SIFT studies of the reactions of H_3O^+, NO^+ and O_2^+ with a series of volatile carboxylic acids and esters

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Abstract

We report the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+ and O_2^+ with some nine carboxylic acids and eight esters. We assume that all the exothermic proton transfer reactions of H_3O^+ with all the acid and esters molecules occur at the collisional rate, i.e. the rate coefficients, k, are equal to k_c; then it is seen that k values for most of the NO^+ and O_2^+ reactions also are equal to or close to k_c. The major ionic products of the H_3O^+ reactions with both the acids and esters are the protonated parent molecules, MH^+, but minor channels are also evident, these being the result of H_2O elimination from the excited $(MH^+)^*$ in some of the acid reactions and an alcohol molecule elimination (CH_3OH or C_2H_5OH) in some of the ester reactions. The NO^+ reactions with the acids and esters result in both ion–molecule association producing $NO^+\cdot M$ in parallel with hydroxide ion (OH^-) transfer with some of the acids, and parallel methoxide ion (CH_3O^-) and ethoxide ion ($C_2H_5O^-$) transfer as appropriate with some of the esters. The O_2^+ reactions proceed by dissociative charge transfer with the production of two or more ionic fragments of the parent molecules, the different isomeric forms of both the acid and the ester molecules resulting in different product ions. © 1998 Elsevier Science B.V.

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1. Introduction

In support of a major development programme of the application of flow tube techniques coupled with chemical ionisation to the analysis of trace gases in air and human breath, we have embarked on a major study of the reactions of three ionic species, H_3O^+, NO^+ and O_2^+ (which are the chosen precursor ions), with a wide range of organic and inorganic gases and vapours, many of which are known to be present in trace quantities in environmental air and human breath [1,2]. Details of our analytical technique, the selected ion flow tube (SIFT) approach, are given in some recent papers [3–5].

To use chemical ionisation (with the SIFT technique) for the analysis of complex gas mixtures, a substantial database of the rate coefficients and ion products of the reactions of the aforementioned precursor ions with a large number and variety of organic and inorganic vapours and gases is needed. Thus we have embarked on several surveys of the kinetics of the gas phase reactions of H_3O^+, NO^+ and O_2^+ and, to date, we have carried out studies of the reactions of these ions with some 17 alcohols, including primary,

Table 1

Rate coefficients for the reactions of H_3O^+, NO^+ and O_2^+ with the acids and esters indicated. Also given are their molecular weights, m, in atomic units, u, their polarisabilities, α, in units of 10^{-24} cm^3 and their permanent dipole moments, μ, in Debye, D. The values of α and μ are known for some of the compounds included in this study and they are shown in regular type (taken from [13]). For the remaining compounds we have estimated their μ value assuming that it does not change significantly with the number of carbon atoms in acid and ester molecules, and their α value by adopting the average values of the known polarisabilities of other organic molecules possessing the same number of carbon atoms. Then the collisional rate coefficients, k_c, for all reactions have been calculated using the parametreised trajectory formulation of Su and Chesnavich [14] and these are given in square brackets. The estimated uncertainty in these calculated rate coefficients is $\pm 20\%$. On the assumption that all the H_3O^+ reactions proceed at the collisional rates, the rate coefficients, k, for the NO^+ and O_2^+ reactions have been experimentally derived by the procedure described in the text. The k and k_c values are given in units of 10^{-9} cm^3 s^{-1}

Molecule	m (u)	α (10^{-24} cm^3)	μ (D)	k_c (H_3O^+) (10^{-9} cm^3 s^{-1})	k_c, k (NO^+) (10^{-9} cm^3 s^{-1})	k_c, k (O_2^+) (10^{-9} cm^3 s^{-1})
HCOOH formic acid	46	3.4	1.41	[2.2]	[1.9] < 0.1	[1.9] 2.0
CH$_3$COOH acetic acid	60	5.1	1.74	[2.6]	[2.2] 0.9	[2.2] 2.3
C$_2$H$_5$COOH propionic acid	74	6.9	1.75	[2.7]	[2.3] 1.5	[2.2] 2.2
C$_3$H$_7$COOH n-butyric acid	88	10 ± 1	1.8 ± 0.3	[2.9]	[2.4] 1.9	[2.4] 2.1
(CH$_3$)$_2$CHCOOH iso-butyric acid	88	10 ± 1	1.8 ± 0.5	[2.9]	[2.4] 2.5	[2.4] 2.5
C$_4$H$_9$COOH valeric acid	102	11 ± 1	1.8 ± 0.5	[2.9]	[2.4] 2.4	[2.4] 2.4
(CH$_3$)$_3$CCOOH trimethylacetic acid	102	11 ± 1	1.8 ± 0.5	[2.9]	[2.4] 1.1	[2.4] 1.0
CH$_2$=CHCOOH acrylic acid	72	7 ± 1	1.8 ± 0.5	[2.7]	2.3] 1.1	[2.3] 2.2
CH$_3$CH(OH)COOH lactic acid	90	8 ± 1	2.0 ± 0.5	[3.0]	[2.5] —	[2.4] —
HCOOCH$_3$ methyl formate	60	6 ± 1	1.77	[2.7]	[2.3] 0.5	[2.3] 2.2
HCOOC$_2$H$_5$ ethyl formate	74	8.1	1.93	[3.0]	[2.5] 1.6	[2.5] 2.5
CH$_3$COOCH$_3$ methyl acetate	74	6.9	1.8 ± 0.3	[2.8]	[2.3] 1.6	[2.3] 2.4
CH$_3$COOC$_2$H$_5$ ethyl acetate	88	9.7	1.78	[2.9]	[2.4] 2.1	[2.4] 2.4
C$_2$H$_5$COOCH$_3$ methyl propionate	88	10 ± 1	$1 8 \pm 0.3$	[2.9]	[2.4] 2.1	[2.4] 2.0
C$_2$H$_5$COOC$_2$H$_5$ ethyl propionate	102	11 ± 1	1.8 ± 0.3	[2.9]	[2.4] 2.5	[2.4] 2.5
C$_3$H$_7$COOCH$_3$ methyl butyrate	102	11 ± 1	1.8 ± 0.3	[2.9]	[2.4] 2.4	[2.4] 2.4
C$_6$H$_5$COOCH$_3$ methyl benzoate	136	16 ± 1	1.8 ± 0.3	[3.1]	[2.6] 1.5	[2.5] 1.4

secondary and tertiary alcohols [6], and 11 aldehydes and nine ketones [7]. As well as providing a wealth of relevant kinetic data for the trace gas analysis, these studies are proving to be extremely interesting from an ion chemist's viewpoint, because several different reaction processes have been observed and a body of data on them is being obtained. Processes such as H_2O elimination following the protonation of alcohols and aldehydes by H_3O^+ [6–8], hydride ion transfer and hydroxide ion transfer in the reactions of NO^+ with oxygen-containing organic species and the fragmentation of organic molecules following charge transfer reactions with O_2^+ ions [6,7,9]

are being catalogued. The present paper reports the results of a study of the reactions of the above ions with some nine volatile carboxylic acids and eight esters, specifically those listed in Table 1.

2. Experimental

Measurements of the rate coefficients, k, and the ion products of ion–molecule reactions at thermal energies using the SIFT technique have been discussed in numerous review and research papers (see Refs. [10,11]) and do not need to be discussed in detail here. It is sufficient to say that a reactant gas or vapour is introduced at a controlled, measured flow rate into the helium carrier gas of the SIFT into which, upstream, a current of mass selected reactant ions has been introduced, and the loss rate of the reactant ions and the production rates of the product ions of the ion–molecule reaction that occurs are determined by the downstream mass spectrometer. From the rate of loss of the primary (precursor) ions and the formation rates of the product ions, together with other critical parameters including the carrier gas flow velocity and the effective reaction time (length of the reaction zone), it is simple to determine k for the reaction and the ion product branching ratios [10].

For permanent reactant gases it is easy to measure and vary their flow rates using some form of flowmeter/controller, but for 'sticky' organic vapours this is a more difficult problem because the thermodynamic data required for capillary calibrations (i.e. heat capacities) are mostly unavailable, and known volume/pressure reduction methods of calibration are inaccurate because such vapours readily adsorb and stick to surfaces. So we have adopted the following procedure for the 'sticky' vapours involved as reactants in these studies.

We assume, with justification [12], that k values for all exothermic proton transfer reactions proceed at the collisional rate, k_c, which can be calculated if the polarisability and the dipole moment of the reactant molecule are known [13,14]. Since all the H_3O^+ proton transfer reactions with which we are concerned in these surveys are exothermic (because the proton affinities of the reactant molecules are greater than the proton affinity of H_2O molecules [15]), then k values for these particular reactions are equal to their respective k_c. Numerous experimental studies over decades have shown that for such reactions k is always equal to k_c [12,16]. However, this is not necessarily so for exothermic reactions that proceed via different processes such as charge transfer and hydride ion transfer via which many of the reactions of O_2^+ and NO^+ with organic molecules occur [16–18]. So the k for the reactions of the latter ions with these sticky organic vapours must be determined experimentally. Since we cannot measure the flow rates of most of the neat organic vapours sufficiently accurately, we simple make a very dilute mixture of the vapour at an unknown partial pressure in dry cylinder air in a plastic bag and use this as the reactant gas in these SIFT experiments. The flow rate of this mixture (essentially air) is readily measured using standard flowmeters. Of course, using this procedure we cannot determine the absolute k for the reactions, but by injecting upstream H_3O^+, NO^+ and O_2^+ ions simultaneously, we can measure the relative decay rates of these three ion species as a function of the flow rate of the vapour/air mixture. Since for the H_3O^+ reactions $k = k_c$, then k for the NO^+ and O_2^+ reactions can be obtained. Further discussion of this procedure is given in our first paper in this series of papers which is concerned with alcohol reactions [6]. The product ion distributions for the reactions are also determined from these measurements in the usual manner [10]. We have included in Table 2 and Table 3 only those ion products which represent more than 2% of the product distribution.

To assess the influence of the presence of any metastable electronically excited states of the primary NO^+ and O_2^+ ions, we measured the branching ratios and the rate coefficients of

Table 2
Products of the reactions of the organic acids indicated with H_3O^+, NO^+ and O_2^+. The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion product is given in parentheses. The neutral products are given only for the H_3O^+ and NO^+ and not the O_2^+ reactions for which the neutral products (and in most cases the ionic products) are not readily defined. Note the production of an additional H_2O molecule in some of the H_3O^+ reactions, an HNO_2 molecule in most of the NO^+ reactions, and the several fragment ions in some of the O_2^+ reactions. I.E. are the ionisation energies in electron volts (eV)

Molecule I.E. (eV)	H_3O^+	NO^+	O_2^+
HCOOH formic acid (11.3 eV)	$HCOOH_2^+(100) + H_2O$	no reaction	$HCOO^+(90)$ $HCOOH^+(10)$
CH_3COOH acetic acid (10.7 eV)	$CH_3COOH_2^+(100) + H_2O$	$NO^+·CH_3COOH(100)$	$CH_3CO^+(50)$ $CH_3COOH^+(50)$
C_2H_5COOH propionic acid (10.5 eV)	$C_2H_5COOH_2^+(90) + H_2O$ $C_2H_5CO^+(10) + 2H_2O$	$NO^+·C_2H_5COOH(70)$ $C_2H_5CO^+(30) + HNO_2$	$C_2H_5COOH^+(80)$ $C_2H_4CO^+(10)$ $C_2H_5COO^+(5)$ $C_2H_5CO^+(5)$
C_3H_7COOH n-butyric acid (10.2 eV)	$C_3H_7COOH_2^+ + H_2O$ $C_3H_7CO^+(10) + 2H_2O$	$NO^+·C_3H_7COOH(50)$ $C_3H_7CO^+(50) + HNO_2$	$CH_3COOH^+(85)$ $C_2H_4COOH^+(10)$ $C_3H_7COOH^+(5)$
$(CH_3)_2CHCOOH$ iso-butyric acid (10.3 eV)	$(CH_3)_2CHCOOH_2^+(90)$ $+ H_2O$ $(CH_3)_2CHCO^+(10) + 2H_2O$	$(CH_3)_2CHCO^+(80) + HNO_2$ $NO^+·(CH_3)_2CHCOOH(20)$	$(CH_3)_2CH^+(50)$ $CH_3CHCOOH^+(30)$ $(CH_3)_2(CHCOOH^+(20)$
C_4H_9COOH valeric acid (10.5 eV)	$C_4H_9COOH_2^+(90) + H_2O$ $C_4H_9CO^+(10) + 2H_2O$	$C_3H_7CO^+(70) + HNO_2$ $NO^+·C_3H_7COOH(30)$	$CH_3COOH^+(80)$ $CH_2CH_2COOH^+(20)$
$(CH_3)_3CCOOH$ trimethylacetic acid (10.1 eV)	$(CH_3)_3CCOOH_2^+(90) + H_2O$ $(CH_3)CCO^+(10) + 2H_2O$	$(CH_3)_3CCO^+(75) + HNO_2$ $NO^+·(CH_3)_3CCOOH(25)$	$(CH_3)_3C^+(90)$ $(CH_3)_2(CH_2)C^+(10)$
$CH_2=CHCOOH$ acrylic acid (10.6 eV)	$CH_2=CHCOOH_2^+(95)$ $+ H_2O$ $CH_2=CHCO^+(5) + 2H_2O$	$NO^+·CH_2=CHCOOH(95)$ $CH_2=CHCO^+(5) + HNO_2$	$CH_2=CHCOOH^+ + (70)$ $CH_2CHOH^+(20)$ $C_2H_3CO^+(10)$
$CH_3CH(OH)COOH$ lactic acid (−)	$CH_3CH(OH)COOH_2^+(25)$ $+ H_2O$ $CH_3CHOH^+(75)$ $+ HCOOH + H_2O$	$CH_3CH(OH)CO^+(50) + HNO_2$ $NO^+·CH_3CH(OH)COOH(50)$	$CH_3CHOH^+(90)$ $CH_3CO^+(10)$

the reactions in two ways; firstly, with only the reactant vapour introduced into the flow tube and secondly, after adding 5 mTorr of air upstream into the flow tube, which quenches ions in these excited states. No significant effects due to excited ions were observed.

For the present study we selected nine volatile carboxylic acids and eight esters. In all, this study involves some 51 reactions, in most of which there are two or more product ions. All the measurements were carried out in helium carrier gas at a pressure of about 0.5 Torr at a temperature of 300 K.

3. Discussion of results

We will discuss the detailed results of this study in two major subsections, the first dealing with the carboxylic acids and in the second with the esters, and within each of these subsections we will discuss separately the H_3O^+, NO^+ and O_2^+ reactions. But first we now make some general observations about the complete data set.

3.1. General comments

On the basis that all the H_3O^+ reactions

Table 3

Product of the reactions of the esters indicated with H_3O^+, NO^+ and O_2^+. The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion product is given in parentheses. The neutral products are given only for the H_3O^+ and NO^+ and not for the O_2^+ reactions for which the neutral products (and the ionic products for the complex molecule menthone) are nt readily defined. Note the production of the alkyl nitrite molecules in some of the NO^+ reactions. I.E. are the ionisation energies in electron volts (eV)

Molecule I.E.(eV)	H_3O^+	NO^+	O_2^+
HCOOCH$_3$ methyl formate (10.8 eV)	$HCOOCH_3 \cdot H^+(> 95)$ $+ H_2O$ $CH_3OH_2^+(< 5)$ $+ H_2O + CO$	$NO^+ \cdot HCOOCH_3(100)$	$CH_3O^+(> 95)$ $HCOOCH_3^+(< 5)$
HCOOC$_2$H$_5$ ethyl formate (10.6 eV)	$HCOOC_2H_5 \cdot H^+(95)$ $+ H_2O$ $C_2H_5OH_2^+(< 5)$ $+ H_2O + CO$	$NO^+ \cdot HCOOC_2H_5(100)$	$C_2H_4^+(> 90)$ $HCOOC_2H_5^+(5)$ $C_2H_5O^+)(< 5)$
CH$_3$COOCH$_3$ methyl acetate (10.3 eV)	$CH_3COOCH_3 \cdot H^+(100)$ $+ H_2O$	$NO^+ \cdot CH_3COOCH_3(80)$ $CH_3CO^+(20) + CH_3NO_2$	$CH_3CO^+(90)$ $CH_3COOCH_3^+(10)$
CH$_3$COOC$_2$H$_5$ ethyl acetate (10.1 eV)	$CH_3COOC_2H_5 \cdot H^+(100)$ $+ H_2O$	$NO^+ \cdot CH_3COOC_2H_5(90)$ $CH_3CO^+(10) + C_2H_5NO_2$	$C_2H_5O_2^+(40)\ CH_3CO^+(20)$ $C_2H_5O^+(20)\ CH_3O^+(20)$
C$_2$H$_5$COOCH$_3$ methyl propionate (10.1 eV)	$C_2H_5COOCH_3 \cdot H^+(95)$ $+ H_2O$ $C_2H_5CO^+(5) + H_2O$ $+ CH_3OH$	$C_2H_5CO^+(80) + CH_3NO_2$ $NO^+ \cdot C_3H_7COOCH_3(20)$	$C_2H_5CO^+(75)$ $C_3H_7COOCH_3^+(25)$
C$_2$H$_5$COOC$_2$H$_5$ ethyl propioate (10.0 eV)	$C_2H_5COOC_2H_5 \cdot H^+(95)$ $+ H_2O$ $C_2H_5CO^+(5)$ $+ H_2O + C_2H_2H_5OH$	$NO^+ \cdot C_2H_5COOC_2H_5(60)$ $C_2H_5CO^+(40) + C_2H_5NO_2$	$C_3H_5O^+(45)C_2H_5O^+(15)$ $C_2H_4^+(5)CH_3O^+(5)$ $CH_3CO^+(5)C_3H_6O_2^+(5)$ $C_2H_5COOC_2H_5^+(5)$
C$_3$H$_7$COOCH$_3$ methyl butyrate (10.1 eV)	$C_3H_7COOCH_3 \cdot H^+(90)$ $+ H_2O$ $C_3H_7CO^+(10)$ $+ H_2O + CH_3OH$	$C_3H_7CO^+(80) + CH_3NO_2$ $NO^+ \cdot C_3H_7COOCH_3(20)$	$C_3H_6O_2^+(45)$ $C_3H_7CO^+(45)$ $C_4H_7O_2^+(5)CH_3O^+(5)$
C$_6$H$_5$COOCH$_3$ methyl benzoate (9.32 eV)	$C_6H_5COOCH_3 \cdot H^+(90)$ $+ H_2O$ $C_6H_5CO^+(10)$ $+ H_2O + CH_3OH$	$C_6H_5CO^+(90) + CH_3NO_2$ $NO^+ \cdot C_6H_5COOCH_3(10)$	$C_6H_5CO^+(65)$ $C_6H_5COOCH_3^+(35)$

proceed at the collisional rate, i.e. $k = k_c$, it is seen by inspection of Table 1 that with few exceptions the reactions of NO^+ and O_2^+ with both the acids and esters, M, also proceed at or near their respective bimolecular collisional rates, although it must be noted that most of the NO^+ reactions with both the acids and esters proceed at least in part by collisional (termolecular) association as we mention again later.

The H_3O^+ reactions all proceed via proton transfer, with the major product ion being MH^+ for all the acids (except lactic acid) and all the esters. In most of the reactions of both the acids and esters, minor ionic products are also evident which are the result of the partial dissociation of the nascent $(MH^+)^*$ excited product ion formed in the initial protonation step. This often involves the elimination of an H_2O molecule (as is also seen in some of the reactions of H_3O^+ with alcohols [6] and aldehydes [7]), and in some of the ester reactions the elimination of an alcohol molecule (see Tables 2 and 3).

The NO^+ reactions with the acids mostly proceed along two obvious parallel channels, i.e.

collisional association forming $NO^+ \cdot M$ ions and hydroxide ion (OH^-) transfer forming $(M-OH)^+$ ions and HNO_2 neutral molecules) as is often seen in the reactions of NO^+ with alcohols [6] and aldehydes [7]. With the esters, analogous reactions in which parallel association and alkoxide ion (CH_3O^- or $C_2H_5O^-$) transfer forming the appropriate carboxyl ion and the neutral nitrite molecule (CH_3NO_2 or $C_2H_5O_2$) occur. Note that charge transfer between NO^+ and all these acids and esters is endothermic because their ionisation energies (I.E.) exceed the I.E. of NO.

Two or more products are formed in the O_2^+ reactions which we presume to occur via charge transfer. The parent molecular ion, M^+, is commonly a product, but in the majority of these reactions the major products are fragment ions which result from the cleavage of specific bonds in the nascent $(M^+)^*$ excited ions.

We comment on these interesting reaction processes below, noting that using the available thermochemical data [15] we are able to determine, in some cases, the structures of the product ions.

3.2. Carboxylic acid reactions

As can be seen in Table 2, we have included in this study formic, acetic, and propionic acid, n- and iso-butyric acid, valeric acid and its isomer trimethylacetic acid, the unsaturated acrylic acid, and lactic acid, a monohydroxycarboxylic acid, in order to obtain some sense of the different reactivities of the isomers, the influence of the presence of the double bond (in acrylic acid) and the additional OH group (in the lactic acid).
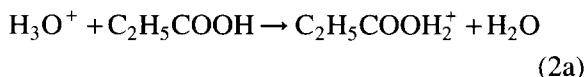
3.2.1. H_3O^+ reactions

A glance at Table 2 reveals that in both the formic and acetic acid reactions there is only a single ionic product, the protonated parent molecule, whereas in the remaining seven reactions there are two ionic products, the protonated parent molecule, MH^+, and the molecular ion which
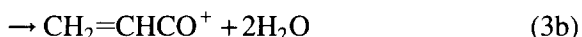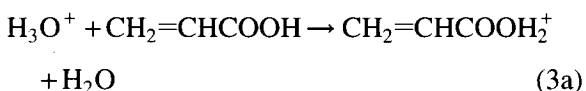
is left after an H_2O molecule has been lost from MH^+ (the lactic acid reaction is an exception; see below). The acetic acid reaction proceeds thus:

$$H_3O^+ + CH_3COOH \rightarrow CH_3COOH_2^+ + H_2O \quad (1)$$
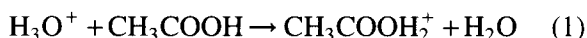
whilst the propionic acid reaction proceeds thus:

$$H_3O^+ + C_2H_5COOH \rightarrow C_2H_5COOH_2^+ + H_2O \quad (2a)$$

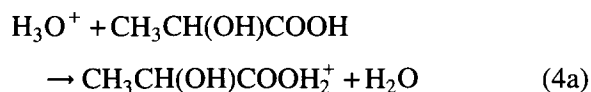$$\rightarrow C_2H_5CO^+ + 2H_2O \quad (2b)$$

The reactions of H_3O^+ with formic and acetic acids were studied previously by Bohme et al. [19] in a flowing afterglow who observed a minor 5% channel of H_2O loss in the acetic acid reaction. However, it can be shown that H_2O elimination in reaction (1) is endothermic by 12.5 kJ mol^{-1} and so it cannot occur under the thermal conditions of the SIFT experiment at 300 K. The same process is also endothermic in the protonation of formic acid by H_3O^+ and is thus not observed (see Table 2). However, reaction (2b) is exothermic by 37.5 kJ mol^{-1} and in these experiments it is seen as a minor (10%) ionic product. This process is also exothermic in the reactions of the butyric acid isomers, and valeric and trimethylacetic acids in which it represents about 10% of the ion product distribution in each case. In acrylic acid, H_2O elimination is seen as only a 5% contribution:

$$H_3O^+ + CH_2\text{=}CHCOOH \rightarrow CH_2\text{=}CHCOOH_2^+ + H_2O \quad (3a)$$

$$\rightarrow CH_2\text{=}CHCO^+ + 2H_2O \quad (3b)$$

Reaction (3b) is exothermic only by 2.5 kJ mol^{-1} (using data from Ref. [15]) which probably explains why it is such a minor product. The indications from this albeit limited number of H_3O^+ protonation reactions is that when H_2O elimination is energetically allowed it occurs as a minor product with the major product being the protonated parent acid molecule.

In this limited study of the reactions of H_3O^+ with carboxylic acids the lactic acid reaction is

unique in that not only is the protonated parent molecule the minor product (25%) but also because H_2O is not the elimination process; it is rather formic acid elimination, thus:

$$H_3O^+ + CH_3CH(OH)COOH$$

$$\rightarrow CH_3CH(OH)COOH_2^+ + H_2O \qquad (4a)$$

$$\rightarrow CH_3CHOH^+ + HCOOH + H_2O \qquad (4b)$$

Unfortunately, thermochemical data for lactic acid are not available, but clearly because reaction (4b) represents 75% of the ion product distribution it is surely quite exothermic. Note that in this reaction three close shell stable species are formed, because the ionic product is most probably protonated acetaldehyde. Further gas phase studies of the hydroxy acids are frustrated by their very low vapour pressures; because of the low vapour pressure of lactic acid we were unable to determine the rate coefficients of its reactions with any of the three primary ions with which this study is concerned. Hence these k values do not appear in Table 1.

3.2.2. NO⁺ reactions

Again, the formic acid reaction is unique in this series in that it is slow if it proceeds at all (we are only able to place an upper limit on the $k < 0.05k_c$; see Table 1). This is simply because there are no exothermic bimolecular reaction channels available (hydroxide ion transfer is 138 kJ mol⁻¹ endothermic). However, within the series from acetic through trimethylacetic acid listed in Table 2, all reactions occur increasingly rapidly, with collisional association and hydroxide ion transfer being the reaction processes, the latter process becoming increasingly important. The acetic acid reaction occurs with a $k = 0.25k_c$, and collisional association is the only observed process under the conditions of these SIFT experiments in which the helium atoms of the carrier gas remove the binding energy to stabilise the adduct ion:

$$NO^+ + CH_3COOH \rightarrow NO^+ \cdot CH_3COOH \qquad (5)$$

Again in this reaction, hydroxide ion transfer is 21 kJ mol⁻¹ endothermic.

Now in the propionic acid reaction, OH⁻ transfer is exothermic by 25 kJ mol⁻¹ and occurs as a significant (25%) channel and the overall reaction is faster than reaction (5) but still does not proceed at the collisional rate (see Table 1):

$$NO^+ + C_2H_5COOH \rightarrow NO^+ \cdot C_2H_5COOH \qquad (6a)$$

$$\rightarrow C_2H_5CO^+ + HNO_2 \qquad (6b)$$

Note the production of a nitrous acid molecule and a stable carboxyl ion in reaction (6b). In the isobutyric acid reaction, for which $k = k_c$, OH⁻ transfer is the dominant process (80%) as it also is for the n-butyric, valeric and trimethylacetic acid reactions. However, for the unsaturated acrylic acid, OH⁻ transfer is only a minor channel (5%) with association dominating:

$$NO^+ + CH_2{=}CHCOOH \rightarrow NO^+ . CH_2{=}CHCOOH$$
$$\qquad (7a)$$

$$\rightarrow CH_2{=}CHCO^+ + HNO_2 \qquad (7b)$$
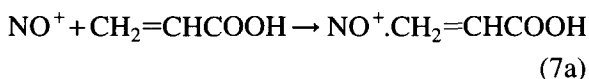
This is because reaction (7b) is endothermic by about 8.4 kJ mol⁻¹ [15]. The 5% product distribution coupled with the overall $k = 0.5k_c$, is consistent with a scenario in which OH⁻ transfer would be the major (perhaps the only) process at higher temperatures (interaction energies) for the reaction, especially so when it is known that the rates of association reactions invariably decrease with increasing temperatures [20]. In the lactic acid reaction, association and OH⁻ transfer are seen to be equally important under these SIFT conditions (see Table 2).

3.2.3. O₂⁺ reactions

All these reactions are fast (see Table 1). There are no obvious trends within the ionic products, and the reaction mechanisms are difficult to positively identify by inspection of the products which are shown in Table 2. The ionisation energies of all these acid molecules are less than that of oxygen molecules, and so charge

transfer with ground state O_2^+ ions is energetically allowed in all these reactions. Indeed, the parent molecular ion is observed as a product of most, but not all, of the reactions, fragment ions being more obvious even in the reaction of formic acid where the parent ion is only a minor (10%) product:

$$O_2^+ + HCOOH \rightarrow HCOOH^+ + O_2 \qquad (8a)$$

$$\rightarrow HCOO^+ + (H + O_2) \qquad (8b)$$

The majority (90%) channel (8b), probably via dissociative charge transfer, produces the observed ion together with a free hydrogen atom and an oxygen molecule, but, as suggested, it is possible that hydride ion (H^-) transfer actually occurs producing a stable HO_2 molecule. H^- transfer is commonly observed in NO^+ reaction with alcohols [6] and some aldehydes [7], but is not commonly observed in O_2 reactions.

It is difficult to determine the neutral products of most of these reactions. The energetics can help in some cases by eliminating some potential products. We do not think a detailed discussion of the possible neutral products is worthwhile here, but it can be done for specific reactions when required.

Radical neutrals must be released in many of these O_2^+ reactions with the simultaneous production of open shell cations. The elimination of COOH radicals from the nascent parent cations is apparent in some of the reactions, for example in the trimethylacetic acid reaction:

$$O_2^+ + (CH_3)_3CCOOH \rightarrow (CH_3)_3C^+ + COOH + O_2 \qquad (9a)$$

$$\rightarrow (CH_3)_2CH_2C^+ + HCOOH + O_2 \qquad (9b)$$
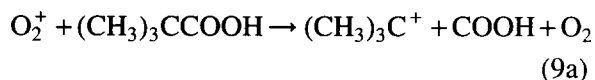
Reaction (9a) is the majority (90%) channel. It appears that formic acid is the neutral product of reaction (9b), although this requires some rearrangement of the excited parent cation before dissociation occurs. It is clear that to produce many of the ionic products of these O_2^+ reactions rearrangement of the respective parent cations is

also necessary. This is most surely the case for the lactic acid reaction (see Table 2).

3.3. Ester reactions

As can be seen in Table 3, we have included in this series of esters the simplest, methyl formate, and three pairs with the same molecular weight, i.e. ethyl formate and methyl acetate, methyl propionate and ethyl acetate, and methyl butyrate and ethyl propionate, principally to see if these isomers can be distinguished via their reactions with our chosen precursor ions. Also included is one ester with an aromatic ring, methyl benzoate.
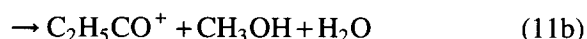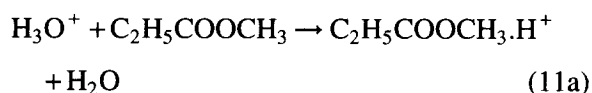
3.3.1. H_3O^+ reactions

A glance at Table 3 shows that the major product of each of these reactions, and in the two acetate ester reactions the only product, is the protonated parent molecule. In the remaining seven reactions, minor products (5% or 10%) are evident. The minor products (< 5%) of the methyl formate and ethyl formate reactions are apparently protonated methanol and ethanol respectively, e.g.

$$H_3O^+ + HCOOCH_3 \rightarrow HCOOCH_3 \cdot H^+ + H_2O \qquad (10a)$$

$$\rightarrow CH_3OH_2^+ + (CO + H_2O) \qquad (10b)$$
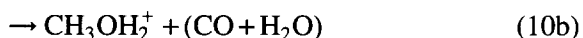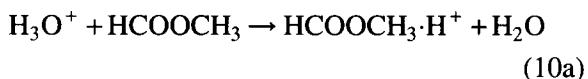
It must be said immediately that we are uneasy about the small, 5%, products because a reaction like (10b) requires some rearrangement in the intermediate ion to produce the protonated alcohol molecule, and there remains the possibility of a small vapour pressure of the alcohol (partial hydrolysis) above the ester liquid. However, two points persuade us that channel (10b) is real. Firstly, there is no evidence of a significant partial pressure of methanol (or ethanol in the analogous ethyl formate reaction) as determined by using NO^+ ions as the precursor to analyse the vapour (see Table 3); the presence of methanol would be detected by the appearance in the mass spectrum of the adduct $NO^+ \cdot CH_3OH$ (and

$C_2H_5O^+$ in the ethanol case; see our previous detailed study of alcohol reactions [6]). Secondly, to produce the products as written in reaction (10b), and the analogous products for the ethyl formate reaction, is energetically favourable, the reaction being 16.7 kJ mol^{-1} exothermic for separated CO and H_2O molecules. However, it is not inconceivable that a single neutral molecule of formic acid, HCOOH, emerges from a reaction which first results in the formation of the adduct ion $(H_3O^+ \cdot HCOOCH_3)^*$ in a small fraction of the collisions, and such a reaction would be much more exothermic. A similar situation might occur in the ethyl formate reaction.

Moving to the methyl acetate and ethyl acetate reactions, Table 3 shows that reactions analogous to (10b) are not observed. This is because they are endothermic according to the available thermochemical data [15]. The ethyl acetate reaction was studied previously by Bohme et al. in a flowing afterglow [21], but they observed an additional $C_2H_5O_2^+$ product ion, probably due to the presence of other more energetic precursor ions in their flowing afterglow. These H_3O^+/acetate reactions are also endothermic to produce the carboxyl ions, RCO$^+$, that are clearly produced in the methyl propionate, ethyl propionate, methyl butyrate and methyl benzoate reactions as, for example,

$$H_3O^+ + C_2H_5COOCH_3 \rightarrow C_2H_5COOCH_3.H^+$$
$$+ H_2O \qquad (11a)$$

$$\rightarrow C_2H_5CO^+ + CH_3OH + H_2O \qquad (11b)$$

In reactions such as (11b) the carboxyl ion is produced and the appropriate alcohol molecule is ejected from the protonated parent molecule. This reaction is exothermic by 12.5 kJ mol^{-1}. The corresponding reaction involving ethyl propionate also results in $C_2H_5CO^+$ ion with the ejection of a C_2H_5OH molecule, this reaction also being 12.5 kJ mol^{-1} exothermic. Since these minority channels producing RCO$^+$ cations can be shown to be endothermic in the methyl

and ethyl acetate reactions with H_3O^+ (typically by 29.3 kJ mol^{-1}), then it is not surprising that there is only a single product in these two reactions (see Table 3).

3.4. NO$^+$ reactions

Note in Table 3 that although the ionisation potentials of these ester molecules are relatively small, they all exceed the ionisation energy of NO molecules (9.26 eV), and so charge transfer between ground state NO$^+$ ions and these ester molecules cannot occur at thermal energies and so it is not observed.

There is only a single ionic product in both the methyl and ethyl formate reactions which proceed relatively rapidly via ion/molecule association under these SIFT conditions, e.g.,

$$NO^+ + HCOOCH_3 \rightarrow NO^+ \cdot HCOOCH_3 \qquad (12)$$

As before, the association energy is removed from the excited adduct during its frequent collisions with the helium atoms of the carrier gas. However, in the other six reactions there are two parallel ionic products, in each reaction one product being the appropriate adduct as exemplified in reaction (12) and the other being the appropriate carboxyl ion, RCO$^+$, e.g.,

$$NO^+ + CH_3COOCH_3 \rightarrow NO^+ \cdot CH_3COOCH_3$$
$$\qquad (13a)$$

$$\rightarrow CH_3CO^+ + CH_3NO_2 \qquad (13b)$$
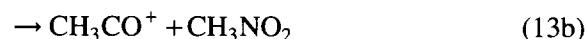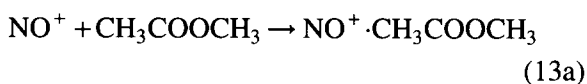
Reaction (13b), as written, indicates the formation of methyl nitrite as the neutral product. Such a reaction can be described as a methoxide ion, CH_3O^-, transfer reaction, and represents 20% of the product distribution. From the available thermochemical data [15] this reaction is apparently 4.2 kJ mol^{-1} endothermic which probably explains why it is only a 20% product of this reaction at 300 K. Significantly, CH_3CO^+ ($+C_2H_5NO_2$) is only a minor (10%) product of the ethyl acetate reaction because it is also slightly endothermic. The latter reaction must

involve ethoxide ion, $C_2H_5O^-$, transfer producing a $C_2H_5NO_2$ molecule since fragmentation of this (and the CH_3NO_2 molecule in reaction (13b)) would be far too endothermic to occur.

However, alkoxide ion transfer is significantly exothermic in the remaining reactions and it is the major reaction process that occurs in all but one of these reactions (ethyl propionate). Thus, for example, the methyl propionate reaction proceeds thus:

$$NO^+ + C_2H_5COOCH_3 \rightarrow C_2H_5CO^+ + CH_3NO_2$$
(14a)

$$\rightarrow NO^+ \cdot C_2H_5COOCH_3$$
(14b)
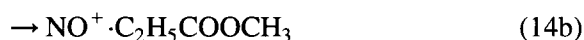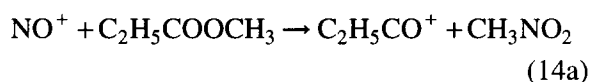
In this reaction the methoxide ion transfer channel (14a) is 80% of the product distribution with the adduct channel being a minor 20%. Reaction (14a) is $37.5 \, kJ \, mol^{-1}$ exothermic; other neutral products such as ($HNO + CH_2O$) and ($NO_2 + CH_3$) would be quite exothermic. Production of the carboxyl ion and the appropriate nitrite molecule is exothermic in the methyl butyrate, ethyl propionate and methyl benzoate reactions with NO^+ and significantly this is the major channel in these reactions with the association reaction being the minor parallel product (see Table 3). So it seems that when the alkoxide ion transfer is exothermic it is favoured over association (stable adduct formation) in these reactions.

3.4.1. O_2^+ reactions

The low ionisation energies of these ester molecules ensure that charge transfer with ground state O_2^+ ions (recombination energy is 12.1 eV) is always possible, and we assume that all these reactions proceed via this process. However, the parent cation, when observed (see Table 3), is never more than a minority product, the charge transfer being sufficiently exothermic, typically by about 2 eV to allow its fragmentation in some cases producing several different ionic species.

There are no obvious trends amongst the products of these reactions, but some types of fragmentation mechanisms are evident. Most obvious is the breaking of the R_1CO-OR_2 bond in the ester commonly producing the R_1CO^+ carboxyl ion as, for example, in the methyl acetate reaction:

$$O_2^+ + CH_3COOCH_3 \rightarrow CH_3CO^+ + CH_3O + O_2$$
(15a)

$$\rightarrow CH_3COOCH_3^+ + O_2$$
(15b)
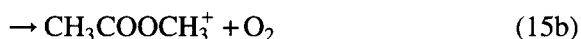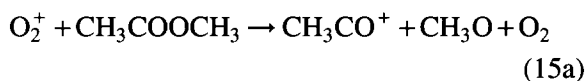
in which it is the major (90%) ion product, and sometimes producing the OR_2^+ alkoxy cation as in the methyl formate reaction:

$$O_2^+ + HCOOCH_3 \rightarrow CH_3^+ + HCO + O_2$$ (16a)

$$\rightarrow HCOOCH_3^+ + O_2$$ (16b)
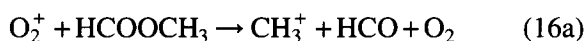
in which it is the major (> 95%) product. In the ethyl propionate reaction there appear seven discernible product ions, with the major ones being the carboxyl ion, $C_2H_5CO^+$ (45%) and the alkoxy ion, $C_2H_5O^+$ (15%).

A rare event in the reaction of O_2^+ ions with carbon–oxygen-containing organic molecules is the production of hydrocarbon ions, but this occurs in the ethyl formate reaction for which $C_2H_4^+$ is observed as the major (> 90%) product:

$$O_2^+ + HCOOC_2H_5 \rightarrow C_2H_4^+ + HCOOH + O_2$$
(17)
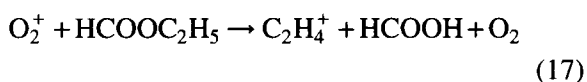
The energetics demand that the neutral product of this reaction is formic acid as indicated.

4. Concluding remarks

Little more can be said about the O_2^+ reactions with both the acids and esters, in which the charge transfer reactions result in fragmentation of the nascent parent cations so formed, and no obvious patterns of reactivity emerge. However, these reactions are of some value in analysis in that the isomeric forms of the acids and esters react with O_2^+ to produce different ion products.

Of greater interest are the H_3O^+ and NO^+ reactions with these acids and esters which have obvious value in analysis because they are fast and the products of the reactions are simpler and more predictable. The major product ions ($>$ or $= 90\%$) of the H_3O^+ reactions with both the acids and esters are the protonated parent molecules. Worthy of note is that the minority product ions largely result form the elimination of H_2O molecules from the protonated acids, and often the elimination of alcohol molecules (CH_3OH or C_2H_5OH) from the protonated esters when this process is exothermic. The NO^+ reactions with both the acids and esters invariably generate, in part, the adduct ions $NO^+ \cdot M$, with parallel hydroxide ion transfer also occurring in most of the acid reactions and parallel alkoxide ion transfer occurring in some of the ester reactions, which apparently becomes the major reaction process when it is exothermic.

Our studies of the reactions of H_3O^+, NO^+ and O_2^+ with several types of organic molecules of which the present study is a part (but also see Refs. [6,7]) are showing the value of H_3O^+ and NO^+ in chemical ionisation mass spectrometry and especially in our SIFT method which has been demonstrated in several studies [22–24]. Following the present studies and the previous studies of the reactions of alcohols [6] and aldehydes and ketones [7], we have initiated similar studies of the reactions of several ethers, organosulphur molecules, amines and hydrocarbons which will be reported in due course. A major objective of this work is to establish a database of rate coefficients and ion product branching ratios in support of our SIFT method of trace gas analysis [3, 4, 5].

Acknowledgements

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