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Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and $O_2{}^+$ with several amines and some other nitrogen-containing molecules

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Abstract

We report the results of a selected ion flow tube study at 300 K of the reactions of H_3O^+, NO^+, and $O_2{}^+$ with ammonia, five primary, three secondary, and two tertiary amines, pyrrole and pyridine, and acetonitrile and benzonitrile. The major product ions of all the H_3O^+ reactions are the protonated parent molecules, MH^+, these being the single product in six of these reactions; $NH_4{}^+$ is seen to be a minor product of three of the primary amine reactions, and ions of the type $(M\text{-}H)^+$ are minor products of the secondary and tertiary amine reactions. The low ionisation energies of all the amines, pyrrole, and pyridine ensures that charge transfer occurs in their reactions with NO^+, this generally being sufficiently exothermic to result in partial fragmentation of the $(M^+)^*$ nascent product ions resulting in $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions. However, charge transfer is endothermic between NO^+ and pyridine and the two nitriles and then ion–molecule association occurs, producing the adduct ions $NO^+ \cdot M$. The reactions of the more energetic $O_2{}^+$ ions with all the amines proceed via dissociative charge transfer, producing major products ions of the type $(M\text{-}R)^+$, where R is the alkyl radicals, CH_3, C_2H_5, etc., as appropriate, but the parent cations, M^+, are the single product ions for the reactions of the more stable aniline, pyrrole, pyridine, and benzonitrile. (Int J Mass Spectrom 176 (1998) 203–211) © 1998 Elsevier Science B.V.

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1. Introduction

We are carrying out detailed surveys of the reactions of the three ionic species H_3O^+, NO^+, and $O_2{}^+$ with various classes of organic (and some inorganic) molecules in support of our development of the selected ion flow tube (SIFT) as a sensitive detector of the trace gases in atmospheric air and human breath [1–3]. These ions are used to chemically ionise [4] the trace gases in an air/breath sample introduced into the SIFT to the exclusion of the major atmospheric gases (N_2, O_2, H_2O, Ar, and CO_2) with which they do not react at appreciable rates. The quantification of the trace gases by this method requires that the rate coefficients and the ionic products of the reactions of these three ions with the trace gases are known, and it is a major purpose of these studies to obtain these

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critical kinetic data and thus to build an extensive database for this analytical procedure. Additionally, such wide ranging studies provide a large amount of information on ionic reaction processes at thermal energies.

To date, we have determined the rate coefficients and the ionic products for the reactions of H_3O^+, NO^+, and $O_2{}^+$ ions with some 17 alcohols [5], 11 aldehydes, and 9 ketones [6], 9 carboxylic acids and 8 esters [7], 10 ethers [8], and 8 organosulphur molecules [9]. These data have revealed the trends in reactivity of these precursor ions with particular molecular types, and many examples of reaction processes hitherto not greatly explored such as the elimination of H_2O molecules after the protonation of some alcohols, aldehydes, and carboxylic acids by H_3O^+ [5–7], hydride ion transfer (H^-), and hydroxide ion (OH^-) transfer in the reactions of NO^+ with some alcohols, aldehydes, acids, and ethers [5–8,10], facile ion–molecule association between NO^+ and most ketones [6], and even alkoxide ion (CH_3O^- and $C_2H_5O^-$) transfer in the reactions of NO^+ with some esters and ethers [7,8]. Our data reveal that the reactions of $O_2{}^+$ with almost all these types of organic compounds proceed via charge transfer, often with the production of several fragment ions [5–9].

Nitrogen-containing molecules are intimately involved in human biology, their dietary origin being proteins and amino acids. It has been reported that dimethylamine and trimethylamine are present at elevated levels on the breath of those suffering from end-stage renal failure [11]. Very recently we have shown that ammonia is greatly elevated on the breath of such patients compared with normal control subjects [12], and increases in concentration on the breath of healthy individuals after the ingestion of a liquid protein meal [10]. Thus, it is important that we include in our surveys the reactions of our chosen precursor ions with ammonia, amines, and other nitrogen-containing species.

In this paper we report the results of a study of the rate coefficients and ion product distributions for the reactions of the three ions with some 10 amines, (5 primary, 3 secondary and 2 tertiary), 2 heterocyclics, and 2 nitriles. We also include ammonia even though its reactions have been studied previously [13,14]. Little previous work has been carried out on the other reactions included in this study. As in our previous papers in this series, we concentrate on the fundamental processes that occur in these reactions, noting the different reactivities of the primary, secondary, and tertiary amines, and of the heterocyclics and the nitriles.

2. Experimental

Measurements of the rate coefficients, k, and the ion products of ion–molecule reactions at thermal energies using the conventional SIFT technique have been discussed in numerous review and research papers [15–17]. So it is sufficient to note here that a reactant gas or vapor is introduced at a controlled, measured flow rate into the helium carrier gas of the SIFT into which a current of mass selected reactant ions has been introduced upstream, 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), the k for the reactions and the ion product branching ratios are determined [15].

It is straightforward to measure the flow rates of most permanent reactant gases, but this is more difficult for many organic vapours because the thermodynamic data required for capillary and flow meter calibrations (i.e. heat capacities) are mostly unavailable, and volume/pressure reduction methods of flow measurements are inaccurate because such vapours often stick to vessel surfaces. So in common with our previous studies in this series we have adopted the following procedure.

It is well known from numerous experimental studies [13,14,18] that proton transfer reactions proceed at their respective collision rates if the proton affinity (PA) of the acceptor molecule, M, exceeds that of the donor molecule (i.e. if these reactions are appreciably exothermic). The PA of all the reactant

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+, and O_2^+ with the organonitrogen molecules indicated[a]

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})
Ammonia	17	2.20	1.47	[2.6]	0.01 [2.4]	2.6 [2.4]
l-Propylamine	59	9.20	1.17	[2.4]	1.4 [2.1]	1.9 [2.0]
Isopropylamine	59	*9.20*	*1.2 ± 0.2*	[2.4]	1.5 [2.1]	1.6 [2.0]
l-Butylamine	73	13.50	*1.2 ± 0.2*	[2.7]	1.6 [2.3]	2.4 [2.2]
l-Pentylamine	87	*14.5 ± 1*	*1.2 ± 0.2*	[2.7]	1.5 [2.3]	2.3 [2.2]
Aniline	93	12.10	1.53	[2.8]	1.8 [2.3]	1.9 [2.3]
Dimethylamine	45	6.37	1.03	[2.1]	1.6 [1.8]	1.8 [1.8]
Methylethylamine	59	*9 ± 1.5*	*1.0 ± 0.2*	[2.3]	1.4 [2.0]	1.6 [1.9]
Diethylamine	73	10.20	0.92	[2.3]	1.2 [1.9]	1.3 [1.9]
Trimethylamine	59	8.15	0.61	[2.0]	1.6 [1.7]	1.5 [1.6]
Triethylamine	101	*16 ± 2*	0.66	[2.5]	2.3 [2.1]	2.1 [2.1]
Pyrrole	67	9.50	1.84	[3.0]	2.5 [2.5]	2.6 [2.5]
Pyridine	79	*10 ± 2*	2.19	[3.3]	2.4[b] [2.8]	2.6 [2.7]
Acetonitrile	41	4.50	3.92	[5.1]	<0.2[b] [4.4]	0.9[b] [4.3]
Benzonitrile	103	12.50	4.18	[5.3]	2.2[b] [4.4]	2.5 [4.3]

[a] 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 in Debye (D). The values of both α and μ are known for only nine of the compounds included in this study, and they are shown in regular type (taken from [21]). For the remaining compounds (numbers shown in italics) we have estimated their μ assuming they do not change significantly with the number of carbon atoms in the organonitrogen molecule, and their α by adopting the average values of the known polarisabilities of similar organic molecules possessing the same number of carbon atoms. The collisional rate coefficients, k_c, for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [20] 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 values are given in units of 10^{-9} cm^{3}s^{-1}.

[b] In these reactions association occurs; the k values are the effective two body rate coefficients.

molecules included in this study are known [19] and they are all greater than that of water. So we can assume that the k for all these proton transfer reactions of H_3O^+ 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 [20,21]. Unfortunately these molecular parameters are not known for all the reactant molecules, and we must make estimates for some of them to obtain approximate values for the k_c. This procedure (outlined in the footnote to Table 1) does not involve large errors, as can be seen from our estimates given in Table 1, and thus we can use with confidence the calculated/estimated k_c for our SIFT analyses [1–3]. However, 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 [22] do not necessarily proceed at the collision rate, i.e. k cannot be assumed to be equal to k_c. So the k for the NO^+ and O_2^+ reactions must be determined experimentally. To do this we make a dilute mixture of the reactant molecule 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. Using this procedure, the absolute k for the reactions is not obtained directly, but by 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. Because for the H_3O^+ reactions $k = k_c$ then the k for the NO^+ and O_2^+ reactions can be obtained. More discussion of this procedure and the possible influence of metastable states of the primary ions together with sample primary ion decay plots are given in the previous papers in this series [5–7]. The product ion distributions for the ion–molecule reactions are also determined from these measurements in the usual manner by introducing H_3O^+, NO^+, and $O_2{}^+$ separately using the upstream quadrupole mass filter [15,16]. All the measurements were carried out in helium carrier gas at a pressure of about 0.5 Torr at a temperature of 300 K.

3. Results and discussion

The calculated values of k_c for the reactions of all three ion species and the derived k for the NO^+ and $O_2{}^+$ reactions are given in Table 1. As can be seen, the rate coefficients for most 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 footnote to Table 1). Their reactions with acetonitrile are obvious exceptions.

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. Also included in this table below each reactant molecule are their ionisation energies volts (in eV) and the proton affinities (in kJ mol^{-1}). Note that the ionisation energies of all the amines and also pyrrole are significantly smaller than that of NO (9.26 eV [19,21]) whereas those of ammonia, the two nitriles, and pyridine exceed that of NO. This determines the processes that can occur in their reactions with NO^+ as we will see. Note also that the proton affinities of all the reactant molecules greatly exceed that of H_2O (697 kJ mol^{-1}) and this fact also has an important bearing on the course of the H_3O^+ reactions. The reactant molecules are grouped in Table 2 as primary, secondary and tertiary amines, heterocyclics and nitriles, because these groups are seen to exhibit characteristic reactions. We now discuss the H_3O^+, NO^+, and $O_2{}^+$ reactions separately.

3.1. H_3O^+ reactions

The initial step in all these reactions is the exothermic transfer of a proton from the H_3O^+ ion to the reactant molecule M, leaving residual energy in the $(MH^+)^*$ ion, which may then partly dissociate. In the ammonia reaction the only product is $NH_4{}^+$, no other exothermic channels being available. However, partial dissociation obviously occurs in the reactions of the primary amine *n*-propylamine and its isomer isopropylamine, where $NH_4{}^+$ is a measurable product together with the protonated parent molecules that are the major product ions:

$$H_3O^+ + (CH_3)_2CHNH_2 \rightarrow (CH_3)_2CHNH_2 \cdot H^+ + H_2O \qquad (1a)$$

$$\rightarrow NH_4{}^+ + C_3H_6 + H_2O \qquad (1b)$$

In this reaction $NH_4{}^+$ production is a 35% product, whereas in the n-propylamine reaction it is only a 10% channel. It is readily shown using the available thermodynamic data that $NH_4{}^+$ production is clearly exothermic for both of these reactions and for either the propene or the cyclopropane structures of the C_3H_6 neutral product. Note in Table 2 that $NH_4{}^+$ is only a very minor product (<2%) in the *n*-butylamine reaction and is not observed at all in the two other primary amine reactions. What then is controlling the branching ratio for these reactions? Clearly, after the protonation at the NH_2 site, producing a transient $NH_3{}^+$ moiety within the $(MH^+)^*$ excited ion, migration of an H atom is required from an adjacent carbon atom to allow $NH_4{}^+$ to be released. Although general conclusions cannot be drawn from the small amount of data in this study, it is evident from the results of our detailed study of the reactions of some 11 isomers of a particular amine (of molecular formula $C_5H_{13}N$, [23]) that the closer the proximity of an alkyl group (CH_3 or C_2H_5) to the N atom the greater is the propensity for $NH_4{}^+$ formation in primary amines. Indeed, $NH_4{}^+$ is the majority product ion when N is bonded to a tertiary carbon [23].

In the reactions of the secondary amines with H_3O^+ another reaction process is observed that, in effect, is the loss of an H_2 molecule from the excited protonated parent molecule:

Table 2
Products of the reactions of the organonitrogen molecules with H_3O^+, NO^+, and O_2^+[a]

	H_3O^+	NO^+	O_2^+
Ammonia NH_3 10.2 *854*	NH_4^+	No reaction	NH_3^+
Primary amines			
Propylamine $C_3H_7NH_2$ 8.8 *912*	$C_3H_7NH_2 \cdot H^+$ (90)+H_2O NH_4^+ (10) + C_3H_6 + H_2O	$C_3H_8N^+$ (75) + HNO $C_3H_7NH_2^+$ (25) + NO	CH_4N^+ (100)
Isopropylamine $(CH_3)_2CHNH_2$ 8.7 *915*	$(CH_3)_2CHNH_2 \cdot H^+$ (65)+ H_2O NH_4^+ (35) + C_3H_6 + H_2O	$C_3H_8N^+$ (45) + HNO $C_2H_6N^+$ (50) + (CH_3 + NO)	$C_2H_6N^+$ (75) CH_5N^+ (10) $C_3H_8N^+$ (5)
l-Butylamine $C_4H_9NH_2$ 8.7 *914*	$C_4H_9NH_2 \cdot H^+$ (>98) + H_2O NH_4^+ (<2) + C_4H_8 + H_2O	$C_4H_{10}N^+$ (65) + HNO $C_4H_9NH_2^+$ (35) + NO	CH_4N^+ (100)
l-Pentylamine $C_5H_{11}NH_2$ 8.7 *916*	$C_5H_{11}NH_2 \cdot H^+$ (100) +H_2O	$C_5H_{12}N^+$ (65) + HNO $C_5H_{11}NH_2^+$ (35) + NO	CH_4N^+ (90) $C_5H_{11}NH_2^+$ (5) $C_2H_7N^+$ (5)
Aniline c-$C_6H_5NH_2$ 7.7 *877*	$C_6H_5NH_2 \cdot H^+$ (100) + H_2O	$C_6H_5NH_2^+$ (100) + NO	$C_6H_5NH_2^+$ (100)
Secondary amines			
Dimethylamine $(CH_3)_2NH$ 8.2 *923*	$(CH_3)_2NH \cdot H^+$ (100) +H_2O	$(CH_3)_2NH^+$ (95) + NO $C_2H_6N^+$ (5) + HNO	$(CH_3)_2NH^+$ (70) $C_2H_6N^+$ (30)
Methylethylamine $C_2H_5CH_3NH$ 8.2 *932*	$C_2H_5CH_3NH \cdot H^+$ (95) +H_2O $C_3H_8N^+$ (5) + H_2 + H_2O	$C_2H_5CH_3NH^+$ (75) + NO $C_2H_6N^+$ (15) + (CH_3 + NO) $C_3H_8N^+$ (10) + HNO	$C_2H_6N^+$ (90) $C_2H_5CH_3NH^+$ (5) $C_3H_8N^+$ (5)
Diethylamine $(C_2H_5)_2NH$ 8.0 *945*	$(C_2H_5)_2NH \cdot H^+$ (95) +H_2O $C_4H_{10}N^+$ (5) + H_2 + H_2O	$(C_2H_5)_2NH^+$ (70) + NO $C_4H_{10}N^+$ (15) + HNO $C_3H_8N^+$ (15) + (CH_3 + NO)	$C_3H_8N^+$ (80) CH_4N^+ (15) $C_4H_{10}N^+$ (5)
Tertiary amines			
Trimethylamine $(CH_3)_3N$ 7.8 *942*	$(CH_3)_3N \cdot H^+$ (90) + H_2O $C_3H_8N^+$ (10) + H_2 + H_2O	$(CH_3)_3N^+$ (100) + NO	$C_3H_8N^+$ (65) $(CH_3)_3N^+$ (35)
Triethylamine $(C_2H_5)_3N$ 7.5 *972*	$(C_2H_5)_3N \cdot H^+$ (80) + H_2O $C_6H_{14}N^+$ (20) + H_2 + H_2O	$(C_2H_5)_3N^+$ (90) + NO $C_5H_{12}N^+$ (10) + (CH_3 + NO)	$C_5H_{12}N^+$ (100)
Heterocyclics with N			
Pyrrole c-C_4H_5N 8.2 *869*	$C_4H_5N \cdot H^+$ (100) + H_2O	$C_4H_5N^+$ (100) + NO	$C_4H_5N^+$ (100)
Pyridine c-C_5H_5N 9.3 *924*	$C_5H_5N \cdot H^+$ (100) + H_2O	$NO^+ \cdot C_5H_5N$ (70) $C_5H_5N^+$ (30) + NO	$C_5H_5N^+$ (100)
Nitriles			
Acetonitrile CH_3CN 12.2 *787*	$CH_3CN \cdot H^+$ (100) + H_2O	$NO^+ \cdot CH_3CN$ (100)	CH_3CN^+ $O_2^+ \cdot CH_3CN$
Benzonitrile c-C_6H_5CN 9.7 *820*	$C_6H_5CN \cdot H^+$ (100) + H_2O	$NO^+ \cdot C_6H_5CN$ (100)	$C_6H_5CN^+$ (100)

[a] The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion product is given in parentheses. The neutral products are given only for the H_3O^+ and NO^+ and not for the O_2^+ reactions, for which the neutral products (and in some cases the structures of the ionic products) are not readily defined. Also given below each reactant molecule are their ionisation energies in electron volts (eV) and their proton affinities (in italics) in kJ mol^{-1}.

$$H_3O^+ + (C_2H_5)_2NH \rightarrow (C_2H_5)_2NH \cdot H^+ + H_2O \quad (2a)$$

$$\rightarrow C_4H_{10}N^+ + H_2 + H_2O \quad (2b)$$

Although this H_2 elimination is only a minor channel (5%) in two of these secondary amine reactions (Table 2), this process is exothermic and becomes a more important channel in the tertiary amine reactions. In the trimethylamine reaction it is a 20% product:

$$H_3O^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3N \cdot H^+ + H_2O \quad (3a)$$

$$\rightarrow C_6H_{14}N^+ + H_2 + H_2O \quad (3b)$$

This H_2 elimination process is clearly exothermic in these reactions because otherwise it could not occur to a measurable extent under the thermal energy conditions of these SIFT experiments.

The greater stability of the heterocyclic rings of pyrrole and pyridine ensure that the only products of their reactions are the protonated parent molecules. Similarly, the lower proton affinities of acetonitrile and benzonitrile ensure that there are no accessible dissociation products for the reactions of these with H_3O^+ (Table 2). That there is only a single product for these last reactions greatly simplifies their quantification in air samples when using our SIFT analytical method.

3.2. NO^+ reactions

The ionisation energy of NO molecules, and hence the recombination energy of NO^+ ions is low when compared with most stable diatomic molecules and so charge transfer between NO^+ ions and the smaller members of some classes of organic compounds with ionisation energies greater than NO (e.g. alcohols [5]) cannot occur. However, all the amines have low ionisation energies (Table 2) and so in their reactions with NO^+ charge transfer is possible and it is indeed observed in all the reactions studied here. The ionisation energies of the secondary amines are smaller than the primary amines and those of the tertiary amines are even smaller. Thus, charge transfer is more exothermic for the secondary and tertiary amine reactions, sufficiently so that dissociative charge transfer becomes energetically allowed in all these reactions.

Two product ions are observed in the aliphatic primary amine reactions. The *n*-propylamine reaction proceeds thus:

$$NO^+ + C_3H_7NH_2 \rightarrow C_3H_8N^+ + HNO \quad (4a)$$

$$\rightarrow C_3H_7NH_2{}^+ + NO \quad (4b)$$

Reaction (4b) is simple charge transfer that produces the parent cation, M^+. Reaction (4a) must proceed by the process of hydride ion (H^-) transfer (producing $(M\text{-}H)^+$ ions) because it can be shown using the available thermochemical data [19] that dissociative charge transfer to produce (H + NO) is endothermic by 67 kJ mol^{-1}. The most likely structure of the product ion of the reaction (4a) is $C_3H_6NH_2{}^+$ because all exothermic channels involve the transfer of H^- from a carbon atom and not from the nitrogen atom [19]. H^- transfer must also be occurring in the *n*-butylamine reaction, again constrained by the energetics; it is probably occurring in the *n*-pentylamine reaction also, but it must be said that in this reaction (H + NO) could be fractional neutral products of the major channel (Table 2) because a consideration of the energetics indicates that dissociative charge transfer is close to thermoneutral. The isopropylamine reaction is unusual in that the parent cation is not an observed product:

$$NO^+ + (CH_3)_2CHNH_2 \rightarrow C_3H_8N^+ + HNO \quad (5a)$$

$$\rightarrow C_2H_6N^+ + (CH_3 + NO) \quad (5b)$$

However, it is most likely that charge transfer is occurring because it can be shown that dissociative charge transfer is energetically allowed to produce the separated neutral products given in the parentheses in (5b). This does not exclude the possibility that $CH_3{}^-$ transfer producing CH_3NO occurs. This process is known to occur in the reaction of NO^+ with diisopropyl ether [8]. Dissociative charge transfer producing (H + NO) cannot be totally ruled out in reaction (5a) because this process is slightly exothermic, as it also is for the analogous reaction of *n*-pentylamine. There are no such problems of interpretation in the aniline reaction where the only allowed product is the parent cation, again a manifestation of the stability of the aromatic ring, so often seen in all our surveys of the reactions of H_3O^+, NO^+, and $O_2{}^+$ [6–8].

In all three of the secondary amine reactions, the parent cation M^+ (with neutral NO) is the major product. $(M\text{-}H)^+$ ions are also minor products in these three reactions and the neutral products in all cases could be (energetically) either (H + NO) or HNO. In two of these reactions there are three products, the third channel being the result of the ejection of a CH_3 radical from M^+ after the charge transfer:

$$NO^+ + (C_2H_5)_2NH \rightarrow (C_2H_5)_2NH^+ + NO \quad (6a)$$

$$\rightarrow C_4H_{10}N^+ + (H + NO) \quad (6b)$$

$$\rightarrow C_3H_8N^+ + (CH_3 + NO) \quad (6c)$$

Again, formation of CH_3NO in reaction (6c) cannot be ruled out.

In the reaction of the tertiary trimethylamine there is only one product ion, charge transfer producing only the parent cation even though H^- transfer and CH_3 radical elimination are both exothermic. However, in the triethylamine reaction two productions are observed, the major product being the parent cation with a minor CH_3 elimination channel (Table 2).

The only energetically allowed bimolecular reaction of NO^+ with pyrrole is nondissociative charge transfer to produce the parent cation as is observed. However, the pyridine reaction is more interesting in that the ionization energy of this molecule is slightly greater than that of NO and consequently charge transfer is slightly endothermic by about 40 meV, i.e. comparable to kT at room temperature. So although charge transfer is inhibited, it is not totally prevented and it is seen as a 30% product together with the adduct ion (70% product), which is the result of a parallel termolecular ion–molecule association reaction:

$$NO^+ + C_5H_5N(+He) \rightarrow NO^+ \cdot C_5H_5N + (He) \quad (7a)$$

$$\rightarrow C_5H_5N^+ + NO \quad (7b)$$

Parallel charge transfer–association reactions are also seen in the reactions of NO^+ with several ketones [6], which also have ionisation energies close to that of NO. These association reactions proceed at high efficiency under the conditions of these SIFT experiments (helium pressure ~0.5 Torr, temperature 300 K), the effective bimolecular rate coefficients being large fractions of the collision rate, k_c, as can be seen for reaction (7a) which is 0.85 k_c. We consider that this efficiency is due to the phenomenon of "charge transfer complexing" [6,7] in which the proximity of the ionisation potentials of the NO and the pyridine molecules (in this case) allows the charge to migrate around the excited transient $(NO^+ \cdot M)^*$ ion, thus increasing its lifetime against unimolecular dissociation back to NO^+ and M. This increases the probability that the $(NO^+ \cdot M)^*$ will be relaxed to the stable $NO^+ \cdot M$ adduct ion in collisions with the helium carrier gas atoms.

Because the ionization energies of both acetonitrile and benzonitrile exceed that of NO, charge transfer cannot occur. No other bimolecular reactions are exothermic and so the only reaction that can occur is ion–molecule association as is observed (Table 2). Note that the acetonitrile association is relatively slow, whereas the benzonitrile reaction is efficient, probably because of the proximity of its ionisation energy (9.7 eV) to that of NO (9.26 eV) and the probable involvement again of charge transfer complexing.

3.3. $O_2{}^+$ reactions

All these reactions proceed via nondissociative (i.e. parent ion formation) or dissociative charge transfer, which essentially are the only reaction processes that $O_2{}^+$ ions undergo efficiently at low energies as our SIFT experiments [5–7,22] and numerous other experiments have shown [13,14]. In the reactions of the (aromatic) aniline, the cyclic molecules pyrrole and pyridine and the two nitriles the single products are the parent cations, whereas in the reactions of the more fragile amines dissociation always occurs. A common product ion of the primary amine reactions is CH_4N^+, which most probably has the structure $CH_2NH_2^+$ and results from the dissociation of the carbon chain at the $(R–CH_2NH_2)^+$ bond in the ion:

$$O_2^+ + CH_3CH_2CH_2NH_2 \rightarrow CH_2NH_2^+ + C_2H_5 + O_2 \qquad (8)$$

In this reaction a C_2H_5 radical is ejected. The same product ion of the *n*-butylamine and *n*-pentylamine reactions results in the ejection of C_3H_7 and C_4H_9 radicals, respectively. But in the isopropylamine reaction the major product ion is the result of the ejection of a CH_3 radical:

$$O_2^+ + (CH_3)_2CHNH_2 \rightarrow CH_3CHNH_2^+ + CH_3 + O_2 \qquad (9)$$

$$\rightarrow CH_5N^+ + C_2H_4 + O_2 \qquad (9b)$$

$$\rightarrow C_3H_8N^+ + H + O_2 \qquad (9c)$$

The minor reaction channel (9b) clearly requires that some rearrangement occurs in the transient parent cation before the dissociation occurs, a common event in ion–molecule reactions.

Reaction (9c) simply is the result of the ejection of an H atom, a process that occurs in all the secondary and tertiary amine reactions with O_2^+ (Table 2), usually as a minor process, except for the trimethylamine reaction where it is the major process that occurs in parallel with parent ion production. In these reactions the most common process is the ejection of a CH_3 radical from the transient excited $(M^+)^*$ ions, this being essentially the only process that occurs in the triethylamine reaction:

$$O_2^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_2CH_2N^+ + CH_3 + O_2 \qquad (10)$$

The minor ions in these reactions (see Table 2) are the result of the rearrangement and fragmentation of the excited parent ions at different bonds.

It is interesting to note that the ionisation energies of CH_3CN (12.2 eV) are somewhat greater than the recombination energy of ground state O_2^+ (12.07 eV) and so charge transfer is endothermic in the reaction:

$$O_2^+ + CH_3CN(+He) \rightarrow O_2^+ \cdot CH_3CN(+He) \qquad (11a)$$

$$\rightarrow CH_3CN^+ + O_2 \qquad (11b)$$

However, a small fraction of the product distribution was the result of endothermic charge transfer [reaction (11b)], but also the collisional association reaction (11a) occurred, resulting in the adduct ion indicated. It seems certain that in this reaction charge transfer, complexing occurs because of the proximity of the ionisation potentials of O_2 and CH_3CN (see also reaction (7)). The branching ratio is not given for this reaction in Table 2 because of its complexity; the ratio is dependent on the helium pressure and is distorted by the occurrence of secondary reactions of the product ions of both reactions (11a) and (11b). In this regard, it is interesting to note that the adduct ion reacts with acetonitrile to generate its dimer ion thus:

$$O_2^+ \cdot CH_3CN + CH_3CN \rightarrow (CH_3CN)_2^+ + O_2 \qquad (12)$$

The production of the parent dimer ion does not occur as a result of the reaction (association) of the separated CH_3CN^+ with CH_3CN because this reaction is exothermic for the production of $CH_3CN \cdot H^+$ and the CH_2CN radical. Formation of parent dimer ions $(M)_2^+$, including $(H_2O)_2^+$ and $(CH_4)_2^+$, has been observed in the reactions of Kr_2^+ ions with some molecules M [24], which proceed first by the formation of the intermediate ions $Kr^+ \cdot M$, which then react with M to form $(M)_2^+$ ions.

4. Conclusions

These kinetic data relating to the reactions of H_3O^+, NO^+, and O_2^+ with a series of amines and some other organonitrogen molecules represent a significant contribution to the data base that is essential for our SIFT trace gas analytical method. The results of this study also reveal some interesting differences in the reactivity of the primary, secondary, and tertiary amines with our chosen reactant ions. Of note are the production of NH_4^+ in the reactions of some of the primary amines with H_3O^+ and ions like $(M\text{-}H)^+$ in the secondary and tertiary amine reactions. The low ionisation energies of amines ensure that charge transfer occurs in their reactions with NO^+, usually resulting in one or two products, commonly M^+ and $(M\text{-}H)^+$ ions. All but 1 of the 12 reactions of H_3O^+, NO^+, and O_2^+ with the more stable cyclic molecules aniline, benzonitrile, pyridine, and pyrrole result in a single product ion (sometimes the adduct ion), which facilitates their detection and quantification in air using our SIFT analytical method.

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