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Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and O_2^+ with several aromatic and aliphatic monosubstituted halocarbons

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Abstract

We describe the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+, and O_2^+ with the monosubstituted halobenzenes, C_6H_5X, the monosubstituted halotoluene isomers 2-$C_6H_5CH_3X$ and 4-$C_6H_5CH_3X$ ($X = F$, Cl, Br, I), benzyl chloride, $C_6H_5CH_2Cl$, benzyl bromide, $C_6H_5CH_2Br$, and the monosubstituted halomethanes and haloethanes CH_3X and C_2H_5X ($X = Cl$, Br, I). The H_3O^+ reactions with the aromatic halocarbons, M, are rapid and mostly proceed via direct proton transfer producing MH^+ ions, the exceptions being the benzyl halides in which only HCl (and HBr) elimination occurs from the nascent MH^+ ions. The H_3O^+ reactions with the aliphatic halocarbons are more varied in their rates and products, and in some reactions association occurs forming $H_3O^+ \cdot M$ ions. The NO^+ reactions with the aromatics mostly proceed rapidly via charge transfer producing the parent cations M^+ only, whereas the NO^+ reaction with the aliphatics are generally slow association reactions resulting in $NO^+ \cdot M$ ions. The O_2^+ reactions are fast mostly proceeding via nondissociative charge transfer producing the parent cations M^+ only, but in some of these reactions minority dissociative charge transfer channels are evident in which a halogen atom is eliminated leaving the corresponding hydrocarbon ion. In conclusion, some general observations are made concerning near-thermoneutral charge transfer and proton transfer processes. (Int J Mass Spectrom 189 (1999) 213–223) © 1999 Elsevier Science B.V.

Keywords: Selected ion flow tube (SIFT); Ion–molecule reactions; Halocarbons; Proton transfer; Charge transfer; Chemical ionisation; Trace gas analysis

1. Introduction

In this paper we report the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+, and O_2^+ with the monosubstituted halomethanes and haloethanes CH_3X and C_2H_5X ($X = Cl$, Br, I), the monosubstituted halobenzenes, C_6H_5X, the monosubstituted halotoluene isomers 2-$C_6H_5CH_3X$ and 4-$C_6H_5CH_3X$ ($X = F$, Cl, Br, I) and benzyl chloride, $C_6H_5CH_2Cl$, and benzyl bromide, $C_6H_5CH_2Br$. This study continues our studies of the reactions of these three ions with several other types of organic compounds including alcohols [1], aldehydes and ketones

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[2], carboxylic acids and esters [3], ethers [4], organosulphur molecules [5], amines and other nitrogen-containing compounds [6], several structural isomers of the amines with the common molecular formula $C_5H_{13}N$ [7], aromatic and aliphatic hydrocarbons [8] and, most recently, several chloroalkanes and chloroalkenes [9]. The kinetic data obtained from these studies comprises the required database of the reactions of these three ionic species, which are our chosen precursor ions for our SIFT mass spectrometric analytical method (SIFT/MS; [10]). This method combines fast flow tube techniques and chemical ionisation [11]); using SIFT/MS we are able to determine the partial pressures of trace gases in air [12] and metabolites in human breath [13] down to the low parts per billion (ppb) regime in real time (from a single exhalation of breath) [14,15].

In addition to providing the extensive database, these studies are providing a great deal of information on the various fundamental processes that occur in ion–molecule reactions at thermal energies [1–9]. Thus, it is seen, as expected, that the process of proton transfer occurs with unit efficiency from H_3O^+ to molecules, M, with proton affinities (PA) appreciably greater than that of H_2O (PA = 691 kJ mol^{-1} [16]), i.e. when these reactions are clearly exothermic. This is the situation for the vast majority of organic molecules when the product ions of these reactions are commonly MH^+ ions. However, when M is an alcohol, an aldehyde, and a carboxylic acid, product ions of the kind $(M–OH)^+$ are often seen which result from the elimination of H_2O molecules from the nascent $(MH^+)^*$ ions [1–3]. Because these reactions invariably proceed with unit efficiency, i.e. the measured rate coefficient for the reactions, k, are equal to their respective collisional rate coefficient, k_c [17], then any small potential barriers that may exist to these nondissociative and dissociative proton transfer reactions can be overcome by their inherent exothermicities [i.e. PA(M)–PA(H_2O)]. The situation is not so clear when the PA of the reactive molecules are close to PA(H_2O). This is the case for most higher-order alkanes [8]. The PA for methane, ethane, *n*-propane, and *n*-butane are all smaller than PA(H_2O) and so proton transfer from H_3O^+ to these molecules is endothermic and does not occur at the thermal energies (300 K) at which these SIFT experiments are carried out. The available values of the PA of these *n*-alkanes indicate increasing values with the chain length up to propane [16], and although no values of the PA for larger *n*-alkanes are available it therefore might be expected that the PA of the larger *n*-alkanes will continue to increase towards that of H_2O molecules. It is therefore somewhat surprising to find that protonated *n*-hexane, *n*-octane, *n*-decane, and *n*-dodecane are not observed as products of the reactions of these hydrocarbons with H_3O^+ [8]. Rather, we observe that association occurs forming $H_3O^+ \cdot M$ adduct ions, the formation rates of which increase with the chain length, the effective bimolecular rate coefficient, k_{eff}, for the H_3O^+/*n*-dodecane reaction becoming equal to k_c under the conditions of these SIFT experiments (helium carrier gas pressure about 0.5 Torr at a temperature of 300 K) [8].

Previous work [18,19] has indicated that the PA of the halomethanes and haloethanes straddle the PA of H_2O and so, following the precedence of the hydrocarbons, we might expect to see adduct ions formed in the reactions of H_3O^+ with some of these halocarbons. Further to this, our most recent study of the reactions of H_3O^+ reactions with several chloroalkanes (which also have relatively low PA [16]) show that direct proton transfer producing MH^+ ions, ion/molecule association producing $H_3O^+ \cdot M$ ions, HCl elimination from the protonated molecule producing $(M–Cl)^+$ ions, and even incorporation of H_2O into the ion with the elimination of one or two HCl molecules occur [9].

The reactions of NO^+ ions with polar organic molecules [1–9] variously proceed via hydride ion transfer producing $(M–H)^+$ ions, hydroxide ion transfer producing $(M–OH)^+$ ions, and ion/molecule association producing $NO^+ \cdot M$ ions, the last being most typical of the reactions with ketones [2]. However, charge transfer is usually facile when the reactant molecule has an ionisation energy less than that of NO (9.26 eV [20]); this is very much the situation for most amines [6] and most aromatic hydrocarbons [8]. For the reactions of NO^+ with some chloroalkanes, Cl^- transfer occurs producing $(M–Cl)^-$ ions and

NOCl molecules [9]. Examples of halide ion transfer are also found in the present study. The reactions of O_2^+ with organic molecules are invariably fast and proceed via charge transfer producing the parent cations M^+ which often dissociate producing fragment ions. These processes are also dominant in the present data for the O_2^+ reactions.

2. Experimental

The SIFT is a standard technique for the study of ion–molecule reactions at thermal energies which has been described in numerous review articles (see, for example, [21]). We have described its use as an analytical tool in some recent review papers [12,13]. The approach we take to the determination of the rate coefficients, k, and the ion product distributions for the reactions of the liquid halocarbons included in this study is essentially identical to that taken for all our previous studies of several other classes of liquid organic compounds. It is described in detail in our alcohols paper [1] and outlined in subsequent papers [2–9], so only a brief outline of the method is required here.

We have been able to reasonably assume in most of our previous studies that the k for the H_3O^+ reactions proceed at the collisional rate with rate coefficient, k_c, because the proton affinities, PA, of most of the organic molecules chosen for these studies exceed the PA of the H_2O molecule; then the $k = k_c$ [22]. The k_c can be calculated [17] if the polarisabilities and dipole moments of the reactant molecules are known [23] or can be estimated [1]. Then the corresponding k for the NO^+ and O_2^+ reactions with each particular molecule are obtained in the usual way [1,21] from the relative decay rates of all three reactant ions (H_3O^+, NO^+, and O_2^+) as they are simultaneously injected into the helium carrier gas of the SIFT whilst the reactant organic vapour or its weak mixture in air is introduced at a measured flow rate into the helium. This approach is taken because of the "sticky" nature of most organic compounds which renders measurements of the absolute flow rates of their neat vapours difficult. The rationale and justification for this approach is given in our previous papers [1,2].

This is an acceptable approach to take in determining the k for the aromatic halocarbons included in this study because they all have PA which appreciably exceed PA(H_2O) (see [16] and Table 4 later). However, the situation for some of the aliphatic halocarbons is not so simple because the available data show that some have smaller PA than PA(H_2O). Thus they cannot undergo efficient proton transfer with H_3O^+ at thermal energies. Obviously, therefore, it cannot be assumed that these compounds will react with H_3O^+ at the collisional rate. Fortunately, however, the available data on the reactions of O_2^+ with halocarbons indicate that they generally react (charge transfer) at or close to the collisional rate [24,25], data which are supported by our crude measurements using neat vapour, and therefore we feel justified in assuming that this is the case for the halocarbon reactions included in this study. So with this assumption we can estimate the rate coefficients for the (often slower) reactions of H_3O^+ and NO^+ from the relative decay rates of all three ions as they simultaneously react with each aliphatic halocarbon as is explained above. However, some doubt must remain on the absolute values of these rate coefficients, but the relative values of the k for the reactions of the H_3O^+, NO^+, and O_2^+ with each halocarbon are accurate. These experimentally derived k values are listed in Tables 1 and 3 and are subject to an uncertainty of ±25%. We discuss these kinetic data in subsequent sections of this paper.

The product ions and their percentages for these reactions are obtained in the usual way for SIFT studies [21] by injecting each of the reactant ions into the helium carrier gas separately and observing the relative count rates of the various product ions with the downstream mass spectrometer. It is worthy of note that the three reactant ion species are formed and then extracted from a microwave cavity discharge in an argon/wet air mixture at a pressure of about 0.1 Torr. Any residual electronic (and vibrational) excitation in these reactant ions is minimised (quenched) by the addition of a small amount of air to the helium carrier gas [1,2]. All these measurements were carried

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the aromatic halides listed. Also given are the molecular weights, m, in atomic units, u, the polarisabilities, α, in units of 10^{-24} cm^3 and the permanent dipole moments, μ, in Debye, D, of these aromatic halides. The values of α and μ are known for some of these aromatic halides and they are shown in regular type (taken from [25]). For the remaining aromatic halides we have estimated their μ and α (given in italics) by adopting the values for similar molecules. The collisional rate coefficients, k_c, given in the square brackets have been calculated using the parameterised trajectory formulation of Su and Chesnavich [17]. The estimated uncertainty in these calculated k_c is ±20%. On the assumption that all the H_3O^+ reactions proceed at their collisional rates, the rate coefficients, k, for the O_2^+ and NO^+ reactions have been experimentally derived by the procedure described in the text. The k and k_c are given in units of 10^{-9} cm^3 s^{-1}.

Molecule	m [u]	α [10^{-24} cm^3]	μ [D]	k, k_c (H_3O^+) [10^{-9} cm^3 s^{-1}]	k, k_c (NO^+) [10^{-9} cm^3 s^{-1}]	k, k_c (O_2^+) [10^{-9} cm^3 s^{-1}]
fluorobenzene	96	10.30	1.60	2.7 [2.7]	2.3 [2.3]	2.1 [2.2]
chlorobenzene	112	12.30	1.69	2.9 [2.9]	2.4 [2.4]	2.4 [2.3]
bromobenzene	156	14.70	1.70	3.0 [3.0]	2.8 [2.5]	2.6 [2.4]
iodobenzene	204	15.50	1.70	3.0 [3.0]	1.1 [2.4]	1.0 [2.4]
benzylchloride	126	*13 ± 0.5*	*2 ± 0.5*	3.2 [3.2]	3.2 [2.6]	2.6 [2.6]
benzylbromide	170	*15 ± 0.5*	*2 ± 0.5*	3.2 [3.2]	3.1 [2.7]	2.5 [2.6]
2-fluorotoluene	110	12.30	1.37	2.7 [2.7]	2.3 [2.2]	2.1 [2.2]
4-fluorotoluene	110	12.30	2.00	3.2 [3.2]	3.2 [2.6]	2.5 [2.6]
2-chlorotoluene	126	*13 ± 0.7*	1.56	2.8 [2.8]	2.0 [2.3]	1.9 [2.3]
4-chlorotoluene	126	*13 ± 0.7*	2.21	3.4 [3.4]	2.7 [2.8]	2.1 [2.7]
2-bromotoluene	170	*15 ± 0.7*	*1.5 ± 0.5*	2.9 [2.9]	2.0 [2.3]	1.9 [2.3]
4-bromotoluene	170	*15 ± 0.7*	*2 ± 0.5*	3.2 [3.2]	2.6 [2.7]	2.4 [2.6]
2-iodotoluene	218	*17 ± 1*	*1.2 ± 0.5*	2.8 [2.8]	2.0 [2.2]	1.9 [2.2]
4-iodotoluene	218	*17 ± 1*	*1.8 ± 0.5*	3.1 [3.1]	2.2 [2.6]	2.2 [2.5]

out in helium carrier gas at a pressure of 0.5 Torr at room temperature.

3. Results and discussion

A glance at Table 1 reveals that the measured rate coefficients, k, for the reactions of all the aromatic halocarbons with both H_3O^+, NO^+, and O_2^+ are fast and equal (within experimental uncertainty) to their respective k_c. The only exceptions amongst these 42 reactions are the charge transfer reactions of NO^+ and O_2^+ with iodobenzene for which the k are about 0.5 k_c. It is not unknown for charge transfer reactions to proceed at rates somewhat less than the collisional rate at thermal energies [24,25] and this is usually attributed to unfavourable Franck–Condon factors [26,27], but for reactions involving polyatomic molecules it is the exception rather than the rule. However, the data in Table 3 reveal that the k for the 18 aliphatic halocarbon reactions with H_3O^+ and NO^+ are generally much less than their respective k_c (based on the assumption that the k for the O_2^+ reactions are equal to their respective k_c; see Sec. 2). These low values of k can be rationalised in terms of the energetics and the reaction processes that are involved as will be discussed below. The ionic products of all these reactions are presented in Tables 2 and 4. We now discuss under separate headings these aromatics and aliphatic halocarbon reactions.

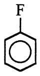
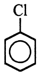
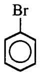
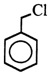
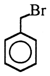
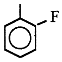
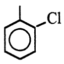
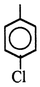
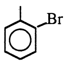
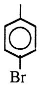
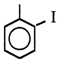
3.1. Aromatic halocarbon reactions

The ionic products of these 42 reactions are given in Table 2. The 14 compounds comprise 4 monohalobenzenes, 8 monohalotoluenes, benzyl chloride, and benzyl bromide. The reactions of the substituted benzenes and toluenes with H_3O^+, NO^+, and O_2^+ are very simple whereas the benzyl halide reactions are more complex.

3.1.1. H_3O^+ reactions

The proton affinities (PA) of all these aromatic halocarbons (see Table 2) exceed that of H_2O (691 kJ mol^{-1} [16]) and so it is no surprise that all these

Table 2
Products of the reactions of H_3O^+, NO^+, and O_2^+ with the aromatic halides listed. The molecular formulae of the ion products do not necessarily represent their structures; the percentage of each ion products is given in brackets. The ionisation energies of the aromatic halides are given in eV [23] in regular type and their proton affinities, when known, are given in kJ/mol [16] in italics.

Compound IP [eV] PA[kJ/mol]		H_3O^+	NO^+	O_2^+
fluorobenzene 9.20 *764*		$C_6H_5F \cdot H^+$(100) + H_2O	$C_6H_5F^+$(75) + NO $C_6H_5F \cdot NO^+$(25)	$C_6H_5F^+$(100) + O_2
chlorobenzene 9.06 *760*		$C_6H_5Cl \cdot H^+$(100) + H_2O	$C_6H_5Cl^+$(100) + NO	$C_6H_5Cl^+$(100) + O_2
bromobenzene 8.98 *763*		$C_6H_5Br \cdot H^+$(100) + H_2O	$C_6H_5Br^+$(100) + NO	$C_6H_5Br^+$(100) + O_2
iodobenzene 8.69		$C_6H_5I \cdot H^+$(100) + H_2O	$C_6H_5I^+$(100) + NO	$C_6H_5I^+$(100) + O_2
benzylchloride 9.14		$C_6H_5CH_2^+$(100) + HCl + H_2O	$C_6H_5CH_2^+$(95) + NOCl $C_6H_5CH_2Cl^+$(5) + NO	$C_6H_5CH_2^+$(60) + Cl + O_2 $C_6H_5CH_2Cl^+$(40) + O_2
benzylbromide 9.0		$C_6H_5CH_2^+$(90) + HBr + H_2O $C_6H_5CH_2BrH^+$(10) + H_2O	$C_6H_5CH_2^+$(70) + NOBr $C_6H_5CH_2Br^+$(30) + NO	$C_6H_5CH_2^+$(95) + Br + O_2 $C_6H_5CH_2Br^+$(5) + O_2
2-fluorotoluene 8.91 *782*		$C_7H_7F \cdot H^+$(100) + H_2O	$C_7H_7F^+$(100) + NO	$C_7H_7F^+$(95) + O_2 $C_7H_7^+$(5) + F + O_2
4-fluorotoluene 8.79 *757*		$C_7H_7F \cdot H^+$(100) + H_2O	$C_7H_7F^+$(100) + NO	$C_7H_7F^+$(100) + O_2
2-chlorotoluene 8.83 *771*		$C_7H_7Cl \cdot H^+$(100) + H_2O	$C_7H_7Cl^+$(100) + NO	$C_7H_7Cl^+$(80) + O_2 $C_7H_7^+$(20) + Cl + O_2
4-chlorotoluene 8.96 *756*		$C_7H_7Cl \cdot H^+$(100) + H_2O	$C_7H_7Cl^+$(100) + NO	$C_7H_7Cl^+$(85) + O_2 $C_7H_7^+$(15) + Cl + O_2
2-bromotoluene 8.58 *783*		$C_7H_7Br \cdot H^+$(100) + H_2O	$C_7H_7Br^+$(100) + NO	$C_7H_7Br^+$(85) + O_2 $C_7H_7^+$(15) + Br + O_2
4-bromotoluene 8.67 *783*		$C_7H_7Br \cdot H^+$(100) + H_2O	$C_7H_7Br^+$(100) + NO	$C_7H_7Br^+$(90) + O_2 $C_7H_7^+$(10) + Br + O_2
2-iodotoluene 8.62 *788*		$C_7H_7I \cdot H^+$(100) + H_2O	$C_7H_7I^+$(100) + NO	$C_7H_7I^+$(75) + O_2 $C_7H_7^+$(15) + I + O_2 I^+(10) + C_7H_7 + O_2
4-iodotoluene 8.6 *788*		$C_7H_7I \cdot H^+$(100) + H_2O	$C_7H_7I^+$(100) + NO	$C_7H_7I^+$(95) + O_2 $C_7H_7^+$(5) + I + O_2

reactions are fast, i.e. $k = k_c$. The initial step in these reactions is proton transfer producing the protonated parent molecule MH^+, and for the reactions of all 12 compounds with the halogen atom bonded to the aromatic ring, the only observed products are MH^+ ions as, for example, in the fluorobenzene reaction,

$$H_3O^+ + C_6H_5F \rightarrow C_6H_5F \cdot H^+ + H_2O \quad (1)$$

However, MH^+ does not appear as a stable product ion in the benzyl chloride reaction, the only ion product being $C_7H_7^+$,

$$H_3O^+ + C_6H_5CH_2Cl \rightarrow C_6H_5CH_2^+ + HCl + H_2O \quad (2)$$

This reaction is exothermic by 41 kJ mol^{-1} (according to the data from [20]) to produce the benzyl cation $C_6H_5CH_2^+$ which must surely be the product because there is a very large barrier (about 270 kJ mol^{-1} [28]) to the rearrangement of the benzyl cation to tropylium. Note (in Table 2) that the reactions of H_3O^+ with both of the chlorotoluene isomers do not result in HCl elimination even though these reactions would also be 41 kJ mol^{-1} exothermic for the formation of the benzyl cation and 70 kJ mol^{-1} exothermic for the production of tropylium [28]. A reaction similar to (2) occurs for benzyl bromide in which HBr is eliminated, but in this case the protonated parent molecule is also observed as a minor (10%) product (see Table 2).

3.1.2. NO^+ reactions

All these reactions are fast; indeed, some of the k values apparently exceed their respective k_c, but not by more than the estimated uncertainties in the measured k. The ionisation energies of all the aromatic halocarbons included in this study (see Table 2) are smaller than that of NO (9.26 eV [20]) and so it is no surprise to see that charge transfer occurs in all of these NO^+ reactions. In 11 of the 14 reactions the parent cation, M^+, is the only observed product ion as can be seen in Table 2. This is because their ionisation energies are not much smaller than that of NO and so these charge transfer reactions are not sufficiently exothermic to allow dissociation to occur (this contrasts with the corresponding O_2^+ reactions). The fluorobenzene reaction is only exothermic by 60 meV and in this case we see a parallel association product,

$$\begin{aligned} NO^+ + C_6H_5F + (He) & \\ &\rightarrow C_6H_5F^+ + NO + (He) \quad (75\%) \quad (3a) \\ &\rightarrow NO^+ \cdot C_6H_5F + (He) \quad (25\%) \quad (3b) \end{aligned}$$

This is yet another example of “charge transfer complexing” of which there are now many examples amongst the numerous reactions of NO^+ that we have studied in these surveys [1–9]. It is apparent that when the ionisation energy of the reactant molecule M is close to the recombination energy of the reactant ion, in this case NO^+, then the delocalisation of charge around the intermediate complex ion $(NO \cdot M)^+$ increases its lifetime against dissociation to NO^+ and M or NO and M^+ (when this is energetically allowed) and this increases the probability that a third body (He atoms of the carrier gas in these SIFT experiments) can intervene to stabilise the $(NO \cdot M)^+$ against dissociation. Hence the adduct ion is seen as a stable product of the reaction. This phenomenon is especially evident in the reactions of NO^+ with ketones [2]. When the ionisation energy of M exceeds that of NO, charge transfer is endothermic and then adduct ion formation generally occurs often in parallel with hydride ion transfer [2,3].

The more reactive halogen in the benzyl halides results in another reaction process as exemplified by the benzyl bromide reaction,

$$\begin{aligned} NO^+ + C_6H_5CH_2Br & \\ &\rightarrow C_6H_5CH_2^+ + NOBr \quad (70\%) \quad (4a) \\ &\rightarrow C_6H_5CH_2Br^+ + NO \quad (30\%) \quad (4b) \end{aligned}$$

Charge transfer is the minor channel with the major channel being due to bromide ion, Br^-, transfer in which the neutral molecule NOBr must be formed (production of NO and Br is clearly endothermic [20]). Similarly, Cl^- transfer occurs as the major channel in the benzyl chloride reaction (see Table 2).

Table 3
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the aliphatic halides listed. Also given are their molecular weights, m, in atomic units, u, the polarisabilities, α, in units of 10^{-24} cm^3 and the permanent dipole moments, μ, in Debye, D (taken from [25]). The collisional rate coefficients, k_c, are given in the square brackets [17]. The estimated uncertainty in these calculated rate coefficients is ±20%. On the assumption that all the O_2^+ reactions proceed at their collisional rates, the rate coefficients, k, for the H_3O^+ and NO^+ reactions have been experimentally derived by the procedure described in the text. The k and k_c are given in units of 10^{-9} cm^3 s^{-1}.

Molecule	m [u]	α [10^{-24} cm^3]	μ [D]	k, k_c (H_3O^+) [10^{-9} cm^3 s^{-1}]	k, k_c (NO^+) [10^{-9} cm^3 s^{-1}]	k, k_c (O_2^+) [10^{-9} cm^3 s^{-1}]
CH_3Cl	50	4.70	1.87	0.04 [2.8][a]	0.01 [2.4][a]	2.4 [2.4]
CH_3Br	94	5.87	1.81	0.2 [2.6][a]	0.02 [2.2][a]	2.2 [2.2]
CH_3I	142	7.97	1.62	1.2 [2.5]	0.1 [2.1][a]	2.0 [2.0]
C_2H_5Cl	64	7.27	2.05	1.6 [3.1][a]	<0.01 [2.6][a]	2.6 [2.6]
C_2H_5Br	108	8.05	2.03	1.7 [3.0][a]	0.4 [2.5][a]	2.4 [2.4]
C_2H_5I	156	10.00	1.91	2.5 [2.9]	1.2 [2.4][a]	2.3 [2.3]

[a] Effective two-body rate coefficients for these three-body reactions in helium at 0.5 Torr.

3.1.3. O_2^+ reactions

All these reactions are fast and proceed via charge transfer. For the halobenzenes the only product ions are the parent cations M^+ (see Table 2), because all dissociative charge transfer channels are endothermic and so cannot occur at thermal energies. However, this is not the case for the two benzyl halides for which dissociative channels are dominant, e.g.

$$O_2^+ + C_6H_5CH_2Cl$$

$$\rightarrow C_6H_5CH_2^+ + (Cl + O_2) \quad (70\%) \qquad (5a)$$

$$\rightarrow C_6H_6CH_2Cl^+ + O_2 \quad (30\%) \qquad (5b)$$

The dissociative channel (5a), producing the benzyl cation and a chlorine atom, is exothermic by 162 kJ mol^{-1} [20]. In the benzyl bromide reaction the dissociative channel represents 95% of the ionic products by virtue of the weaker C–Br bond. Dissociation occurs to varying degrees in the halotoluene reactions releasing the halogen atom, e.g.

$$O_2^+ + 2\text{-}C_6H_4CH_3Cl$$

$$\rightarrow C_7H_7Cl^+ + O_2 \quad (80\%) \qquad (6a)$$

$$\rightarrow C_7H_7^+ + (Cl + O_2) \quad (20\%) \qquad (6b)$$

although, as can be seen in Table 2 these are always minority channels. Presumably, the $C_7H_7^+$ product ions of these dissociative charge transfer reactions are of the form $C_6H_4CH_3^+$ although we cannot exclude the possibility that rearrangement takes place to produce the benzyl cation or even tropylium, both of which would be quite exothermic. It can also be seen in Table 2 that there is a tendency for more dissociation to occur in the ortho (2-) isomers of these halotoluenes. Note that in the 2-iodotoluene reaction a minor additional channel leads to the production of I^+ ions which is energetically possible by virtue of the very low ionisation energy of iodine atoms (10.45 eV [20]).

3.2. Aliphatic halocarbon reactions

The k for the H_3O^+ and NO^+ reactions are very varied as can be seen in Table 3 and the reaction processes involved are quite different from those for the aromatic halocarbon reactions as can be seen in Table 4. Ion–molecule association plays a dominant role because other reaction processes are often inhibited energetically. The H_3O^+ reactions especially require careful interpretation.

3.2.1. H_3O^+ reactions

The course of these reactions is determined to a large extent by the proton affinities (PA) of the reactant molecules relative to PA(H_2O). The PA values are given in Table 4 where it can be seen that PA(CH_3Cl) and PA(CH_3Br) are about 40 kJ mol^{-1} smaller than PA(H_2O). So for the reactions of H_3O^+ with these molecules, proton transfer is very endo-

Table 4
Products of the reactions of H_3O^+, NO^+, and O_2^+ with the aliphatic halides listed. The molecular formulae of the ion products do not necessarily represent their structures; the percentage of each ion products is given in brackets. The ionisation energies of the aliphatic halides are given in eV [23] in regular type and their proton affinities are given in kJ/mol [16] in italics.

Compound I.P. [eV] PA [kJ/mol]	H_3O^+	NO^+	O_2^+
CH_3Cl 11.26 *647.3*	$H_3O^+ \cdot CH_3Cl(100)$	$NO^+ \cdot CH_3Cl(100)$	$CH_3Cl^+(100)$
CH_3Br 10.54 *664.3*	$H_3O^+ \cdot CH_3Br(100)$	$NO^+ \cdot CH_3Br(100)$	$CH_3Br^+(100)$
CH_3I 9.54 *691.7*	$CH_3I \cdot H^+(100) + H_2O$	$NO^+ \cdot CH_3I(100)$	$CH_3I^+(100)$
C_2H_5Cl 10.98 *693.4*	$H_3O^+ \cdot C_2H_5Cl(50)$ $C_2H_5OH_2^+(50) + HCl$	$NO^+ \cdot C_2H_5Cl(100)$	$C_2H_4^+(60) + HCl + O_2$ $C_2H_5^+(30) + Cl + O_2$ $C_2H_5Cl^+(10) + O_2$
C_2H_5Br 10.29 *696.2*	$CH_3CH_2Br \cdot H^+(40) + H_2O$ $H_3O^+ \cdot C_2H_5Br(30)$ $C_2H_5OH_2^+(30) + HBr$	$NO^+ \cdot C_2H_5Br(100)$	$C_2H_5Br^+(60) + O_2$ $C_2H_5^+(40) + Br + O_2$
C_2H_5I 9.35 *724.8*	$CH_3CH_2I \cdot H^+(100)$	$NO^+ \cdot C_2H_5I(100)$	$C_2H_5^+(35) + I + O_2$ $C_2H_5I^+(65) + O_2$

thermic and cannot occur at SIFT energies and only termolecular association occurs, e.g.

$$H_3O^+ + CH_3Br + He \rightarrow H_3O^+ \cdot CH_3Br + He \tag{7}$$

The CH_3Cl association reaction is relatively inefficient (see Table 3), but the CH_3Br reaction (7) proceeds with an effective bimolecular rate coefficient, k_{eff}, which is about 0.1 k_c under the conditions of helium pressure and temperature of these SIFT experiments. $PA(CH_3I)$ is apparently greater than $PA(H_2O)$ by only about 1 kJ mol^{-1} [16] and yet proton transfer does occur but at less than unit efficiency ($k = 0.5\ k_c$) and the adduct ion $H_3O^+ \cdot CH_3I$ is not an observed product. This is because the probability that $(H_3O^+ \cdot CH_3I)^*$ will dissociate back to reactants is significant when the reaction is exothermic by less than about 20 kJ mol^{-1} [29] and also there may exist a small apparent barrier (~1 kJ mol^{-1}) to proton transfer reactions [29].

In the experimental paper by Beauchamp et al. [18], $PA(C_2H_5Cl)$ is estimated to be 9 kJ/mol greater than that of H_2O, but this figure has been reduced to about 2 kJ mol^{-1} [16] by correcting for entropy change. Yet proton transfer is not observed in the H_3O^+ reaction with C_2H_5Cl but rather adduct ion formation and HCl elimination occur,

$$H_3O^+ + C_2H_5Cl + (He)$$
$$\rightarrow H_3O^+ \cdot C_2H_5Cl + (He) \quad (50\%) \tag{8a}$$
$$\rightarrow C_2H_5OH_2^+ + HCl \quad (50\%) \tag{8b}$$

Reaction (8b) has been described by Holtz et al. [30] to occur via nucleophilic displacement in the reaction complex $H_3O^+ \cdot C_2H_5Cl$, a phenomenon which occurs when proton transfer from the protonated substrate to the nucleophile is endothermic. The present observation that the reaction complex is effectively stabilised in collisions with He atoms [reaction (8a)] at a pressure of 0.5 Torr implies that the lifetime of this complex is $\geq 10^{-7}$ s. These collected observations indicate that $PA(C_2H_5Cl)$ is somewhat less than $PA(H_2O)$.

$PA(CH_3Br)$ exceeds $PA(H_2O)$ by only 5 kJ mol^{-1} [16] and the protonated molecule does appear as the major product,

$$H_3O^+ + C_2H_5Br + (He)$$
$$\rightarrow C_2H_5Br \cdot H^+ + H_2O \quad (40\%) \tag{9a}$$
$$\rightarrow H_3O^+ \cdot C_2H_5Br + (He) \quad (30\%) \tag{9b}$$
$$\rightarrow C_2H_5OH_2^+ + HBr \quad (30\%) \tag{9c}$$

Again, as a result of this small proton affinity difference, this reaction most probably occurs within a complex with a lifetime sufficiently long [29] to allow a fraction of the $(H_3O^+ \cdot C_2H_5Br)^{+*}$ ions to be stabilised in helium atom collisions against dissociation and in which exothermic proton transfer and HBr elimination also occur.

PA(C_2H_5I) exceeds PA(H_2O) by about 34 kJ mol^{-1} and so according to the above ideas the lifetime of the intermediate complex will be very short and thus direct proton transfer proceeds very efficiently to produce only $C_2H_5I \cdot H^+$ ions (see Table 4) even though the production of $C_2H_5OH_2^+$ (+HI) [by analogy with reaction (9c)] would be exothermic by 49 kJ mol^{-1} [20]. This demonstrates that when direct proton transfer is sufficiently exothermic then it is facile.

3.2.2. NO^+ reactions

All these reactions proceed via termolecular ion–molecule association producing $NO^+ \cdot M$ ions and again there is evidence for the involvement of the phenomenon of "charge transfer complexing" alluded to in Sec. 3.1.2 above. The ionisation energies of CH_3Cl, CH_3Br, and C_2H_5Cl are much greater than that of NO (see Table 4) and thus we would predict that association would be inefficient in their reactions with NO^+. This is indeed the case, the k values being only about 1% of their k_c value (see Table 3). Now the ionisation energies of C_2H_5Br, CH_3I and especially C_2H_5I are closer to that of NO and the k values for these reactions are appreciable fractions of their respective k_c values. The ionisation energy of C_2H_5I exceeds that of NO by only 9 meV and for the termolecular reaction,

$$NO^+ + C_2H_5I + He \rightarrow NO^+ \cdot C_2H_5I + He \quad (10)$$

the k is 0.5 k_c.

3.2.3. O_2^+ reactions

The only process that occurs for the three methyl monohalides is nondissociative charge transfer producing the parent cations, but additional product channels occur for the ethyl monohalides as can be seen in Table 4. In all three ethyl halide reactions with O_2^+ the dissociative product channels which produce $C_2H_5^+$ (and the halogen atom) represent about 35% of the branching ratios, but in the C_2H_5Cl reaction an additional ion, $C_2H_4^+$, appears as the major product,

$$O_2^+ + C_2H_5Cl$$

$$\rightarrow C_2H_4^+ + (HCl + O_2) \quad (60\%) \quad (11a)$$

$$\rightarrow C_2H_5^+ + (Cl + O_2) \quad (30\%) \quad (11b)$$

$$\rightarrow C_2H_5Cl^+ + O_2 \quad (10\%) \quad (11c)$$

$C_2H_4^+$ is not a product of the C_2H_5Br and C_2H_5I reactions even though its production would be quite exothermic [20]. It is interesting and instructive to compare the product ions of these O_2^+/ethyl halide reactions with the mass spectra of these halides obtained using 70 eV electron impact (EI). The EI spectra (from [31]) are reproduced in Fig. 1, where it can be seen that the mass 28 u ion is dominant in the EI spectrum of C_2H_5Cl, but is only a minor ion in the C_2H_5Br and C_2H_5I spectra. The similarity of these results is because similar amounts of excess energy are available in both the O_2^+/halide charge transfer reactions and in the electron impact in which only 1–3 eV of energy is deposited in the molecules even at incident electron energies of 70 eV [32].

4. Concluding remarks

Some interesting conclusions can be drawn from the kinetic data reported in this paper and also the data obtained in our previous studies of H_3O^+, NO^+, and O_2^+ reactions [1–9]. When charge transfer reactions of NO^+ with organic molecules, M, are exothermic by a few tenths of an eV or more, then charge transfer invariably occurs rapidly. The parent molecular ion, M^+, is often the only product ion especially so when M is aromatic. Similarly, when H_3O^+ ions react with molecules with proton affinities which are greater than PA(H_2O) by a few kJ mol^{-1} then proton transfer to form MH^+ ions is facile in accordance with the ideas presented in [29]. For molecules with even

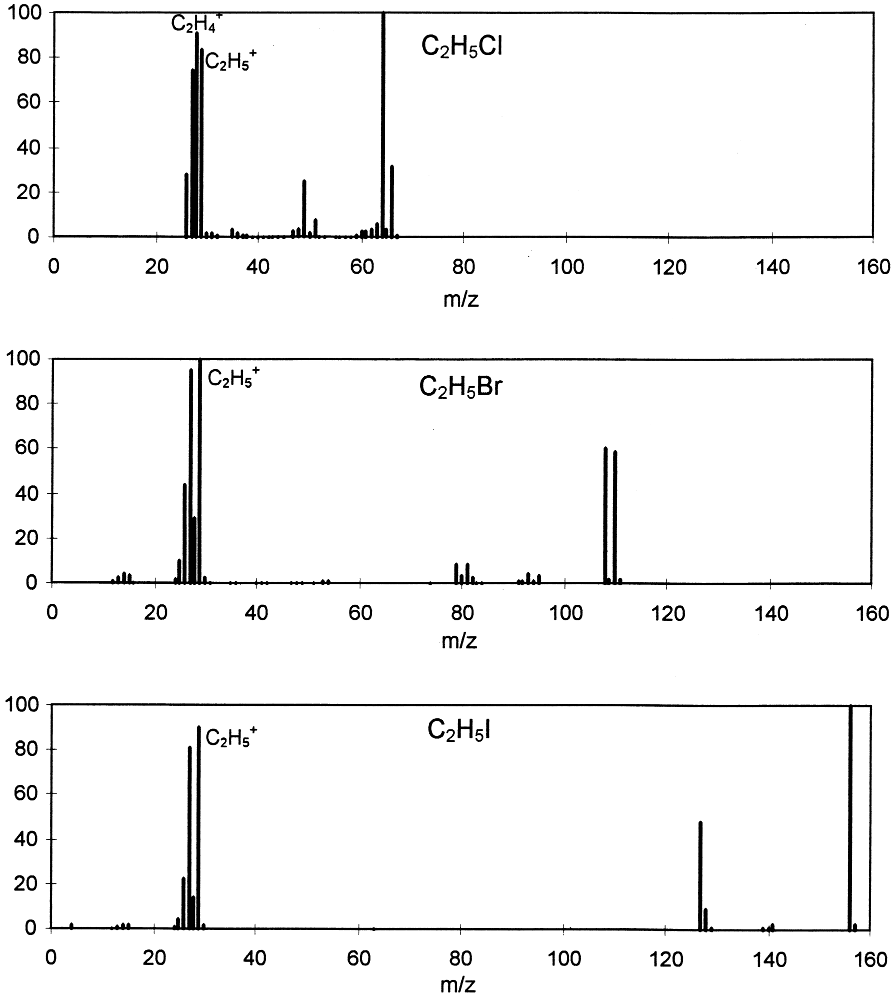


Fig. 1. Electron impact mass spectra (cracking patterns) for 70 eV electrons according to the NIST database [31] for C_2H_5Cl, C_2H_5Br, and C_2H_5I. Note the relative intensities of the ion signals at *m/z* = 28 ($C_2H_4^+$) and *m/z* = 29 ($C_2H_5^+$). See Table 4 for the products of the analogous O_2^+ reactions.

greater PA(M) elimination of stable molecules can occur from $(MH^+)^*$, examples being the elimination of H_2O molecules following the protonation of some alcohols [1], aldehydes [2], and carboxylic acids [3] by H_3O^+ and (from the present study) the elimination of HCl from benzyl chloride [see Eq. (2)].

When these charge transfer and proton transfer processes are close to thermoneutral, then ion–molecule association reactions are seen to occur forming the species $NO^+ \cdot M$ and $H_3O^+ \cdot M$, respectively. It seems that the phenomenon of “charge transfer complexing” enhances the lifetime of the $(NO^+ \cdot M)^{+*}$ excited complexes and that “proton bound complexes” of the kind $(H_2O \cdot H^+ \cdot M)^*$ can form in which “shuttling” or “tunnelling” of the proton between H_2O and M prolongs the lifetime of the complex [33]. Both these phenomena result in an increase in the efficiency of formation of stable adduct ions. It is evident that these observations need to be underpinned by further theoretical work.

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References

[1] P. Španěl, D. Smith, Int. J. Mass. Spectrom. Ion Processes 167/168 (1997) 375.
[2] P. Španěl, Y. Ji, D. Smith Int. J. Mass Spectrom. Ion Processes 165/166 (1997) 25.
[3] P. Španěl, D. Smith, Int. J. Mass Spectrom. Ion Process 172 (1998) 137.
[4] P. Španěl, D. Smith, Int. J. Mass Spectrom. Ion Processes 172 (1998) 239.
[5] P. Španěl, D. Smith, Int. J. Mass Spectrom. 176 (1998) 167.
[6] P. Španěl, D. Smith, Int. J. Mass Spectrom. 176 (1998) 203.
[7] P. Španěl, D. Smith, Int. J. Mass Spectrom. 185/186/187 (1998) 139.
[8] P. Španěl, D. Smith, Int. J. Mass Spectrom. 181 (1998) 1.
[9] P. Španěl, D. Smith, Int. J. Mass Spectrom. 184 (1998) 175.
[10] D. Smith, P. Španěl, Int. Rev. Phys. Chem. 15 (1996) 231.
[11] A.G. Harrison, Chemical Ionisation Mass Spectrometry, 2nd ed., CRC, Boca Raton, FL, 1992.
[12] D. Smith, P. Španěl, Rapid Commun. Mass Spectrom. 10 (1996) 1183.
[13] P. Španěl, D. Smith, Med. Biol. Eng. Comput. 34 (1996) 409.
[14] S. Davies, P. Španěl, D. Smith, Kidney International 52 (1997) 223.
[15] P. Španěl, S. Davies, D. Smith, Rapid Commun. Mass Spectrom. 12 (1998) 763.
[16] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.
[17] T. Su, and W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[18] J.L. Beauchamp, D. Holtz, S.D. Woodgate, S.L. Patt, J. Am. Chem. Soc. 94 (1972) 2798.
[19] M.N. Glukhovtsev, J.E. Szuleiko, T.B. McMahon, J.W. Gauld, A.P. Scott, B.J. Smith, A. Pross, L. Radom, J. Phys. Chem. 98 (1994) 13099; S.A.H. Petri, C.G. Freeman, M.J. McEwan, M. Meot-Ner, Int. J. Mass Spectrom. Ion Processes 90 (1989) 241.
[20] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (suppl. 1) (1988).
[21] D. Smith, N.G. Adams, Adv. At. Mol. Phys. 24 (1987) 1.
[22] D.K. Bohme, in P. Ausloos (Ed.), Interactions Between Ions and Molecules, Plenum, New York, 1975, p. 489.
[23] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC, Boca Raton, 1991.
[24] Y. Ikezoe, S. Matsuoka, M. Takebe, A. Viggiano, Gas Phase Ion–molecule Reaction Rate Constants Through 1986, Maruzen, Tokyo, 1987.
[25] V. Anicich, J. Phys. Chem. Ref. Data 22 (1993) 1469.
[26] J.B. Laudenslager, in Kinetics of Ion Molecule Reaction, P. Ausloos (Ed.), Plenum, New York, 1979, p. 405.
[27] C.A. Mayhew, D. Smith, Int. J. Mass Spectrom. Ion Processes 100 (1990) 737.
[28] B.J. Smith, N.E. Hall, Chem. Phys. Lett. 279 (1997) 165.
[29] G. Bouchoux, J.Y. Salpin, D. Leblanc, Int. J. Mass Spectrom. Ion Processes 153 (1996) 37.
[30] D. Holtz, J.L. Beauchamp, S.D. Woodgate, J. Am. Chem. Soc. 92 (1970) 7484.
[31] NIST Mass Spectra Data Center, S.E. Stein, director, in W.G. Mallard, P.J. Linstrom (Eds.), NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, 1997.
[32] F.W. McLafferty, F. Tureček, Interpretation of Mass Spectra, University Science Books, Mill Valley, CA, 1993.
[33] M.J. Henchman, D. Smith, N.G. Adams, J.F. Paulson, Z. Herman, Int. J. Mass Spectrom. Ion Processes 92 (1989) 15.