Chemistry of H_2O^+ with C_2F_4 , C_2F_6 , and CF_3X (X = F, Cl, Br, I)

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The reactions of H₂O⁺ with CF₄, C₂F₆, C₂F₄, CF₃Cl, CF₃Br, and CF₃I have been studied at 300 and 499 K. The measurements were conducted using a variable-temperature-selected ion flow tube apparatus. H_2O^+ reacts via charge transfer with C_2F_4 with rate constants equal to 1.4×10^{-9} and 1.5×10^{-9} cm³ s⁻¹ at 300 and 499 K, respectively. The reactions with CF₃X (X = Cl, Br, I) all proceed at the collision rate at 300 and 499 K within experimental uncertainty. The rate constants are in the range $1.6 \times 10^{-9} - 2.1 \times 10^{-9}$ cm³ s⁻¹. The reactions of H₂O⁺ with CF₃X produce CF₃⁺ and CF₂X⁺ for X = Cl, Br, I, CF_2OH^+ for X = Cl, Br, and CF_3X^+ for X = Br, I. The reaction with CF_3Cl also forms the ionic product $CF_3OH_2^+$. No reaction was observed between H_2O^+ and the reactant neutrals CF_4 and C_2F_6 ; the rate constants are less than 5×10^{-12} cm³ s⁻¹ at 300 and 499 K. Upper limits to the heats of formation of CF₂Cl⁺, CF₂Br⁺, and CF₂I⁺ have been derived from the data and are <506, <566, and <624 kJ mol⁻¹, respectively.

Introduction

Gaseous halocarbons are used in plasma techniques for microcircuit fabrication. They are employed in chemical techniques such as plasma etching, in physical techniques including ion milling and sputter etching, and in reactive ion etching and reactive ion beam etching, processes which are both physical and chemical in nature.¹ While plasma etching is believed to involve mainly the neutral species in the plasma, these other techniques make use of ions to achieve etching. Despite the long-standing use of these ion techniques for microcircuit fabrication, little is known about the gas-phase ion chemistry of many of the species involved.²

Water is sometimes included intentionally in the feed gas mixture to the plasma to control the etching chemistry.³ Water has been added to a plasma reactor to provide a source of hydrogen in the destruction of waste trichloroethylene.⁴ Water may also be present as a contaminant in plasmas used in semiconductor manufacturing. Small concentrations of water in an Ar plasma have been found to affect dramatically the erosion of Cu electrodes.⁵ Perhaps more significantly, water has been shown to slow and even stop the etching of Si in CF_4/O_2 plasmas.^{6,7} This is believed to be the result of a reduction in the concentration of F atoms when water is present in the plasma.⁶ This leads to a reduction in the F:C ratio which in turn controls the SiO₂:Si etch rate ratio.^{7,8} It has been shown that high SiO₂:Si etch rate ratios can be achieved by adding controlled amounts of water to the reactor.

Because of the paucity of published work on the ion chemistry of halocarbons, we have undertaken a study of reactions of various ions with selected halocarbons. In this article we report the first measurements of the rate constants and product branching fractions for the reactions of H_2O^+ with the halocarbons C_2F_4 , C_2F_6 , and CF_3X (X = F, Cl, Br, I).

Experimental Section

The measurements were made using a variable-temperatureselected ion flow tube apparatus.9 Instruments of this type have been the subject of review,¹⁰ and only those aspects important to the present study will be discussed in detail.

 H_2O^+ ions were produced from water in the ion source by electron impact ionization. The ions were then mass selected in a quadrupole mass filter and injected into the flow tube using a Venturi inlet. The neutral halocarbon reactant was introduced downstream through one of two ring inlets and allowed to react with the ions for a known reaction time ($\sim 2 \text{ ms}$) in a fast flow of He buffer gas maintained at ~ 0.4 Torr. The reactant and product ions were mass analyzed in a second quadrupole mass filter and detected by a channel particle multiplier. Rate constants were extracted from least-squares fits of the plot of logarithm of

the reactant ion signal versus concentration of reactant neutral. The reaction time was determined from ion time-of-flight measurements. For the experiments conducted at 499 K, the temperature of the flow tube was raised using electrical resistance heaters attached to a copper heat exchanger in contact with the flow tube. The accuracy of the measured overall rate constants is $\pm 25\%$, and the relative accuracy is $\pm 15\%$.⁹

Unit mass resolution and accurate mass calibration were necessary to identify unambiguously the product ions, e.g., to distinguish charge transfer from proton transfer. Product masses were identified in separate experiments in which ions of known mass were injected into the flow tube. A mass scan over the range of interest was recorded on a strip chart recorder when the ions of known mass were being injected into the flow tube. Subsequently, H_2O^+ was injected into the flow tube and the neutral reactant added to the flow tube so that the product ions could be detected. The mass scan was repeated and recorded on top of the first scan. For example, the Xe⁺ isotopes were injected in order to calibrate the product ion masses near 130 Da in the reaction of H_2O^+ with CF_3Br , which turned out to be masses 129 and 131 from the ionic product CF_2Br^+ .

The product branching fractions were determined by recording the product ion count rates as a function of the flow rate of the reactant neutral. Because of complications introduced by secondary reactions of the product ions with the reactant neutral, the reported branching fractions were found by plotting the measured branching fractions versus reactant neutral flow rate and extrapolating the fractions to zero reactant flow. The loss of reactant ion signal with added reactant neutral was approximately equal to the sum of the product ion signals. Therefore no attempt was made to account for the possible effects of either mass discrimination or differing rates of diffusion to the walls by the reactant and product ions. These two effects tend to cancel one another since they both depend on mass but in opposite senses.11

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TABLE I: Rate Constants for the Reactions of H_2O^+ with Several Halocarbons

	rate constant, 10 ⁻⁹ cm ³ s ⁻¹					
reactant neutral	300 K		499 K			
	exptl	collisional ^a	exptl	collisional ^a		
CF ₄	<0.005	1.19	<0.005	1.19		
$C_2 F_6$	<0.005	1.53	<0.005	1.53		
C_2F_4	1.4	1.23	1.5	1.23		
CF ₃ Cl	1.6	1.58	1.6	1.53		
CF ₃ Br	1.8	1.63	1.7	1.56		
CF ₃ I	2.1	2.08	1.9	1.96		

^a Calculated using the method in ref 12.

TABLE II: Product Branching Percentages for the Reactions of H_2O^+ with CF₃X (X = Cl, Br, I)

 $H_2O^+ + CF_3X \rightarrow products$

	Cl		Br		I	
products	300 K	499 K	300 K	499 K	300 K	499 K
$CF_{3}^{+} + H_{2}O + X$	15	53	83	89	73	84
$CF_{1}X^{+} + H_{2}O$	0	0	6	<1	14	9
$CF_{1}OH_{2}^{+} + X$	48	13	0	0	0	0
$CF_{2}X^{+}$ (+ HF + OH)	8	16	5	7	12	7
$CF_{2}OH^{+}$ (+ H, F, X)	30	19	5	4	<2	<1

The reported branching percentages are precise to within 3 percentage points. The absolute uncertainty in the branching measurements is difficult to assess because of the mass-dependent effects mentioned above. The uncertainty is no greater than 30%, which is the largest difference observed between the reactant ion signal loss and the total product ion signal. However, the uncertainty depends upon the masses of the ions being compared and, in general, will be less than 30% since this value results from a comparison of the loss of H_2O^+ reactant ion signal at 18 Da with the sum of the signals from the product ions.

Reactant gases were obtained commercially and used without further purification. The He buffer gas was high-purity grade (99.997%) and was passed through a zeolite trap, cooled by liquid nitrogen, before use. The trap helped to remove impurity H_2O present in the He. H_2O^+ reacts rapidly with H_2O producing $H_3O^{+,2}$ The H_3O^+ signal at the detector was typically less than 5% of the H_2O^+ signal. The H_3O^+ ions did not react rapidly with any of the neutrals under investigation.

Results and Discussion

Rate constants for the reactions studied are presented in Table I. Also included are the collisional rate constants calculated from parameterized trajectory theory calculations.¹² The rate constants for the reactions of H_2O^+ with C_2F_4 and CF_3X (X = Cl, Br, I) are equal to the collision-limiting values at both 300 and 499 K within experimental uncertainty. This is often the case for exothermic ion-molecule reactions. Product branching percentages for the reactions which produced multiple ionic products, i.e., those of H_2O^+ with CF_3X (X = Cl, Br, I), are given in Table II. The neutral products are inferred from mass balance and available thermochemistry and are discussed in more detail below. All thermochemistry is derived from data in the compilation of Lias et al.¹³ unless otherwise noted. The heat of formation of CF_3^+ is taken to be +360.8 kJ mol⁻¹, a revised value published by Fisher and Armentrout.¹⁴

CF₃**CI.** The reaction of H_2O^+ with CF₃Cl was found to produce four different ionic products:

$$H_2O^+ + CF_3Cl \rightarrow CF_3^+ + H_2O + Cl$$

 $\Delta H = -27.4 \text{ kJ mol}^{-1} (1a)$

 \rightarrow CF₂Cl⁺ + HF + OH ΔH = +29.5 kJ mol⁻¹ (see text) (1b)

$$\rightarrow$$
 CF₂OH⁺ + (H,F,Cl) ΔH (see text) (1c)

$$\rightarrow CF_3OH_2^+ + Cl \qquad \Delta H = ? \tag{1d}$$

Reaction channel 1a, which leads to CF_3^+ , is exothermic only if the neutral products are $H_2O + Cl$. Using published thermochemistry,^{13,15} the channel producing CF_2Cl^+ (1b) is endothermic for all possible neutral product combinations. The least endothermic of these possibilities is the channel leading to $CF_2Cl^+ +$ HF + OH. Formation of the CF_2Cl^+ product with ~8% efficiency at 300 K suggests that this reaction is exothermic or at most 8 kJ mol⁻¹ endothermic. Therefore, the published heat of formation of $CF_2Cl^{+13,15}$ is too large, assuming that the heats of formation of the other species involved in the reaction are known more accurately than is the heat of formation of CF_2Cl^+ . From our data, we can set an upper limit on the heat of formation of CF_2Cl^+ of <506 kJ mol⁻¹.

For channel 1c leading to CF_2OH^+ , two sets of neutral products are energetically possible: HF + Cl (exothermicity of 197 kJ mol⁻¹) and HCl + F (59 kJ mol⁻¹). For this reason, the neutral products for this channel have not been assigned. The final channel (1d), forming $CF_3OH_2^+$, is the major channel at 300 K. The enthalpy of reaction for this channel is not known because the heat of formation of $CF_3OH_2^+$ is not known, but the observation of this very efficient reaction channel indicates that the heat of formation of $CF_3OH_2^+$ is <144 kJ mol⁻¹. It is interesting to note that nondissociative charge transfer, producing CF_3Cl^+ , is not observed, despite a 22 kJ mol⁻¹ exothermicity, while nondissociative charge transfer was observed for the reactions of H_2O^+ with CF_3Br , CF_3I , and C_2F_4 , as discussed below.

The temperature dependence of the product branching fractions is shown in Table II. Interestingly, although the major product changes from $CF_3OH_2^+$ at 300 K to CF_3^+ at 499 K, the sum of the branching fractions for these two products is independent of temperature within experimental uncertainty. Similarly, the sum of the CF_2Cl^+ and CF_2OH^+ products is essentially invariant with temperature. The apparent correlation of these branching fractions suggests that, for each of these product pairs, the two products are linked in the reaction mechanism. This feature of the data will be discussed later in the paper.

CF₃Br. The reaction of H_2O^+ with CF₃Br produces four ionic products, three of which are the same as or are analogous to products observed for the CF₃Cl reaction. The fourth product channel, that of charge transfer, was not observed in the reaction of H_2O^+ with CF₃Cl. The product ion CF₃OH₂⁺, the major product at 300 K in the reaction with CF₃Cl, was not observed in the reaction with CF₃Br.

$$H_2O^+ + CF_3Br \rightarrow CF_3^+ + H_2O + Br$$

ΔH = -94.1 kJ mol⁻¹ (2a)

$$\rightarrow CF_2Br^+ + (HF + OH) \qquad \Delta H = ? \qquad (2b)$$

$$\rightarrow$$
 CF₂OH⁺ + (H,F,Br) ΔH (see text) (2c)

$$\rightarrow CF_3Br^+ + H_2O \qquad \Delta H = -117 \text{ kJ mol}^{-1} \qquad (2d)$$

Channel 2a, leading to CF_3^+ , is the major reaction channel and is exothermic only if the neutral products are $H_2O + Br$. Neither the reaction energetics nor the neutral products can be assigned for channel 2b because the heat of formation of CF_2Br^+ is not known. The neutrals HF + OH are given parenthetically because this channel is most exothermic if these are the neutral products. An upper limit to the heat of formation of CF_2Br^+ of <566 kJ mol⁻¹ is derived from the observed rate for this channel and from published thermochemistry.¹³

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As in the CF₃Cl reaction, the channel leading to CF_2OH^+ (2c) is exothermic for two possible sets of neutral products: HF + Br (exothermicity = 267 kJ mol^{-1}) and HBr + F (63 kJ mol^{-1}). The charge-transfer channel (2d) is observed at 300 K but not at 499 K. The decrease in this channel upon raising the temperature from 300 to 499 K was accompanied by an increase of equal magnitude in the channel leading to CF_3^+ . Such a correlation of branching fractions can indicate a coupling of these two channels in the reaction mechanism. We note also that the sum of the branching fraction for the two products CF_2Br^+ and CF_2OH^+ is approximately constant over the temperature range studied. These aspects of the data will be discussed in more detail later in the paper.

 CF_3I . The reaction of H_2O^+ with CF_3I forms three ionic products analogous to products observed for the CF₃Br reaction. No CF_2OH^+ is formed in this reaction although this ion is produced in the reactions of H_2O^+ with CF_3Cl and CF_3Br .

$$H_2O^+ + CF_3I \rightarrow CF_3^+ + H_2O + I \qquad \Delta H = -159 \text{ kJ mol}^{-1}$$
(3a)

+
$$CF_2I^+$$
 + (HF + OH) $\Delta H = ?$ (3b)

$$\rightarrow CF_3I^+ + H_2O \qquad \Delta H = -230 \text{ kJ mol}^{-1} \qquad (3c)$$

As also noted for the reactions of H_2O^+ with CF_3Cl and CF_3Br , formation of CF_3^+ is exothermic only if the neutral products are water and the halogen atom. No value for the heat of formation of CF_2I^+ has been published, and therefore the energetics and neutral products cannot be assigned. Using the measured rate for this channel and the available thermochemistry,¹³ we derive an upper limit to the heat of formation for CF_2I^+ of <624 kJ mol⁻¹.

The observation of the highly exothermic charge-transfer channel (3c) is somewhat surprising since other energetically allowed dissociative channels could better dissipate the large heat of reaction. It is possible that the CF_3I^+ is produced in an excited state which is closer to being in energy resonance with the recombination energy of the H_2O^+ reactant ion, 12.61 eV. The higher energy spin-orbit ${}^{2}E_{1/2}$ state of CF₃I⁺ lies only 0.73 eV above the ground ${}^{2}E_{3/2}$ state giving it an ionization potential of 10.96 eV.¹⁶ However, the ${}^{2}A_{1}$ excited state of CF₃I⁺ shows an onset in the photoelectron spectrum at approximately 12.6 eV and a maximum at 13.25 eV.¹⁶ Therefore, it is possible that this state is formed by near-resonant charge transfer.

 C_2F_4 . The H_2O^+ ion reacts with tetrafluoroethylene by nondissociative charge transfer.

$$H_2O^+ + C_2F_4 \rightarrow C_2F_4^+ + H_2O \qquad \Delta H = -242 \text{ kJ mol}^{-1}$$
 (4)

The unit efficiency of this highly exothermic nondissociative charge-transfer reaction suggests that the number of internal degrees of freedom in the products may be sufficient to incorporate most of the excess energy. At least two other less exothermic pathways exist for this system, but formation of the products requires extensive rearrangement. In an analogous reaction, that of H_2O^+ with ethylene, proton transfer¹⁷ is observed in addition to nondissociative charge transfer.^{17,18}

 CF_4 and C_2F_6 . H_2O^+ is unreactive toward the perfluoroalkanes CF_4 and C_2F_6 at both 300 and 499 K. The rate constants are less than 5×10^{-12} cm³ s⁻¹ at 300 and 499 K. The lack of reactivity with CF_4 is due to a lack of exothermic reaction channels.

The reactivity of H_2O^+ toward the analogous alkanes is very different. H_2O^+ reacts rapidly with both CH_4^{17-19} and $C_2H_6^{20}$, primarily by hydrogen atom abstraction. While there are exothermic pathways for the alkane reactions,¹³ there may not be for those of the perfluoroalkanes. Fluorine abstraction by H_2O^+ is endothermic by 234 and 210 kJ mol⁻¹ for CF_4 and C_2F_6 , respectively, on the basis of an estimated heat of formation for FH_2O^+ of 735 kJ mol⁻¹. The heat of formation of FH_2O^+ was estimated by assuming the proton affinity of HOF is the same as that of H_2O . The uncertainty in this estimate is not great enough to cause the heat of reaction to change sign.

Trends in the Series of Halides. Both the measured and the collisional¹² rate constants for the reactions of H₂O⁺ with CF₃X (X = Cl, Br, I) increase with increasing molecular weight of CF_3X as expected from the increasing values of molecular polarizability and the dipole moment of CF_3X with heavier X. The contribution by nondissociative charge transfer to the total products also increases in this series for heavier X. While this process is exothermic for X = Cl, Br, and I, it was not observed for CF_3Cl , was observed only at 300 K for CF₃Br, and was observed at both 300 and 499 K for CF₃I. The contribution by charge transfer, where observable, increases with increasing reaction exothermicity and decreases with increasing temperature (see Table II).

The decrease of nondissociative charge transfer with temperature in the reactions with CF_3Br and CF_3I is compensated by an increase in the dissociative pathway forming $CF_3^+ + H_2O +$ Br(I). This correlation can be explained if reaction is initiated by charge transfer (see discussion of mechanism below). After initial charge transfer, some fraction of the charge-transfer product ions will dissociate, and this fraction will increase as the temperature or internal energy of the reactants and products is increased.

The observed trend of increasing formation of CF_3X^+ with increasing exothermicity of this channel seems to contradict this explanation at first glance but is consistent with this picture when one considers the different bond energies involved. Electron impact ionization and dissociation studies^{21,22} of CF_3X have shown that the abundance ratio of CF_3X^+ to CF_3^+ increases from CF_3Cl to CF_3Br to CF_3I , a similar trend to that in the present data. Using photoionization, Noutary²³ found that the relative abundance of CF_3I^+ is larger than that of CF_3Br^+ . The photoionization data reveal that the increase in yields of CF_3Cl^+ , ^{24,25} CF_3Br^+ , ^{21,22,26} and CF₃I⁺²⁷ with increasing photon energy is promptly interrupted at the onset of CF_3^+ production, indicating that the formation of the parent molecular ion is favored only within a narrow range of energies. This range of energies is the gap between the ionization potential of CF_3X and the appearance potential of CF_3^+ from \hat{CF}_3X and is larger for CF_3I than for \hat{CF}_3Br , which is in turn larger than that for $CF_3Cl^{23,24,26,27}$ This energy gap is related to the bond dissociation energy for CF_3^+ -X, where X is the halogen atom, and these data indicate that this bond energy increases as the halogen atom is changed from Cl to Br to I. The increase in nondissociative charge transfer in the reactions of H_2O^+ with CF_3X in the series X = Cl, Br, I observed in our work may simply reflect the increasing bond energy. As mentioned above, if the reaction is initiated by charge transfer, the fraction of chargetransfer products which dissociate will decrease as the CF_3^+ -X bond energy increases; i.e., the nondissociative charge-transfer channel will become relatively more efficient as is observed.

Nondissociative charge transfer is not observed in the reaction with CF_3Cl presumably because the CF_3^+ -Cl bond is too weak. We note that, according to the most recent published thermochemistry,^{13,14} the CF₃⁺-Cl bond dissociation energy is nearly zero; the value is actually negative, -2.9 kJ mol^{-1} . However, CF₃Cl⁺ is a stable/bound species, at least on the time scale of the photoionization mass spectrometer experiments.^{23-25,28} It is likely

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$$\begin{array}{c} H_2O^{+} + CF_3X \\ \downarrow \\ [H_2O^{+} + CF_3X] \\ \downarrow \\ CF_3X^{+} + H_2O \leftarrow [H_2O + CF_3-X^{+}] \rightarrow CF_3X^{+} + H_2O \\ \downarrow \\ CF_2X^{+} + H_2O + F \leftarrow [CF_2X^{+} + H_2O + F] [CF_3^{+} + H_2O + X] \rightarrow CF_3^{+} + H_2O + X \\ \downarrow \uparrow \\ \downarrow \uparrow \\ [CF_2X^{+} + OH + HF] [CF_2XOH_2^{+} + F] [CF_3OH_2^{+} + X] \rightarrow CF_3OH_2^{+} + X \\ \downarrow \\ CF_2X^{+} + OH + HF \\ [CF_2OH^{+} + HF + X] \\ \downarrow \\ CF_2OH^{+} + HF + X \end{array}$$

Figure 1. Proposed reaction mechanism for the reactions of H_2O^+ with CF₃X (X = Cl, Br, I).

that the problem with the bond energy arises from the relative heats of formation of CF_3Cl^+ and CF_3^+ . More specifically, the ionization potential of CF_3Cl was obtained from photoionization mass spectrometry^{13,23,24,28} while the heat of formation of CF_3^+ was derived from guided ion beam measurements¹⁴ of the threshold energy for production of CF_3^+ in the reaction of Kr^+ ($^2P_{3/2}$) with CF_4 . The current value¹⁴ for the heat of formation of CF_3^+ represents a 38 kJ mol⁻¹ reduction of the previous value²⁹ obtained from a photoelectron-photoion coincidence study of CF_3I .

The contribution by the channel leading to CF_2OH^+ decreases with heavier X and with increasing temperature. No obvious trend in the CF_3X series was observed for the branching fraction to produce CF_2X^+ .

Mechanism for $H_2O^+ + CF_3X$. A general mechanism for the reactions of H_2O^+ with CF_3X (X = Cl, Br, I) is proposed and shown schematically in Figure 1. According to the postulated mechanism, an initial ion-dipole complex is formed by the mutual capture of the reactant particles. An electron is then transferred (possibly at long range) from CF_3X to H_2O^+ to form the second complex, $[H_2O + CF_3X^+]$. According to photoelectron spectroscopic data, 16,25,30-32 the electron is removed from the lone pair on X. This complex may lead directly to the charge-transfer product, CF_3X^+ . The charge-transfer product may possess enough energy to decompose into either CF3+ or CF2X+ plus the associated halogen atom before or after separation of the complex. Decomposition of excited CF_3X^+ into CF_3^+ (and to some extent into CF_2X^+) is evident in the photoionization mass spectra.^{23-25,27} Decomposition within the complex will lead to either of two subsequent complexes in which either F or X is lost from the parent ion. Separation of the species in these complexes leads to the products CF_2X^+ or CF_3^+ , respectively. Before separation, a fraction of these ions may add to H₂O, leading to formation of $CF_2XOH_2^+$ and $CF_3OH_2^+$, respectively. The complex containing $CF_3OH_2^+$ may simply separate into products while the complex containing $CF_2XOH_2^+$ eliminates HX to produce CF_2OH^+ . We do not know the details of this elimination so we have written the neutral products as HF + X because this is the most exothermic pathway. Similarly, since the neutral products are not known for the channel(s) producing CF_2X^+ , we have allowed for the two most likely possibilities in the mechanism, formation of $CF_2X^+ + H_2O$ + F and CF_2X^+ + OH + HF.

One possibility not included in the mechanism is that the $CF_3OH_2^+$ product could be formed directly from the complex $[H_2O + CF_3Cl^+]$ by nucleophilic displacement. The proposed

mechanism also does not include the possibility that some of the charge transfers occur at long distances, either before or without formation of the initial ion-dipole complex. The present data do not address the likelihood of these possibilities.

The proposed mechanism can explain some of the experimental observations. It was noted earlier that the branching fractions for formation of CF₃⁺ and CF₃OH₂⁺ in the CF₃Cl reaction appeared coupled in that the decrease in the $CF_3OH_2^+$ abundance with higher temperature was matched by an increase in the CF_3^+ abundance. Similarly, the CF_2X^+ and CF_2OH^+ products appeared to be coupled. In the mechanism, $CF_3OH_2^+$ is formed from CF_3^+ and its associated neutrals and CF_2OH^+ is formed from CF_2X^+ and its associated neutrals. For both pairs of coupled ions, the branching fraction for the species which appears earliest in the reaction mechanism increases with increasing temperature; i.e., increased energy results in a relatively rapid separation of the first-formed ion and associated neutrals into products as compared with rearrangement to form another complex. The constant value for the sum of the branching fractions within these pairs of product ions with temperature suggests that once the fragmentation pathway (loss of F or X) has been made in this reaction, there is little (if any) chance of returning to the charge-transfer ion to change that pathway. The data are also consistent with the possibility of the $CF_3OH_2^+$ product ion decomposing into CF_3^+ and H₂O.

For the reactions with CF_3Br and CF_3I , the decrease in CF_3X^+ production at higher temperature with concomitant increase in CF_3^+ abundance is consistent with increased fragmentation of CF_3X^+ directly or in the complex $[H_2O + CF_3X^+]$ as the internal and translational energy of the reactants increases. Similarly, decreasing production of $CF_3OH_2^+$ and CF_2OH^+ with increasing molecular weight of CF_3X is consistent with the fact that the channels preceding them in the reaction mechanism increase in exothermicity with heavier CF_3X . Dissociation of the complex would occur before these two products could be formed.

Summary

The reactions of H_2O^+ with the halocarbons CF_3X (X = Cl, Br, I) and C_2F_4 proceed at the collision rate at both 300 and 499 K. The neutrals CF_4 and C_2F_6 are unreactive with H_2O^+ at 300 and 499 K within experimental sensitivity. While the reaction of H_2O^+ with C_2F_4 involves only nondissociative charge transfer, the reactions with CF_3X exhibit a number of product channels, some of which depend strongly on temperature. The temperature dependences of the product branching fractions indicate that some of the product channels are coupled. The contribution by nondissociative charge transfer to CF_3X increases for heavier X, consistent with trends observed in published studies of the ionization and dissociation of CF_3X .

There is a need for reliable heats of formation for a number of simple halogenated carbocations, including CF_2X^+ and $CF_3OH_2^+$. Observation of the production of CF_2Cl^+ , with a rate constant on the order of 2×10^{-10} cm³ s⁻¹, from the reaction H_2O^+ + CF_3Cl indicates that the published heat of formation of CF_2Cl^+ should be lowered to a revised limit of <506 kJ mol⁻¹. Similarly, the observed rate constants for production of CF_2Br^+ from CF_3Br and of CF_2I^+ from CF_3I lead to derived upper limits for the heats of formation of CF_2Br^+ and CF_2I^+ of <566 and <624 kJ mol⁻¹, respectively. Finally, the high reactivity of H_2O^+ with some of the halocarbons studied indicates the potential importance of these reactions in certain halocarbon plasmas containing H_2O .

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Registry No. H_2O^+ , 56583-62-1; CF_4 , 75-73-0; C_2F_6 , 76-16-4; C_2F_4 , 116-14-3; CF_3Cl , 75-72-9; CF_3Br , 75-63-8; CF_3I , 2314-97-8; chlorodifluoromethylium, 40640-71-9; bromodifluoromethylium, 67000-50-4; difluoroiodomethylium, 96607-14-6.