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

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Abstract

We describe the results of a selected ion flow tube study of the reactions of H_3O^+, NO^+, and O_2^+ with the 10 aromatic hydrocarbons benzene, toluene, 1,2-, 1,3-, and 1,4-dimethylbenzene, ethylbenzene, propylbenzene, 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene, and 11 aliphatic hydrocarbons which are the alkanes *n*-butane and 2-methyl propane, *n*-pentane and 2-methyl butane, *n*-hexane, *n*-octane, *n*-decane and *n*-dodecane, the alkenes 1-pentene and 2-methyl-2-butene, and the dialkene 2-methyl butadiene (isoprene). All 30 reactions of the aromatic hydrocarbons are fast, the rate coefficients k being close to their respective collisional rate coefficients k_c. The H_3O^+ reactions all proceed by proton transfer producing the protonated parent molecules MH^+, the NO^+ reactions proceed largely via nondissociative charge transfer producing M^+ ions, and the O_2^+ reactions proceed via charge transfer which is partially dissociative in most cases producing M^+ and $(M–CH_3)+$ ions. The k for the 33 aliphatic hydrocarbon reactions are much more varied, ranging from the immeasurable to k_c. Proton transfer is endothermic in the reactions of H_3O^+ with the smaller hydrocarbons whilst for the larger hydrocarbons reactions ion–molecule association occurs producing $H_3O^+.M$ ions. The NO^+ reactions proceed largely via hydride ion transfer producing $(M–H)^+$ ions, although partial incorporation of the NO^+ into the larger hydrocarbons with subsequent fragmentation occurs producing minority ions like $RHNO^+$ (where R are radicals like C_3H_7, C_4H_9, etc). The O_2^+ reactions all proceed by rapid dissociative charge transfer, the number of fragment ions increasing with the atomicity of the aliphatic hydrocarbon. (Int J Mass Spectrom 181 (1998) 1–10) © 1998 Elsevier Science B.V.

Keywords: Selected ion flow tube; Ion–molecule reactions; Hydrocarbons; Proton transfer; Charge transfer; Hydride ion transfer; Trace gas analysis; 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 several aromatic and aliphatic hydrocarbons, which follow 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], and most recently of several structural isomers of the amines with the common molecular formula $C_5H_{13}N$ [7]. The kinetic data obtained from the present hydrocarbon

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study extends the required database on the reactions of these three ionic species, which are our chosen precursor ions for our SIFT analytical method [8] (which relies on chemical ionisation [9]) using which we are able to determine the partial pressures of trace gases in air [10] and metabolites in human breath [11] 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).

Hydrocarbons occur widely in nature, some aliphatic hydrocarbons being emitted from plants and fruits [12] and from vertebrates (2-methyl-2-butadiene, isoprene, is present in human breath at the 100 ppb level [8,11,13,14]), and aromatic hydrocarbons in particular are present in polluted town air often in the 10–1000 ppb range or even greater [10]. It is important therefore to explore the potential of our chemical ionisation SIFT analytical method for the detection and quantification of hydrocarbons in air and breath.

Chemical ionisation studies have a long history (see the excellent review by Harrison [9]). Various precursor ions have been investigated previously including CH_5^+, NH_4^+, and indeed, H_3O^+ and NO^+. For our analytical purposes, it is obviously necessary that the ions chosen for air and breath analysis do not react with the major components of air, and this immediately rules out CH_5^+ which reacts rapidly (via proton transfer) with N_2 and H_2O. Hence the value of H_3O^+ and NO^+ which do not react rapidly with these gases but do react rapidly with most other organic (and many inorganic) species [1–7]. Previous work has shown that aromatic hydrocarbons undergo efficient proton transfer reactions with H_3O^+, i.e. their rate coefficients k are usually close to their respective collisional rate coefficient k_c and undergo charge transfer reactions with both NO^+ and O_2^+ (see the data compilations [15,16]), observations which are confirmed by the findings of the present study. However, the reactions of aliphatic hydrocarbons with these ions are more varied and complex; neither H_3O^+ nor NO^+ react with the smaller hydrocarbons, and their reactions with the larger hydrocarbons apparently vary widely in efficiency [15]. Previous studies of NO^+ reactions with aliphatic hydrocarbons, M, using high pressure mass spectrometry [17] and ion cyclotron resonance [18] methods have shown that hydride ion (H^-) transfer is the most common process producing $(M–H)^+$ ions (presumably with the neutral product HNO). We will show in this article that amongst the reactions chosen for study here, H^- transfer commonly occurs, but that it is not the only process that occurs in some reactions. Further, we will show for the reactions of H_3O^+ with the larger *n*-alkanes that the presence of water vapour in the reaction cell can intervene in the ion chemistry and “catalyse” the production of hydrated hydronium ions. The reactions of O_2^+ ions with aromatics are relatively simple charge transfer reactions usually resulting in only two product ions, whereas the reactions with the aliphatics result in multiple product ions, the numbers of which increase with the complexity of the reactant hydrocarbon.

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 Ref. [19]). We have described its use as an analytical tool in some more recent review articles [8,10,11]. The approach we take for the determination of the rate coefficients k and ion product distributions for the reactions of the liquid hydrocarbons 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 article [1] and outlined in our subsequent articles [2–7], so only a brief outline of the method is required here. The k for the H_3O^+ reactions with all the ten aromatic molecules are reasonably assumed to proceed at the collisional (gas kinetic) rate, with a rate coefficient, k_c, since these reactions proceed via exothermic proton transfer because the proton affinities, PA, of these aromatic molecules exceed the PA of the H_2O molecule [20]. The k_c can be calculated if the polarisabilities and dipole moments of the reactant molecules are known or can be estimated [21]. Then the corresponding k for the NO^+ and O_2^+ reactions with each aromatic molecule are obtained in the usual way [19] 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 a weak mixture of the reactant aromatic vapour 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 flow rates of their neat vapours difficult. The rationale and justification for this approach is given in our previous articles [1–7]. The situation for the three aliphatic alkenes included in this study is the same in that their PA values each exceed that of H_2O [22] and so proton transfer to these molecules from H_3O^+ will also occur at the collisional rate as the available previous work on some of these reactions has indicated [15]. However, the situation for the aliphatic alkanes is not so simple because the PA for the smaller ones (low molecular weight) included in this study are significantly smaller than that of H_2O and thus they cannot undergo proton transfer with H_3O^+ at thermal energies. The PA of the larger alkanes are not known, so we did not know what to expect when H_3O^+ reacts with these alkanes (actually, the results obtained are extremely surprising and interesting; see later). Obviously, therefore, it cannot be assumed that these alkanes will react with H_3O^+ at the collisional rate, i.e. that $k = k_c$. Fortunately, however, all the available data on the reactions of O_2^+ with alkanes indicates that they all react (charge transfer) at or close to the collisional rate [15,16] (except for methane which is quite exceptional [23]), and so we assume that this is so for the alkane reactions included in this study. Our experimental data gives strong support to this assumption as we will see. So with this assumption we can estimate the rate coefficients for the more interesting, often slower, reactions of H_3O^+ and NO^+ from the relative decay rates of all three ions as they react with each alkane as is explained above.

The product ions and their percentages for these reactions are obtained in the usual way for SIFT studies [19] by injecting each of the reactant ions into the helium carrier gas separately, so as to avoid confusion, 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 is diminished by the additions of a small amount of air to the helium carrier gas [1,2]. All these measurements were carried at room temperature.

3. Results and discussion

The calculated k_c and the experimentally derived k for the reactions of all three ion species are given in Table 1 for the aromatic hydrocarbons and Table 2 for the aliphatic hydrocarbons. It can seen that the reactions of the aromatics with $H_3O^+.NO^+$ and O_2^+ are all similar implying that they all proceed at all close to their respective collisional rates, i.e. $k = k_c$. This is also the case for the three alkenes as can be seen in Table 2 where it can also be seen that the k values for the alkanes vary from the immeasurable to k_c. We discuss these differences in the section below devoted to the products of these alkane reactions. We now discuss under separate headings these aromatic and aliphatic hydrocarbon reactions.

3.1. Aromatic hydrocarbons

As is mentioned above, all these reactions (30 in all) proceed efficiently with their k being close to k_c. The products of these reactions are given in Table 3. We now discuss the H_3O^+, NO^+, and O_2^+ reactions separately.

3.1.1. H_3O^+ reactions

All these reactions proceed via exothermic proton transfer resulting in a single product ion which is the protonated parent aromatic molecule exemplified by the toluene reaction:

$$H_3O^+ + C_6H_5CH_3 \rightarrow C_6H_5CH_3.H^+ + H_2O \qquad (1)$$

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the aromatic hydrocarbons 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 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 Ref. [24]). For the remaining compounds we have estimated their μ and α by adopting the values of similar aromatic molecules. Then the collisional rate coefficients k_c for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [21] and these are given in the square brackets. The estimated uncertainty in these calculated rate coefficients is ±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} cm^3 s^{-1}

Molecule	m (u)	α (10^{-24} cm^3)	μ (D)	k, k_c (H_3O^+) (10^{-9} cm^3 s^{-1})	k, k_c (NO^+) (10^{-9} cm^3 s^{-1})	k, k_c (O_2^+) (10^{-9} cm^3 s^{-1})
Benzene	78	10.3	0	1.9 [1.9]	1.5 [1.6]	1.6 [1.6]
Toluene	92	12.3	0.36	2.2 [2.2]	1.7 [1.8]	1.8 [1.8]
o-Xylene	106	14.9	0.62	2.4 [2.4]	2.1 [2.0]	2.1 [2.0]
m-Xylene	106	14.9	*0.3 ± 0.2*	2.3 [2.3]	1.9 [1.9]	1.9 [1.9]
p-Xylene	106	14.1	0	2.2 [2.2]	1.8 [1.8]	1.8 [1.8]
Ethylbenzene	106	14.2	0.59	2.4 [2.4]	2.0 [2.0]	2.0 [1.9]
Propylbenzene	120	*16.0 ± 0.5*	*0.6 ± 0.2*	2.5 [2.5]	2.0 [2.1]	2.1 [2.0]
1,2,3 Trimethyl benzene	120	*16.0 ± 0.5*	*0.6 ± 0.2*	2.5 [2.5]	1.9 [2.1]	2.0 [2.0]
1,2,4 Trimethyl benzene	120	*16.0 ± 0.5*	*0.4 ± 0.2*	2.4 [2.4]	1.9 [2.0]	2.0 [1.9]
1,3,5 Trimethyl benzene	120	*16.0 ± 0.5*	0	2.3 [2.3]	1.9 [1.9]	1.9 [1.9]

This is a very satisfactory situation regarding the use of H_3O^+ to protonate and thus detect these hydrocarbons as trace gases in air using our SIFT analytical technique, but it offers no help in distinguishing between the structural isomers of xylene or trimethyl benzene.

3.1.2. NO^+ reactions

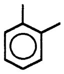
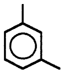
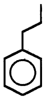
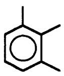
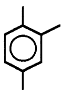
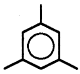
Nine of these ten reactions proceed via nondissociative charge transfer resulting in the parent cation as the single product ion, e.g.

$$NO^+ + C_6H_5CH_3 \rightarrow C_6H_5CH_3^+ + NO \qquad (2)$$

Table 2
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with aliphatic hydrocarbons. The procedure used to calculate the k_c are as indicated in the caption to Table 1. Since many of the H_3O^+ reactions are slow we cannot assume that they proceed at the collisional rate. In this case we assume that the O_2^+ reactions proceed at the collisional rate (see the text) and then the k for the H_3O^+ and NO^+ reactions are obtained from the relative decay rates of the ions in the SIFT as described in the text. The quoted k for the H_3O^+ association reactions are their effective two-body rate coefficients (the helium pressure is 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})
Alkanes						
n-Butane	58	8.2	0	. . . [1.8]	. . . [1.5]	1.5 [1.5]
2-Methyl propane	58	*8.2 ± 0.5*	0.13	. . . [1.8]	0.9 [1.5]	1.5 [1.5]
n-Pentane	72	10.0	0	. . . [1.9]	. . . [1.6]	1.6 [1.6]
2-Methyl butane	72	*10.0 ± 0.5*	0.13	. . . [1.9]	1.4 [1.6]	1.6 [1.6]
n-Hexane	86	11.9	0	<0.1 [2.0]	0.1 [1.7]	1.7 [1.7]
n-Octane	114	15.9	0	0.9 [2.3]	0.7 [1.9]	1.9 [1.9]
n-Decane	142	*20.0 ± 0.5*	0	1.6 [2.6]	1.5 [2.1]	2.0 [2.0]
n-Dodecane	170	*24.0 ± 0.5*	0	2.8 [2.8]	1.5 [2.3]	1.5 [2.2]
Alkenes						
1-Pentene	70	*9.5 ± 0.5*	*0.3 ± 0.1*	1.9 [1.9]	1.6 [1.6]	1.7 [1.6]
2-Methyl-2-butene	70	*9.5 ± 0.5*	*0.3 ± 0.1*	1.9 [1.9]	1.7 [1.6]	1.7 [1.6]
Diene						
2-Methyl butadiene	68	10.0	0.25	2.0 [2.0]	1.7 [1.7]	1.7 [1.6]

Table 3
Products of the reactions of H_3O^+, NO^+, and O_2^+ with aromatic hydrocarbons. The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion products is given in brackets. O_2 is always a product of the O_2^+ reactions and so it is not included

Compound (structure) I.P.[eV]	H_3O^+	NO^+	O_2^+
benzene 9.25 	$C_6H_6.H^+$(100)	$C_6H_6^+$(85)+NO $NO.C_6H_6^+$(15)	$C_6H_6^+$(100)
toluene 8.82 	$C_7H_8.H^+$(100)	$C_7H_8^+$(100)+NO	$C_7H_8^+$(100)
o-xylene 8.56 	$C_8H_{10}.H^+$(100)	$C_8H_{10}^+$(100)+NO	$C_8H_{10}^+$(75) $C_7H_7^+$(25)+CH_3
m-xylene 8.56 	$C_8H_{10}.H^+$(100)	$C_8H_{10}^+$(100)+NO	$C_8H_{10}^+$(80) $C_7H_7^+$(20)+CH_3
p-xylene 8.44 	$C_8H_{10}.H^+$(100)	$C_8H_{10}^+$(100)+NO	$C_8H_{10}^+$(80) $C_7H_7^+$(20)+CH_3
ethylbenzene 8.77 	$C_8H_{10}.H^+$(100)	$C_8H_{10}^+$(100)+NO	$C_7H_7^+$(70)+CH_3 $C_8H_{10}^+$(30)
propylbenzene 8.72 	$C_9H_{12}.H^+$(100)	$C_9H_{12}^+$(100)+NO	$C_7H_7^+$(80)+C_2H_5 $C_6H_6^+$(20)+C_3H_6
1,2,3-trimethylbenzene 8.42 	$C_9H_{12}.H^+$(100)	$C_9H_{12}^+$(100)+NO	$C_9H_{12}^+$(85) $C_8H_9^+$(15)+CH_3
1,2,4-trimethylbenzene 8.27 	$C_9H_{12}.H^+$(100)	$C_9H_{12}^+$(100)+NO	$C_9H_{12}^+$(85) $C_8H_9^+$(15)+CH_3
1,3,5-trimethylbenzene 8.41 	$C_9H_{12}.H^+$(100)	$C_9H_{12}^+$(100)+NO	$C_9H_{12}^+$(95) $C_8H_9^+$(5)+CH_3

Charge transfer is possible because of the low ionisation energies of these aromatic hydrocarbons (which are given in Table 1) compared to the recombination energy of NO^+ (9.26 eV [24]). The only exception in this selection of aromatics is the benzene reaction:

$$NO + C_6H_6 + (He) \rightarrow C_6H_6^+ + NO + (He) \quad (3a)$$

$$\rightarrow NO^+.C_6H_6 + He \quad (3b)$$

The ionisation energy of benzene (9.25 eV) is almost equal to that of NO and this allows charge transfer to occur in the majority of the NO^+/benzene molecule collisions (85%) but in the remainder three-body association results producing the adduct ion as shown in reaction (3b). Association of the reactant ion/molecule pair often results when the ionisation energies of the two molecules involved (in this case NO and C_6H_6) are comparable, as we have also observed in the reactions of NO^+ with several ketones [2]. This phenomenon is often termed "charge transfer complexing" [2] since apparently the lifetime of the transient excited complex ion, in this case $(NO^+.C_6H_6)^*$, is prolonged by the sharing of the charge between the two molecules which thus increases the probability of a superelastic (quenching) collision between the excited ion and the helium atoms of the carrier gas in these SIFT experiments.

3.1.3. O_2^+ reactions

All these reactions of O_2^+ (recombination energy = 12.07 eV) proceed via charge transfer which is partially dissociative in all but the benzene and toluene reactions in which the only ion products are the parent cations (see Table 3). In the reactions of the three xylene isomers and the three trimethylbenzene isomers the parent cations are again the majority products but in all these six reactions partial elimination of a CH_3 radical from the nascent parent cation occurs, e.g.

$$O_2^+ + C_6H_4(CH_3)_2 \rightarrow C_6H_4(CH_3)_2^+ + O_2 \quad (4a)$$

$$\rightarrow C_6H_4CH_3^+ + CH_3 + O_2 \quad (4b)$$

As can be seen by a glance in Table 3 there is little variation in the product ratios in these reactions, the parent cation usually being about 80% of the product distribution. However, in both the ethylbenzene and propylbenzene reactions the major product ion is the dissociative product $C_7H_7^+$, e.g.

$$O_2^+ + C_6H_5C_3H_7 \rightarrow C_6H_5CH_2^+ + C_2H_5 + O_2 \quad (5a)$$

$$\rightarrow C_6H_6^+ + C_3H_6 + O_2 \quad (5b)$$

In reaction (5b) the benzene cation is produced together with a propene molecule, $CH_3CH{=}CH_2$. The production of $C_6H_5^+$ and C_3H_7 radical is easily shown to be endothermic in this reaction [22].

3.2. Aliphatic hydrocarbons

As is mentioned above, the k for these reactions (33 in all) vary greatly from the immeasurable to collisional (see Table 2). The products of these reactions are given in Table 4. We now discuss the H_3O^+, NO^+, and O_2^+ reactions separately. Before doing so, we note that the 9 reactions of the three ions with the two unsaturated alkenes and the one dialkene proceed at the collisional rate.

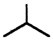
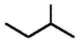
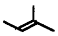
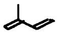
3.2.1. H_3O^+ reactions

The reactions of 1-pentene and its isomer 2-methyl-2-butene, and 2-methyl butadiene with H_3O^+ are simple in that the single product ion in each case is the protonated hydrocarbon (see Table 4), and the reactions thus proceed at the collisional rate via exothermic proton transfer (by virtue of the relatively high PA of these unsaturated compounds [22]).

The situation for the alkanes included in this study is quite different because in none of these reactions is the protonated parent molecule, MH^+, observed as a product ion. Indeed, a search through the published literature reveals no evidence that protonated *n*-alkanes larger than $C_3H_8.H^+$ have been observed, and no data apparently exists on the proton affinities of the larger *n*-alkanes [22]. A value of the PA of isobutane (2-methyl propane) is reported at 163.3 kcal/mol [22] which is significantly lower than the PA of H_2O which is 166.5 kcal/mol, and so proton transfer from H_3O^+ to this organic molecule is too endothermic to occur at thermal energies.

The very interesting observation from these studies is that for the larger *n*-alkanes a different reaction process occurs with the H_3O^+ ion, that of ion/molecule association producing ions of the type $H_3O^+.M$. This first became evident in the *n*-pentane reaction which proceeds only very slowly, the estimated effective two-body rate coefficient under the conditions of these SIFT experiments k_2 being only about 1% of k_c. For the isopentane reaction association again occurs but in this case k_2 is about 10% of k_c, and for the *n*-hexane reaction $k_2 \sim 0.2k_c$. These three-body association reactions increase in efficiency as the alkane increases in size; for *n*-octane, $k_2 \sim 0.5k_c$; for *n*-decane, $k_2 \sim 0.8k_c$ and for *n*-dodecane, $k_2 \sim k_c$. All these reactions proceed, for example, like the *n*-decane reaction thus:

Table 4
Products of the reactions of H_3O^+, NO^+, and O_2^+ with aliphatic hydrocarbons. 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 NO and HNO neutral products of the NO^+ reactions are included to indicate that these reactions proceed via charge transfer and hydride ion transfer, respectively

Compound (structure) I.P.[eV]	H_3O^+	NO^+	O_2^+
Alkanes			
n-butane 10.53 	no reaction	no reaction	$C_4H_{10}^+$(20) $C_3H_7^+$(65) $C_3H_6^+$(10) $C_2H_4^+$(5)
2-methyl propane 10.57 	no reaction	$C_4H_9^+$(100)+HNO	$C_3H_7^+$(40) $C_4H_9^+$(25) $C_3H_6^+$(25) $C_4H_8^+$(10)
n-pentane 10.35 	no reaction	no reaction	$C_5H_{12}^+$(10) $C_3H_7^+$(45) $C_4H_9^+$(5) $C_3H_6^+$(40)
2-methyl butane 10.22 	no reaction	$C_5H_{11}^+$(100)+HNO	$C_5H_{12}^+$(10) $C_3H_7^+$(20) $C_4H_9^+$(15) $C_3H_6^+$(45) $C_4H_8^+$(10)
n-hexane 10.13 	$H_3O^+.C_6H_{14}$(100)	$C_6H_{13}^+$(100)+HNO	$C_6H_{14}^+$(20) Σ R^+(45) Σ $(R\text{-}H)^+$(35)
n-octane 9.8 	$H_3O^+.C_8H_{16}$(100)	$C_8H_{17}^+$(>80)+HNO Σ $RHNO^+$(<20)	$C_8H_{18}^+$(30) Σ R^+(40) Σ $(R\text{-}H)^+$(30)
n-decane 9.65 	$H_3O^+.C_{10}H_{22}$(100)	$C_{10}H_{21}^+$(>90)+HNO Σ $RHNO^+$(<10)	$C_{10}H_{22}^+$(35) Σ R^+(45) Σ $(R\text{-}H)^+$(20)
n-dodecane 	$H_3O^+.C_{12}H_{26}$(100)	$C_{12}H_{25}^+$(>90)+HNO Σ $RHNO^+$(<10)	$C_{12}H_{26}^+$(40) Σ R^+(40) Σ $(R\text{-}H)^+$(20)
Alkenes			
1-pentene 9.52 	$C_5H_{10}.H^+$(100)	$NOCH_4^+$(65) $C_4H_7^+$(15) $C_5H_9^+$(15) $NO^+.C_5H_{10}$(10)	$C_5H_{10}^+$(20) $C_4H_7^+$(25) $C_3H_6^+$(55)
2-methyl 2-butene 8.68 	$C_5H_{10}.H^+$(100)	$C_5H_{10}^+$(100)+NO	$C_5H_{10}^+$(15) $C_4H_7^+$(50) $C_3H_6^+$(35)
Diene			
2-methyl butadiene 8.84 	$C_5H_8.H^+$(100)	$C_5H_8^+$(100)+NO	$C_5H_8^+$(45) $C_5H_7^+$(45) $C_4H_5^+$(10)

$$H_3O^+ + C_{10}H_{22} + He \rightarrow H_3O^+.C_{10}H_{22} + He \quad (6)$$

The adduct ions are clearly observed as the only ion products of these reactions, significantly the protonated parent molecules are not observed, again apparently indicating that they are not stable species. There is a great need for theory in this area. That the observed rates of these association reactions increase with the complexity of the reactant hydrocarbon is consistent with the idea that the bond energy of the excited transient complex ions (H_3O^+.M)* is dispersed temporarily into the vibrational degrees of freedom of the transient ion, and the more degrees of freedom the longer the lifetime of the complex against unimolecular dissociation [25]. Since the *n*-dodecane reaction occurs with a k_2 equal to k_c this sets a lower limit to lifetime of the transient complex as greater than the collision time of the excited ions with helium carrier gas atoms which is of the order of 10^{-7} s under the pressure and temperature conditions of these SIFT experiments. This also equates to a very large three-body association rate coefficient k_3 ($= k_2$/[He], where [He] is the helium atom number density) of $>10^{-25}$ cm^6/s.

A further interesting phenomenon observed when studying these reactions is that when a trace of water vapour is present in the carrier gas of the SIFT then a very rapid ligand “switching” reaction occurs between the H_3O^+.M ions and H_2O molecules thus:

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

Switching reactions such as reaction (7) usually occur at the collisional rate and those involving the alkanes are no exception. The three-body reactions between H_3O^+ ions and H_2O molecules which can also produce $H_3O^+.H_2O$ ions are relatively slow [15] and so we have the situation that small traces of higher-order alkanes in ionised moist air can catalyse the production of the hydrated hydronium ion via reactions such as reactions (6) and (7). This observation may have some relevance to the ion chemistry of polluted air.

3.2.2. NO^+ reactions

The reactions with both 2-methyl-2-butene and 2-methyl butadiene proceed via charge transfer, this being a reflection of the low ionisation energies of these two species (see Table 4). However, the 1-pentene reaction is much more complex, charge transfer in this case being endothermic but by only 0.26 eV. The reaction results in four ionic products:

$$NO^+ + C_5H_{10} \rightarrow CH_4NO^+ + C_4H_6 \quad (8a)$$

$$\rightarrow C_4H_7^+ + CH_3NO \quad (8b)$$

$$\rightarrow C_5H_9^+ + HNO \quad (8c)$$

$$\rightarrow NO^+.C_5H_{10} \quad (8d)$$

This is a very curious ion–molecule reaction. The production of the CH_4NO^+ ion [reaction (8a)] occurs in 65% of the collisions, and also occurring are hydride ion transfer (8c), association (8d), and also chemistry resulting in the production of the neutral CH_3NO (production of CH_3 and NO is clearly endothermic for all acceptable structures of the product $C_4H_7^+$ ion [22]). We cannot say what the structure of the majority product ion is, but of the few possibilities the protonated formamide ion is possible, $HCONH_3^+$, but considerable rearrangement is required to produce this. Its production is certainly exothermic for any of the likely structures of the neutral C_4H_6 (see the database [22]).

There is no measurable reaction between NO^+ and both *n*-butane and *n*-pentane but their corresponding structural isomers isobutane (2-methyl propane) and isopentane (2-methyl butane) react rapidly with NO^+ via hydride ion transfer, e.g.

$$NO^+ + (CH_3)_2\ CHCH_2CH_3 \rightarrow C_5H_{11}^+ + HNO \quad (9)$$

These findings are in agreement with previous work [15]. The remaining *n*-alkanes in this study, *n*-hexane, *n*-octane, *n*-decane, and *n*-dodecane do react with NO^+, but the rate coefficients are all measurably smaller than k_c, the *n*-hexane reaction being especially slow (see Table 2). The major process occurring in all four reactions is hydride ion transfer resulting in product ions of the kind $(M–H)^+$ and a HNO radical (see Table 4). However, in these reactions a series of minority product ions of the kind RHNO+ are clearly formed, where R is one of the radicals C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, and even C_8H_{17} in the

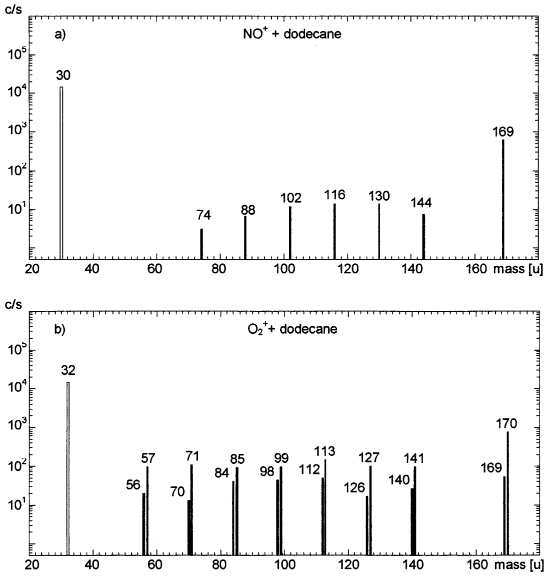


Fig. 1. Ion products of the dodecane reactions with (a) NO^+ and (b) O_2^+ as obtained using the SIFT apparatus represented as the mass spectra in the semilogarithmic form. The ^{13}C isotopic variants of the products are not shown for clarity.

n-dodecane reaction. In all these reactions these unusual ions represent less than 20% of the product ions; in Table 4 these ions are given as Σ $RHNO^+$ ions to avoid overcomplicating Table 4. A sample SIFT product ion spectrum obtained for the NO^+/dodecane reaction which shows these ions together with the major ion formed via simple hydride ion transfer is given in Fig. 1(a). The formation of these unusual ions, the structures of which are debatable but which again may be protonated formamide derivatives, $HCONHR.H^+$ as for the product ion of reaction (8a), must also result in the simultaneous formation of the appropriate alkene neutral molecule as, e.g.

$$NO^+ + C_{12}H_{26} \rightarrow C_6H_{14}NO^+ + C_6H_{12} \qquad (10)$$

It must be stressed that reaction (10) represents only one of the minor products of the overall reaction of NO^+ with dodecane [see Fig. 1(a) and Table 4].

3.2.3. O_2^+ reactions

All these reactions proceed via efficient charge transfer ($k \sim k_c$) which in every reaction is largely dissociative and result in multiple products (see Table 4). The parent cation is a product in every reaction but is never greater than a 45% product (as it is for the 2-methyl butadiene reaction). For the larger *n*-alkanes (*n*-hexane and larger) the number of products increases with the atomicity of the molecule and thus for these reactions it is impractical to include the many products in Table 4. Series of ions are observed as products which are R^+ and $(R–H)^+$, where as before R is one of the radicals C_4H_9, C_5H_{11}, C_6H_{13}, etc., so again, we represent these many fragmentation products using the formulation Σ R^+ and Σ $(R–H)^+$ in Table 4. A sample SIFT product ion spectrum for the O_2^+/dodecane reaction is shown in Fig. 1(b), which shows the many products of this reaction (typical of all the higher-order alkanes) and the pairs of ions produced, i.e. R^+ and $(R–H)^+$ ions. Thus, for example, two of the products of the dodecane reaction are at masses 113 and 112 u which result from the reactions:

$$O_2^+ + C_{12}H_{26} \rightarrow C_8H_{17}^+ + C_4H_9 + O_2 \qquad (11a)$$

$$\rightarrow C_8H_{16}^+ + C_4H_{10} + O_2 \qquad (11b)$$

Again, it is important to stress that these are just two of the many product channels of the O_2^+/dodecane reaction. Note that in each of the similar pairs of ion products a close shell ion plus a radical is formed in one case and in the other an open shell ion and a stable molecule is formed (thus conserving spin in these reactions). The collected data on all these alkane reactions with O_2^+ show that in all cases the former combination [represented by reaction (11a)] is favoured by about a factor of 2; we do not know why this should be so. Again, this highlights the need for theoretical work on these processes.

4. Conclusions

These SIFT studies indicate that the reactions of H_3O^+, NO^+, and O_2^+ ions with aromatic hydrocarbons, M, are all fast and that the H_3O^+ and NO^+ reactions produce MH^+ and M^+ ions, respectively (see Tables 1 and 3). These reactions are therefore very useful in detecting the presence of these hydrocarbons in air and determining their concentrations using our SIFT analytical method. Unfortunately, however, these reactions cannot distinguish between the structural isomers of these aromatic hydrocarbons and so additional analytical support is required to achieve this, for example by the use of gas chromatography.

The reactions of the aliphatic hydrocarbons with our chosen precursor ions are much more varied in both the rate coefficients (Table 2) and the ionic products (Table 4), and except for particular molecules they are not readily analysed as trace gases using our SIFT method. The exceptions are the alkenes which are efficiently protonated by H_3O^+ (see Table 4). Thus, we have used both the H_3O^+ and the NO^+ reactions to detect and quantify 2-methyl butadiene (isoprene) on human breath [11]. The most interesting finding of the present study is that H_3O^+ reactions undergo efficient association with the higher-order alkanes producing $H_3O^+.M$ ions which then undergo rapid ligand switching reactions with H_2O molecules producing the monohydrated hydronium ion $H_3O^+.H_2O$. Thus the presence of trace amounts of these higher-order alkanes in ionised air catalyses the production of hydrated hydronium ions which are known to be major components of the ions in the stratosphere and the troposphere [26].

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