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International Journal of Mass Spectrometry 185/186/187 (1999) 139–147

Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and O_2^+ with eleven amine structural isomers of $C_5H_{13}N$

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Received 18 May 1998; accepted 20 July 1998

Abstract

We describe the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+, and O_2^+, which are the chosen ions for chemical ionisation in our SIFT trace gas analytical method, with eleven structural amine isomers having the molecular formula $M = C_5H_{13}N$. These isomers comprise seven primary, two secondary, and two tertiary amines. The product of the reactions of H_3O^+ with the primary amines progress from only the parent protonated molecule MH^+ for the linear chain 1-pentylamine towards an increasing fraction of NH_4^+ as the carbon chain becomes more branched, until for the very branched 2-methyl-2-butylamine reaction, NH_4^+ is the major product (>90%). For the secondary and tertiary amine reactions with H_3O^+ the major product ion is MH^+ in parallel with product ions $(M–H)^+$ that result from H_2 elimination from MH^+, the latter ions being 30% of the product distribution for the tertiary amine, N,N-diethylmethylamine reaction. The NO^+ reactions with the primary amines mostly proceed via parallel nondissociative charge transfer (producing M^+ ions) and hydride ion transfer [producing $(M–H)^+$ ions]. With increased branching of the primary amines and for the secondary and tertiary amines, dissociative charge transfer occurs, mainly producing $(M–R)^+$ ions and various alkyl radicals, R (= CH_3, C_2H_5, C_3H_7). The O_2^+ reactions with all these amine isomers proceed via dissociative charge transfer, mainly producing $(M–R)^+$ ions. Comparisons of the products of these O_2^+ reactions with the “cracking patterns” produced by 70 eV electron impact on these amines show remarkable similarities except for one or two of the isomers. (Int J Mass Spectrom 185/186/187 (1999) 139–147) © 1999 Elsevier Science B.V.

Keywords: Selected ion flow tube; Ion-molecule reactions; Amine isomers; Proton transfer; Charge transfer; Trace gas analysis; Chemical ionisation

1. Introduction

To establish the selected ion flow tube (SIFT) technique as an analytical method for the detection and quantification of trace gases in multicomponent mixtures such as human breath [1,2], it is necessary for us to survey the reactions of the ions H_3O^+, NO^+, and O_2^+, which are the chosen ions for chemical ionisation [3] on which our SIFT analytical method depends [4], with a wide variety of organic and inorganic compounds that are found in such complex mixtures. Thus, we have previously determined the

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Dedicated to Professor Michael T. Bowers in recognition of his major contributions to ion chemistry and on the occasion of his 60th birthday.

PII S1387-3806(98)14099-X

rate coefficients and product ion distributions for the reactions of these ions with several alcohols [5], aldehydes and ketones [6], carboxylic acids and esters [7], ethers [8], organosulphur compounds [9], and (most recently) amines [10], that in total involve some 300 reactions and as such are the beginning of the substantial database which we are building as an integral part of our SIFT system for trace gas analysis. Within this wide survey of reactions there are examples of most of the well-characterised ion/molecule reaction processes such as proton transfer, hydride ion transfer, charge transfer, and ion-molecule association, and other little-known processes such as alkoxide ion transfer.

Throughout these studies we have looked not only for reaction processes that characterise groups of organic molecules (e.g. how the reactions of aldehydes with our chosen ions compare with the reactions of ketones or alcohols, some of which are emitted by plants [11]), but also for differences in the reactivity of the isomeric forms of particular classes of molecules (especially for different product ions and different product ion distributions). In this respect we observed, for example, that the reactions of NO^+ with some tertiary alcohols obviously differ from the reactions of their primary and secondary isomers [5]. Recently, in our study of amine reactions, we observed that NH_4^+ was a significant product ion in the reactions of H_3O^+ with primary amines but not with secondary and tertiary amines [10]. It is thus obvious that studies of the reactions of isomeric forms of organic compounds are required to underpin our SIFT analytical work, and especially those of the structural isomers of amines that are intimately involved in human biochemistry (and are elevated on the breath of patients suffering from renal failure [12,13]).

Here, we present the results of a study of the rate coefficients and production ion distributions for the reactions of H_3O^+, NO^+, and O_2^+ with 11 amines having the common molecular formula $C_5H_{13}N$, chosen because they are the smallest amines with enough isomeric structures to allow a worthwhile survey, and because several of the isomers are readily available from the suppliers. The 11 isomers include 7 primary, 2 secondary, and 2 tertiary amines as given in Tables 1 and 2. As usual, the studies were carried out using the conventional SIFT technique [14] with some slight modifications (see below and [5]) at room temperature and in helium carrier gas at a pressure of 0.5 Torr.

2. Experimental

The SIFT, a standard technique for the study of ion-molecule reactions at thermal energies, has been described in numerous review articles (see for example [14]). We have described its use as an analytical tool in some more recent review articles [4, 15, 16]. The approach we take for the determination of the rate coefficients, k, and ion product distributions for these amine reactions is identical to that taken for all our previous studies of several other classes of organic compounds. It is described in detail in our alcohols article [5] and outlined in our subsequent articles [6–10]. Thus it is sufficient to say here that the k for the H_3O^+ reactions, the initial step of which is exothermic proton transfer to the amines, are reasonably assumed to proceed at the collisional (gas kinetic) rate, with a rate coefficient, k_c, that can be calculated if the polarisabilities and dipole moments of the reactant molecules are known or can be estimated [17]. Then the corresponding k for the NO^+ and O_2^+ reactions with each amine are obtained 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 while a weak mixture of the reactant amine 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 that renders measurements of the flow rates of their neat vapours difficult. The rationale and justification for this approach is given in our previous articles [5,6]. The product ions and their percentages are obtained in the usual way for SIFT studies [14] by injecting each of the reactant ions separately, so as to avoid confusion, and observing the relative count rates of the various product ions with

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the amine isomers indicated. Also given are the molecular weights of the reactant molecules, m, in atomic units, u, their polarisabilities, α, in units of 10^{-24} cm^3 and their permanent dipole moments, μ, in Debye, D. We have estimated the μ values by adopting average values for primary, secondary, and tertiary amines, assuming that they do not change significantly with the number of carbon atoms in the amine molecule, and the single value of α for all the amines by adopting the average value of the known polarisabilities of similar organic molecules possessing the same number of carbon atoms (taken from [19]). Then the collisional rate coefficients, k_c, for all the reactions have been calculated using the parametrised trajectory formulation of Su and Chesnavich [17], as shown in the square brackets. The estimated uncertainty in these calculated rate coefficients is ±25%. On the assumption that all the H_3O^+ reactions proceed at their respective 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}]
Primary amines						
1-pentylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	1.5 [2.3]	2.3 [2.2]
3-methylbutylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	1.4 [2.3]	2.3 [2.2]
2-methylbutylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	2.0 [2.3]	2.2 [2.2]
2-pentylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	2.3 [2.3]	2.3 [2.2]
3-methyl-2-butylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	2.4 [2.3]	2.3 [2.2]
3-pentylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	2.3 [2.3]	2.2 [2.2]
2-methyl-2-butylamine	87	14.5 ± 1	1.2 ± 0.2	[2.7]	2.2 [2.3]	2.3 [2.2]
Secondary amines						
N-methylbutylamine	87	14.5 ± 1	1.0 ± 0.2	[2.6]	2.2 [2.2]	2.2 [2.1]
N-ethyl-2-propylamine	87	14.5 ± 1	1.0 ± 0.2	[2.6]	2.2 [2.2]	2.2 [2.1]
Tertiary amines						
N,N-diethylmethylamine	87	14.5 ± 1	0.7 ± 0.2	[2.5]	1.5 [2.1]	1.6 [2.0]
N,N-dimethyl-2-propylamine	87	14.5 ± 1	0.7 ± 0.2	[2.5]	2.2 [2.1]	2.1 [2.0]

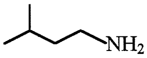
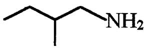
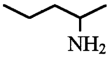
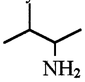
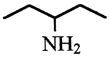
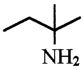
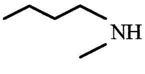
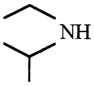
the downstream mass spectrometer. It is worthy of note that the three reactant ion species are formed and extracted from a microwave cavity discharge in an argon/wet air mixture at a pressure of about 0.1 Torr. Any residual electronic (and vibrational) excitation in these reactant ions is diminished by the additions of a small amount of air to the helium carrier gas [5,6].

3. Results and discussion

The calculated k_c for the reactions of all three ion species and the experimentally derived k for the NO^+ and O_2^+ reactions are given in Table 1. As can be seen, the rate coefficients for the majority of the NO^+ and O_2^+ reactions are equal to or a large fraction of their respective calculated collisional rate coefficients k_c (as calculated using the procedure outlined in the caption to Table 1).

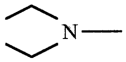
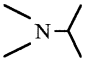
The ion product distributions for all the reactions are shown in Table 2, where the structure of each isomer is also represented to facilitate the discussions of the reaction mechanisms. Only those ion products which represent more than 3% of the product distribution have been included and these are rounded to the nearest 5%. The ionisation energies of all these amine isomers [18] are significantly smaller than that of NO (9.26 eV [18, 19]). This allows for charge transfer to occur in all their reactions with NO^+ as we will see. The proton affinities of all the reactant molecules [18] greatly exceed that of H_2O (697 kJ mol^{-1} [18]) and this has an important bearing on the course of the H_3O^+ reactions. The recombination energy of the ground state O_2^+ ion is 12.06 eV [19] which allows dissociative charge transfer to proceed in its reactions with these amines as is observed in every case. The reactant molecules are grouped in Table 2 as primary, secondary, and tertiary amines. We now discuss the H_3O^+, NO^+, and O_2^+ reactions separately.

Table 2
Products of the reactions of H_3O^+, NO^+, and O_2^+ with the amine structural isomers shown as determined in the SIFT at 300 K. The percentage of each ion product is given in brackets. The listed molecular formulas of the ion products do not necessarily represent their structures. The brackets around the neutral products in some of the NO^+ reactions signifies uncertainty in these products (see the text for clarification). Note that in two of the primary amine reactions with NO^+ two of the product ions are uncertain (see the text)

Compound (structure)	H_3O^+	NO^+	O_2^+
Primary amines			
1-pentylamine 	$C_5H_{11}NH_2 \cdot H^+ + H_2O$	$C_5H_{10}NH_2^+(65) + HNO$ $C_5H_{11}NH_2^+(35) + NO$	$CH_2NH_2^+(90) + C_4H_9$ $C_2H_5NH_2^+(5) + C_3H_6$ $C_5H_{11}NH_2^+(5)$
3-methylbutylamine 	$C_5H_{11}NH_2 \cdot H^+(>95)$ $+ H_2O$ $NH_4^+(<5) + C_5H_{10} + H_2O$	$C_5H_{10}NH_2^+(75) + HNO$ $C_5H_{11}NH_2^+(25) + NO$	$CH_2NH_2^+(85) + C_4H_9$ $C_4H_6NH_2^+(10)$ $+(CH_3 + H_2)$ $C_5H_{11}NH_2^+(5)$
2-methylbutylamine 	$C_5H_{11}NH_2 \cdot H^+(50)$ $+ H_2O$ $NH_4^+(50) + C_5H_{10} + H_2O$	$C_5H_{10}NH_2^+(50) + HNO$ $C_5H_{11}NH_2^+(35) + NO$ $C_3H_6NH_2^+(15)$ $+ (C_2H_5 + NO)$	$CH_2NH_2^+(90)^+ + C_4H_9$ $C_2H_4NH_2^+(10)^+ + C_3H_7$
2-pentylamine 	$NH_4^+(60) + C_5H_{10} + H_2O$ $C_5H_{11}NH_2 \cdot H^+(40)$ $+ H_2O$	$C_2H_4NH_2^+(65)$ $+ (C_3H_7 + NO)$ $C_5H_{10}NH_2^+(25) + HNO$ $C_5H_{11}NH_2^+(10) + NO$	$C_2H_4NH_2^+(95) + C_3H_7$ $C_4H_8NH_2^+(5) + CH_3$
3-methyl-2-butylamine 	$NH_4^+(65) + C_5H_{10} + H_2O$ $C_5H_{11}NH_2 \cdot H^+(30)$ H_2O $C_2H_5C(CH_3)_2^+(5)$ $+ NH_3 + H_2O$	$C_2H_4NH_2^+(70)$ $+ (C_3H_7 + NO)$ $C_5H_{10}NH_2^+(15) + HNO$ $C_2H_3NH_2^+(15)$ $+(C_3H_8 + NO)$ or $C_3H_7^+(15)$ $+ (C_2H_4NH_2 + NO)$	$C_2H_4NH_2^+(90) + C_3H_7$ $C_4H_8NH_2^+(10) + CH_3$
3-pentylamine 	$NH_4^+(70) + C_5H_{10} + H_2O$ $C_5H_{11}NH_2 \cdot H^+(30)$ $+ H_2O$	$C_3H_6NH_2^+(75)$ $+(C_2H_5 + NO)$ $C_5H_{10}NH_2^+(20) + HNO$ $C_5H_{11}NH_2^+(5) + NO$	$C_3H_6NH_2^+(100) + C_2H_5$
2-methyl-2-butylamine 	$NH_4^+(>90) + C_5H_{10} + H_2O$ $C_5H_{11}NH_2 \cdot H^+(<5)$ $+ H_2O$ $C_2H_5C(CH_3)_2^+(5)$ $+ NH_3 + H_2O$	$C_3H_6NH_2^+(85)$ $+ (C_2H_5 + NO)$ $C_4H_8NH_2^+(5)$ $+ (CH_3 + NO)$ $C_4H_7NH_2^+(10)$ $+ (CH_3 + H + NO)$ or $C_2H_5C(CH_3)_2^+(10)$ $+ NH_2NO$	$C_3H_6NH_2^+(80) + C_2H_5$ $C_4H_8NH_2^+(20) + CH_3$
Secondary amines			
N-methylbutylamine 	$C_5H_{12}NH \cdot H^+(90)$ $+ H_2O$ $C_5H_{12}N^+(10)$ $+ H_2 + H_2O$	$C_2H_5NH^+(50)$ $+ (C_3H_7 + NO)$ $C_5H_{12}NH^+(40) + NO$ $C_5H_{12}N^+(10) + HNO$	$C_2H_5NH^+(>95) + C_3H_7$ $C_3H_7NH^+(<5) + C_2H_5$
N-ethyl-2-propylamine 	$C_5H_{12}NH \cdot H^+(90)$ $+ H_2O$ $C_5H_{12}N^+(10)$ $+ H_2 + H_2O$	$C_4H_9NH^+(70)$ $+ (CH_3 + NO)$ $C_5H_{12}NH^+(30) + NO$	$C_4H_9NH^+(90) + CH_3$ $C_2H_5NH^+(10) + C_3H_7$

(*continued*)

Table 2 (*continued*)

Compound (structure)	H_3O^+	NO^+	O_2^+
Tertiary amines			
N,N-diethylmethylamine 	$C_5H_{13}N \cdot H^+(70) + H_2O$ $C_5H_{12}N^+(30) + H_2 + H_2O$	$C_5H_{13}N^+(90) + NO$ $C_4H_{10}N^+(10)$ $+ (CH_3 + NO)$	$C_4H_{10}N^+(100) + CH_3$
N,N-dimethyl-2-propylamine 	$C_5H_{13}N \cdot H^+(80) + H_2O$ $C_5H_{12}N^+(20) + H_2 + H_2O$	$C_5H_{13}N^+(65) + NO$ $C_4H_{10}N^+(35)$ $+ (CH_3 + NO)$	$C_4H_{10}N^+(95) + CH_3$ $C_2H_6N^+(5) + C_3H_7$

3.1. H_3O^+ reactions

The initial step in all these reactions is efficient exothermic proton transfer producing the excited protonated parent molecules $(MH^+)^*$ which in some cases are sufficiently excited to partially undergo dissociation producing fragment ions. As can be seen by a glance at Table 2, MH^+ is an observed product in all these primary, secondary, and tertiary amine reactions which supports the premise that $(MH^+)^*$ formation is the initial step in the reactions. Note that exothermic proton transfer always occurs with unit efficiency, i.e. the measured rate coefficient, k, is always equal to the collisional rate coefficient, k_c [20, 21,22].

3.1.1. Primary amine reactions

Among the primary amine reactions, MH^+ is the single product ion of the 1-pentylamine amine reaction but only a minor product of the 2-methyl-2-butylamine amine reaction. But of greatest interest here is the appearance of NH_4^+ as a product ion in most of these reactions. Inspection of the product ratios in Table 2 apparently reveals that the percentage of NH_4^+ is correlated with both the proximity of a CH_3 group to the NH_2 group and the number of CH_3 groups in the molecule, implying that the additional H required to form NH_4^+ is provided by a CH_3 group. An alternative view is that the C–N bonds involving the "secondary carbon" in the, 2-pentylamine, 3-methyl-2-butylamine, and 3-pentlyamine molecules and the "tertiary carbon" in the 2-methyl-2-buylamine molecule are weaker, thus promoting NH_4^+ production in these reactions at the expense of the stabilisation rate of the $(MH^+)^*$ to MH^+. However, the N atom is bound to a primary C atom in the 2-methylbutylamine and 3-methylbutylamine molecules and NH_4^+ is consequently a lesser product. NH_4^+ is not a product of the 1-pentylamine reaction, even though its formation would be quite exothermic for any likely structure of the neutral C_5H_{10} that would also be formed in such a reaction [18]. Thus it is likely that the reactions of the RNH_2 amines proceed first by forming RNH_3^+ which rearranges to a carbenium ion/ammonia molecule complex $R^+ \cdots NH_3$ (when energetically possible), that further rearranges to $(R–H) \cdots NH_4^+$ and then dissociates to the alkene (R–H) and the closed shell ion NH_4^+. Thus NH_4^+ is >90% of the product ratio in the 2-methyl-2-butylamine reaction:

$$H_3O^+ + C_2H_5C(NH_2)(CH_3)_2$$

$$\rightarrow NH_4^+ + CH_3CH{=}C(CH_3)_2 + H_2O \qquad (1a)$$

$$\rightarrow C_2H_5C(NH_3^+)(CH_3)_2 + H_2O \qquad (1b)$$

$$\rightarrow C_2H_5C(CH_3)_2^+ + NH_3 + H_2O \qquad (1c)$$

Reaction (1c) indicates that $R^+ \cdots NH_3$ is a likely intermediate complex because R^+ and NH_3 are separate products. Such elimination of NH_3 after proton transfer also occurs in the 3-methyl-2-butylamine reactions (see Table 2). Both these reaction processes are exothermic according to the available thermochemical data [18] provided that the product ion is the very stable $C_2H_5C^+(CH_3)_2$.

Unfortunately, there are no thermochemical data available to substantiate the results for these individual reactions. Theoretical structure calculations with a view to determining the energetics of the reaction intermediates involved in these reactions are therefore desirable. Further experimental observations could also help; for example, we would predict on the basis of the present work that NH_4^+ would be the only product of the protonation of $(CH_3)_3CNH_2$ by H_3O^+.

3.1.2. Secondary and tertiary amine reactions

NH_4^+ is not a product of any of the reactions of H_3O^+ with the two secondary and two tertiary amines because such a process would require the breaking of two C–N bonds. However, another process occurs in all four reactions, this being the elimination of an H_2 molecule following the protonation step as exemplified by the N,N-diethylmethylamine reaction:

$$H_3O^+ + (C_2H_5)_2NCH_3$$

$$\rightarrow (C_2H_5)_2NCH_3 \cdot H^+ + H_2O \qquad (2a)$$

$$\rightarrow C_5H_{12}N^+ + H_2 + H_2O \qquad (2b)$$

In all four reactions the protonated parent molecule is the major product (see Table 2) but in reaction (2) H_2 elimination (channel 2b) represents 30% of the product ratio. The energetically preferred structure of the $C_5H_{12}N^+$ product ions in these primary and tertiary amine reactions would be the immonium ions as exemplified by $CH_3CH{=}N^+(CH_3)(C_2H_5)$ in reaction (2b), implying that the H_2 is eliminated from the hydrocarbon chain. Theoretical work is desirable to clarify these situations.

3.2. NO^+ reactions

The reactions of NO^+ with these amines are rich and varied, much more so than with most other organic molecules that we have studied [5–10, 23]. This is partly because of the relatively low ionisation energies of these amines that vary from 8.7 eV for the primary amine 1-pentylamine to 7.5 eV and 7.3 eV for the tertiary amines N,N-diethylmethylamine and N,N-dimethyl-2-propylamine, respectively [18]. Thus, the possibility of dissociative charge transfer arises, although the lack of appropriate thermochemical data in some cases leaves the actual mechanisms of some of the reactions in doubt. However, the thermochemical data are available to show the reactions of 1-pentylamine and 3-methylbutylamine proceed only via parallel hydride ion (H^-) transfer (producing HNO and not H + NO) and direct charge transfer, e.g.:

$$NO^+ + C_5H_{11}NH_2 \rightarrow C_5H_{10}NH_2^+ + HNO \qquad (3a)$$

$$\rightarrow C_5H_{11}NH_2^+ + NO \qquad (3b)$$

The H^- ion is most probably taken from the carbon atom that is bonded to the N atom producing the energetically favoured immonium ion, although there are no useful thermochemical data available to support this presumption. H^- transfer apparently occurs in other primary amine reactions (see Table 2) and, additionally, in some of these reactions ion products appear that are equivalent to the elimination of alkyl radicals R (variously CH_3, C_2H_5, and C_3H_7) or RNH_2 moieties. The 3-methyl-2-butylamine reaction most probably proceeds thus:

$$NO^+ + (CH_3)_2CHCH(CH_3)NH_2$$

$$\rightarrow CH_3CH{=}NH_2^+ + (C_3H_7 + NO) \qquad (4a)$$

$$\rightarrow C_2H_3NH_2^+ + (C_3H_8 + NO) \qquad (4b)$$

$$\rightarrow C_5H_{10}NH_2^+ + HNO \qquad (4c)$$

Thus reaction (4a) probably results in the stable immonium ion as indicated. Under these circumstances reaction (4a) could involve the transfer of a $C_3H_7^-$ anion to the NO^+ cation producing the neutral C_3H_7NO. Such R^- transfer reactions have been characterised previously in the reactions of NO^+ ions with some ethers [8]. A further possibility is that the neutral products are (C_3H_6 + HNO), which is certainly exothermic, both for the propene and cyclopropane structures of C_3H_6 [18]. The brackets around the neutral products in reactions (4a) signifies these uncertainties. Reaction (4b) most likely results in the production of the $C_2H_3NH_2^+$ ion with (C_3H_8 + NO) as the neutral products (exothermic according to the data from [18]). An alternative product ion with the same molecular weight would be $C_3H_7^+$ with $(CH_3)_2NNO$ as a neutral product, which is less likely, because of the rearrangement required. Reaction (4c) is probably H^- transfer, but again we cannot be sure of this because the required thermochemical data are not available. However, because of the propensity of NO^+ to form complexes, $(NO^+ \cdot M)^*$ with many organic species M [6, 7], some of which live long enough to be stabilised to $NO^+ \cdots M$, it seems sensible to expect all these NO^+/amine reactions to proceed within a short-lived complex followed by their dissociation into the observed product ions and not via discreet processes such as H^- transfer or charge transfer that are usually considered to occur at appreciable internucleur distances [24].

The secondary and tertiary amine reactions result in products that can be described as resulting from dissociative charge transfer [e.g. (5a)] and direct, nondissociative charge transfer [e.g. (5b)], and in one of the four reactions H^- transfer apparently occurs [(5c)]:

$$NO^+ + C_4H_9NHCH_3$$

$$\rightarrow CH_2{=}NHCH_3^+ + (C_3H_7 + NO) \tag{5a}$$

$$\rightarrow C_4H_9NHCH_3^+ + NO \tag{5b}$$

$$\rightarrow C_5H_{12}N^+ + HNO \tag{5c}$$

In reaction (5a) the butyl chain breaks, producing the ion indicated (again most likely having the immonium structure as indicated) and a C_3H_7 radical that is an exothermic process. However, we cannot be certain that C_3H_7NO is not formed. The other three reactions result in parallel nondissociative and dissociative charge transfer products, the latter process in these three reactions most probably resulting in the elimination of a CH_3 radical (see Table 2).

3.3. O_2^+ reactions

The reactions of O_2^+ with all these primary, secondary, and tertiary amines can be described as dissociative charge transfer reactions because in only 2 of the 11 reactions is the parent cation observed as a very minor product ion (~5%; see the first two primary amines listed in Table 2). This contrasts with the corresponding NO^+ reactions in which the parent cation is a major product in several of the reactions. Clearly this is due to the greater recombination energy of O_2^+ (12.07 eV) compared to NO^+. The dissociation pathways are understandable in terms of the structures of the individual amines, simple cleavage of C–C bonds occurring in all cases producing N-bearing ions, and alkyl radicals (as a glance at Table 2 reveals).

Among the primary amines a simple pattern is evident, which shows that the majority product ions are those which result from the elimination of the largest radical by a one C–C bond cleavage, as is exemplified by the 3-methyl-2-butylamine reaction:

$$O_2^+ + (CH_3)_2CHCH(CH_3)NH_2$$

$$\rightarrow CH_3CH{=}NH_2^+ + C_3H_7 \tag{6a}$$

$$\rightarrow C_3H_7CH{=}NH_2^+ + CH_3 \tag{6b}$$

Again, the product ions most likely have the immonium structures as indicated.

In the reaction of the secondary amine N-methylbutylamine, the above trend is continued with the elimination of C_3H_7 as the very dominant channel, and in the reaction of the tertiary amine N,N-diethylmethylamine, the most likely option within the above scenario is CH_3 elimination as is observed (see Table 2.). Also, in the N-ethyl-2-propylamine and N,N-dimethyl-2-propylamine reactions, the dominant channels result from the elimination of CH_3 radicals and the cleaving of C–C bonds. But now minor products are evident from these two reactions which apparently result in the elimination of a C_3H_7 radical and thus the cleaving of a C–N bond in these molecules (this process is exothermic by 350 kJ mol^{-1} for N,N-dimethyl-2-propylamine).

It is interesting and instructive to compare the product ions of these O_2^+/amine reactions with the mass spectra of these amines obtained using 70 eV electron impact (EI) [25]. The major ions of these mass spectra are the same as the products of the amine reactions with O_2^+ in which the excess energy is only a few electron volts compared to the 60 eV or more that is potentially available in the electron impact. However, only about 2–3 eV of this energy is deposited on average into the amine molecules [26].

In order to illustrate some of the similarities and differences between the chemical ionisation of these amines by O_2^+ ions and by EI, we reproduce in Figs. 1(a)–(f) the EI mass spectra for the primary amines 1-pentylamine, 2-pentylamine, and 2-methyl-2-butylamine, for the secondary amine N-ethyl-2-propylamine, and for the tertiary amines N,N-diethylmethylamine and N,N-dimethyl-2-propylamine, together with the product ion branching ratios for their O_2^+ reactions.

It can be seen that for the first three primary amines [Figs. 1(a)–(c)] the O_2^+ and the EI data are remarkably similar, although minor additional ions are evident in the EI mass spectra. But for the secondary amine represented in Fig. 1(d) there are obviously more ions in the EI mass spectrum than are formed in the O_2^+ reaction, although the major ion is the same (at 72 u). Also, it is interesting to note that the other ion formed in the O_2^+ reaction at 44 u, which is likely to be $C_2H_5NH^+$, and which can only be formed by the cleaving of a C–N bond, is the second most abundant ion in the EI mass spectrum. However, an ion at 30 u (probably $CH_2{=}NH_2^+$), is clearly evident in the EI mass spectrum but it is not formed in the lower energy O_2^+ reaction, presumably because the formation of these ions requires some molecular rearrangement for which the energy is not available in the O_2^+ reaction. Finally, the major ions in the cracking patterns of the two tertiary amines are the same as those formed in the O_2^+ reactions. However, the parent cations (at 87 u) appear as minor components of the cracking patterns but they do not survive (against dissociation) as significant products of the O_2^+ charge transfer reactions.

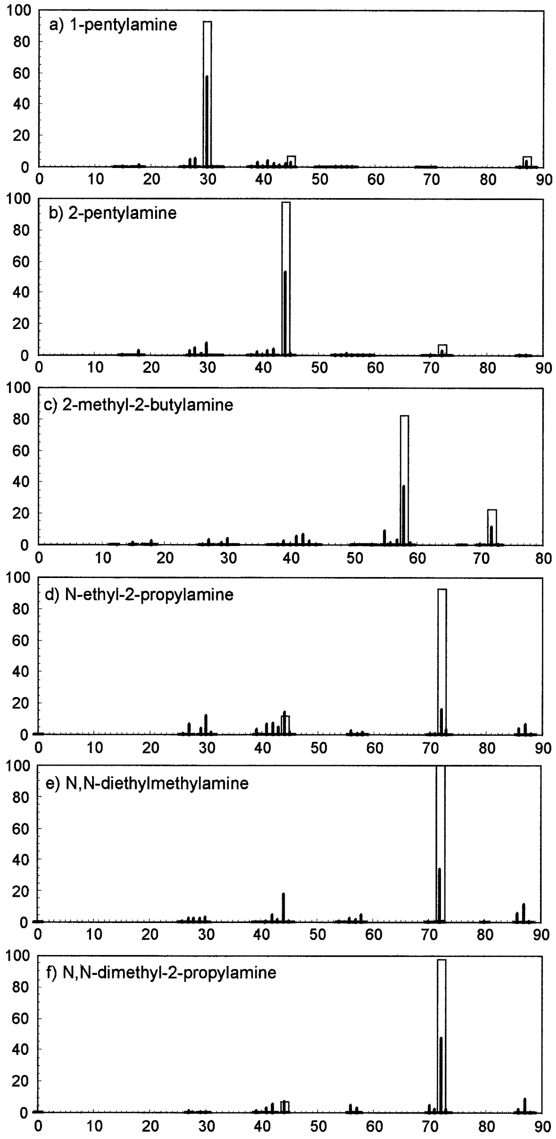


Fig. 1. Ion product branching ratios for the reactions of O_2^+ with the six amine isomers shown as percentages of products (ordinates) at the mass to charge ratios indicated (abscissa), obtained using the SIFT (open bars) as compared with the electron impact mass spectra according to the NIST database [25] (solid bars).

4. Concluding remarks

Our hope in initiating these studies was that the reactions of H_3O^+, NO^+, and O_2^+ with these amine structural isomers would reveal product ions that are characteristic of the different structure, and to some extent this is the way it turns out. The most obvious results are that in the reactions of H_3O^+, NH_4^+ ions are only formed with some primary amines and H_2 elimination occurs with the secondary and especially the tertiary amines. These observations have some value in our SIFT analyses of amines, and especially serve as a warning that when NH_4^+ appears on a mass spectrum where H_3O^+ is the chemical ionisation precursor, it does not necessarily indicate the presence of ammonia in the sample of gas being analysed. To differentiate between these primary amines and NH_3 when they are both present in a gas (such as human breath) and to separately quantify them, it is also necessary to use O_2^+ as the precursor ion which uniquely generates NH_3^+ in reaction with NH_3 [10, 21, 22]. Note in Table 2 that none of the O_2^+ reactions result in the production of NH_3^+ ions. The great advantage of our SIFT analytical method is that we can readily switch between H_3O^+ and O_2^+ (and indeed NO^+) precursor ions [4, 15, 16] to avoid possible confusions such as this, and also to provide additional information on the nature of unidentified ions in the analytical spectra.

The low ionisation energies of amines, especially secondary and tertiary amines, allows charge transfer to occur in their reactions with NO^+ ions, and this process is commonly observed. Thus the parent cation is often a product that usually occurs along with products resulting from dissociative charge transfer (in which alkyl radicals are eliminated from the parent amine cation) or hydride ion transfer. But in the more energetic O_2^+ ion reactions with these amines, dissociative charge transfer is the major process, the parent amine cation being barely observed. The comparison of the products of the O_2^+ reactions and the 70 eV cracking patterns for the amine isomers reveals that both ways of ionising these molecules result in the same major ion, but in some cases the cracking patterns result in more ions. Thus the analysis of mixtures containing some of these amines and other gases is better carried out using the soft ionisation that O_2^+ provides to avoid multiple ion peaks on analytical mass spectra. In this regard, our SIFT method has much to offer, especially because of the ability to use selected precursor ions on a given gas mixture. Of course, the information on the reactions of our chosen precursor ions, H_3O^+, NO^+, and O_2^+, with the wide variety of organic and inorganic molecules that our surveys are providing [5–10], are vital to our SIFT analytical work.

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