J. Phys. Chem. A **1997,** *101,* 8489−8495

Reactions of H_3O^+ and H_2O^+ with Several Fully Halogenated Bromomethanes

R. D. Thomas,[†] R. A. Kennedy,*[‡] C. A. Mayhew,[†] and P. Watts[§]

Chemical Physics Laboratory, School of Physics and Space Research, University of Birmingham, School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K., and PLSD, CBD, Porton Down, Salisbury, Wiltshire SP4 0JQ, U.K.

Received: June 16, 1997[⊗]

The bimolecular rate coefficients and ion products for the reactions of H_3O^+ and H_2O^+ with the bromine-containing molecules CF_3Br, CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ at 300 K are reported. With the exception of the reactions of H_3O^+ with CF_3Br and CF_2BrCl, the rate coefficients are near the collisional values ($k \approx 10^{-9}$ cm^3 molecule^{-1} s^{-1}). The most efficient exit pathway for the majority of the H_3O^+ reactions is the formation of a trihalomethyl cation, together with water and a hydrogen halide as the neutral products. In each case, more than one trihalomethyl cation can be formed. The branching ratios are largest for the products resulting from the breaking of a C−F bond. This is attributed to the high bond strength of HF relative to HCl and HBr. Similarly for $CBrCl_3$, the major product cation is CCl_2Br^+. The H_2O^+ reactions are found to proceed predominantly via charge transfer. For the reaction of H_2O^+ with CF_3Br there is clear evidence for intimate reaction pathways in which bonds are broken and formed.

Introduction

The monitoring of atmospheric concentrations of chlorofluorocarbons (CFCs) and their replacements, the perfluorocarbons (PFCs), the hydrofluorocarbons (HFCs), and the hydrochlorofluorocarbons (HCFCs) has in the past few years taken on great importance. This is due to the adverse effects some of these molecules have in the atmosphere. Depletion of the ozone layer is intimately linked to increased atmospheric concentrations of CFCs. The PFCs, HFCs, and HCFCs are significant greenhouse gases. Gaseous ions can be used as powerful probes for the purposes of monitoring these halogenated compounds. This in part, together with growing interest in atmospheric ion chemistry, has led to much attention being paid to the ion−molecule reactions of CFCs, PFCs, HFCs, and HCFCs with various cations.[1−5] Little attention has been given to their brominated equivalents, yet the presence of bromine in the stratosphere can, like chlorine, lead to the catalytic destruction of stratospheric ozone. Although bromine compounds are present in the atmosphere in much smaller quantities than their CFC equivalents, bromine (atom for atom) leads to a much higher destruction of ozone than chlorine.[6,7]

In this article we present the first results from a much larger study of the reactions of a series of cations with a large number of bromocarbons. Here, we concentrate on the reactions of H_3O^+ and H_2O^+ with the bromomethanes CF_3Br, CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$. The interest in the H_3O^+ and H_2O^+ reactant ions is twofold. First, H_3O^+ and H_2O^+ are important atmospheric cations. Second, the reaction chemistry involved will be very different for the two ions, and it was primarily for this reason that the study was undertaken. H_2O^+ can react by charge transfer nondissociatively ($H_2O^+ + BC \rightarrow BC^+ + H_2O$) and/or dissociatively ($H_2O^+ + BC \rightarrow B^+ + C + H_2O$). H_3O^+ cannot react via either of these processes because its recombination energy is far below the ionization potentials of any of the neutral reagents. Therefore, a reaction with an H_3O^+ ion requires an ion−molecule complex to be first formed. Charge transfer does not require such a complex and can occur by a long-range process.

To our knowledge, of the ion−molecule reactions reported here, only one has been previously investigated and reported. Morris et al.[3] have studied the reaction of H_2O^+ with CF_3Br, and our results are in good agreement with their values of the reaction rate coefficient and branching ratios.

Experimental Details

This study was carried out using a selected ion flow tube (SIFT) apparatus. The SIFT technique and the analysis of the data to obtain product ion distributions and reaction rate coefficients have been described in detail by Smith and Adams.[8] Therefore, only a few points pertinent to the present study will be mentioned here. Ions were generated in an enclosed high-pressure electron impact ion source. H_2O was used to create both the ions: H_2O^+ via primary ionization and H_3O^+ via proton transfer from H_2O^+ to H_2O. The reactant ions were mass selected by a quadrupole mass filter and then injected into a fast flowing (~150 Torr L s^{-1}) helium buffer gas (0.5 Torr) where they were collisionally thermalized to 300 K. Measured quantities of the neutral reactant of interest were introduced into the carrier gas/reactant ion flow downstream from the ion inlet. All the reactant samples, CF_3Br, CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$, were obtained commercially. CF_2Br_2 and $CFBr_2Cl$ have stated purities of 97% and 90%, respectively. CF_3Br, $CFBr_3$, and $CBrCl_3$ have stated purities of 99%. The purity of the sample of CF_2BrCl was not reported by the supplier. CF_2Br_2, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ are liquids at room temperature and therefore prior to use were subjected to several freeze−pump−thaw cycles to remove dissolved gases.

Parent and product ions enter a second quadrupole mass filter where they are detected by a channeltron electron multiplier. The product ion distribution and reaction rate coefficient are obtained by relating the neutral flow rate to the product ion and reactant ion count rates, respectively. The accuracy of the measured reaction rate coefficients is ±20%. The mass discrimination of the detection system was taken into account in the usual way.[9]

A key aspect of the SIFT technique is the injection of mass-selected ions of a given single *m*/*e* ratio into the flow tube. This

---

[*] Corresponding author. E-mail: R.A.Kennedy@bham.ac.uk. Fax: 0121 414 3722.

[†] School of Physics and Space Research.

[‡] School of Chemistry.

[§] Porton Down.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5639(97)01962-2 CCC: $14.00

TABLE 1: Total Reaction Rate Coefficients, the Product Ions, and the Branching Percentages for the Reactions of H_3O^+ and H_2O^+ with CF_3Br, CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ at 300 K

	CF_3Br (IP = 11.40)[a]	CF_2Br_2 (IP = 11.07)[a]	CF_2BrCl (IP = 11.21)[a,b]	$CFBr_3$ (IP = 10.67)[a]	$CFBr_2Cl$ (IP = 10.87)[a,c]	$CBrCl_3$ (IP = 10.60)[a]
			Reaction of H_3O^+			
k_{exp}[d]		1.23	0.254	1.78	1.64	1.84
k_c[d,e]	1.72	1.90				1.99
product ions[f]		$CFBr_2^+$ (73) $CFBr_2^+{\cdot}H_2O$ (23) $CF_2Br^+{\cdot}H_2O$ (4)	$CFBrCl^+$ (55) $CFBrCl^+{\cdot}H_2O$ (42) $CF_2BrCl{\cdot}H_3O^+$ (3)	CBr_3^+ (90) $CFBr_2^+$ (10)	CBr_2Cl^+ (96) $CFBr_2^+$ (4)	CCl_2Br^+ (70) CCl_3^+ (30)
			Reaction of H_2O^+			
k_{exp}[d]	1.56	1.69	1.72	1.78	1.74	2.06
k_c[d,e]	1.76	1.95				2.05
product ions[f]	CF_3^+ (71) CF_2Br^+ (16) CF_3Br^+ (8) CF_2OH^+ (5)	CF_2Br^+ (100)	CF_2Cl^+ (86) $CFBrCl^+$ (8) CF_2Br^+ (6)	$CFBr_2^+$ (100)	$CFBrCl^+$ (97) $CFBr_2^+$ (3)	CCl_3^+ (76) CCl_2Br^+ (24)

[a] Ionization potentials of the neutral molecules are in eV. [b] The value for the ionization potential of CF_2BrCl has been taken from the paper by Wang and Leroi.[14] [c] The ionization potential for $CFBr_2Cl$ was estimated from that of $CFBr_3$ (10.67 eV). Replacing Br by Cl increases the ionization potential by ~0.20 eV, a value obtained by comparing the ionization potentials of the pairs of molecules CF_2Br_2/CF_2BrCl (0.23 eV), CH_2Br_2/CH_2BrCl (0.27 eV), and $CHBr_3/CHBr_2Cl$ (0.11 eV). [d] The reaction rate coefficients (both calculated and experimental) are given in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. The measured rate coefficients and the product ion distributions are considered to be accurate to ±20%. [e] The calculated 300 K collisional reaction rate coefficient is given for those molecules with known polarizabilities and dipole moments. [f] Branching percentages are in parentheses.

was possible for H_3O^+ but not for H_2O^+. Significant quantities of H_3O^+ were produced under the best ion source conditions for H_2O^+ production, and the injection quadrupole mass resolution was not sufficient to reject all the H_3O^+. A smaller additional contribution to the H_3O^+ concentration in the flow tube resulted from the reaction of H_2O^+ with trace water in the helium buffer gas. This was minimized by passing the helium gas through a liquid nitrogen trap. In practice, when tuned to inject H_2O^+, a mixture of 70% H_2O^+ and 30% H_3O^+ was recorded using the second quadrupole mass filter and channeltron electron multiplier. By use of the SIFT results for the reactions of H_3O^+, the ion products of the reactions of H_2O^+ were extracted from the data.

Results and Discussion

The measured rate coefficients (k_{exp}), the product ions, and their branching ratios for all the reactions included in this study are summarized in Table 1. The reactant molecules are listed at the top of the table in order of decreasing fluorination (CF_3Br → $CBrCl_3$), and their ionization potentials are given in brackets below each molecule. Also included in the table are the collisional rate coefficients (k_c) when calculable. These have been determined using the trajectory method.[10] It is clear from Table 1 that, with the exception of the reactions of H_3O^+ with CF_3Br and CF_2BrCl, the measured rate coefficients are close to the expected collisional values.

For the analysis of the reaction pathways, thermochemical data have been taken from Lias et al.[11] and Lide,[12] unless indicated otherwise in the text. Enthalpies of formation of some of the observed ion products have not been reported. The observation of a reaction pathway to one of these ions implies that the enthalpy of the reaction is less than 0, and so this allows the determination of an upper limit to its enthalpy of formation. These upper limits can then be used to place bounds on the enthalpies of other reactions.

For simplicity, in the following discussion "M" will be used to indicate the halogenated methane molecule.

Reactions with H_3O^+. Four reaction pathways need to be considered.

(i) Proton Transfer.

$$H_3O^+ + M \rightarrow MH^+ + H_2O$$

This was not observed with any of the molecules of this study, suggesting that the proton affinities of the molecules are all less than that of H_2O (697 kJ mol^{-1}). Thermodynamic data are available for only one of the protonated molecules—CF_3BrH^+, and for CF_3Br the proton-transfer reaction is endothermic:

$$H_3O^+ + CF_3Br \rightarrow CF_3BrH^+ + H_2O \qquad \Delta H = +112 \text{ kJ mol}^{-1} \quad (1)$$

(ii) Charge Transfer.

$$H_3O^+ + M \rightarrow M^+ + H + H_2O$$

The recombination energy of H_3O^+ ($+ e^- \rightarrow H_2O + H$, 615 kJ $mol^{-1} \equiv 6.37$ eV) is much less than the ionization potential of any of the reactant molecules of this study, and therefore, charge transfer is impossible.

(iii) Attack of H_3O^+ on a Halogen Atom Followed by the Release of Water and the Formation of a Hydrogen Halide.

$$H_3O^+ + M \rightarrow [M-X]^+ + HX + H_2O$$

This is the only pathway observed for $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ and is the predominant pathway for CF_2Br_2 and CF_2BrCl. Only CF_3Br is found to be unreactive with H_3O^+. In Table 2 we list all the channels of this type, together with the reaction enthalpies. Two very different values for the enthalpy of formation of CF_2Br^+ have been reported. A photoionization mass spectrometric (PIMS) study of CF_3Br by Clay et al.[13] yielded a value of $\Delta_fH(CF_2Br^+) = 640$ kJ mol^{-1} at 0 K, while PIMS studies by Wang and Leroi lead to an upper limit of $\Delta_fH(CF_2Br^+) \leq 544$ kJ mol^{-1}.[14] There is no obvious explanation for the large difference between these values. The table contains entries derived from both values. In the construction of Table 2 an estimate for the heat of formation of $CFBr_2Cl$ (-181 ± 10 kJ mol^{-1}) has been taken from an earlier study of ours.[15]

With the exception of the formation of CBr_3^+ from $CFBr_3$, the existing thermodynamic data are consistent with our observations. The enthalpy of formation of CBr_3^+ reported by Lias et al., $\Delta_fH(CBr_3^+) = 1000$ kJ mol^{-1}, appears to be too high. Our results require $\Delta_fH(CBr_3^+) < 869$ kJ mol^{-1}. This and other bounds established from the identification of the product ions are collected in Table 3.

TABLE 2: Ion and Neutral Products and Enthalpies for the Reaction of H_3O^+ with the Bromomethanes Presented in This Study

bromomethane	products	ΔH/kJ mol^{-1}	ion products observed?
CF_2Br_2	$CFBr_2^+ + H_2O + HF$	$\Delta_fH(CFBr_2^+) -726$	yes
	$CF_2Br^+ + H_2O + HBr$	150 or ≤ 54	no
CF_2BrCl	$CFBrCl^+ + H_2O + HF$	$\Delta_fH(CFBrCl^+) - 667$	yes
	$CF_2Br^+ + H_2O + HCl$	153 or ≤ 57	no
	$CF_2Cl^+ + H_2O + HBr$	$\leq 75^a$	no
$CFBr_3$	$CBr_3^+ + H_2O + HF$	$\Delta_fH(CBr_3^+)^b - 869$	yes
	$CFBr_2^+ + H_2O + HBr$	$\Delta_fH(CFBr_2^+) - 633$	yes
$CFBr_2Cl$	$CBr_2Cl^+ + H_2O + HF$	$\Delta_fH(CBr_2Cl^+) - 924$	yes
	$CFBr_2^+ + H_2O + HCl$	$\Delta_fH(CFBr_2^+) - 744$	yes
	$CFBrCl^+ + H_2O + HBr$	$\Delta_fH(CFBrCl^+) - 688$	no
$CBrCl_3$	$CBrCl_2^+ + H_2O + HCl$	$\Delta_fH(CBrCl_2^+) - 882$	yes
	$CCl_3^{+\,c} + H_2O + HBr$	5 ± 7	yes

[a] $\Delta_fH(CF_2Cl^+) \leq 506$ kJ mol^{-1}, taken from Morris et al.,[3] is used in the calculation. [b] CBr_3^+ is observed with a large branching ratio. This is only possible if the heat of formation of CBr_3^+ reported by Lias et al.[11] ($\Delta_fH(CBr_3^+) = 1000$ kJ mol^{-1}) is incorrect (and it should be noted that the heat reported by Lias et al. has been estimated). [c] The heat of formation of CCl_3^+ reported by Lias et al.[11] ($\Delta_fH(CCl_3^+) \approx 831$ kJ mol^{-1}) is between 824 and 837 kJ mol^{-1} owing to the experimental observation of CCl_3^+ from the reaction $H_3O^+ + CFCl_3$ ($\rightarrow CCl_3^+ + H_2O + HF$) and the nonobservation of the reaction *sec*-$C_3H_7^+ + CFCl_3$ ($\rightarrow CCl_3^+ + C_3H_7F$). The observation of CCl_3^+ from the reaction of $H_3O^+ + CCl_3Br$ would seem to indicate that $\Delta_fH(CCl_3^+)$ lies closer to 824 kJ mol^{-1} than to 837 kJ mol^{-1}.

TABLE 3: Thermodynamic Upper Limits Established from the Thermochemistry of the Reported Reactions by Requiring That for Any Observed Reaction $\Delta H < 0$

species	ΔH(300 K)/kJ mol^{-1}
CBr_3^+	≤ 869
$CFBr_2^+$	≤ 633
$CFBrCl^+$	≤ 667
CBr_2Cl^+	≤ 924
CCl_2Br^+	≤ 882

The failure of H_3O^+ to react with CF_3Br is seen to be due to the endothermicity of the dissociative pathways leading to both CF_2Br^+ and CF_3^+. For example,

$$H_3O^+ + CF_3Br \rightarrow CF_2Br^+ + H_2O + HF \qquad \Delta H = +185 \text{ or } \leq 89 \text{ kJ mol}^{-1} \quad (2)$$

is the least endothermic dissociative pathway. The reactions of H_3O^+ with CF_2Br_2, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ have rate coefficients close to the collisional values, so for these systems there is evidently no significant potential barrier on the exit pathway to the trihalomethyl cations. The rate coefficient for H_3O^+ reacting with CF_2BrCl is at least a factor of 5 below any reasonable estimate of the collisional rate coefficient; in this case there must be some barrier to the exothermic pathway:

$$H_3O^+ + CF_2BrCl \rightarrow CFBrCl^+ + H_2O + HF \qquad \Delta H = \Delta_fH(CFBrCl^+) - 667 \text{ kJ mol}^{-1} \quad (3)$$

Only one trihalomethyl cation product is observed from CF_2Br_2 ($CFBr_2^+$) and CF_2BrCl ($CFBrCl^+$), and this is in accord with the available thermochemical data. Where more than one trihalomethyl cation product is observed, the pathways to the different trihalomethyl cations will be similar. On this basis, we suggest that the branching ratios will correlate with the relative exothermicities of the channels. This cannot be tested with the available thermochemical data. However, if this assertion is correct, then the following inequalities can be obtained from our observations.

from $H_3O^+ + CFBr_3$:

$$\Delta_fH(CFBr_2^+) > \Delta_fH(CBr_3^+) - 236 \text{ kJ mol}^{-1}$$

from $H_3O^+ + CFBr_2Cl$:

$$\Delta_fH(CFBr_2^+) > \Delta_fH(CBr_2Cl^+) - 180 \text{ kJ mol}^{-1}$$

and from $H_3O^+ + CBrCl_3$:

$$\Delta_fH(CBrCl_2^+) < 882 \text{ kJ mol}^{-1}$$

The inequalities can also be expressed in terms of bond strengths. Consider, for example, the reaction between H_3O^+ and $CFBr_3$:

$$H_3O^+ + CFBr_3 \rightarrow CBr_3^+ + H_2O + HF \qquad (4a)$$

$$\rightarrow CFBr_2^+ + H_2O + HBr \qquad (4b)$$

$$\Delta H(4b) - \Delta H(4a) = D(CBr_2^+{-}Br) + D(H{-}F) - D(CBr_2^+{-}F) - D(H{-}Br)$$

Channel 4a will be preferred if

$$D(H{-}F) - D(H{-}Br) > D(CBr_2^+{-}F) - D(CBr_2^+{-}Br)$$

The difference between the HF and HBr bond strengths is 204 kJ mol^{-1}. Our observation that channel 4a is preferred implies that

$$D(CBr_2^+{-}F) - D(CBr_2^+{-}Br) < 204 \text{ kJ mol}^{-1}$$

and that the greater difference between the HF and HBr bond strengths compared to the CF and CBr bonds in CBr_2F^+ and CBr_3^+, respectively, is the enthalpic driving force that distinguishes the two channels.

The same analysis can be applied to the product branching ratios for the reaction of H_3O^+ with $CFBr_2Cl$ and with $CBrCl_3$, giving

$$D(CBr_2^+{-}F) - D(CBr_2^+{-}Cl) < 139 \text{ kJ mol}^{-1}$$

$$D(CBrCl^+{-}F) - D(CBrCl^+{-}Br) < 204 \text{ kJ mol}^{-1}$$

$$D(CFBr^+{-}Cl) - D(CFBr^+{-}Br) < 65 \text{ kJ mol}^{-1}$$

and

$$D(CCl_2^+{-}Cl) - D(CCl_2^+{-}Br) < 65 \text{ kJ mol}^{-1}$$

(iv) Other Pathways. Two additional products are observed from the reaction of H_3O^+ with CF_2Br_2:

$$H_3O^+ + CF_2Br_2 \rightarrow CFBr_2^{+}\cdot H_2O + HF \qquad (5a)$$

$$\rightarrow CF_2Br^{+}\cdot H_2O + HBr \qquad (5b)$$

The observation of these ion products supports the proposal that the reactions of H_3O^+ with the bromomethanes proceed via an ion–molecule complex. In the bimolecular pathways, reactions 5a and 5b, the H_2O is not released as the reaction proceeds from the initially formed ion–molecule complex to the products. The binding between the cation and the H_2O increases the exothermicity of the reactions:

$$\Delta H(5a) = \Delta_f H(CFBr_2^{+}) - D(CFBr_2^{+}\cdot H_2O) - 726\ \text{kJ mol}^{-1}$$

$$\Delta H(5b) = -D(CF_2Br^{+}\cdot H_2O) + (150\ \text{or} < 54)\ \text{kJ mol}^{-1}$$

The observation of $CF_2Br^+\cdot H_2O$ is particularly interesting, since bare CF_2Br^+ is not a product of the reaction of H_3O^+ with CF_2Br_2. The binding of the product CF_2Br^+ with H_2O releases sufficient energy to make the pathway to $CF_2Br^+\cdot H_2O$ exothermic, while the pathway to CF_2Br^+ is endothermic:

$$D(CF_2Br^{+}\cdot H_2O) > \Delta_f H(CF_2Br^{+}) - 490\ \text{kJ mol}^{-1}$$

Using the two PIMS values for $\Delta_f H(CF_2Br^+)$ gives either

$$\Delta_f H(CF_2Br^{+}) - 490 = 150\ \text{kJ mol}^{-1}$$

or

$$\Delta_f H(CF_2Br^{+}) - 490 \leq 54\ \text{kJ mol}^{-1}$$

The binding between H_2O and CF_2Br^+ is unlikely to be greater than 150 kJ mol^{-1}. Thus, the detection of $CF_2Br^+\cdot H_2O$ indicates that the best value for $\Delta_f H(CF_2Br^+)$ is the upper bound reported by Wang and Leroi:[14]

$$\Delta_f H(CF_2Br^{+}) \leq 544\ \text{kJ mol}^{-1}$$

This is confirmed by our studies of the reactions of H_2O^+ with CF_3Br (see later) and is in accord with the bound reported by Morris et al., ≤566 kJ mol^{-1}.[3]

In the case of the reaction of H_3O^+ with CF_2BrCl, there are in addition to $CFBrCl^+$ two other ion products. One is due to a bimolecular reaction

$$H_3O^+ + CF_2BrCl \rightarrow CFBrCl^{+}\cdot H_2O + HF$$
$$\Delta H = \Delta_f H(CFBrCl^{+}) - D(CFBrCl^{+}\cdot H_2O) - 667\ \text{kJ mol}^{-1} \qquad (6)$$

The other is due to a three-body associative process:

$$H_3O^+ + CF_2BrCl \xrightarrow{He} CF_2BrCl\cdot H_3O^{+} \qquad (7)$$

Based on our thermochemical analysis for the formation of $CF_2Br^+\cdot H_2O$ from the reaction of H_3O^+ with CF_2Br_2, the pathway

$$H_3O^+ + CF_2BrCl \rightarrow CF_2Br^{+}\cdot H_2O + HCl \qquad (8)$$

is likely to be exothermic, but $CF_2Br^+\cdot H_2O$ was not observed.

The overall reaction between H_3O^+ and CF_2BrCl is relatively slow. There is some barrier to reactive breakup of the intermediate ion–molecule complex. This causes the complex lifetime to be much longer than for the other systems, and a small fraction of the complexes are stabilized by collisions with the helium buffer gas. The resulting association product $CF_2BrCl\cdot H_3O^+$ is a minor product, and no attempt was made to investigate the dependence of the association rate on the helium pressure. With CF_3Br no bimolecular products were observed, and attempts to detect $CF_3Br\cdot H_3O^+$ were unsuccessful. Both kinetic and thermodynamic reasons can be advanced to explain the failure to observe $CF_3Br\cdot H_3O^+$. A kinetic argument is that the initially formed collision complex may break up to CF_3Br and H_3O^+ at a rate much faster than it can be stabilized by collisions with He at 0.5 Torr. Thermodynamically, although the formation of $CF_3Br\cdot H_3O^+$ from CF_3Br and H_3O^+ is exothermic, the process will be opposed by the large decrease in entropy accompanying the association reaction. As a result, the equilibrium (maximum) concentration of $CF_3Br\cdot H_3O^+$ may be too small to be detectable. However, it is curious that association was observed between CF_2BrCl and H_3O^+, but under the same conditions CF_3Br is not observed to associate with H_3O^+.

Reactions with H_2O^+. All the molecules reacted with H_2O^+ with rate coefficients at or close to the collisional values. The recombination energy of H_2O^+ (1217 kJ mol^{-1} ≡ 12.61 eV) is far higher than that of H_3O^+ and considerably exceeds the ionization potential of each of the molecules in this study. As a consequence, the major reaction products can all be identified as resulting from processes initiated by charge transfer. A detailed mechanistic scheme has been proposed by Morris et al. from their results for the reaction of H_2O^+ with various CF_3X molecules.[3]

Three reaction pathways need to be considered.

(i) Nondissociative Charge Transfer.

$$M + H_2O^{+} \rightarrow M^{+} + H_2O$$

This channel is exothermic for all the molecules. If sufficient excess energy remains in the ion M^+, fragmentation of the parent ion may occur. Nondissociative charge transfer is thus most likely to be seen for CF_3Br, which has the highest ionization potential of the molecules investigated in this study. But even for CF_3Br it is observed to be a relatively minor channel:

$$CF_3Br + H_2O^{+} \rightarrow CF_3Br^{+} + H_2O \quad \Delta H = -117\ \text{kJ mol}^{-1} \qquad (9)$$

A further requirement for the formation of the parent cation is the existence of an adequate energy range over which the cation is stable to fragmentation. The recent threshold photoelectron–photoion coincidence (TPEPICO) study of CF_3Cl and CF_3Br[16] shows that a clear region of stability exists for CF_3Br^+, and included in this region is the energy corresponding to the recombination energy of H_2O^+, but such a region does not exist for CF_3Cl^+. This correlates with the observations of Morris et al.;[3] CF_3Cl^+ is not formed in the reaction of CF_3Cl with H_2O^+, but CF_3Br^+ is a product of the reaction of CF_3Br with H_2O^+. TPEPICO results have not been reported for the other molecules of this study, and the question of an adequate region of stability remains open.

(ii) Dissociative Charge Transfer. From the list of observed ion products (Table 1), M^+ is evidently formed with energy in excess of one or more dissociative ionization limits:

$$M + H_2O^{+} \rightarrow (M^{+})^{*} + H_2O$$

$$(M^{+})^{*} \rightarrow [M-X]^{+} + X$$

In Table 4 are collected the enthalpies for all the dissociative charge-transfer pathways of the type above, that is, for

TABLE 4: Enthalpies for All the Dissociative Charge-Transfer Pathways of the Type $M + H_2O^+ \rightarrow (M^+)^* + H_2O \rightarrow [M-X]^+ + X + H_2O$ and for All the Pathways $M + H_2O^+ \rightarrow [M-X]^+ + HX + OH$[a]

M	X	ΔH/kJ mol^{-1} $M + H_2O^+ \rightarrow [M-X]^+ + H_2O + X$	ΔH/kJ mol^{-1} $M + H_2O^+ \rightarrow [M-X]^+ + HX + OH$	$[M-X]^+$ observed?
CF_3Br	Br	−47	77	yes (71)
	F	≤57	≤−15	yes (16)
CF_2Br_2	Br	≤−182	≤−49	yes (100)
	F	≤−125	≤−197	no
CF_2BrCl	Br	≤−161 [b]	≤−28 [b]	yes (86)
	Cl	≤−114	≤−46	yes (6)
	F	≤−32	≤−104	yes (8)
$CFBr_3$	Br	≤−236	≤−103	yes (100)
	F	≤−32	≤−104	no
$CFBr_2Cl$	Br	≤−257	≤−124	yes (97)
	Cl	≤−282	≤−214	yes (3)
	F	≤−32	≤−104	no
$CBrCl_3$	Br	−231	−98	yes (76)
	Cl	≤−171	≤−104	yes (24)

[a] Note that the heat of formation taken for CF_2Br^+ is that reported by Wang and Leroi.[14] Other inequalities are a result of the heat of formation of the product ion being taken as the upper limit derived from the H_3O^+ study (Table 3). The numbers in parentheses are the branching ratios to the observed $[M-X]^+$ products. [b] $\Delta_f H(CF_2Cl^+) \leq 506$ kJ mol^{-1}, reported by Morris et al.,[3] is used in the calculation.

$$M + H_2O^+ \rightarrow [M-X]^+ + H_2O + X \qquad (10)$$

The bounds of Table 3 were used to calculate many of the entries in Table 4. With the possible exception of

$$CF_3Br + H_2O^+ \rightarrow CF_2Br^+ + H_2O + F \qquad \Delta H = 153 \text{ or } \leq 57 \text{ kJ mol}^{-1} \quad (11)$$

these fragmentation pathways to the trihalomethyl cations are all exothermic. For most of the molecules there are other exothermic pathways to the trihalomethyl cations of the form

$$M + H_2O^+ \rightarrow [M-X]^+ + HX + OH \qquad (12)$$

and the enthalpies of these pathways are also given in Table 4.

For pathway 10 the exothermicities increase in the order $X = Br < Cl < F$, reflecting the relative strengths of the C−X bonds in the trihalomethyl cations. For pathway 12 the overall thermochemistries are the result of the balance between C−X and H−X bond strengths, and these pathways are most exothermic for $X = F$.

There is a strong correlation between the exothermicity for the simple dissociative charge-transfer mechanism 10 and the observed branching ratios, indicating that mechanism 10 is the preferred pathway by which the trihalomethyl cations are formed. There is one definite exception, the formation of CF_2Br^+ from CF_3Br, for which the most exothermic pathway is

$$CF_3Br + H_2O^+ \rightarrow CF_2Br^+ + HF + OH \qquad \Delta H = 82 \text{ or } \leq -15 \text{ kJ mol}^{-1} \quad (13)$$

The observation of CF_2Br^+ as a product of the reaction between CF_3Br and H_2O^+ is only consistent with the second of these two values for ΔH. This value is derived from Wang and Leroi's upper limit to $\Delta_f H(CF_2Br^+)$ (≤544 kJ mol^{-1}).[14] The value of $\Delta_f H(CF_2Br^+) = 640$ kJ mol^{-1} obtained by Clay et al. from a PIMS study of CF_3Br appears to be much too high.[13] It has thus been rejected in the construction of Table 4, and Wang and Leroi's bound for the heat of formation of CF_2Br^+ has been used.

The formation of CF_2Br^+ from CF_3Br indicates the occurrence of reaction within an ion−molecule complex, while the other reactions could result from long-range charge transfer. The significance of this observation is discussed further below.

(*iii*) *Formation of Protonated Carbonic Dihalides.* CF_2OH^+ is one of the products observed from the reaction of CF_3Br with H_2O^+:

$$CF_3Br + H_2O^+ \rightarrow CF_2OH^+ + HF + Br \qquad \Delta H = -267 \text{ kJ mol}^{-1} \quad (14)$$

This is the most exothermic pathway to CF_2OH^+. Its observation again suggests that the reaction of CF_3Br with H_2O, at least in part, proceeds via an intimate mechanism within an ion−molecule complex. The product is assumed to be protonated carbonic difluoride rather than the difluoromethoxy cation CHF_2O^+, since a comparison of the enthalpies of formation of CH_2OH^+ (703 kJ mol^{-1}) and CH_3O^+ (842 kJ mol^{-1}) leads to the conclusion that CF_2OH^+ will be the lower energy isomer.

Protonated carbonic dihalides are not observed as products of any of the other reactions, although there are exothermic pathways to CF_2OH^+ production for both CF_2Br_2 and CF_2BrCl:

$$CF_2Br_2 + H_2O^+ \rightarrow CF_2OH^+ + HBr + Br \qquad \Delta H = -301 \text{ kJ mol}^{-1} \quad (15)$$

$$CF_2BrCl + H_2O^+ \rightarrow CF_2OH^+ + HCl + Br \qquad \Delta H = -298 \text{ kJ mol}^{-1} \quad (16)$$

There are no thermochemical data for the other protonated carbonic dihalides. The proton affinities of carbonic difluoride and methanal are quite similar, 672 and 718 kJ mol^{-1}, respectively. This suggests that the proton affinity may be regarded as a transferable property of the carbonyl group (∼700 kJ mol^{-1}). This value was used to make reasonable estimates of the enthalpies of formation of CCl_2OH^+ (610 kJ mol^{-1}) and CBr_2OH^+ (717 kJ mol^{-1}). The following pathways are likely to be exothermic:

$$CF_2Br_2 + H_2O^+ \rightarrow CBr_2OH^+ + HF + F$$

$$CFBr_3 + H_2O^+ \rightarrow CBr_2OH^+ + HF + Br$$

$$CFBr_2Cl + H_2O^+ \rightarrow CBr_2OH^+ + HF + Cl$$

$$CBrCl_3 + H_2O^+ \rightarrow CCl_2OH^+ + HCl + Br$$

None of these pathways were observed. Similarly, by use of values of the heats of formations of CFBrO (−377 kJ mol^{-1}),[15] CBrClO (−167 kJ mol^{-1}),[15] and CFClO (−430 kJ mol^{-1}),[17]

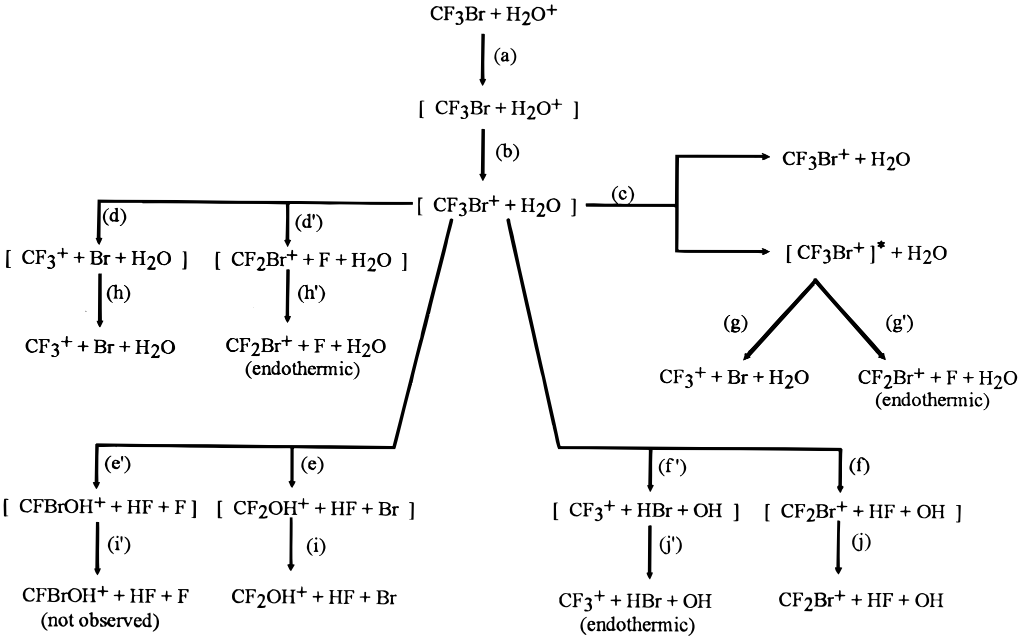

Figure 1. Mechanistic scheme for the reaction of H_2O^+ with CF_3Br (adapted from ref 3).

estimates of the heats of formation of $CFBrOH^+$ (453 kJ mol^{-1}), $CBrClOH^+$ (664 kJ mol^{-1}), and $CFClOH^+$ (400 kJ mol^{-1}) have been determined. These estimated heats of formation indicate that there are exothermic reaction pathways leading to protonated carbonic dihalides for all the molecules of this study.

Mechanisms of the Reactions of H_2O^+ with the Bromomethanes. The results show that the reaction of H_2O^+ with CF_3Br is different from the reactions of H_2O^+ with the other fully halogenated bromomethanes of this study. The parent cation product CF_3Br^+ is observed. Two of the other products CF_2Br^+ and CF_2OH^+ are indicative of intimate reactions within an ion−molecule complex—their formation requires the making and breaking of bonds, together with charge transfer. On the basis of the reactions of the other bromomethanes, the only product to be expected from CF_3Br is CF_3^+. The general mechanistic scheme proposed by Morris et al.[3] provides a framework within which to examine these observations. For the specific case of the reaction of CF_3Br with H_2O^+, an adapted version of the scheme of Morris et al. is illustrated in Figure 1. The steps in this scheme are (a) the initial formation of an ion−molecule complex and (b) charge transfer within this complex.

The efficiency of charge transfer at long range can be assessed by combining the separate Franck−Condon factors for the recombination of the ion (here, $H_2O^+ + e^- \rightarrow H_2O$) and ionization of the molecule.[5,18−20] Energy conservation requires that the energy released by recombination is equal to that supplied to ionize the molecule. The geometry of the ground state of H_2O^+ differs little from that of H_2O, and the largest Franck−Condon (F−C) factor starting from H_2O^+ in its zero-point level is to H_2O in its zero-point level. The energy released is 12.61 eV (the adiabatic and vertical ionization potential of H_2O). The relative F−C factor for ionization of the molecule at this energy can be judged by inspection of the photoelectron spectrum of the molecule in which relative intensities are usually set by F−C factors for ionization. For the case of charge transfer to H_2O^+, this is only likely to be efficient if there is a peak in the photoelectron spectrum of the molecule with an ionization energy close to 12.61 eV. An inspection of the photoelectron spectra of CF_3Br,[21] reproduced in Figure 2, shows no peak at 12.61 eV. When the match is poor, as for $H_2O^+ + CF_3Br$, a large distortion of the potential energy surface of the neutral would be required to obtain good F−C factors. Charge transfer must then occur within an ion−molecule complex, as indicated in the mechanism. Step b is exothermic. The energy released is partitioned between internal energy of the cation CF_3Br^+, internal energy of the H_2O, and relative motion of CF_3Br^+ and H_2O. There are a number of possible fates of the complex indicated by steps c−f. Step c is the breakup of the complex to release the parent cation. If the parent cation contains sufficient internal energy, it may fragment (step g). Step c is in competition with step d, dissociation of the cation within the complex, and steps e and f, which are reactions within the complex.

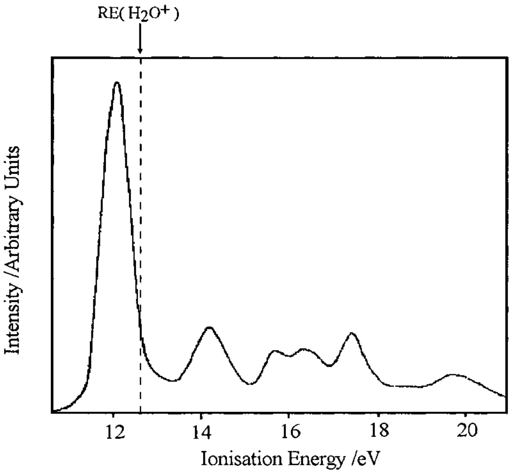

Figure 2. Photoelectron spectrum of CF_3Br in the ionization energy range 11.5−20.5 eV (adapted from ref 21). The vertical dashed line is drawn at the recombination energy (RE) of the H_2O^+ ion, 12.61 eV.

Steps d−f lead to steps h−j, respectively; i.e., each of the complexes formed by reactions within the initially generated ion−molecule complex will break up to release the respective product cations.

To observe the parent cation, step c must compete against steps d−f and the parent cation must not break up after release from the complex (step g). Step b is least exothermic for CF_3Br, and CF_3Br^+ is known to have a fairly wide energy range over which it is stable to dissociation. The formation of stable parent cations is most likely for CF_3Br and was only observed for CF_3Br.

Steps e and f are intimate reactions within the ion−molecule complex, involving the making and breaking of bonds. Compared to charge transfer, these are relatively slow processes, which will only compete with steps c and d if the complex lifetime is long and the parent cation does not rapidly dissociate. The energy released within the complex by the initial charge transfer, step b, will determine the lifetime of the ion−molecule complex between the parent cation and H_2O. The charge transfer is least exothermic for CF_3Br, and it is only for CF_3Br that a product corresponding to steps e and i is observed. Steps f and j are the route to CF_2Br^+ for CF_3Br.

For completeness, illustrated in Figure 1 are the pathways ending in steps h′, g′, and j′, all of which are overall endothermic, and the pathway ending in step i′, which although overall exothermic, is not observed.

Considering the other molecules of this study, an inspection of the photoelectron spectra of CF_2BrCl,[22] $CFBr_3$,[23] and $CBrCl_3$[24] shows that for these molecules there are no F−C accessible ionic states at the vertical recombination energy of H_2O^+. There is a partial match for CF_2Br_2.[22] Charge transfer must again occur within an ion−molecule complex, and reaction is initiated by steps a and b of the mechanism. The very different pattern of products, exclusive formation of trihalomethyl cations, observed from CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$, when compared to CF_3Br, indicates a change in the dynamics of the complex $[M^+ + H_2O]$ so that the only significant steps are step c followed by step g and/or step d followed by step h. For CF_2Br_2, CF_2BrCl, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$ more energy is released by charge transfer during step b. This energy will appear both in the internal energy of the cation, leading to its dissociation (steps d and g), and in the relative motion of the molecules within the complex, accelerating its destruction (steps c and h). The net effects are a short complex lifetime and the exclusive production of trihalomethyl cations, for which the branching ratios will parallel the exothermicities of the competing dissociative charge-transfer reactions. Whether the route is via steps c and g or via steps d and h will depend on the relative rates for dissociation of the parent cation and breakup of the ion−molecule complex.

To conclude, the observed branching ratios for the reaction of H_2O^+ with CF_3Br appear to be due to the high ionization potential of CF_3Br, compared to the other molecules of this study, and the stability of CF_3Br^+ to dissociation at the recombination energy of H_2O^+.

Summary

There are important reasons for undertaking fundamental and comprehensive investigations of the ion chemistry of bromomethanes. These include applications of ion−molecule reactions in pollutant monitors and an understanding of atmospheric ion chemistry. Furthermore, the ion chemistry of the bromomethanes is essentially unexplored.

In this paper the results from a study of the reactions of two important atmospheric cations, H_3O^+ and H_2O^+, with six brominated molecules have been presented. Of the 12 reactions detailed here, only one has previously been reported in the literature by Morris et al.[3] H_3O^+ reacts with a rate coefficient close to the collisional value with four of the molecules (CF_2Br_2, $CFBr_3$, $CFBr_2Cl$, and $CBrCl_3$) at a decreased efficiency with CF_2BrCl and has no observable reaction with CF_3Br, whereas H_2O^+ is found to react at the collisional rate with all six of the molecules studied.

H_3O^+ can only react through the formation of an intimate reaction complex. We suggest that after the formation of the complex, the first reaction step is attack of the acidic H^+ in the H_3O^+ ion on a halogen in the neutral. Preferentially, an HF is ejected together with H_2O from the complex for the fluorine-containing molecules, and HCl and H_2O are ejected from the complex for the reaction involving $CBrCl_3$. Such a reaction pathway is endothermic for the reaction of H_3O^+ with CF_3Br, and this explains the lack of an observable reaction with this molecule. In the case of CF_2Br_2 and CF_2BrCl, it is observed that the H_2O may bind to the trihalomethyl cation as the ion−molecule complex breaks up.

H_2O^+ reacts predominantly via dissociative charge transfer, which probably takes place at short range, since the Franck−Condon factors connecting the ground state of the bromine-containing molecule to any ionic state are small at the vertical recombination energy of H_2O^+. Clear evidence of this has been found from the reaction of H_2O^+ with CF_3Br, for which other ion products that can only result from intimate reactions occurring within an ion−molecule complex are observed in addition to charge transfer.

Acknowledgment. Financial support from the PLSD (CBD), Porton Down, U.K., is gratefully acknowledged. One of the authors (R.D.T.) especially thanks Professor G. C. Morrison, Head of the School of Physics and Space Research, for a School studentship.

References and Notes

(1) Fehsenfeld, F. C.; Crutzen, P. J.; Schmeltekopf, A. L.; Howard, C. J.; Albritton, D. L.; Ferguson, E. E.; Davidson, J. A.; Schiff, H. I. *J. Geophys. Res.* **1976**, *81*, 4454.

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

(3) Morris, R. A.; Viggiano, A. A.; Van Doren, J. M.; Paulson, J. F. *J. Phys. Chem.* **1992**, *96*, 3051.

(4) Morris, R. A.; Viggiano, A. A.; Arnold, S. T.; Paulson, J. F.; Liebman, J. F. *J. Phys. Chem.* **1995**, *99*, 5992.

(5) Jarvis, G. K.; Mayhew, C. A.; Tuckett, R. P. *J. Phys. Chem.* **1996**, *100*, 17166.

(6) McElroy, M. B.; Salawitch, R. J.; Wofsy, S. C.; Logan, J. A. *Nature* **1986**, *321*, 759.

(7) Washida, N.; Imamura, T.; Bandow, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 535.

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

(9) Adams, N. G.; Smith, D. *Int. J. Mass Spec. Ion. Phys.* **1976**, *21*, 349.

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

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

(12) *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press Inc.: Boca Raton, FL, 1996.

(13) Clay, J. T.; Walters, E. A.; Grover, J. R.; Willcox, M. V. *J. Chem. Phys.* **1994**, *101*, 2069.

(14) Wang, F.; Leroi, G. E. *Ann. Isr. Phys. Soc.* **1983**, *6*, 210.

(15) Thomas, R.; Liu, Y.; Mayhew, C. A.; Peverall, R. *Int. J. Mass Spectrom. Ion Processes* **1996**, *155*, 163.

(16) Creasey, J. C.; Smith, D. M.; Tuckett, R. P.; Yoxall, K. R.; Codling, K.; Hatherly, P. A. *J. Phys. Chem.* **1996**, *100*, 4350.

(17) Mayhew, C. A.; Peverall, R.; Watts, P. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 81.

(18) Bowers, M. T.; Elleman, D. D. *Chem. Phys. Lett.* **1972**, *16*, 486.

(19) Gauglhofer, J.; Kevan, W. T., Jr. *Chem. Phys. Lett.* **1972**, *16*, 492.

(20) Laudenslager, J. B.; Huntress, W. T., Jr.; Bowers, M. T. *J. Chem. Phys.* **1974**, *61*, 4600.

(21) Doucet, J.; Sauvageau, P.; Sandorfy, C. *J. Chem. Phys.* **1973**, *58*, 3708.

(22) Doucet, J.; Gilbert, R.; Sauvageau, P.; Sandorfy, C. *J. Chem. Phys.* **1975**, *62*, 366.

(23) Chau, F. T.; McDowell, C. A. *J. Electron Spectrosc. Related Phenom.* **1975**, *6*, 357.

(24) Novak, I.; Cvitaš, T.; Klasinc, L.; Güsten, H. *Faraday Trans. 2* **1981**, *77*, 2049.