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International Journal of Mass Spectrometry 184 (1999) 175–181

International Journal of Mass Spectrometry

Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and O_2^+ with some chloroalkanes and chloroalkenes

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Received 3 November 1998; accepted 17 December 1998

Abstract

We describe the results of a selected ion flow tube study of the reactions of H_3O^+, NO^+, and O_2^+ with the chloromethanes CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, the chloroethanes CH_2ClCH_2Cl, CH_3CHCl_2, CH_3CCl_3, and $CHCl_2CHCl_2$, and the chloroethylenes $CHClCCl_2$ and C_2Cl_4. The H_3O^+ reactions with these molecules, M, are mostly rapid but unusually varied, the most evident processes being direct proton transfer producing MH^+ ions, ion/molecule association producing $H_3O^+.M$ 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. The NO^+ reactions are generally slow and proceed largely via ion/molecule association producing $NO^+.M$ ions. Only one of the reactions, that of CH_3CCl_3, is fast and proceeds via Cl^- transfer producing $CH_3CCl_2^+$ and an NOCl molecule. The O_2^+ reactions are apparently all fast and proceed via charge transfer producing the parent cations M^+ and via dissociative charge transfer with the elimination of Cl atoms and HCl molecules. In only one of these O_2^+ reactions (that with $CHCl_2CHCl_2$) is the carbon–carbon bond broken. (Int J Mass Spectrom 184 (1999) 175–181) © 1999 Elsevier Science B.V.

Keywords: Selected ion flow tube, SIFT; Ion/molecule reactions; Chlorocarbons; Proton transfer; Charge transfer; Ion/molecule association; Chemical ionisation

1. Introduction

In this article we report the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+, and O_2^+ with the chloromethanes CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, the chloroethanes CH_2ClCH_2Cl, CH_3CHCl_2, CH_3CCl_3, $CHCl_2CHCl_2$, and the chloroethylenes $CHClCCl_2$ and C_2Cl_4. This study follows our studies of the reactions of these ions with several other types of organic compounds including alcohols [1], aldehydes and ketones [2], carboxylic acids and esters [3], ethers [4], organosulphur molecules [5], amines [6], several structural isomers of the amines with the common molecular formula $C_5H_{13}N$ [7] and, most recently, of several aromatic and aliphatic hydrocarbons [8]. The kinetic data obtained from the present study extends the required database on the reactions of these three ionic species, which are our chosen precursor ions for our SIFT

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PII S1387-3806(98)14296-3

analytical method [9] (which relies on chemical ionisation [10]) by which we are able to determine the partial pressures of trace gases in air [11] and metabolites in human breath [12] down to the low parts per billion (ppb) regime in real time (e.g. from a single exhalation of breath). These extensive studies are also providing a wealth of information on the various fundamental processes that occur in ion–molecule reactions at thermal energies (see the references cited above).

Chlorocarbons are used extensively in industry as solvents and for dry cleaning. If ingested (via skin absorption or breathing) they are a potential health hazard and have thus attracted the attention of the occupational hygiene inspectors. We have used our SIFT analytical technique to study the breath of volunteers following their controlled exposure to trichloro- and tetrachloroethylene, noting that they can persist on breath for many hours following exposure [13]. Some of these chlorocarbons are also present in the wider atmosphere as low level pollutants [14]. Hence the reason for including some of these compounds in our surveys of the reactions of H_3O^+, NO^+, and O_2^+ thus exploring the potential of our chemical ionisation SIFT analytical method for the detection and quantification of these compounds in air and breath.

Previous work on these chloromethanes has shown that they are relatively unreactive [15,16], particularly with protonated molecules such as H_3O^+, presumably because of their relatively low proton affinities [17], and with low energy species like NO^+ because of their relatively large ionisation energies [17], and the present study supports these findings. However, the present work shows that the chloroethanes and chloroethylenes are more reactive with the three reactant ions and so these should be amenable to detection and quantification using our SIFT analytical method.

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, [18]). We have described its use as an analytical tool in some recent review papers [11,12]. The approach we take to determine the rate coefficients, k, and 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 our subsequent papers [2–8], so only a brief outline of the method is required here. We have been able to reasonably assume in our many previous studies that the k for the H_3O^+ reactions proceed at the collisional (gas kinetic) rate, rate coefficient, k_c, because the proton affinities, PA, of most of the molecules chosen for study exceed the PA of the H_2O molecule [17]; then $k = k_c$ [19]. The k_c can be calculated if the polarisabilities and dipole moments of the reactant molecules are known or can be estimated [20]. Then the corresponding k for the NO^+ and O_2^+ reactions with each particular molecule are obtained in the usual way [18] 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 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 [1–8].

The situation for these chlorocarbons is not so simple because the sparse amount of data available on their PA values show that they are probably smaller than that of H_2O and 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, i.e. that $k = k_c$. Fortunately, however, the available data on the reactions of O_2^+ with chlorocarbons indicated that they generally react (charge transfer) at or close to the collisional rate [15,16], data which are supported by our crude measurements using neat vapour, and therefore we feel justified in assuming that this is so for those chlorocarbon reactions included in this study. So with this assumption we can

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the chlorocarbons 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 in debye, D, of the chlorocarbons. The values of α and μ are known for most of these chlorocarbons and they are shown in regular type (taken from [25]). For two of them we have estimated their μ and α by adopting the values of 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 [20]. 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}. An asterisk indicates effective two-body rate coefficients for these three-body reactions in helium at 0.5 Torr

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]	— [2.4]	2.4 [2.4]
CH_2Cl_2	84	6.48	1.60	*0.04 [2.5]	— [2.1]	2.0 [2.0]
$CHCl_3$	118	9.50	1.01	*0.06 [2.2]	— [1.8]	1.8 [1.8]
CCl_4	152	11.00	0	1.7 [1.9]	0.1 [1.6]	1.5 [1.5]
CH_2ClCH_2Cl	98	8.00	1.90	*1.2 [2.9]	*0.2 [2.4]	2.3 [2.3]
CH_3CHCl_2	98	8.64	1.34	2.4 [2.4]	*0.2 [2.0]	1.9 [1.9]
CH_3CCl_3	132	10.70	1.78	2.7 [2.9]	2.1 [2.4]	2.3 [2.3]
$CHCl_2CHCl_2$	166	12.10	1.32	*0.7 [2.5]	*0.2 [2.1]	2.0 [2.0]
$CHClCCl_2$	130	*9.0 ± 1*	*1.0 ± 0.3*	2.0 [2.1]	*<0.1 [1.8]	1.7 [1.7]
C_2Cl_4	164	*9.0 ± 1*	*0*	0.6 [1.7]	*0.5 [1.4]	1.4 [1.4]

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 react with each chlorocarbon 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 chlorocarbon are accurate. These k values are listed in Table 1 where it can be seen that the k for the reactions of a few of these chlorocarbons with both H_3O^+ and O_2^+ are fast and in approximate proportion to their respective k_c values (i.e. for the CCl_4, CH_3CHCl_2, CH_3CCl_3, and the $CHClCCl_2$ reactions). For these reactions it is very likely that they proceed at the collisional rate ($k = k_c$). Note that only one of the reactions of NO^+ with of these four chlorocarbons (CH_3CCl_3) proceeds at the collisional rate.

The product ions and their percentages for these reactions are obtained in the usual way for SIFT studies [18] 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 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 as they enter the flow tube is minimised by the additions of a small amount of air to the helium carrier gas [1,2]. All these measurements were carried out in helium carrier gas at a pressure of 0.5 Torr at room temperature.

3. Results and discussion

Relative to the fast O_2^+ reactions the rates of the H_3O^+ and NO^+ reactions varied from very fast (collisional) to immeasurably slow (see Table 1). The ionic and neutral products of all these reactions and the product branching ratios where there is more than one product channel are given in Table 2. We now discuss the H_3O^+, NO^+, and O_2^+ reactions separately.

3.1. H_3O^+ reactions

The reactions of these chlorocarbons, M, with H_3O^+ are more diverse than with any of the many other types of organic compounds we have surveyed in our work [1–8]. In these reactions there are

Table 2
Products of the reactions of H_3O^+, NO^+, and O_2^+ with chlorocarbons listed. The molecular formulae of the ion products do not necessarily represent their structures; the percentage of each ion products is given in brackets. Brackets around the neutral products indicate that they may be bonded. The ionisation energies of the chlorocarbons (in eV [17]) are given in the square brackets

	H_3O^+	NO^+	O_2^+
Chloromethanes			
CH_3Cl [11.22]	$H_3O^+.CH_3Cl$(100)	—	CH_3Cl^+(100) + O_2
CH_2Cl_2 [11.32]	$H_3O^+.CH_2Cl_2$(100)	—	$CH_2Cl_2^+$(100) + O_2
$CHCl_3$ [11.37]	$H_3O^+.CHCl_3$(100)	—	$CHCl_2^+$(100) + (Cl + O_2)
CCl_4 [11.47]	CCl_3^+(100) + (HCl.H_2O)	CCl_3^+(95) + NOCl $NO^+.CCl_4$(5)*	CCl_3^+(100) + (Cl + O_2)
Chloroethanes			
CH_2ClCH_2Cl [11.04]	$H_3O^+.CH_2ClCH_2Cl$(55)* $CH_2ClCH_2OH_2^+$(35) + HCl $CH_2ClCH_2Cl.H^+$(10) + H_2O	$NO^+.CH_2ClCH_2Cl$(100)	$C_2H_3Cl^+$(95) + (HCl + O_2) $C_2H_4Cl^+$(5) + (Cl + O_2)
CH_3CHCl_2 [11.06]	$CH_3CHClOH_2^+$(50) + HCl CH_3CHOH^+(50) + 2HCl	$NO^+.CH_3CHCl_2$(100)	$C_2H_4Cl^+$(100) + (Cl + O_2)
CH_3CCl_3 [11.00]	$CH_3CCl_2^+$(100) + (HCl + H_2O)	$CH_3CCl_2^+$(100) + NOCl	$CH_3CCl_2^+$(100) + (Cl + O_2)
$CHCl_2CHCl_2$ [11.6]	$H_3O^+.CHCl_2CHCl_2$(100)	$NO^+.CHCl_2CHCl_2$(100)	$CHCl_2^+$(75) + $CHCl_2$ + O_2 $C_2HCl_3^+$(20) + (HCl + O_2) $C_2H_2Cl_3^+$(5) + (Cl + O_2)
Chloroethylenes			
$CHClCCl_2$ [9.47]	$CHClCCl_2.H^+$(100) + H_2O	$NO^+.CHClCCl_2$(100)	$C_2HCl_3^+$(100) + O_2
C_2Cl_4 [9.32]	$C_2Cl_4.H^+$(95) + H_2O $C_2Cl_3^+$(5) + (HCl + H_2O)	$NO^+.C_2Cl_4$(100)	$C_2Cl_4^+$(100) + O_2

examples of direct proton transfer producing MH^+ ions, HCl elimination following protonation producing $(M–Cl)^+$ ions, association producing adduct ions $H_3O^+.M$ and even the incorporation of H_2O into the ion with the elimination of HCl molecules!

There is no information available on the proton affinities of these chlorocarbons, but because in the majority of these reactions the protonated halocarbons are not observed the implication is that their PA are less than that of H_2O (696 kJ mol^{-1} [17]). The PA of the fully hydrogenated equivalents to these chlorinated hydrocarbons included in this study, i.e. CH_4, C_2H_6 and C_2H_4, also have PA which are less than that of H_2O and thus H_3O^+ cannot undergo efficient proton transfer with these hydrocarbons. However, the data obtained in the present study clearly indicates that chlorine substitution tends to increase the PA of the molecule. This is especially obvious for the chlorinated ethylenes included in this study, $CHClCCl_2$ and C_2Cl_4. In the reaction of the former, the only product ion is the protonated molecule and the reaction occurs at the collisional rate:

$$H_3O^+ + CHClCCl_2 \rightarrow CHClCCl_2.H^+ + H_2O \tag{1}$$

This certainly shows that exothermic proton transfer is occurring thus indicating that the PA of $CHClCCl_2$ exceeds 696 kJ mol^{-1} (this is greater than the PA of C_2H_4, which is 680 kJ mol^{-1} [21]). Similarly, the C_2Cl_4 reaction proceeds thus:

$$H_3O^+ + C_2Cl_4 \rightarrow C_2Cl_4.H^+ + H_2O \tag{2a}$$

$$\rightarrow C_2Cl_3^+ + (HCl + H_2O) \tag{2b}$$

In this reaction the direct proton transfer channel (2a) represents 95% of the branching ratio. The minor channel (2b) involves the elimination of a HCl molecule from the protonated molecule, a process that occurs with unit efficiency in the CCl_4 and the CH_3CCl_3 reactions, e.g.

$$H_3O^+ + CCl_4 \rightarrow CCl_3^+ + (HCl + H_2O) \tag{3}$$

It appears that Reaction (3) is very close to thermoneutral and even slightly endothermic within the uncertainties of the thermochemical data [17] and yet it proceeds at the collisional rate (see Table 1). It therefore seems very likely that the weakly bound dimer molecule $HCl.H_2O$ is formed in this reaction, the binding energy (which we estimate to be about 20 kJ mol^{-1}) rendering the reaction significantly exothermic. This dimer may also be formed in Reaction (2b) as is indicated by the enclosing brackets.

Ion–molecule association is evident in some of these reactions, sometimes in parallel with other processes, and then the reactions proceed less efficiently with the measured k being less than the respective k_c. This is the only process occurring in the CH_3Cl, CH_2Cl_2, and $CHCl_3$ reactions which are slow (see Tables 1 and 2) and in the $CHCl_2CHCl_2$ reaction, but this is faster

$$H_3O^+ + CHCl_2CHCl_2(+He) \rightarrow H_3O^+.CHCl_2CHCl_2(+He) \qquad (4)$$

These are presumably three-body association reactions in which a fraction of the excited $(H_3O^+.M)^*$ intermediate ions are stabilised against unimolecular dissociation in collisions with the He atoms of the carrier gas [22]. Association is the major channel in the reaction

$$H_3O^+ + CH_2ClCH_2Cl \rightarrow H_3O^+.CHCl_2CHCl_2 \qquad (5a)$$

$$\rightarrow CH_2ClCH_2OH_2^+ + HCl \qquad (5b)$$

$$\rightarrow CH_2ClCH_2Cl.H^+ + H_2O \qquad (5c)$$

In this curious reaction, $(H_3O^+.M)^*$ ions are first formed a fraction of which (55%) are stabilised in He collisions, a fraction of which result in HCl elimination (35%) and a fraction of which an H_2O molecule is eliminated (10%). These observations strongly indicate that the PA of this molecule is a little smaller than that of H_2O (696.6 kJ mol^{-1}), and given that proton transfer occurs in 10% of the collisions at 300 K, the energetics require that the PA of CH_2ClCH_2Cl must be larger than 691 kJ mol^{-1}. In the CH_3CHCl_2 reaction the $(H_3O^+.M)^*$ excited ion is first formed but dissociates rapidly and completely (before it can be stabilised) along two approximately equally probable channels

$$H_3O^+ + CH_3CHCl_2 \rightarrow CH_3CHClOH_2^+ + HCl \qquad (6a)$$

$$\rightarrow CH_3CHOH^+ + 2HCl \qquad (6b)$$

This reaction is remarkable in that it requires considerable rearrangement in the (presumed) very short lifetime of the intermediate complex ion, even resulting in the formation of what seems to be protonated acetaldehyde (6b) following the elimination of two HCl molecules!

It is interesting to note that the adduct ions formed in the reactions of some of these chlorocarbons with H_3O^+ undergo rapid switching reactions with H_2O molecules when they are present in the helium carrier gas, thus

$$H_3O^+.M + H_2O \rightarrow H_3O^+.H_2O + M \qquad (7)$$

We have also observed this process to occur when H_3O^+ ions associate with higher-order aliphatic hydrocarbons (n-hexane to n-dodecane [8]). Thus these association processes catalyse the production of hydrated hydronium ions when occurring in wet air such as the troposphere and the stratosphere [23].

3.2. NO^+ reactions

In contrast to the reactions of H_3O^+ these NO^+ reactions are relatively simple. They are generally slow, the k being only a small fraction of the k_c or even immeasurably small (see Table 1). All but two of the observed reactions proceed via three-body association, e.g.

$$NO^+ + C_2Cl_4 + (He) \rightarrow NO^+.C_2Cl_4 + (He) \qquad (8)$$

This particular association reaction is unusual in this series in that it proceeds relatively efficiently, the effective two-body rate coefficient, k_2, being 5×10^{-10} cm^3 s^{-1}. At the helium pressure at which these studies were carried out (0.5 Torr) this is equivalent to a large three-body rate coefficient, k_3, of 3×10^{-26} $cm^6\ s^{-1}$. Why should this particular association reaction be so efficient? It is probably because the ionisation energy of C_2Cl_4 (9.32 eV; see Table 2) is close to that of NO (9.26 eV) and so the reaction may involve charge transfer complexing in which the positive charge on the $(NO.C_2Cl_4)^{+*}$ intermediate excited ion can be shared between the two molecules, a process which is considered to enhance the lifetime of the complex ion against unimolecular dissociation [1,2]. The larger ionisation energies of the other chlorocarbons included in this study inhibit this charge transfer complexing and the three-body association reactions are consequently less efficient.

It is clear that the $NO^+.M$ product ions are relatively weakly bound because in the presence of H_2O they undergo rapid switching reactions thus:

$$NO^+.M + H_2O \rightarrow NO^+.H_2O + M \tag{9}$$

This indicates that the NO^+–M bond energies are less than the NO^+–H_2O bond energy which has been determined to be (0.85 ± 0.15) eV [24]. Switching reactions of this type (where M is N_2, O_2 and CO_2) are known to be involved in the formation of hydrated hydronium ions in the lower atmosphere [22].

The reaction of NO^+ with CH_3CCl_3 is anomalous in these NO^+ reactions in that it proceeds rapidly, with k close to k_c, thus

$$NO^+ + CH_3CCl_3 \rightarrow CH_3CCl_2^+ + NOCl \tag{10}$$

This may be described as a chloride (Cl^-) ion transfer reaction producing the ion indicated and a NOCl molecule. Dissociative charge transfer producing the observed ion together with NO and Cl can be excluded since the ionisation energy of CH_3CCl_3 (11.0 eV) greatly exceeds that of NO. The formation of the NO–Cl bond releases 162 kJ mol^{-1} of energy [17] which obviously renders reaction (10) exothermic. Unfortunately, the heat of formation of the $CH_3CCl_2^+$ ion is not available, but the rapid occurrence of reaction (10) indicates that it must be less than 790 kJ mol^{-1} (using the available thermochemical data [17]). This Cl^- transfer process also occurs in the CCl_4 reaction but much more slowly ($k = 0.03k_c$) and in parallel with the association product $NO^+.CCl_4$ at the 5% level (see Tables 1 and 2). According to the thermochemical data [17] this Cl^- transfer reaction is slightly endothermic (by about 4 kJ mol^{-1}) which probably explains why the reaction is slow and why parallel adduct formation occurs.

3.3. O_2^+ reactions

All these reactions are observed to proceed via charge transfer, generally producing a single ionic product (see Table 2). The most common process is chlorine atom loss, e.g.

$$O_2^+ + CCl_4 \rightarrow CCl_3^+ + Cl + O_2 \tag{11}$$

although the parent molecular ion is produced in some cases, e.g.

$$O_2^+ + C_2Cl_4 \rightarrow C_2Cl_4^+ + O_2 \tag{12}$$

A third process is apparent, that of HCl elimination following the charge transfer,

$$O_2^+ + CH_2ClCH_2Cl \rightarrow CH_2ClCCl^+ + HCl + O_2 \tag{13}$$

It can be readily shown from the available thermochemical data [17] that Cl + H elimination is endothermic in this reaction. Note that the carbon–carbon bond is broken only in the CH_2ClCH_2Cl reaction producing the $CHCl_2^+$ ion and the neutral radical $CHCl_2$. This process is 16 kJ mol^{-1} exothermic [17] and occurs in parallel with both HCl molecule and Cl atom elimination (see Table 2).

4. Concluding remarks

The mechanisms of the reactions of H_3O^+ with the chlorocarbons included in this limited study are quite varied. Protonation of the reactant molecules producing MH^+ ions is the exception rather than the rule except for the two chloroethylenes which must have proton affinities that exceed that of H_2O. The value of the PA of CH_2ClCH_2Cl as indicated by these results must lie between 691 and 696 kJ mol^{-1}. The NO^+ reactions generally proceed via very slow association producing $NO^+.M$ ions, whereas the O_2^+ reactions are fast proceeding via charge transfer and the production of the parent cations of the reactant chlorocarbons, M^+, or via the elimination of a Cl atom producing $(M–Cl)^+$ ions. An unusual result is that the reactions of H_3O^+, NO^+, and O_2^+ with CH_3CCl_3 and CCl_4 produce the same ionic product, $CH_3CCl_2^+$ for the former and CCl_3^+ for the latter (see Table 2), a result we have not seen before in the large number of different molecules (exceeding 100) included in our surveys of the reactions of these ions [1–8]. Finally, it is perhaps worthy of note that our additional studies of the reactions of these ions shows that both H_3O^+ and NO^+ are unreactive with CF_2Cl_2, CF_3Br, CH_2Br_2 whereas these halomethanes undergo dissociative charge transfer with O_2^+ ions. It is clear from this study that O_2^+ is the preferred ion for the detection and quantification of these chlorocarbons in air using our SIFT analytical technique [9,11,12].

Acknowledgement

This work was partly supported by the Grant Agency of the Czech Republic under project no. 203/97/P130.

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