

SIFT studies of the reactions of H_3O^+ , NO^+ and O_2^+ with several ethers

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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 10 ethers, M. We assume that all the exothermic proton transfer reactions of H_3O^+ with all the ether molecules occur at the collision rate, i.e. the rate coefficients, k , are equal to k_c , then it is seen that the k 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 are unusually complicated compared to the reactions of these reactant ions with many ketones, alcohols, aldehydes and carboxylic acids in which the products are predominantly MH^+ and $(\text{M}-\text{H}_2\text{O})^+$ ions (water molecule elimination). In these ether reactions, water elimination is not observed, but rather MH^+ and ions resulting from the elimination of alcohol and hydrocarbon molecules are the common products. The NO^+ reactions mostly proceed via hydride ion (H^-) transfer producing $(\text{M}-\text{H})^+$ ions and an HNO molecule, with parallel alkyl radical ion, R^- , abstraction (producing $(\text{M}-\text{R})^+$ ions (and RNO molecules) being evident in two of the reactions and aikoxide ion, RO^- , abstraction (producing hydrocarbon ions and RONO molecules) in two of the other reactions. The NO^+ /anisole reaction proceeds exclusively via charge transfer, this being allowed because of the low ionization energy of anisole. The O_2^+ reactions proceed by dissociative charge transfer with the production of two or more ionic fragments of the parent molecular ion, the different isomeric forms of these ether molecules resulting in different product ions. © 1998 Elsevier Science B.V.

Keywords: SIFT; Ion-molecule reactions; Proton transfer; Hydride ion transfer; Charge transfer; Trace gas analysis; Chemical ionization

1. Introduction

In support of our development of the selected ion flow tube (SIFT) as a sensitive method for the detection and quantification of trace gases in air and human breath [1,2], we have embarked upon an extensive survey of the reactions of H_3O^+ , NO^+ and O_2^+ ions with a wide variety of organic and inorganic molecular species, including many that are known to be present in atmospheric air and human breath and are emitted by fruit and

food products. These precursor ionic species are selectively used for chemical ionization of the trace gases; they are the most suitable for air analyses because they do not react at a significant rate with the major air components (N_2 , O_2 , CO_2 , H_2O and Ar), yet they do react rapidly with most of the known trace gas molecules in the air/breath samples. Of course, to be used successfully as chemical ionization agents for the identification of specific trace gas molecules and for their quantification, the product ions of the ion-molecule reactions must be identified and the rate coefficients for the reactions, k , must be known. Given

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the complexities of the air mixtures noted above (for example, it is reported that some 300 species are present in human breath [3,4]) this could be an endless exercise, but a knowledge of the trends in reactivity of our chosen precursor ions with particular molecular types has obvious advantages in the interpretation of complex mass spectra.

To date, we have studied the reactions of H_3O^+ , NO^+ and O_2^+ ions with some 17 alcohols [5], 11 aldehydes and nine ketones [6], and nine carboxylic acids and eight esters [7]. The results of these studies represent a valuable extension of our database and a better understanding of the fundamental aspects of this ion–molecule chemistry. The data reveal many examples of reaction processes hitherto not greatly explored, such as the elimination of H_2O molecules following the protonation of some alcohols, aldehydes and carboxylic acids by H_3O^+ , hydride ion transfer (H^-) and hydroxide ion (OH^-) transfer in the reactions of NO^+ with some alcohols, aldehydes and acids, facile ion–molecule association between NO^+ and most ketones, and even

alkoxide ion (CH_3O^- and $\text{C}_2\text{H}_5\text{O}^-$) transfer in the reactions of NO^+ with some esters. NO^+ ions were investigated previously as precursors for chemical ionization and it was observed that with ethers the typical product ions are $(\text{M}-\text{H})^+$ ions and that no association occurs [8,9]. The reactions of almost all these organic compounds with O_2^+ proceed via charge transfer, often with the productions of several fragment ions [5–7].

In this article, we report the results of a limited study of the reactions of the three ions with some 10 ethers, including four structural isomers of the saturated $\text{C}_6\text{H}_{14}\text{O}$ ethers, one unsaturated ether, one diether, a heterocyclic and an aromatic ether as given in Table 1. As always, we were searching for trends in the reactivity of these species.

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

Table 1

Rate coefficients for the reactions of H_3O^+ , NO^+ and O_2^+ with the ethers indicated. Also given are the molecular weights of the ethers, 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 [15]). For the remaining compounds (in italics) we have estimated their μ assuming they do not change significantly with the number of carbon atoms in the ether molecule, and their α by adopting the average values of the known polarisabilities of similar organic molecules possessing the same number of carbon atoms. Then, the collisional rate coefficients, k_c , for all reactions have been calculated using the parameterized trajectory formulation of Su and Chesnavich [14] and these are given in the 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 are given in units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$

Molecule	m [u]	α [10^{-24} cm^3]	μ [D]	k, k_c (H_3O^+) [$10^{-9} \text{ cm}^3 \text{ s}^{-1}$]	k_c, k (NO^+) [$10^{-9} \text{ cm}^3 \text{ s}^{-1}$]	k_c, k (O_2^+) [$10^{-9} \text{ cm}^3 \text{ s}^{-1}$]
Tetrahydrofuran	72	9 ± 1	1.63	[2.8]	[2.3] 2.5	[2.3] 2.5
Diethyl ether	74	10.2	1.15	[2.4]	[2.1] 1.8	[2.0] 2.0
Allyl ethyl ether	86	10.7 ± 1	1.2 ± 0.2	[2.5]	[2.1] 2.3	[2.0] 2.2
Butyl methyl ether	88	11 ± 1	1.2 ± 0.2	[2.5]	[2.1] 2.2	[2.0] 2.1
Ethylene glycol dimethyl ether	90	11.5 ± 1	1.4 ± 0.2	[2.7]	[2.2] 2.3	[2.2] 2.2
Tertiary pentyl methyl ether	102	12.8 ± 1	1.2 ± 0.2	[2.6]	[2.2] 2.3	[2.1] 2.3
Butyl ethyl ether	102	12.8 ± 1	1.2 ± 0.2	[2.6]	[2.2] 2.2	[2.1] 2.3
Dipropyl ether	102	12.8	1.21	[2.6]	[2.2] 2.4	[2.1] 2.3
Diisopropyl ether	102	12.8 ± 1	1.2 ± 0.2	[2.6]	[2.2] 2.3	[2.1] 2.4
Anisole	108	13.3	1.38	[2.7]	[2.3] 2.2	[2.2] 2.1

papers (see Refs [10–12]). So 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/detection system. From these data, together with other critical parameters including the carrier gas flow velocity and the length of the reaction zone (i.e. the effective reaction time), it is simple to determine the k for the reaction and the ion product branching ratios [10].

It is straightforward to measure the flow rates of permanent reactant gases, but for 'sticky' organic vapours this is more difficult because the thermodynamic data required for capillary and flow meter calibrations (i.e. heat capacities) are mostly unavailable, and known volume/pressure reduction methods of flow measurements are inaccurate because such vapours stick to vessel surfaces. Therefore, we have adopted the following procedure for the 'sticky' vapours involved as reactants in these studies.

We justifiably assume [13] that the k for all appreciably exothermic proton transfer reactions proceed at the collision rate, k_c , which can be calculated if the polarisability and the dipole moment of the reactant molecule, M , are known [14,15]. Since all the H_3O^+ proton transfer reactions with which we are concerned in these surveys are exothermic (because the proton affinities, PA , of M are greater than the PA of H_2O molecules [16]), the k -values for these particular reactions are equal to their respective k_c . Numerous experimental studies have shown that for such reactions the values of k are always equal to or close to k_c [13,17]. However, this is not necessarily so for other exothermic reactions that proceed via processes such as charge transfer and hydride ion transfer by which many of the O_2^+ and NO^+ reactions with organic molecules occur [18]. So the k for such reactions must be

determined experimentally. To do this we make a very dilute mixture of the reactant vapour at an unknown (but low) 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 flow meters. Of course, using this procedure we cannot determine the absolute values of k for the reactions, but introducing H_3O^+ , NO^+ and O_2^+ ions simultaneously into the carrier gas, 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 the k for the NO^+ and O_2^+ reactions can be obtained. Further discussion of this procedure is given in the first in this series of papers, which is concerned with alcohol reactions [5]. To illustrate the quality of the decay curves thus obtained, those for the three di-isopropyl ether reactions are reproduced in Fig. 1. The product ion distributions for the reactions are also determined from these measurements in the usual manner [10].

The presence of metastable electronically excited states of the primary NO^+ and O_2^+ ions in the injected ion swarm is a potential problem, in particular they could influence the product ion distributions, but excited ions were shown not to be important by simply adding 5 mTorr of air upstream into the flow tube (which is known to quench these excited 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. In all, 30 reactions were studied and in most of them two or more product ions were observed.

3. Discussion of results

The calculated k_c for the H_3O^+ proton transfer reactions and the experimentally derived k (with their respective k_c) for the NO^+ and O_2^+ reactions with these 10 ethers are shown in Table 1. The k_c

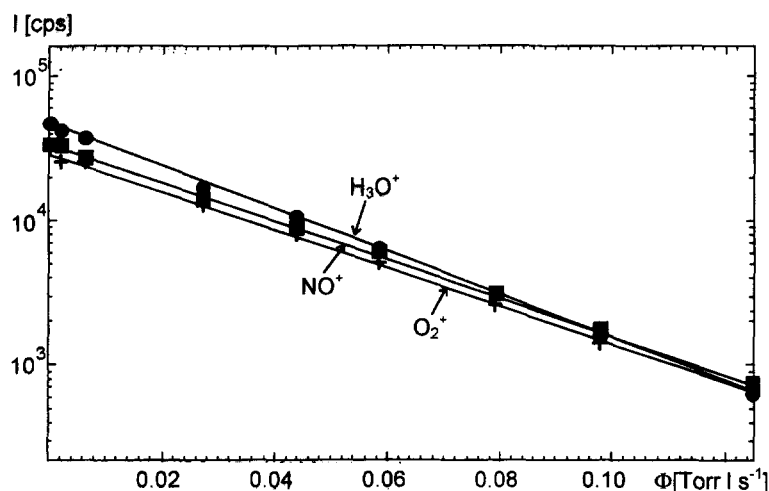


Fig. 1. Semi-logarithmic decay plots of the count rates, I (in counts per second, cps), of the simultaneously injected H_3O^+ , NO^+ and O_2^+ primary ions as functions of the flow rate, Φ (in Torr/litres per second), of air containing the vapour of diisopropyl ether. Because these three primary ions do not react at a significant rate with the major components of air at the flow rates used, their decay rates are due only to their reactions with the ether molecules. Therefore, the slopes of these plots provide the relative rate coefficients of the reactions of the three ions with diisopropyl ether. Assuming that the H_3O^+ reactions proceed at the collisional rate (i.e. $k = k_c$) then the k for the NO^+ and O_2^+ reactions can be derived and these values are given in Table 1. See Table 2 for the products of these reactions.

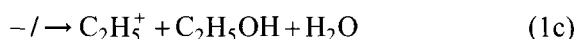
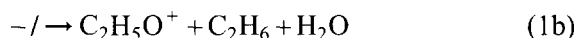
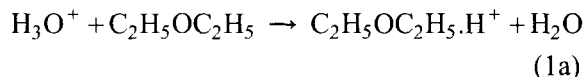
were calculated using the procedure outlined in the caption to the table. As can be seen, with few exceptions the NO^+ and O_2^+ reactions proceed at or near the collision rate. The ion product distributions for all the reactions are shown in Table 2. Only those ion products which represent more than 2% of the product distribution have been included. We now discuss the H_3O^+ , NO^+ and O_2^+ reactions separately.

3.1. H_3O^+ reactions

The ethers are listed in the tables in order of their relative molar masses, but for clarity we discuss the reactions in order of their observed complexity.

In each of the tetrahydrofuran, diethyl ether and anisole reactions only a single ionic product is observed, these being the protonated parent molecules. This is because no other realistic exothermic products can be identified for the tetrahydrofuran and anisole reactions, remembering that they are studied under truly thermalized conditions in the SIFT at 300 K. However, in the diethyl ether reaction it can be considered (on

the basis of some of the other ether reactions with H_3O^+ included in this study; see Table 2) that hydrocarbon and/or alcohol molecule elimination could occur, thus:




However, reactions 1b and 1c are not observed under the conditions of these SIFT experiments, even though it can be shown using the available thermochemical data [16] that they are both exothermic. The reaction of H_3O^+ with dimethyl ether (not included in this study) was previously studied by Bohme and co-workers [19] who observed in their flowing afterglow experiment that non-dissociative proton transfer at the gas kinetic rate is the only process that occurs and interestingly that dimethyl ether forms hydrated ions in reaction with $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}_{1,2,3}$ [20].

Contrasting with these three simple H_3O^+ reactions are the remaining seven reactions for which

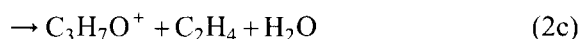
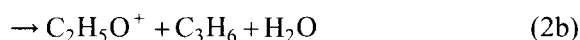
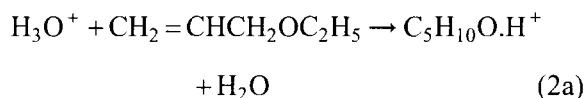
Table 2

Products of the reactions of the ethers 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 products is given in brackets. 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 in some cases the ionic products) are not readily defined

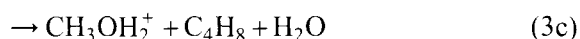
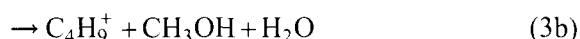
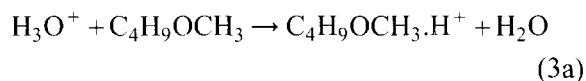
	H_3O^+	NO^+	O_2^+
$\text{C}_4\text{H}_8\text{O}$,  tetrahydrofuran	$\text{C}_4\text{H}_8\text{O}.\text{H}^+(100) + \text{H}_2\text{O}$	$\text{C}_4\text{H}_7\text{O}^+(100) + \text{HNO}$	$\text{C}_4\text{H}_7\text{O}^+(55)$ CH_2CO^+ or $\text{C}_3\text{H}_6^+(40)$ CH_3CO^+ or $\text{C}_3\text{H}_5^+(5)$
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ diethyl ether	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5.\text{H}^+(100) + \text{H}_2\text{O}$	$\text{C}_4\text{H}_9\text{O}^+(100) + \text{HNO}$	$\text{C}_2\text{H}_5\text{OCH}_2^+(65)$ $\text{C}_4\text{H}_9\text{O}^+(20)$ $\text{CH}_3\text{O}^+(15)$
$\text{C}_3\text{H}_5\text{OC}_2\text{H}_5$ allyl ethyl ether	$\text{C}_3\text{H}_5\text{OC}_2\text{H}_5.\text{H}^+(60) + \text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{O}^+(20) + \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ $\text{C}_3\text{H}_7\text{O}^+(20) + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	$\text{C}_5\text{H}_9\text{O}^+(100) + \text{HNO}$	$\text{C}_3\text{H}_6\text{O}^+(70)$ $\text{C}_3\text{H}_5\text{O}^+(15)$ $\text{C}_5\text{H}_{10}\text{O}^+(10)$ $\text{C}_3\text{H}_5^+(5)$
$\text{C}_4\text{H}_9\text{OCH}_3$ butyl methyl ether	$\text{C}_4\text{H}_9\text{OCH}_3.\text{H}^+(40) + \text{H}_2\text{O}$ $\text{CH}_3\text{OH}_2^+(10)$ $+ \text{C}_4\text{H}_8 + \text{H}_2\text{O}$	$\text{C}_5\text{H}_{11}\text{O}^+(100) + \text{HNO}$	$\text{CH}_3\text{OCH}_2^+(70)$ $\text{C}_4\text{H}_8^+(30)$
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ ethylene glycol dimethyl ether	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3.\text{H}^+(40) + \text{H}_2\text{O}$ $\text{CH}_3\text{OCH}_2\text{CH}_2^+(55)$ $+ \text{CH}_3\text{OH} + \text{H}_2\text{O}$ $\text{CH}_3\text{O}_2^+(5)$ $+ \text{CH}_3\text{OCH}_3$ $+ \text{H}_2\text{O}$	$\text{C}_4\text{H}_9\text{O}_2^+(80) + \text{HNO}$ $\text{C}_4\text{H}_{10}\text{O}_2^+(10) + \text{NO}$ $\text{CH}_3\text{OCH}_2\text{CH}_2^+(10)$ $+ \text{CH}_3\text{ONO}$	$\text{CH}_3\text{OCH}_2^+(70)$ $\text{C}_4\text{H}_{10}\text{O}_2^+(10)$ $\text{CH}_3\text{OCH}_2\text{CH}_2^+(10)$ $\text{CH}_3\text{OCH}_2\text{CH}^+(5)$ $\text{C}_4\text{H}_9\text{O}_2^+(5)$
$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{OCH}_3$ tertiary pentyl methyl ether	$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2.\text{H}^+(95) + \text{CH}_3\text{OH}$ $+ \text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{OCH}_3.\text{H}^+(5)$ $+ \text{H}_2\text{O}$	$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2^+(90)$ $+ \text{CH}_3\text{ONO}$ $\text{C}_4\text{H}_9\text{O}^+(10) + (\text{C}_2\text{H}_5 + \text{NO})$	$\text{CH}_3\text{OC}(\text{CH}_3)_2^+(75)$ $\text{C}_5\text{H}_{11}\text{O}^+(15)$ $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2^+(10)$
$\text{C}_4\text{H}_9\text{OC}_2\text{H}_5$ butyl ethyl ether	$\text{C}_4\text{H}_9\text{OC}_2\text{H}_5.\text{H}^+(45) + \text{H}_2\text{O}$ $\text{C}_2\text{H}_7\text{O}^+(55) + \text{C}_4\text{H}_8 + \text{H}_2\text{O}$	$\text{C}_6\text{H}_{13}\text{O}^+(100) + \text{HNO}$	$\text{C}_2\text{H}_5\text{OCH}_2^+(70)$ $\text{C}_4\text{H}_8^+(25)$ $\text{C}_6\text{H}_{13}\text{O}^+(5)$ $\text{C}_3\text{H}_7^+(50)$ $\text{C}_3\text{H}_7\text{OCH}_2^+(50)$
$\text{C}_3\text{H}_7\text{OC}_3\text{H}_7$ dipropyl ether	$\text{C}_3\text{H}_7\text{OC}_3\text{H}_7.\text{H}^+(70) + \text{H}_2\text{O}$ $\text{C}_3\text{H}_9\text{O}^+(25) + \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ $\text{C}_3\text{H}_7^+(5) + \text{C}_3\text{H}_7\text{OH} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_{13}\text{O}^+(100) + \text{HNO}$	$\text{C}_2\text{H}_5\text{O}^+(60)$ $\text{C}_5\text{H}_{11}\text{O}^+(40)$
$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$ diisopropyl ether	$\text{C}_3\text{H}_9\text{O}^+(80) + \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2.\text{H}^+(20)$ $+ \text{H}_2\text{O}$	$\text{C}_6\text{H}_{13}\text{O}^+(50) + \text{HNO}$ $\text{C}_5\text{H}_{11}\text{O}^+(20) + (\text{CH}_3 + \text{NO})$ $(\text{CH}_3)_2\text{COH}^+(30) + \text{C}_3\text{H}_7\text{NO}$	$\text{C}_2\text{H}_5\text{O}^+(60)$ $\text{C}_5\text{H}_{11}\text{O}^+(40)$
$\text{C}_6\text{H}_5\text{OCH}_3$ anisole	$\text{C}_6\text{H}_5\text{OCH}_3.\text{H}^+(100) + \text{H}_2\text{O}$	$\text{C}_7\text{H}_8\text{O}^+(100) + \text{NO}$	$\text{C}_7\text{H}_8\text{O}^+(100)$

there are two or three ionic products. Three ion products are rare in the reactions of H_3O^+ with alcohols (the exceptions being the long-chain octanols [5]), aldehydes, ketones, esters and acids [6,7]. Note in Table 2 that there are three products in the allyl ethyl ether, butyl methyl ether and ethylene glycol dimethyl ether reactions, their protonated parent molecules being important, but not always the majority product ions. The minor channels in the allyl ethyl ether

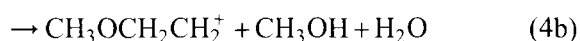
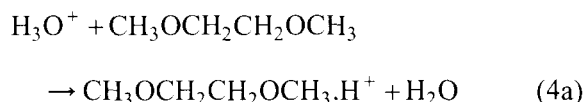
reaction involve hydrocarbon elimination from the protonated parent molecule:



Clearly, following protonation the ion partially splits at the third carbon–oxygen bond releasing a propene molecule and equivalently at the second–third carbon releasing an ethene molecule. A similar splitting of protonated butyl methyl ether occurs:



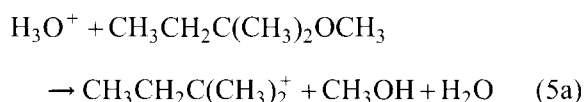
In this reaction, the split occurs at the fourth carbon–oxygen bond eliminating a methanol molecule in most dissociations, but with a fraction resulting in the elimination of a butene molecule (see Table 2). The energetics show that the C_4H_9^+ ion product of reaction (3b) must be either the secondary $(\text{CH}_3)_2\text{CHCH}_2^+$ ion or the tertiary $(\text{CH}_3)_3\text{C}^+$ ion, thus requiring during the reaction a rearrangement of the C_4H_9 moiety. Methanol elimination is the major channel (reaction (4b)) in the reaction of ethylene glycol dimethyl ether:



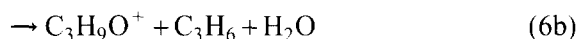
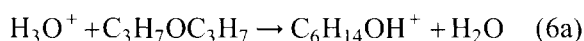
showing a much greater propensity for splitting at one of the carbon–oxygen bond and a small probability for splitting at the central carbon–carbon bond producing two ether structures.

The reactions of the four structural isomers with the common molecular formula $\text{C}_6\text{H}_{14}\text{O}$ (see Table 2) result in quite different products. The reaction of tertiary pentyl methyl ether results in almost total dissociation producing a hydrocarbon ion with the elimination of a methanol molecule, the protonated parent molecule being

only a very minor product:



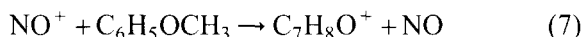
This reaction is very reminiscent of the reactions of H_3O^+ with many higher-order alcohols which also result in the appropriate hydrocarbon ion [5], but in those alcohol reactions it is an H_2O molecule that is eliminated. The reaction of butyl ethyl ether is quite analogous to the reaction of butyl methyl ether (reaction (3c)) in that hydrocarbon molecule elimination occurs (see Table 2). The dipropyl and diisopropyl ether reactions result in the same two major product ions, $\text{C}_6\text{H}_{14}\text{OH}^+$ and $\text{C}_3\text{H}_9\text{O}^+$, but the product percentages are essentially reversed, as can be seen in Table 2. Both reactions proceed thus:



The elimination of a C_3H_6 molecule presumably leaves a protonated 1-propanol or 2-propanol molecule as appropriate.

3.2. NO^+ reactions

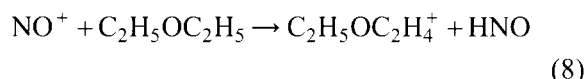
There is only a single ionic product in seven of the 10 reactions. Of these, the anisole reaction is unique in that it proceeds via charge transfer only:



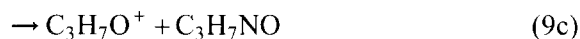
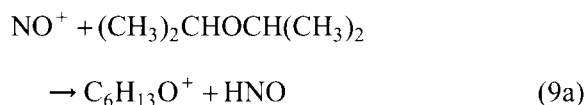
Charge transfer is possible because the ionization energy (IE) of anisole ($IE = 8.2$ eV) is much smaller than that of NO ($IE = 9.26$ eV). The IE s of the other ethers in this series [16] are somewhat greater than that of NO which thus inhibits charge transfer at the low interaction energies of the SIFT experiment. However, charge transfer is a minor channel in the reaction of ethylene glycol dimethyl ether even though it is slightly endothermic based on the published value [16]

of the IE ($= 9.3$ eV) of this molecule. There is no real contradiction here, because of the possible small uncertainty in the IE and the thermal spread in the ion/molecule interaction energies in the SIFT at 300 K.

The most common reaction mechanism in these reactions is hydride ion (H^+) transfer. It is the single process that occurs for six of these reactions (see Table 2) and is exemplified by:



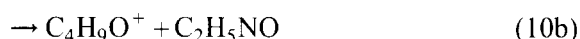
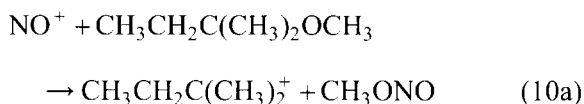
These reactions are, thus, characterized by the production of an $(M-H)^+$ ion and an HNO molecule. This is a common process in the reactions of NO^+ ions, also occurring in their reactions with many alcohols [5] and aldehydes [6]. It is also the major process in two of the other ether reactions, occurring in parallel with other processes. The diisopropyl ether reaction proceeds thus:



H^- transfer (reaction (9a)) is the major channel, but now two other parallel channels appear which involve the transfer (abstraction) of CH_3^- and $C_3H_7^-$ ions to the NO^+ forming CH_3NO and C_3H_7NO molecules. The energetics show [16] that reactions (9b) and (9c) would be very endothermic to result in the separated alkyl radicals and the NO molecule. There are several possible structures for the product ions and neutrals of reactions (9b) and (9c) according to the thermochemical database [16] and within these there are several exothermic combinations. Therefore, it is surprising that the dipropyl ether isomer results in but a single product due to H^- transfer even though there would appear to be exothermic channels corresponding to reactions (9b) and (9c). Whatever the reason for this

difference in the reactions of these two isomers, it offers a clear opportunity to distinguish them using NO^+ chemical ionization.

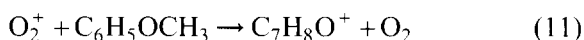
The reaction of tertiary pentyl methyl ether is unique in this series in that the major product is a hydrocarbon ion. It proceeds thus:



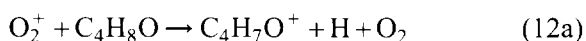
Here the methoxide ion (CH_3O^-) is transferred (abstracted) to the NO^+ in 90% of the interactions, thus forming the hydrocarbon ion and a methyl nitrite molecule, and in the other 10% the ethide ion ($C_2H_5^-$) is transferred from the opposite end of the molecule (see also reactions (9b) (9c)). We have observed that methoxide ion transfer commonly occurs in the reactions of NO^+ with methyl esters [7]. Note also (in Table 2) that this process occurs as a minor channel in the glycol ether reaction.

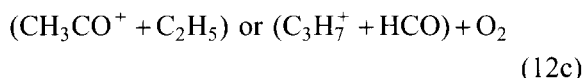
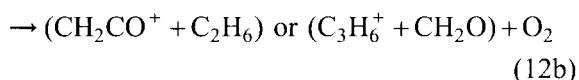
3.3. O_2^+ reactions

We class all these as charge transfer reactions, but in only one, the anisole reaction, is the parent cation the only product:

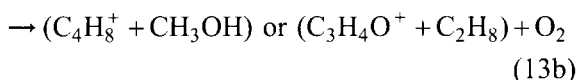
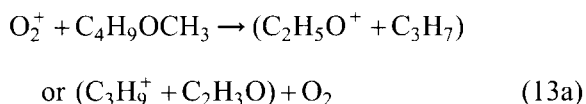


The remaining nine reactions must be classed as dissociative charge transfer reactions. In each reaction, after the electron transfer has taken place, the nascent parent cation dissociates at more than one position leading to the observed product distributions. In the tetrahydrofuran reaction there is some doubt which product ions are formed because there are two valid options at a given product ion mass. Sometimes under these circumstances, the energetics may exclude one of the options, but in this case the available thermochemical data indicate that both options (see Table 2) are energetically permitted:



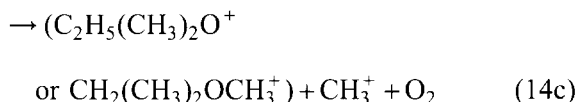
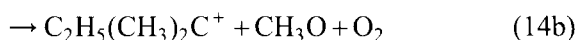
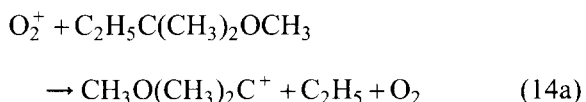


Each product ion is feasible from a consideration of the dissociation of the parent ion (little rearrangement required) so we cannot identify the products of reactions (12b) and (12c). Indeed, it is possible that both of the ions are products in each case. Similarly, it is not simple to identify the products of the butyl methyl ether reaction:



Energetically, the C_2H_8 in reaction (13b) could either be $(\text{C}_2\text{H}_6^+ + \text{H}_2)$ or 2CH_4 . We favour the production of the $\text{C}_2\text{H}_5\text{O}^+$ in reaction (13a) because the alternative ion, C_3H_9^+ (protonated propane), would rapidly be lost by proton transfer with the H_2O which is always present in the carrier gas when air is introduced. However, we favour the hydrocarbon ion C_4H_9^+ in reaction (13b) because the product ion at this mass did not form an adduct with water and throughout our extensive studies of these reactions we have observed that hydrocarbon ions show little propensity to form adducts with water (see Ref. [21]). Should it be necessary, the ion chemistry of these product ions could be investigated to obtain further clues as to their nature.

Few doubts exists concerning the products of the other O_2^+ reactions, in which following the charge transfer the nascent parent cation splits at particular bonds. For example the reaction of tertiary pentyl methyl ether proceeds thus:



Note in Table 2 that the products of the dipropyl and diisopropyl ether reactions are quite different, which may have some value in analysis.

4. Concluding remarks

The H_3O^+ reactions with the ethers included in this limited survey are more complicated than those with other compounds we have studied (alcohols, aldehydes, ketones, carboxylic acids and esters), some of the ether reactions resulting in three ionic products which diminishes their value in chemical ionization mass spectrometry (trace gas analysis). In this regard the NO^+ reactions are more useful for the identification and quantification of ethers because they generally react via hydride ion transfer resulting in a single product ion, although this is not a 'golden rule' for these reactions, as a glance at Table 2 confirms. Charge transfer is generally endothermic for these NO^+ /ether reactions, the notable exception being the anisole reaction in which only this process occurs producing the ionized parent molecule. In contrast, charge transfer is the process that occurs in all the O_2^+ reactions and it is often dissociative charge transfer producing two or more fragment ions; the exception again is the reaction of the aromatic anisole for which there is a single product ion. The mass equivalence of the possible ion products of the O_2^+ reaction with tetrahydrofuran prevents their positive identification as is indicated in Table 2. Clearly, there are different product ion distributions for the reactions of the isomeric forms of the $\text{C}_6\text{H}_{14}\text{O}$ ethers (see Table 2) and these differences afford some help in distinguishing between them in trace gas analysis.

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