

Reactions of H_3O^+ with a number of bromine containing fully and partially halogenated hydrocarbons

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We wish to dedicate this work to the memory of Professor W. Lindinger.

Abstract

The thermal bimolecular rate coefficients and product ion branching ratios for the reactions of H_3O^+ with the bromine containing molecules CH_3Br , CH_2Br_2 , CH_2FBr , CHF_2Br , CHFBr_2 , CH_2BrCl , CHBrCl_2 , CHBr_2Cl , $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_2\text{BrCF}_2\text{Br}$ at 300 K are reported. H_3O^+ reacts with an experimental rate coefficient (k_{exp}) close to the collisional value ($k_c \approx 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with CHFBr_2 , CHBrCl_2 , CHBr_2Cl , $\text{CH}_2\text{BrCH}_2\text{Cl}$, and $\text{CH}_2\text{BrCH}_2\text{Br}$, at a decreased efficiency with $\text{CH}_3\text{CH}_2\text{Br}$ ($k_{\text{exp}}/k_c \approx 0.3$). The other neutral reactant molecules, CH_3Br , CH_2FBr , CHF_2Br , $\text{CF}_3\text{CF}_2\text{Br}$, and $\text{CF}_2\text{BrCF}_2\text{Br}$ react through a three-body associative process. There is no observable reaction with CH_2Br_2 and CH_2BrCl . Mechanistic arguments are given that go some way to explaining the observed range in both reactivity and reaction pathways. (Int J Mass Spectrom 223–224 (2003) 627–637)

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1. Forward

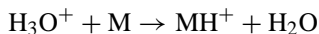
Reactions of protonated water, H_3O^+ , with various volatile organic compounds (VOCs) was a major research area for Professor W. Lindinger. In the early 1990s, Werner and his colleagues, at the Institut für Ionenphysik der Leopold-Franzens-Universität Innsbruck, Austria, exploited the proton donating properties of H_3O^+ to develop a unique and transportable instrument to analyse trace gases (ppbv or better) in air [1,2]. This instrument, called the proton transfer reaction mass spectrometer (PTR-MS), has its origins in

chemical ionisation mass spectrometry (CIMS). The basic idea behind CIMS is to form reagent ions which undergo exothermic reactions with the trace gas of interest in the CI source. The reagent ion is “tailored” so that ionisation of the neutral reactant is “soft,” i.e., the reaction has a low exothermicity, so that fragmentation is limited. The detected product ion is then a fingerprint of the neutral reactant. For the majority of analytical applications CIMS uses gas chromatography for separation purposes. This introduces time delays so that real-time continuous flow analysis is not possible. Even on-line monitoring of mixtures with changing concentrations on a timescale of minutes remains problematic. This problem was overcome to

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some extent with the development of the selected ion flow drift tube (SIFDT), an instrument Werner was intimately involved with. Whilst the detection limit of the SIFDT is higher than that of CIMS, because a much longer reaction chamber is used, its sensitivity lies in the range of several tens to a hundred part per billion by volume (ppbv) and the system is not transportable. For many applications VOCs concentrations of the order of few ppbv need to be detected, often at sites where an instrument would have to be taken. Werner and his colleagues reached such sensitivities with their PTR-MS, which generates and maintains a swarm of H_3O^+ ions through a drift tube. This major breakthrough allows quantitative real-time detection of VOCs providing detailed signatures of, for examples, pollution, biological activity, pyrolysis, and health.

At the heart of the PTR-MS is the proton donating capabilities of H_3O^+ . H_3O^+ transfers a proton to a neutral molecule, M, in the air if the proton affinity of M is higher than that of H_2O ($691.0 \text{ kJ mol}^{-1}$) usually by a non-dissociative mechanism:



M includes most VOCs, but none of the major constituents of air, all of which have proton affinities lower than that of H_2O .

With the development of the PTR-MS, and its growing use in atmospheric, environmental, technological and health applications, attention is focused on the investigation of the fundamental process of proton transfer reactions and other reactions of molecules with H_3O^+ . Werner always welcomed new data on H_3O^+ reactions in order to assemble a database of experimental rate coefficients and product ion distributions. In the following paper we present a study of H_3O^+ reactions with several molecules, which have had little or no previous investigation.

2. Introduction

The reactions of positive ions with neutral molecules play a significant, and sometimes dominant, role

in the chemistry of many gaseous plasma environments. These include the interstellar medium, planetary ionospheres and industrial plasmas. Reaction rate and product ion distribution data are invaluable if we are to understand the formation and abundance of ions and neutrals present in plasmas, and to understand how these plasmas evolve.

Many studies have investigated the positive ion chemistry of chlorofluorocarbons (CFCs) [3], and a number of studies have explored the positive ion chemistry of their replacements, the perfluorocarbons (PFCs) [4–7]. This is a direct result of the use and influence of these molecules in plasma environments and atmospheric chemistry. For example, gaseous halocarbons are used in plasma etching. In contrast, little attention has been directed to the reactions of positive ions with brominated species. Yet a systematic study of these reactions permits useful comparison with the ion chemistry of fluorinated and/or chlorinated compounds. This in turn improves our fundamental understanding of ion–molecule reactions. There is also an atmospheric motivation to such studies. Whilst 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 [8,9].

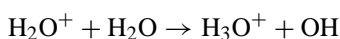
To begin to address the paucity of data on the ion chemistry of brominated molecules, we have made a number of selected ion flow tube (SIFT) studies investigating the reactions of positive ions and anions with a large number of brominated molecules. We have presented a study of the reactions of H_3O^+ and H_2O^+ with several fully halogenated bromomethanes [10], and an investigation of the reactions of O^- , O_2^- , and OH^- with a variety of hydrogen-containing and fully halogenated halocarbons [11]. In this paper, we concentrate on the reactions of the reagent ion H_3O^+ with the following halogenated methanes; CH_3Br , CH_2Br_2 , CH_2FBr , CHF_2Br , CH_2BrCl , CHBrCl_2 , and CHBr_2Cl , together with a series of bromine containing ethanes; $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_2\text{BrCF}_2\text{Br}$. This represents a natural extension to our earlier study, and to other studies involving halogenated molecules. H_3O^+ is an important

and abundant atmospheric ion [12]. Thus, if H_3O^+ reacts with a bromine-containing molecule, the reaction may influence the atmospheric lifetime of the molecule. Another motivation for this study is the application of the PTR-MS, developed by the Professor W. Lindinger and his colleagues, for the detection and concentration measurements of trace gases. Fundamental studies of the reactions of H_3O^+ with molecules are essential for underpinning the use and development of this mass spectrometer.

To our knowledge the majority of the data is being presented here for the first time, with a few exceptions. Only the reactions of H_3O^+ with CHF_2Br [13] and with CH_3Br and $\text{CH}_3\text{CH}_2\text{Br}$ [14] have been reported before.

3. Experimental details

The selected ion flow tube (SIFT) apparatus used to obtain the reaction rate coefficients and product ion branching ratios has been described in detail elsewhere [15,16], so only a brief overview of the salient points of the experimental technique is included here. Ions were generated in an enclosed high-pressure electron impact ion source. H_2O was used to create H_3O^+ via proton transfer from the H_2O^+ , initially produced in the ion source, to H_2O :



The reagent ions were mass selected using a quadrupole mass filter, before being injected into a 300 K helium carrier gas at a pressure of ca. 0.5 Torr. The helium gas (high-purity grade (99.997%)) was passed through a liquid nitrogen cooled zeolite trap before use. The reagent ions were transported along the flow tube and detected by a downstream quadrupole mass spectrometer detection system. Neutral reactant gas was added in controlled amounts to the ion swarm/carrier gas. All the reactant samples, CH_3Br , CH_2Br_2 , CH_2FBr , CHF_2Br , CH_2BrCl , CHBrCl_2 , CHBr_2Cl , $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_2\text{BrCF}_2\text{Br}$ were obtained commercially, all with stated purities greater than 95%.

Liquids were subjected to several freeze-pump-thaw cycles to remove dissolved gases. Otherwise all samples were used without further purification.

The loss of the reagent ions and the appearance of product ions were monitored by the detection system. Relaxed resolution on the quadrupole mass spectrometer was used to minimise mass discrimination effects, i.e., the resolution was set to the smallest possible value on the controller which corresponded to mass peaks having a FWHM of about 2 amu. (Higher resolution (>1 amu) was used to assign the peaks in the mass spectra.) This minimises the error in determining the branching ratios. The reaction rate coefficients and ion product distributions were then determined in the usual way [15–17]. Reaction rate coefficients, which were extracted from least-squares fits of the plot of logarithm of the reagent ion signal vs. reactant neutral concentration, are considered to be accurate to $\pm 20\%$. The percentage product ion branching ratios, determined from the product ion counts as a function of reactant neutral concentration and extrapolated to zero reactant gas concentration to allow for any secondary reactions, are only used to provide a qualitative indication of the important ion channels, and therefore accurate values are not important in our discussions. However, a statistical analysis on the branching ratios indicates a fractional accuracy of better than 20% for the reaction channels with branching ratios greater than 10%. For ion channels with branching ratios less than this value, the accuracy is reduced.

4. Results

The experimental rate coefficients, k_{exp} , the product ions, and product ion branching ratios for the reactions of H_3O^+ with the bromine containing methane molecules CH_3Br , CH_2Br_2 , CH_2FBr , CHF_2Br , CH_2BrCl , CHBrCl_2 , CHBr_2Cl are presented in Table 1. Table 2 provides the rate and branching ratio data for the reactions of H_3O^+ with the bromine containing C_2 molecules $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CF}_3\text{CF}_2\text{Br}$. Included in these two tables are the collisional rate coefficients

Table 1
Reaction rate coefficients, the product ions, and the branching percentages for the reactions of H_3O^+ with CH_3Br , CH_2Br_2 , CH_2FBr , CHFBBr_2 , CHF_2Br , CH_2BrCl , CHBrCl_2 and CHBr_2Cl at 300 K

	CH_3Br	CH_2Br_2	CH_2FBr	CHFBBr_2	CHF_2Br	CH_2BrCl	CHBrCl_2	CHBr_2Cl
$k_{\text{exp}}^{\text{a}}$	0.04	NR	0.28	1.9	0.02	NR	1.7	1.7
$k_{\text{c}}^{\text{a,b}}$	2.7	2.4			1.4			
Product ion(s) ^c	$\text{CH}_3\text{Br} \cdot \text{H}_3\text{O}^+$ (100)	–	$\text{CH}_2\text{FBr} \cdot \text{H}_3\text{O}^+$ (100)	CHBr_2^+ (54), $\text{CHBr}_2\text{O}^+\text{H}_2$ (40), CHFBBr^+ (5), $\text{CHFBBrO}^+\text{H}_2$ (1)	$\text{CHF}_2\text{Br} \cdot \text{H}_3\text{O}^+$ (100)	–	$\text{CHBrClO}^+\text{H}_2$ (69), CHBrCl^+ (22), $\text{CHCl}_2\text{O}^+\text{H}_2$ (7), CHClOH^+ (1), CHBrOH^+ (1)	CHBr_2^+ (38), $\text{CHBr}_2\text{O}^+\text{H}_2$ (35), CHBrCl^+ (20), $\text{CHBrClO}^+\text{H}_2$ (6), CHBrOH^+ (1)

NR refers to no observable reaction, which provides an upper limit of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^a The reaction rate coefficients, both experimental (k_{exp}) and calculated (k_{c}) are given in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and are considered to be accurate to $\pm 20\%$.

^b The calculated 300 K collisional reaction rate coefficients are given for reactant neutral molecules with known polarisabilities and dipole moments. For CHF_2Br only the polarisability is available, and hence the collisional rate refers to the Langevin value.

^c Ion branching percentages are given in parentheses [18].

Table 2

Reaction rate coefficients, the product ions, and the branching percentages for the reactions of H_3O^+ with $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_2\text{BrCF}_2\text{Br}$ at 300 K

	$\text{CH}_3\text{CH}_2\text{Br}$	$\text{CH}_2\text{BrCH}_2\text{Cl}$	$\text{CH}_2\text{BrCH}_2\text{Br}$	$\text{CF}_3\text{CF}_2\text{Br}$	$\text{CF}_2\text{BrCF}_2\text{Br}$
$k_{\text{exp}}^{\text{a}}$	1.2	1.8	1.9	<0.0005	0.19
$k_{\text{c}}^{\text{a,b}}$	3.0	2.3	2.4		
Product ion(s) ^c	$\text{CH}_3\text{CH}_2\text{Br}\cdot\text{H}^+$ (46), $\text{CH}_3\text{CH}_2\text{O}^+\text{H}_2$ (32), $\text{CH}_3\text{CH}_2\text{Br}\cdot\text{H}_3\text{O}^+$ (22)	$\text{CH}_2\text{BrCH}_2\text{O}^+\text{H}_2$ (78), $\text{CH}_2\text{BrCH}_2^+$ (22)	$\text{CH}_2\text{BrCH}_2\text{O}^+\text{H}_2$ (92), $\text{CH}_2\text{BrCH}_2^+$ (7), $\text{CH}_2\text{BrCH}_2\text{Br}\cdot\text{H}^+$ (1)	$\text{CF}_3\text{CF}_2\text{Br}\cdot\text{H}_3\text{O}^+$ (100)	$\text{CF}_2\text{BrCF}_2\text{Br}\cdot\text{H}_3\text{O}^+$ (100)

^a The reaction rate coefficients, both experimental (k_{exp}) and calculated (k_{c}) are given in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and are considered to be accurate to $\pm 20\%$.

^b The calculated 300 K collisional reaction rate coefficients are given for reactant neutral molecules with known polarisabilities and dipole moments.

^c Ion branching percentages are given in parentheses.

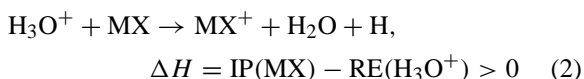
(k_{c}). These have either been determined using the trajectory method when the polarisability and dipole moment of the molecule are known [18], or by the Langevin equation when only the polarisability is available [19]. When neither of these physical quantities is available in the literature, no k_{c} is given. Polarisabilities and dipole moments have been taken from the CRC Handbook [20].

Unless otherwise stated, the enthalpy of the reactions presented in the text have been calculated using enthalpies of formation from the NIST website [21], supplemented with data from the tables of Lias et al. [22].

H_3O^+ has a very low recombination energy; 6.37 eV (298 K) [22], which corresponds to:



This value is far below the ionisation potentials of any of the neutral reagents (the lowest being 10.29 eV for $\text{CH}_3\text{CH}_2\text{Br}$). Charge transfer, which is a commonly encountered mechanism in the reactions of molecules with positive ions resulting in a transfer of an electron from the neutral to the reagent cation, is thus ruled out because of its large endothermicity:



where MX represents one of the bromine containing molecules, IP(MX) the ionisation potential of MX, and RE(H_3O^+) is the recombination energy of H_3O^+ .

Although H_3O^+ is unable to react with any of the brominated molecules via charge transfer, it can react in a number of ways which will be discussed in turn.

4.1. Association reactions

Three-body associative process with H_3O^+ is the reaction channel observed for $\text{M} = \text{CH}_3\text{Br}$, CH_2FBr , CHF_2Br , $\text{CF}_3\text{CF}_2\text{Br}$, and, in trace amounts, $\text{CF}_2\text{BrCF}_2\text{Br}$. It is also observed, but not as the only product ion, with $\text{CH}_3\text{CH}_2\text{Br}$. With the exception of $\text{CH}_3\text{CH}_2\text{Br}$, whose behaviour will be discussed separately, it can be concluded that all of these compounds together with CH_2Br_2 and CH_2BrCl which do not react, have proton affinities less than that of water.

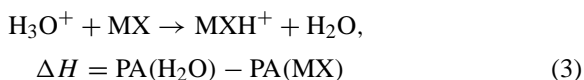
No attempt has been made to investigate the dependence of the association rate on the helium pressure for any of the association reactions. Hence the rate coefficient given for these reactions represent an effective two-body value. The effective two-body rate coefficient at a helium pressure of 0.5 Torr for the reaction of H_3O^+ with $\text{CF}_3\text{CF}_2\text{Br}$ is extremely slow, and only a small signal of the association product ion was detected. Therefore, only an upper limit for the rate coefficient is provided. The small rate coefficient implies that ($\text{CF}_3\text{CF}_2\text{Br}\cdot\text{H}_3\text{O}^+$) must break-up to the initial reactants in a time shorter than that required to stabilise the complex through collisions with the helium buffer gas, assuming that it is formed efficiently initially.

Morris et al. [13] report an effective two-body reaction rate coefficient of $1.5 \pm 0.3 \times 10^{-11} \text{ cm}^3$

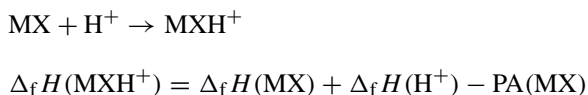
molecule⁻¹ s⁻¹ at a helium pressure 0.41 Torr, for the reaction of H₃O⁺ with CHF₂Br. This value agrees well with our value of $2.1 \pm 0.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ obtained at a higher helium pressure 0.5 Torr. Španel and Smith [14] report an effective two-body reaction rate coefficient of 0.2×10^{-9} cm³ molecule⁻¹ s⁻¹ at a helium pressure 0.5 Torr, for the reaction of H₃O⁺ with CH₃Br, which represents an extremely efficient three-body stabilisation, and which is significantly larger than our value of 0.04×10^{-9} cm³ molecule⁻¹ s⁻¹ obtained at the same helium pressure.

4.2. Proton transfer

Non-dissociative proton transfer can occur when the proton affinity of the neutral reactant molecule is greater than that of H₂O, but not so great that sufficient energy is liberated to promote fragmentation of the protonated molecule.



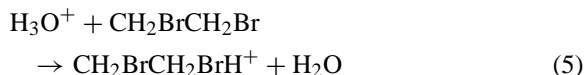
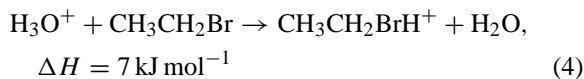
where PA(H₂O) and PA(MX) represent the proton affinities of H₂O and MX, respectively. The proton affinity is defined to be the negative of the enthalpy change of the protonation reaction at 298 K [22]:



Reaction (3) is exothermic providing PA(MX) > PA(H₂O). If PA(MX) is sufficiently greater than PA(H₂O) = 691.0 kJ mol⁻¹, the MXH⁺ ion resulting from the proton transfer may have sufficient energy deposited into it that it may subsequently fragment (dissociative proton transfer).

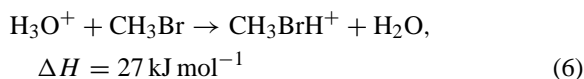
Proton transfer was not observed to be a major reaction channel in this study. None of the reactions with the C₁ molecules resulted in proton transfer. For the C₂ molecules the proton transfer product MH⁺ was only observed for two of the reactant molecules and

then not as the only product ion:



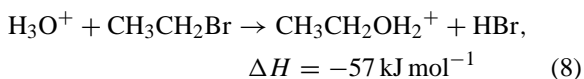
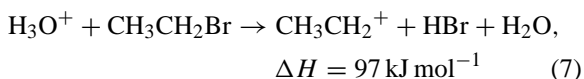
Proton transfer (4) is an important channel (branching ratio 46%) in the reaction of H₃O⁺ with CH₃CH₂Br, and our results are in good agreement with those of Španel and Smith [14]. For CH₂BrCH₂Br, only a small branching ratio (1%) is associated with reaction (5). The enthalpy change for reaction (4) has been calculated using PA(CH₃CH₂Br) = 684 kJ mol⁻¹, determined in recent thermokinetic experiments on proton transfer from CH₃CH₂Br·H⁺ [23]. (The PA(CH₃CH₂Br) in the NIST tabulation is given as 696 kJ mol⁻¹ making the enthalpy change for reaction (4) to be exothermic by 5 kJ mol⁻¹ but these differences are sufficiently small to be considered inconsequential.) For the forward reaction (4), the results in Table 2 give a rate coefficient $k_4 = 5.5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The rate coefficient for the reverse reaction, $k_{-4} = 3.31 \times 10^{-10}$ cm³ [23]. Combining these results gives an equilibrium constant for reaction (4), $k_4 = 1.67$, and a Gibbs free energy change $\Delta G_{298}^\circ(4) = -1.3$ kJ mol⁻¹. Combining this Gibbs free energy with known gas phase basicity of H₂O (GB(H₂O) = 660.0 kJ mol⁻¹) gives GB(CH₃CH₂Br) = GB(H₂O) - $\Delta G_{298}^\circ(4) = 661.3$ kJ mol⁻¹, which is in very good agreement with GB(CH₃CH₂Br) = 660.5 kJ mol⁻¹ obtained by the thermokinetic method [23].

The failure to observe proton transfer from H₃O⁺ to any of the other reactant molecules suggests that their proton affinities are all significantly less than PA(H₂O). The validity of this statement can be tested in only one case, CH₃Br. The proton affinity of CH₃Br has been determined, and the failure to observe CH₃BrH⁺ from the reaction of H₃O⁺ with CH₃Br is consistent with the relative proton affinities of CH₃Br (664 kJ mol⁻¹) and H₂O (691 kJ mol⁻¹):

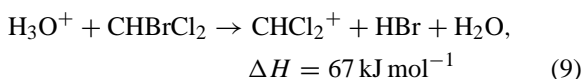


4.3. Hydrogen halide elimination and other reactions

These are observed for the compounds CHFBr_2 , CHBrCl_2 , CHBr_2Cl , $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, and $\text{CH}_3\text{CH}_2\text{Br}$. In general a common pattern is observed; one or two pairs of ions are observed, a carbocation, formed by the loss of a halogen (as the hydrogen halide), and the corresponding protonated alcohol where the water from the H_3O^+ is retained. An exception is CHBrCl_2 , where two protonated alcohols are formed but only one carbocation observed. Whilst formation of the carbocation is formally and thermodynamically equivalent to dissociative proton transfer it is not suggested that this is the mechanism of carbocation formation. It is suggested that in all cases the protonated alcohol is the initial product ion and that if this has sufficient internal energy it can fragment into water and the carbocation before being collisionally stabilised. Unfortunately few thermodynamic data on the halogenated alcohols and related carbocations are available but where they are, they tend to support this argument, viz. for $\text{CH}_3\text{CH}_2\text{Br}$

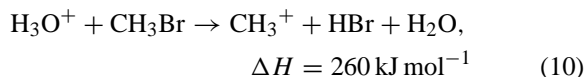


and for CHBrCl_2 whilst formation of the observed protonated alcohol can be presumed to be exothermic, formation of the non-observed associated carbocation is endothermic.

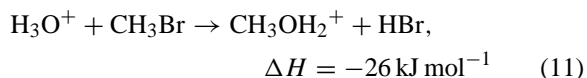


Such thermodynamic arguments, whilst superficially attractive, are of limited value ignoring as they do potential energy barriers to reaction, i.e., activation energies; they merely indicate what may be observed. Three examples will suffice to demonstrate this postulate. CH_3Br reacts exclusively to give the associa-

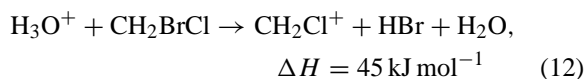
tion product $\text{CH}_3\text{Br} \cdot \text{H}_3\text{O}^+$. Whilst formation of the methyl carbocation is endothermic



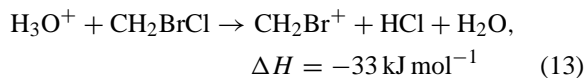
formation of protonated methanol, not observed, is exothermic



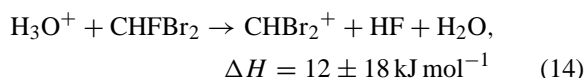
CH_2BrCl is not observed to react. Yet although formation of CH_2Cl^+ is endothermic



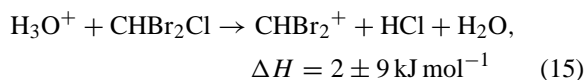
formation of CH_2Br^+ is exothermic



In contrast, formation of CH_2Br^+ from CHFBr_2 is thermoneutral

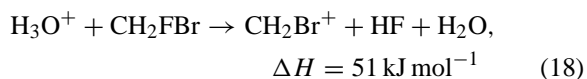
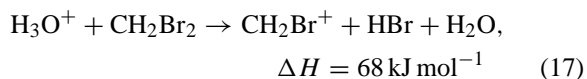
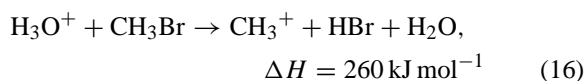


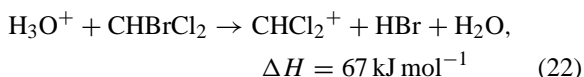
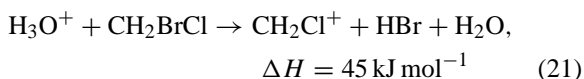
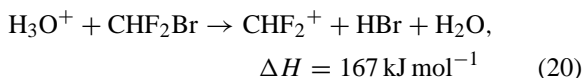
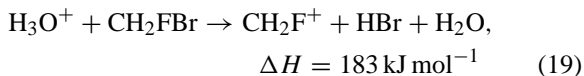
yet is formed close to the collisional rate. Similarly, formation of CHBr_2^+ from CHBr_2Cl is thermoneutral



yet is formed close to the collisional rate.

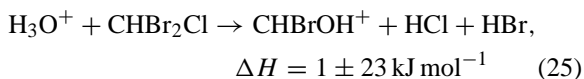
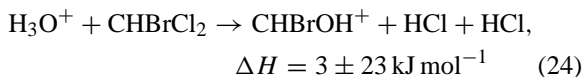
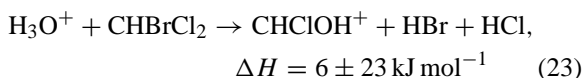
Thermodynamic data are available for the formation of carbocations for a number of the compounds studied





and these are consistent with their non-observation.

An additional and unexpected reaction is the elimination of a hydrogen halide from a protonated alcohol to produce a protonated aldehyde. This is observed for both CHBrCl_2 and CHBr_2Cl albeit in only trace amounts. The proton affinities of CHClO and CHBrO are not reported in the literature, but they can be estimated from the proton affinities of CH_2O ($=713 \text{ kJ mol}^{-1}$) and CF_2O ($=667 \text{ kJ mol}^{-1}$) together with the values of $\Delta_f H(\text{CHClO})$ and $\Delta_f H(\text{CHBrO})$ from Thomas et al. [11], $\Delta_f H(\text{CHClOH}^+)$ and $\Delta_f H(\text{CHBrOH}^+)$ to be 676 kJ mol^{-1} and 729 kJ mol^{-1} . The reaction enthalpies for the production of CHClOH^+ and CHBrOH^+ from the reaction of H_3O^+ with CHBrCl_2 and CHBr_2Cl are therefore



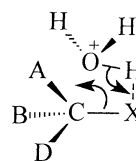
which are not inconsistent with the observations.

5. A discussion of the reaction mechanisms

The discussion of the results presented above leaves several questions unaddressed. These are:

- why do some reactions have activation barriers and others, when superficially similar, do not?
- why are F–C and Cl–C bonds broken preferentially to Br–C bonds when they are the stronger?
- what is the mechanism for the formation of the protonated alcohols?
- $\text{CH}_3\text{CH}_2\text{Br}$ is unusual in that it undergoes all three types of reaction (proton transfer, hydrogen halide ejection and association). Why?

A start can be made to answer these question by considering the structure of the H_3O^+ –molecule complex, schematically represented below:

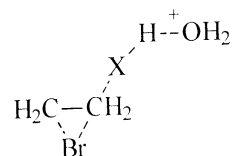


where X is a halogen and A, B and D can be hydrogens, halogens, or carbon containing groups. Ignoring for the present the mechanistic arrows, the initially formed species is H_3O^+ hydrogen bonded to the halogen X. If this hydrogen bonding is not too strong the structure can be easily stabilised by collisions with the helium bath gas. The range of rates for the production of the association complex (see Tables 1 and 2) indicates that there is a fine balance between the initial structure being strong enough to be stabilised by collision before it reverts back to the starting species but not having sufficient internal energy to allow further reaction before collisional stabilisation. If the hydrogen bond is strong enough to allow more than a transient existence of the complex and sufficient energy is present in the complex to allow further reaction then the electrophilic rearrangement indicated by the mechanistic arrows in the structure can occur.¹ Such a mechanism requires

¹ Beauchamp and coworkers [24] studying the gas phase reactions of protonated methyl and ethyl chlorides with water by ion cyclotron resonance (ICR) suggested a similar process to explain their observations. They found that protonated methyl chloride transferred a proton to water whereas protonated ethyl chloride reacted via a similar reaction complex to that shown above to yield protonated ethanol. These differences in reactivity they ascribed to methyl chloride having a lower proton affinity than water

the intramolecular rearrangement leading to the elimination of HX and the formation of the protonated alcohol to be fast as otherwise collisional stabilisation (cooling) of the complex will occur and the complex will not have sufficient internal energy to overcome the barrier for rearrangement/elimination. The data in Tables 1 and 2 show this to be the case with all compounds that produce the protonated alcohol reacting with H_3O^+ close to the collisional rate. The proposed mechanism involves the concerted breaking of a C–X bond and formation of an H–X bond and it might be thought that some useful information might be gained by considering the enthalpy difference between the two bonds for the different halogens. However, taking mean bond enthalpies [25] it can be seen that the differences between the two bonds are 81, 93, and 90 kJ mol^{-1} for $\text{X} = \text{F}$, Cl , and Br , respectively, i.e., very little difference whereas, in practice, the difference can be much larger. For instance for the reaction of H_3O^+ with CH_2BrCl the difference between breaking the C–Cl and C–Br bonds and the formation of the corresponding hydrogen halides is 78 kJ mol^{-1} (see reactions (17) and (19)) not the 3 kJ mol^{-1} expected from the mean bond enthalpies. What then is the determining force(s) for selectivity of reaction? As stated above formation of a hydrogen bond between H_3O^+ and a halogen is the initial process and the strength of that bond and thus the excess internal energy in the initially formed complex determines whether or not further reaction occurs. It is seen that the halogen to be eliminated as H–X is the one to which hydrogen bonding occurs even if this forms the strongest C–X bond. Mechanistically this has to be so but despite what was said above over the use of mean bond energies, the increase in internal energy as a consequence of forming a strong hydrogen bond will at least compensate in part for the increase in energy required to break the C–X bond, which will in

any event have been weakened by the formation of the strong hydrogen bond. Hydrogen bonding will be strongest when X is F. It will be much weaker when X is Br and this is demonstrated by the $\sim 20:1$ ratio of $\text{HF}:\text{HBr}$ production from CH_2FBr_2 . In the chlorine and bromine containing compounds CH_2BrCl_2 and $\text{CH}_2\text{Br}_2\text{Cl}$ the ratio of $\text{HCl}:\text{HBr}$ production is expected (and indeed is seen) to be greater than 1:1 but less than the 20:1 seen for the $\text{HF}:\text{HBr}$ production from CH_2FBr_2 as the hydrogen bond to Cl is expected to be greater than that to Br. The arguments thus far do not explain satisfactorily the apparent discrepancy in reactivity between the halogenated bromomethanes CH_3Br , CH_2Br_2 , and CH_2BrCl and the halogenated bromoethanes $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Cl}$. We ascribe the enhanced reactivity of the bromoethanes to neighbouring group participation of a bromine leading to a structure schematically shown below:



Since hydrogen bonding to Cl is, as stated above, stronger than that to Br and coupled to the greater degree of anchimeric assistance expected from Br compared to that expected from Cl, this also explains why breaking of the C–Cl bond occurs but not that of the C–Br bond in $\text{CH}_2\text{BrCH}_2\text{Cl}$. Such neighbouring group participation cannot explain the difference in behaviour between CH_3Br and $\text{CH}_3\text{CH}_2\text{Br}$. That non-dissociative proton transfer is observed with $\text{CH}_3\text{CH}_2\text{Br}$ but not with CH_3Br is consistent with the published proton affinities but, that said, it is interesting that the PAs should be so different. This question may repay *ab initio* study. But why is $\text{CH}_3\text{CH}_2\text{OH}_2^+$ produced whereas CH_3OH_2^+ is not? Both are exothermic (see reactions (8) and (11), respectively) and both association complexes are formed with sufficiently low exothermicities that they can be collisionally stabilised. It is however likely that during the substitution (or potential substitution of the Br by O) the reacting carbon atom develops some

(17 kJ mol^{-1}) whereas ethyl chloride had a higher proton affinity (12 kJ mol^{-1}) thus allowing the oxygen of water to retain some nucleophilic character in the reaction complex. More recent values of the proton affinities of methyl and ethyl chlorides suggest that these differences are 44 and 2 kJ mol^{-1} but this does not affect their basic argument.

carbocationic character. This will be stabilised in the ethyl compound compared to the methyl compound by mesomeric and hyperconjugative effects and these effects may be sufficient to increase the likelihood of intramolecular reaction within the complex before collisional stabilisation of the complex occurs.

In conclusion, these arguments are consistent with the initial suggestion that which reaction pathway occurs (if any) is determined by a very fine balance of energetics. It is apparent that some of the arguments given above lead to predictions of reactivity that can be explored by an extension of the series of compounds studied here, and such an extension is planned.

6. Summary

The ion chemistry of bromine containing molecules is essentially unexplored. This lack of information, the use of H_3O^+ as the reagent ion in the proton transfer reaction mass spectrometer and because H_3O^+ is an important atmospheric ion provide the motivation for this study.

In this paper the reaction of bromine containing fully and partially halogenated C_1 and C_2 hydrocarbons with H_3O^+ is reported. Of the 13 reactions investigated, only the reactions of H_3O^+ with CHF_2Br [13] and with CH_3Br and $\text{CH}_3\text{CH}_2\text{Br}$ [14] have been reported in the literature. H_3O^+ reacts with CHFBr_2 , CHBrCl_2 , CHBr_2Cl , $\text{CH}_2\text{BrCH}_2\text{Cl}$, and $\text{CH}_2\text{BrCH}_2\text{Br}$ with a rate coefficient close to the collisional value to give predominantly protonated alcohols and corresponding carbocations as the main ionic products.

Proton transfer is not a dominant reaction mechanism, indicating that for the majority of bromine molecules investigated in this study, their proton affinities are less than that of water ($\text{PA}(\text{H}_2\text{O}) = 691.0 \text{ kJ mol}^{-1}$). Mechanistic arguments have been given that go some way to explaining the observed range of both reactivity and reaction pathways. It would be interesting to repeat some of the above experiments with D_3O^+ as the reagent cation, or to investigate the corresponding deuterated organic

reagent neutrals to determine which hydrogen takes part in the halogen halide elimination, in order to test the proposed reaction mechanisms.

In Section 2, we mentioned that this investigation was in part inspired by the development of the PTR-MS by Professor W. Lindinger and his colleagues at the Institut für Ionenphysik der Leopold-Franzens-Universität. A final comment should therefore be made with respect to the use of the PTR-MS. The operation of the PTR-MS is based on the proton donating properties of H_3O^+ . What this present study has illustrated is that the reactions of H_3O^+ with molecules can be more varied than just simple proton transfer. Such reactions have the potential of extending the use of the PTR-MS for trace gas detection and other applications. This study also serves to illustrate the need for fundamental studies of ion–molecule studies to provide rate data, product ion distributions, and mechanistic information. These feed into the applied areas of trace gas detection to which the PTR-MS is so well suited. This parallels Professor W. Lindinger's research activities, which drew extensively from fundamental and applied science.

Acknowledgements

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