}_3\text{CHF}_2$  ( $679 \text{ kJ mol}^{-1}$ ) and  $\text{CF}_3\text{CH}_2\text{CF}_3$  vs  $\text{CF}_3\text{CH}_3$  ( $660 \text{ kJ mol}^{-1}$ ), which yields an average  $\text{CF}_3/\text{H}$  difference of  $670 \text{ kJ mol}^{-1}$ . Imposing this difference on the substitution of  $\text{CF}_3$  for H in  $\text{CF}_3\text{CH}_2\text{F}$  whose heat of formation is known to be  $-896 \text{ kJ mol}^{-1}$ , we derive a value of  $-1566 \text{ kJ mol}^{-1}$  for the heat of formation of  $\text{CF}_3\text{CHF}_2$ . Finally, we take the average of the two values derived by the two methods to arrive at a best estimate of  $-1573 \pm 40 \text{ kJ mol}^{-1}$ .

For  $\text{CF}_3\text{CHFCH}_2$ , we use the heat of formation for  $\text{CF}_3\text{CHF}_2$  derived above and data for other fluorinated species under the assumption of thermoneutrality for the reaction  $\text{CF}_3\text{CHFCH}_2 + \text{RCHF}_2 \rightarrow \text{CF}_3\text{CHFCH}_2 + \text{RCF}_3$  for  $\text{R} = \text{CF}_3$ ,  $\text{CH}_2\text{F}$ , and  $\text{CH}_3$ . We obtain, respectively,  $-1334$ ,  $-1368$ , and  $-1324 \text{ kJ mol}^{-1}$  for the heat of formation of  $\text{CF}_3\text{CHFCH}_2$ , with an average "best" estimate of  $-1342 \pm 30 \text{ kJ mol}^{-1}$ .

Reaction channel 4c appears to result from fluoride transfer; in this case the product ion would have the structure  $\text{CF}_3\text{CHFCH}_2^+$ . The thermochemistry for this ion is formally derived from the proton affinity of  $\text{CF}_3\text{CFCH}_2$ , but neither this proton affinity nor the heat of formation of  $\text{CF}_3\text{CFCH}_2$  are known. The heat of formation of  $\text{CF}_3\text{CFCH}_2$  is consistently estimated as  $-959 \text{ kJ mol}^{-1}$  by assuming thermoneutrality for the following H/F exchange reactions:  $\text{CF}_3\text{CF}_2\text{CF}_3 + \text{CHFCH}_2 \rightarrow \text{CF}_3\text{CFCH}_2 + \text{CF}_2\text{CHF}$  and  $\text{CF}_3\text{CH}_2\text{CF}_3 + \text{CHFCH}_2 \rightarrow \text{CF}_3\text{CFCH}_2 + \text{CH}_2\text{CF}_2$ . The differences between proton affinities of  $\text{CF}_3\text{CFCH}_2$  and  $\text{CF}_3\text{CH}_2\text{CF}_3$  are generally small.<sup>24</sup> From the experimentally determined proton affinity of  $\text{CF}_2\text{CHF}$  ( $707 \text{ kJ mol}^{-1}$ ) and  $\Delta_f H(\text{H}^+)$  and the estimated  $\Delta_f H(\text{CF}_3\text{CFCH}_2)$ , we derive  $\Delta_f H(\text{CF}_3\text{CHFCH}_2^+) = -136 \text{ kJ mol}^{-1}$ . There are also the isomers  $\text{CF}_3\text{CH}^+\text{CHF}_2$  and  $\text{CF}_3\text{CH}_2\text{CF}_2^+$ , similarly derived by protonating  $\text{CF}_3\text{CHCF}_2$ ; a value of  $-186 \text{ kJ mol}^{-1}$  is estimated for the heat of formation of both of these isomers, leading to a minimum exothermicity of  $248 \text{ kJ mol}^{-1}$  for reaction 4c.

**B. Reactions of  $\text{O}_2^+$ .** Table 2 lists the results for the  $\text{O}_2^+$  ion. The reactivity of  $\text{O}_2^+$  with the four neutrals varies considerably.

For  $\text{CHBrF}_2$ , the reaction proceeds at the collisional rate by dissociative and nondissociative charge transfer.



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  $115 \text{ kJ mol}^{-1}$  exothermicity for charge transfer (reaction 5b) is estimated by assuming a value of  $10.9 \text{ eV}$  for the ionization potential (IP) of  $\text{CHBrF}_2$  based

on IP's of similar molecules. The analogous PFC case,  $\text{O}_2^+ + \text{CF}_4$ , is unreactive at thermal energy,<sup>4</sup> and here, charge transfer would be endothermic. The chemistry of reaction 5 differs from that of  $\text{O}_2^+$  with  $\text{CHClF}_2$ , which is slower than collisional and produces  $\text{CF}_2\text{Cl}^+$  (74%) and  $\text{CHF}_2^+$  (26%).<sup>25</sup> The nondissociative charge transfer reported here for  $\text{CHBrF}_2$  was not observed in the  $\text{CHClF}_2$  study<sup>25</sup> in spite of the fact that the C-Cl bond is stronger than the C-Br bond. If the reported  $\text{CF}_2\text{Cl}^+$  product were in fact  $\text{CHClF}_2^+$  (1 amu difference in mass), then those results would be consistent with the present data.

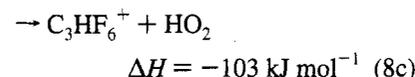
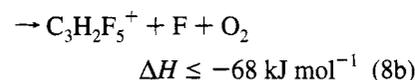
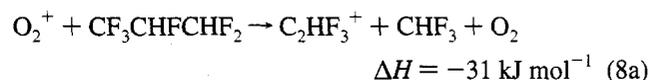
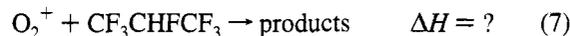
The reaction of  $\text{O}_2^+$  with  $\text{CF}_3\text{CH}_2\text{F}$  proceeds exclusively by slow association.



The bond strength for this ion-molecule cluster is not known. The corresponding PFC system ( $\text{O}_2^+ + \text{C}_2\text{F}_6$ ) showed no association within experimental uncertainty,<sup>4</sup> which is not surprising since  $\text{C}_2\text{F}_6$  has no dipole moment.

The results for reaction 6 were found to depend on whether  $\text{CO}_2$  quenching gas was added to the reaction region (to relax vibrationally excited  $\text{O}_2^+$ ; see Experimental Section). Without  $\text{CO}_2$  added, curvature was seen in the normally linear pseudo-first-order kinetics plot of logarithm of  $\text{O}_2^+$  signal vs added  $\text{CF}_3\text{CH}_2\text{F}$  flow rate, and an additional ionic product  $\text{C}_2\text{H}_2\text{F}_3^+$  was detected. With sufficient  $\text{CO}_2$  added to quench  $\text{O}_2^+(\nu > 0)$  into the  $\nu = 0$  level, based on the known rate constant for this process, both the curvature and the  $\text{C}_2\text{H}_2\text{F}_3^+$  product were absent. These observations indicate that vibrationally excited  $\text{O}_2^+$  was present and reacts faster with  $\text{CF}_3\text{CH}_2\text{F}$  than does  $\text{O}_2^+(\nu = 0)$ , producing  $\text{C}_2\text{H}_2\text{F}_3^+$ .

The two fluorinated propanes show quite different reactivity.



The reaction of  $\text{O}_2^+$  with  $\text{CF}_3\text{CHF}_2$ , 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  $\text{CF}_3\text{CHF}_2$  was  $\text{C}_2\text{F}_3^+$ , a product pathway which is highly endothermic ( $>250 \text{ kJ mol}^{-1}$ ) for all conceivable combinations of neutral products. The most likely explanation is that the  $\text{C}_2\text{F}_3^+$  product is in fact due to an impurity in the  $\text{CF}_3\text{CHF}_2$  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 ( $k_7 \leq 1.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) since no ionic products which could be attributed to the reaction were detected. The results for reaction 7 were independent of whether or not  $\text{CO}_2$  quenching gas was added.

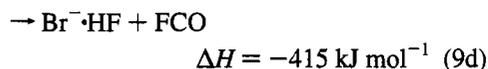
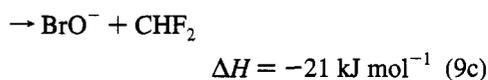
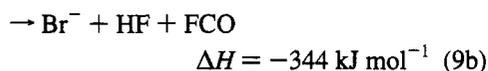
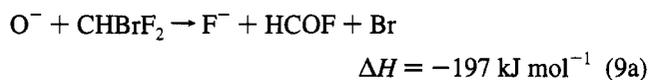
The reaction of  $\text{O}_2^+$  with  $\text{CF}_3\text{CHFCH}_2$  (reaction 8) is at least 30 times faster than reaction 7, and it proceeds by three different pathways. The fluoride transfer channel (8b) results in formation of either  $\text{FO}_2$  or  $\text{F} + \text{O}_2$ , both of which are exothermic pathways. Reaction 8b is exothermic by at least  $68 \text{ kJ mol}^{-1}$  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  $-291 \text{ kJ mol}^{-1}$  from the measured proton affinity of  $CF_2CHF$  and by noting that  $CF_3$  substitution for F decreases proton affinities by about  $38 \text{ kJ mol}^{-1}$ .<sup>24</sup> Formation of separated  $H + O_2$  in reaction 8c would be endothermic by  $104 \text{ kJ mol}^{-1}$ .

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.

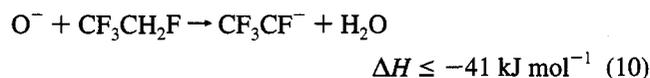
**C. Reactions of  $O^-$ .** Table 3 lists the results for the  $O^-$  ion. All four of the neutrals react at the collisional rate with  $O^-$ , producing a variety of products in most cases.

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



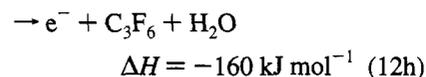
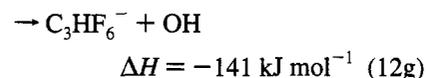
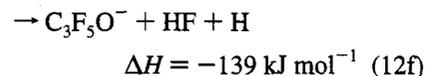
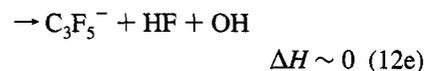
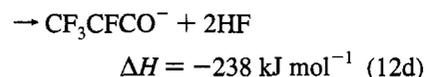
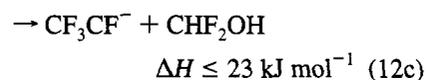
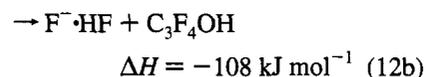
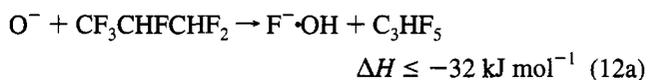
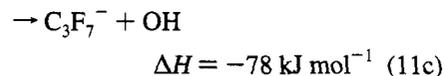
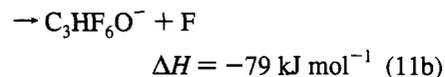
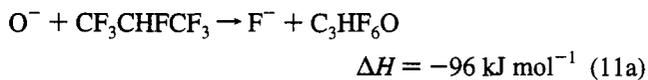
Additional reaction paths are bromine abstraction forming  $BrO^-$  (9c) and formation of the cluster species  $Br^- \cdot HF$  (9d). The latter may be linked to the  $Br^-$  displacement pathway in the following sense. When the initial ion-dipole complex begins to dissociate, it may separate into  $Br^- \cdot HF + FCO$  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  $-101 \text{ kJ mol}^{-1}$ , derived from the measured 2.353 eV electron affinity of  $BrO$ .<sup>26</sup>  $O^-$  is unreactive with  $CF_4$ <sup>27</sup> but does react with  $CH_4$  by hydrogen abstraction,<sup>28</sup> 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  $BrF^-$ .<sup>27</sup>

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  $CF_3CF^- + H_2O$ .



Effective transfer of  $H_2^+$  to  $O^-$  is a well-known process for a variety of organic neutral reactants.<sup>29</sup> 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  $\Delta_f H^-(CF_3CF^-) < 587 \text{ kJ mol}^{-1}$ , which leads to a minimum exothermicity of  $41 \text{ kJ mol}^{-1}$  for reaction 10.  $O^-$  is unreactive with the analogous PFC,  $C_2F_6$ .<sup>4</sup>

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

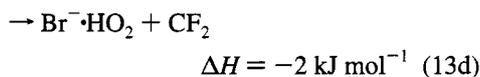
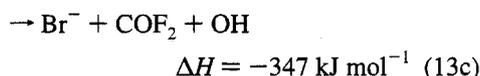
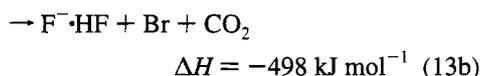
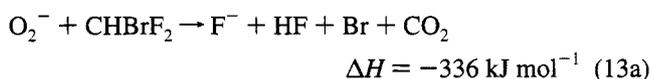


Reactions 11 and 12 have no ionic products in common. However, reaction 11 proceeds mainly by proton transfer, and proton transfer represents the most important pathway in reaction 12 as well (channel 12g). The occurrence of efficient proton transfer in reactions 11 and 12 indicates that the gas-phase 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,  $\Delta H_{acid}$ , than the  $1599 \text{ kJ mol}^{-1}$  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  $25 \text{ kJ mol}^{-1}$  for the increase from  $\Delta_f H(R-F)$  to  $\Delta_f H(R-OH)$ , which is typical for this type of replacement,<sup>30</sup> we derive  $\Delta_f H(n-C_3F_6-OH) = -1312 \text{ kJ mol}^{-1}$ , leading to an exothermicity of  $96 \text{ kJ mol}^{-1}$  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,  $CF_3-CFCHF$ , was estimated (in the discussion of reaction 4) to be  $-959 \text{ kJ mol}^{-1}$ . We estimate  $\Delta_f H(F^{\cdot}OH) = -307 \text{ kJ mol}^{-1}$  by assuming thermoneutrality for the process  $F^{\cdot}H_2O + OH \rightarrow F^{\cdot}OH + H_2O$ , leading to a minimum exothermicity of  $32 \text{ kJ mol}^{-1}$  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  $CF_2CFCHOH$  or  $CF_2C(OH)CF_2$ , which should have nearly identical heats of formation due to offsetting F/OH replacements. In order to estimate  $\Delta_f H(C_3F_4OH)$ , we first estimate  $\Delta_f H(C_3F_5) = -730 \text{ kJ mol}^{-1}$  from the electron affinity of  $C_3F_5$  and from  $\Delta_f H(C_3F_5^-)$ . Then, from the expected  $25 \text{ kJ mol}^{-1}$  increase from  $\Delta_f H(R-F)$  to  $\Delta_f H(R-OH)$  discussed above,<sup>30</sup> we derive  $\Delta_f H(C_3F_4OH) = -705 \text{ kJ mol}^{-1}$  and an exothermicity of  $108 \text{ kJ mol}^{-1}$  for reaction 12b. In reaction 12c, we assume that the neutral product is  $CHF_2OH$ , and using the usual  $25 \text{ kJ mol}^{-1}$  increase in heat of formation in going from  $CHF_3$  to  $CHF_2OH$ , we derive  $\Delta_f H(CHF_2OH) = -670 \text{ kJ mol}^{-1}$ . Combining this with the value for  $\Delta_f H(CF_3CF^-)$  derived for reaction 10, we estimate a minimum exothermicity of  $23 \text{ kJ mol}^{-1}$  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  $-264 \text{ kJ mol}^{-1}$  for  $Br^{\cdot}HO_2$ . This estimate was made by assuming thermoneutrality for the following ligand-switching reaction:  $Br^{\cdot}H_2O + HO_2 \rightarrow Br^{\cdot}HO_2 + H_2O$ .



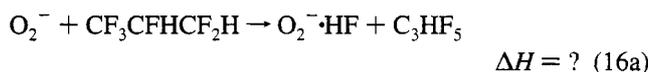
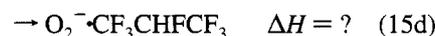
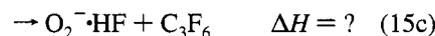
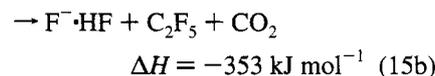
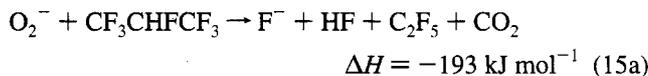
If the small amount of  $F^-$  tentatively identified is a true product, it is likely to arise from dissociation of a portion of the  $F^{\cdot}HF$  produced in reaction 13b.

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



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.



Association (bond strengths unknown) as well as formation of the cluster ion  $O_2^{\cdot}HF$  occur for both  $CF_3CHF_2$  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  $CF_3CHF_2$  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  $148 \text{ kJ mol}^{-1}$ , the energy needed for the dehydrofluorination reaction  $CF_3CHF_2 \rightarrow CF_2CF + HF$ . This may be reconciled by the somewhat large error bars we estimate for the heat of formation of  $CF_3CHF_2$ ,  $40 \text{ kJ mol}^{-1}$ . We also note for comparison that  $F^-$  bonds to HF with an energy of  $161 \text{ kJ mol}^{-1}$ . In channel 16a, an  $O_2^{\cdot}HF$  cluster bond strength of only  $60 \text{ kJ mol}^{-1}$  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  $CF_3CHF_2$  reacts more rapidly than does  $CF_3CHFCHF_2$ . However, association is a smaller contributor to the overall reactivity in the case of  $CF_3CHF_2$ , and the absolute rate constant for association is similarly smaller in this case. The larger rate constant for the overall reactivity of  $CF_3CHF_2$  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  $H_3O^+$ ,  $H_3O^+(H_2O)$ , and  $H_3O^+(H_2O)_2$ .** Table 5 lists the results for the  $H_3O^+$  ion and its hydrates  $H_3O^+(H_2O)$  and  $H_3O^+(H_2O)_2$ . 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  $H_3O^+-HFC$ '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

$\text{CF}_3\text{CHFCHF}_2$  is about 25 times faster than that of  $\text{CF}_3\text{CHFCF}_3$ . While the larger dipole moment of the less symmetric  $\text{CF}_3\text{-CHFCHF}_2$  would be expected to lead to a larger association rate, the factor of 25 is somewhat surprising.

**F. Reactions of  $\text{NO}_3^-$  and  $\text{NO}_3^- \cdot \text{HNO}_3$ .** Table 6 lists the results for  $\text{NO}_3^-$  and  $\text{NO}_3^- \cdot \text{HNO}_3$ . The association product was observed in the  $\text{NO}_3^-$  reactions for all four neutrals, but for  $\text{CHBrF}_2$  and  $\text{CF}_3\text{CH}_2\text{F}$  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  $\text{NO}_3^- \cdot \text{HNO}_3$  cluster ion was unreactive with all four neutrals, as expected since this cluster is expected to be more strongly bound than the  $\text{NO}_3^- \cdot \text{HFC}$  clusters. As was found for  $\text{H}_3\text{O}^+$ , the less symmetric and thus more highly polar  $\text{CF}_3\text{CHFCHF}_2$  reacts by association more rapidly than does  $\text{CF}_3\text{CHFCF}_3$ . Unlike the  $\text{H}_3\text{O}^+$  case, on the other hand, the  $\text{CF}_3\text{CHFCHF}_2$  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  $\text{O}^-$  and  $\text{O}_2^-$  include some interesting cluster ion products. In one case, the reaction of  $\text{O}^-$  with  $\text{CF}_3\text{-CHFCHF}_2$ , eight product channels are observed. The monatomic ions  $\text{O}^+$  and  $\text{O}^-$  are most reactive with the studied neutrals, reacting at the collisional rate within uncertainty in all cases. The less reactive ions  $\text{O}_2^+$ ,  $\text{O}_2^-$ ,  $\text{H}_3\text{O}^+$ , and  $\text{NO}_3^-$  react by association in many cases. The solvated ions  $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2$ , and  $\text{NO}_3^- \cdot \text{HNO}_3$ , 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  $\text{CF}_3\text{CHFCF}_3$  and  $\text{CF}_3\text{-CHFCHF}_2$  to  $\text{O}^-$  allows a lower bound to the gas-phase acidities of these HFC's to be assigned:  $\Delta H_{\text{acid}}(\text{CF}_3\text{CHFCF}_3)$  and  $\Delta H_{\text{acid}}(\text{CF}_3\text{CHFCHF}_2) < 1599 \text{ kJ mol}^{-1}$ .

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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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