dictionaries of the formula are accurate within ±2 kcal/mol. Even complexes of a delocalized carbanion can be accommodated with a small correction of −3 kcal/mol. However, not surprisingly, the formula is not useful for complexes that are not properly hydrogen bonded, such as carbanions bonded to aprotic molecules.

After ∆H°∞solvent relations are accounted for, the intrinsic hydrogen-bonding strengths of proper carbanions, i.e., carbanions without heteroatoms, to protic solvent molecules are weaker by 4–8 kcal/mol than for carbanions with electronegative oxygen or nitrogen functions. In the latter, experimental trends are consistent with ab initio calculations, indicating that the hydrogen-donor bonds to the electronegative heteroatom.

In c-C₆H₄₊ and c-C₆H₅N⁺, trends in complexing energies suggest that the anionic aromatic π systems can serve as electron donors to protons and possibly to aprotic hydrogen-bonding ligands.

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Registry No. H₂NCH₃, 78-03-1; N₂H₅, 78-04-2; CH₃CN, 75-05-8; CD₃CN, 75-50-8; CH₂COCH₂, 67-64-1; c-C₆H₄NH₂, 109-57-7; c-C₆H₅O.

Distonic Ions as Reacting Species

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Abstract: The characteristic reactions of a family of distonic radical cations show that the gas-phase chemistry of these species differs considerably from that of the isomeric conventional molecular ions. Fifteen distonic radical cations, derived from "CH₂CH₂NH₂⁺" by introduction of alkyl substituents at C or N, have been demonstrated to be stable species whose reactions are the predominant fragmentation and isomerization processes of their structure. The particular structure and isomerization properties are the following: (i) simple cleavage of a C-N bond with formation of alkene ions or alkene molecules, and (ii) 1,2-migration of protonated amino groups, and (iii) formation of ammonium ions by elimination of alkenyl radicals. Chain length permitting, these reactions may be preceded or accompanied by specific intramolecular hydrogen abstraction reactions, which lead to isomeric distonic ions with characteristic different reactions. The hydrogen abstraction reactions are generally reversible, in the presence of long alkyl groups isomerization to amine molecular ions (et vice versa) can occur. Correspondingly, the reactions of many low-energy amine molecular ions require isomerization to distonic intermediates prior to fragmentation.

A considerable number of recent papers have demonstrated the existence in the gas phase of stable distonic radical cations, and distonic ions are with increasing frequency being suggested as key intermediates in unimolecular fragmentation reactions.

The collision-induced reactions of these species have often been used to establish their structural integrity, but the question of how the particular properties of distonic ions influence their reactions has not been addressed in the literature. We have studied the isomerization and dissociation reactions of a family of distonic amine ions, in order to discover the characteristic reactions of these species and to examine the difference between these reactions and those of the corresponding conventional molecular ions.

The term distonic was coined by Radom and co-workers to describe radical cations arising (formally) by ionization of zwitterions or diradicals. The difference between the properties of stable distonic ions and those of conventional molecular ions generated by direct ionization of neutral molecules can be considerable, and Radom's neologism has rapidly gained acceptance among gas-phase ion chemists. However, the properties of distonic ions often vary with the number of heavy atoms separating the charge and radical bearing sites. In the present paper we employ the adjectives α-distonic, β-distonic, γ-distonic, etc., to denote respectively species with charge and radical at adjacent atoms (α-distonic ions or ylions, e.g., 1), with charge and radical separated by one heavy atom (β-distonic ions, e.g., 2), by two heavy atoms (γ-distonic ions), etc.

Recent experimental and ab initio studies of various CH₂NH⁺ and C₅H₅N⁺ isomers have shown that α- and
Distonic Ions as Reacting Species

β-distonic ions such as 1 and 2 exist alongside their conventional counterparts and that there are high energy barriers toward interconversion. Distonic amine ions with charge and radical position further separated also exist in potential wells, but the energy barriers for isomerization to conventional amine molecular ions (et vice versa) are in these cases lower.14,21 Neutralization-reionization studies14 have shown that the C3H9N+ ion population that exists microseconds after electron ionization of propylamine is a mixture of ions with conventional and distonic structure (eq 1). Similar conclusions were reached in studies of other low molecular weight amines.14,20

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NH}_2^+ & \rightarrow \text{CH}_3\text{CH}_2\text{NH}^+ + \text{H}_2^+ \\
\text{C}_2\text{H}_5\text{NH}_2^+ & \rightarrow \text{C}_2\text{H}_5\text{NH}^+ + \text{H}_2^+
\end{align*}
\]

In this study the experimental strategy has been to examine the reactions of a relatively large number of distonic ions, to study the characteristic properties of these species, rather than to examine the fragmentation of individual ions in great detail. In general, distonic ions have no corresponding stable neutral molecule. For this reason distonic ions cannot be produced by direct ionization of suitable precursor molecules but must be formed by isomerization or fragmentation processes. The distonic ions examined in the present study were generated in the mass spectrometer ion source by fragmentation of alkoxyalkylamine molecules. For this reason distonic ions cannot be produced by ions examined in the present study were generated in the mass spectrometer ion source by fragmentation of alkoxyalkylamine (see eq 2 for an example). Alkoxyalkylamines were chosen as specifically substituted or isotope labeled distonic ions. The target ion yield26 and because they can be readily tailored to yield precursor molecules because they produce the distonic ions in high yield26 and because they can be readily tailored to yield specifically substituted or isotope labeled distonic ions. The target ions were separated from other ionic species by the magnetic (mass) analyzer of a double focusing mass spectrometer with reversed geometry. The spontaneous and collision-induced reactions were studied in the field-free region between the magnetic and electric sectors.

Previous experimental studies have shown that the β-distonic ion \(\text{C}_3\text{H}_7\text{N}^+=\text{(2)}\) is formed from 2-alkoxyethylamine molecular ions and that ion 2 can also be formed from a number of other precursors.21,23 Results presented by Eckhardt26 indicate that fragmentation of 2-alkoxyethylamines and 3-alkoxypropylamines in general yields β- and γ-distonic ions. This is confirmed by the spontaneous and collision-induced reactions of the product ions examined in the present study. The identity of the ions has been further confirmed by isotope labeling and by comparison of the Collision Induced Dissociation spectra (CID spectra) of the distonic ions with the CID spectra of isomeric conventional molecular ions.

**Experimental Section**

Mass analyzed Ion Kinetic Energy spectra (MIKE spectra) and CID spectra were recorded on a ZAB-2F mass spectrometer (VG Analytical, Manchester, UK) under standard operating conditions (electron energy 70 eV, trap current 100 μA, accelerating voltage 6 kV, ion source temperature 180-190 °C, nominal ion source pressure 2-5 × 10⁻⁷ Torr). Samples were introduced from a septum inlet heated to 150-200 °C. Mass analyzed Ion Kinetic Energy spectra (MIKE spectra) and CID spectra were recorded on a ZAB-2F mass spectrometer (VG Analytical, Manchester, UK) under standard operating conditions (electron energy 70 eV, trap current 100 μA, accelerating voltage 6 kV, ion source temperature 180-190 °C, nominal ion source pressure 2-5 × 10⁻⁷ Torr). Samples were introduced from a septum inlet heated to 150-200 °C. Spectra were recorded at both low and high ionizing energy, as a probe for the possible presence of mixtures of isobaric parent ions.27 Where two ions of the same nominal mass were present it was in most cases possible to suppress the ion of lower exact mass (probably oxygen con-
The collision-induced alkene loss (eq 10) is an important and structurally significant reaction also for β-distonic ions with long N-alkyl substituents, even though the relative importance of alkene loss diminishes as the alkyl chain increases. In addition, these ions show a number of reactions initiated by intramolecular hydrogen abstraction (eq 6–8), which are also among the spontaneously occurring processes. The major difference between the MIKE and CID spectra in these cases consists in the peaks corresponding to ions resulting from collision-induced alkene loss. Cleavage of the carbon–heteroatom bond also gives rise to abundant ions in the collision-induced reactions of related distonic ions,5–9 such as \( \text{CH}_3\text{CH}_2\text{CH}_2\text{H}^+ \) and \( \text{CH}_3\text{CH}_2\text{CH}_3\text{H}^+ \).

Fragmentation of \( \beta \)-substituted neutral radicals is a well-described reaction,10 which is often reversible. Also the alkene elimination from \( \beta \)-distonic ions is reversible; the reverse process, addition of alkene to amine radical cations, has been observed in bimolecular gas-phase reactions as well as in condensed phase.

Many small \( \alpha \) and \( \beta \)-distonic ions form doubly charged ions upon collision that show up as intense narrow peaks in the CID spectra.12,13,32 These peaks are not prominent for conventional molecular ions.33 Among the distonic ions examined in the present study only the ions without \( N \) substituents give rise to abundant doubly charged ions.

### Spontaneous Unimolecular Reactions. Formation of Ammonium Ions.

\( \beta \)-Distonic ions with a free \( \text{NH}_3^+ \) group (13–17) react with formation of ammonium ions, \( \text{NH}_4^+ \). This reaction proceeds specifically by transfer of a \( \gamma \)-hydrogen atom; in particular, fragmentation of the \( \alpha \)-labeled ion, \( \text{(CH}_3\text{)}_2\text{CD}_2\text{NH}_3^+ \) (15a), gives rise exclusively to unlabeled ammonium ions (eq 12). N-Substituted \( \beta \)-distonic ions form alkylammonium ions provided that \( \gamma \)-hydrogen atoms are available (eq 13). Analogously, \( \text{N,N-dialkyl} \) \( \beta \)-distonic ions give rise to \( \text{N,N-dialkyl ammonium ions (e.g.,} \) \( \text{C}_3\text{H}_7\text{H}^+\text{NH}_2\text{CH}_3 \) is formed from 12).

\[
\begin{align*}
\text{CH}_3\text{CD}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ & \rightarrow \text{CD}_2\text{NH}_2\text{CH}_3^+ + \text{CH}_3^+ \quad (12) \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CD}_2\text{NH}_3^+ & \rightarrow \text{CD}_2\text{NH}_2\text{CH}_3^+ + \text{CH}_3^+ \\
\text{C}_3\text{H}_7\text{H}^+\text{NH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CD}_2\text{CH}_2\text{CH}_2\text{NH}_2^+ \\
\end{align*}
\]

### Alkene Loss. Spontaneous elimination of a neutral alkene molecule proceeds in high yield for \( \text{N,N-dialkyl} \) \( \beta \)-distonic ions. The most abundant product ion formed from \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ \) (11) arises by loss of ethylene, and the homologous ion, 12, loses \( \text{C}_2\text{H}_4 \) after 1,5-hydrogen migration to give the second most abundant product ion. The fragmenting \( \beta \)-distonic ion is in this case formed by isomerization of the initial \( \beta \)-distonic ion prior to fragmentation, as shown in eq 14.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}^=\text{CH}_2 + \text{NH}_3^+ \\
\]

Alkene loss proceeds in lower yield for \( \beta \)-distonic amine ions with only one \( N \)-alkyl group (3–10), possibly owing to the higher energy requirements for formation of an alkene molecule and a primary amine radical cation. A more favorable reaction for the \( \text{N,N-dialkyl} \) \( \beta \)-distonic ion is loss of an \( \alpha \) radical from the \( \alpha \)-distonic ion formed after 1,4-hydrogen atom transfer (eq 6; see also below).

Spontaneous alkene loss is not observed for \( \beta \)-distonic ions with a free \( \text{NH}_3^+ \) group.

### 1,2-Migration of Protonated Amino Groups.

A previous study13 has provided unambiguous experimental evidence for the occurrence of the \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ \) ion (eq 15) as \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2^+ \) and \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}^=\text{CH}_2 \) (eq 16). The reaction involves \( \alpha \)–\( \gamma \) migration of the protonated amino group, which is a characteristic feature of the unimolecular reactions of \( \beta \)-distonic ions.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CH}^=\text{CH}_2 + \text{NH}_3^+ \\
\end{align*}
\]


---


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Figure 2. MIKE and CID spectra of 'CH3CD2NH2CH2CH3 (5a). m/z 89. m/z 60: loss of 29 (C2H5) from CH3CD2NHCH2CH3. m/z 59: loss 30 (CH3CD2+) from CH3CD2NHCH2CH3. m/z 58: loss 31 (CH3CD2+) from CH3CD2*NH2CH2CH3 after a 1,4-H shift. m/z 48: loss 41 (C3H7+) from CH3CD2*NH2CH2CH3 after 1,5-H shift. m/z 47: loss 42 (C3H6) from CH3CD2*NH2CH2CH3 after 1,5-H shift, primarily CID. m/z 46: 1,2-RNH2 migration. (b) Successive 1,5; 1,6; and 1,4 H-shifts. (c) 1,2-RNH2 migration. (d) Successive 1,5; 1,6; and 1,4 H-shifts.

Figure 3. Enlargement of the m/z 58 peak in the MIKE spectrum of 'CH3CD2*NH2CH2CH3 (9a).

result in loss of ethyl radicals. Examination of the reactions of the deuterium labeled analogue, *CH3CD3*NH2CH(CH3)2 (9a), confirms this; loss of C2H5* as well as C2H3D* is observed. The latter reaction occurs via an α-distonic isomer formed by a 1,4-H shift (cf. eq 18). Elimination of the unlabeled ethyl group requires a multistep isomerization involving 1,2-migration of the protonated alkylamino group within the tertiary isopropyl group (eq 16). A closely analogous sequence of reactions precedes loss of C2H5* from *CH3CD3*NH2CH(CH3)2 (10), which does not possess a readily expelled C2 fragment.

A similar reaction was reported for the oxygen analogue: CH3CH2*OCH3, to a 1-methylalkyl group, CH3(CH3)R; loss of the radical (R) is an α-cleavage of the isomerized ion (eq 22). These reactions are discussed in more detail below.

The loss of C2H5* from CH3CD2*NH2CH(CH3)2 (12) shows that also 1,2-migration of protonated dialkylamino groups occurs, in competition with other low-energy reactions.

Intramolecular Hydrogen Abstraction. Many fragmentation reactions of β-distonic ions with long N-alkyl chains is loss of an alkyl radical from the β-carbon atom in the N-alkyl group. The key step in this reaction is 1,2-migration of the amino group, which converts the N-alkyl substituent, CH3CH2R, to a 1-methylalkyl group, CH3CH(R); loss of the radical (R) is an α-cleavage of the isomerized ion (eq 22). These reactions are discussed in more detail below.

The reactions of α-distonic ions require initial isomerization by hydrogen atom abstraction, which converts β-distonic ions to isomeric distonic species (eq 6–8). The presence of these isomers, in particular of more than one α-distonic ion, is shown by the CID spectra (see below); the intermediacy of α- and γ-distonic isomers can be inferred from the unimolecular reactions of ions that are initially β-distonic species.

1,4-Abstraction of an α-hydrogen atom from the N-alkyl chain of N-substituted β-distonic ions results in formation of an intermediate α-distonic ion (eq 6), which expels an alkyl radical by simple cleavage of the C–N bond (eq 17). For CH3CH2*NH2CH3 (3) this process gives rise to the most abundant product ion. The reactions of the CD3 analogue (3a) (eq 17) show that the hydrogen abstraction is specific and apparently not readily reversible: one deuterium atom is transferred from the methyl group, accompanied by very little hydrogen/deuterium exchange. The α-distonic intermediate is expected to be a stable species; however, it possesses considerable internal energy when formed via 1,4-hydrogen abstraction (see below) and therefore reacts rapidly by simple fission of the C–N bond. Analogous behavior is observed for ions with longer N-alkyl groups (4–6, 9), that is, loss of CH3CD3* from the labeled ions 4a–6a and loss of CH3CD3* from 9. A similar reaction was reported for the oxygen analogue, *CH3CH2*OCH3; cleavage of the carbon-heteroatom bond in


other α-distonic ions has also been observed.8,32

The absence of H/D exchange prior to alkyl loss from 3a indicates that the rate-limiting step is the hydrogen abstraction and not the subsequent C-N cleavage (eq 17). For the N,N-diethyl analogue, *CH2CH2+NH(CD3), isomer loss is favored over alkyl loss by a factor of 20. These reactions are likewise not accompanied by H/D exchange (m/z 51:50:49 = 20:1:1). The specific loss of DCH2CH2* also from 11a confirms that hydrogen abstraction is followed immediately by alkyl loss. This indicates that the competition between alkyl and alkene loss is governed by the heats of formation of the products, which are in all cases slightly lower for the alkyl loss (by 10–40 kJ/mol).34 The energy barrier for alkene loss from 3 and 11 can be estimated from the reaction thermochemistry to be 160 and 120 kJ/mol, respectively, plus any critical energy for the reverse reaction (the addition of an amine cation radical to an alkene). The energy barrier for 1,4-hydrogen abstraction must be less than that for alkene elimination, since alkyl loss competes successfully even though it has a tighter transition state. This is supported by studies showing that 1,4-hydrogen atom abstraction reactions in alkyl radicals9 have critical energies around 90 kJ/mol.

\[
\text{C}^+\text{H}_2\text{CD}_2\text{NH}^+ \rightarrow \text{DCH}_2\text{CH}_2\text{NH}_2^+ + \text{CH}_3
\]

Loss of the alkyl group in reactions analogous to eq 17 often results in broad metastable peaks (see Figures 2 and 3), indicating an energy barrier for the reverse reaction (T_d = 10–20 kJ/mol). The presence of this barrier could be taken to indicate a more complicated reaction pathway than simple cleavage of the α-distonic ion. One possibility would be that 1,2-alkyl migration from nitrogen to carbon in the α-distonic intermediate gives rise to a conventional amine molecular ion, for which alkyl radical loss (by cleavage) is the expected reaction. 1,2-Alkyl migration from the heteroatom has been described for other α-distonic ions,8 but reactions of this kind do not seem to take place for distonic amine ions; deuteron labeling demonstrates that the two ethyl groups in 5a have not become equivalent prior to ethyl loss (eq 18). Either ethyl group may be expelled, but the shapes of the corresponding metastable peaks are strikingly different, indicating different fragmentation pathways (note the m/z 58 and 60 peaks in Figure 2). This strongly suggests that loss of the deuterated ethyl group occurs directly by C-N cleavage in the α-distonic intermediate, while the unlabeled ethyl group is lost after isomerization to the corresponding secondary amine molecular ion (see below, eq 21). The presence of an energy barrier for the reverse reaction has been suggested to be a general phenomenon for alkyl radical loss from α-distonic ions and related species.40

\[
\text{CH}_3\text{C}^+\text{H}_2\text{NH}_2^+ \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2^+ \rightarrow \text{CH}_3\text{CH}_2\text{H} + \text{NH}_2^+ + \text{H}^+
\]

Isomerization by 1,5-hydrogen abstraction converts N-alkyl α-distonic ions to isomeric β-distonic species (eq 7 and 19). Either can react by C-N cleavage, and loss of both alkene fragments are important collision-induced reactions for 4, 5, 9, and 12, demonstrating that isomerization proceeds efficiently prior to dissociation (eq 19; see also Figure 2). Reactions proceeding by 1,4-hydrogen abstraction are also observed for the β → β' isomerized species, as illustrated by the loss of the isopropyl group from *CH2CH2*NH2CH3 (eq 19). Loss of the isopropyl group from the labeled analogue *CH2CD2*NH2CH3 (9a) leads to ions of m/z 45 and 46 in approximately a 1:1 ratio. The transfer of either H or D shows that 1,2-migration of the protonated amino group in the initial β-distonic ion can precede 1,5-hydrogen abstraction. Ions 4 and 5 exhibit similar behavior.

The heavy-atom skeleton is changed as a result of 1,2-migration of the amino group in the β-distonic ion formed by 1,5-hydrogen transfer; this is discussed further below.

\[
\beta \rightarrow \beta'
\]

1,6-Hydrogen abstraction leads for 5–8 to γ-distonic ions (eq 8 and 21). These do not undergo characteristic direct fragmentation reactions; indeed, there is no unambiguous evidence to show that they are other than short-lived intermediates when formed by isomerization of β-distonic ions. However, isomerization to γ-distonic species opens an additional reaction channel, namely isomerization of distonic ions to the corresponding amine molecular ions (eq 21). Reactions typical of the latter—in particular a-cleavage, which for the deuteriated species in Table I leads predominantly to ions of m/z 60—are observed for ions with N-alkyl groups longer than ethyl (5–8, 12), that is, when formation of a γ-distonic ion is possible. By contrast, a-cleavage (methyl loss) is not observed for 4a, nor for 3 or 11. It seems that isomerization to conventional amine molecular ions requires at least a 5-membered cyclic transition state for intramolecular abstraction of the nitrogen-bonded hydrogen atom in order to compete with other low-energy reactions.

Confirmation of the occurrence of 1,4-hydrogen transfer from nitrogen to carbon comes from the reactions of γ-distonic ions formed by fragmentation of 3-alkoxypropylamines (18–20, eq 9). The MIKE and CID spectra of these γ-distonic ions are nearly identical with the spectra of the corresponding amine molecular ions (Table II).

\[
\beta \rightarrow \gamma
\]

Formation of γ-distonic ions by isomerization of long-chain β-distonic ions may be preceded by skeletal rearrangement—1,2-migration of the protonated amino group after 1,5-hydrogen abstraction—and the fragmentation of 6–8 shows that two different amine molecular ions are in fact formed. The MIKE spectrum of 8a (Figure 4a) illustrates that both processes are efficient; the two most intense peaks correspond to loss of C,H9+ from ions with an intact hexyl group and loss of C,H9+ from ions with a 1-methylpentyl group (eq 22).

Rearrangement to amine molecular ions is in some cases possible even for ions that do not, initially, possess γ-hydrogen atoms. The
Distonic Ions as Reacting Species

Reactions leading to loss of C_2H_5* from 9a (eq 16) and of C_3H_5* from 10 illustrate that 1,2-migration of the protonated amino group can prepare the way for such isomerization reactions.

C alkyl β-distonic ions show analogous behavior: the short-chain ions 13-16 do not isomerize to conventional amine molecular ions. In fact, no reactions common to the distonic and conventional radical cations are observed. The presence of longer alkyl chains (as in C_6H_5CHCH_3NH_3*) (17) makes 1,4-hydrogen abstraction possible, given that 1,2-migration of the amino group occurs. The predominant product ion, CH_3CH=NH_3*, is formed by α-cleavage of the intermediate sec-alkylamine molecular ion (eq 23).

Low-Energy Amine Molecular Ions React via Distonic Intermediates. The formation of amine molecular ions as intermediates prior to fragmentation of long-chain distonic amine ions does not demonstrate that the initial distonic ion population has to a large extent isomerized to ions of conventional structure. Isomerization to the latter occurs only en route to fragmentation. Most of the distonic ions examined in the present study are lower in energy than the corresponding amine molecular ions, and the collision-induced reactions of long-chain distonic ions include processes that are not observed for amine molecular ions, whereas the converse does not apply. Extensive isomerization to ions of conventional structure is not even observed for 'CH_2CH_2+NH_3' (17).

The only reaction observed for low-energy tertiary amines is the conversion of conventional and distonic isomers, regardless of the initial structure of the reactant ions, is particularly obvious when the chain length permits intermediate formation of primary amine molecular ions and their conventional counterparts, CH_3CD,NHC_6H_5*+, illustrate this point (Figure 4). The spectra are almost identical, differing slightly in peak intensities, which indicates that the same mixture of reacting ions is formed. In particular, the formation of abundant ions by loss of C_2H_5* from both precursors is a direct consequence of isomerization by 1,2-migration of the protonated amino group (eq 22).

The intermediacy of α-distonic isomers in the reactions of amine molecular ions is illustrated by the fragmentation of low-energy N-isopropylpentylamine molecular ions, where the second most abundant product ion (m/z 58) arises by direct loss of C_2H_5*.

Cleavage of the C-N bond is not commonly encountered for amine molecular ions, but it is a characteristic reaction of α-distonic ions (see above). Deuterium labeling confirms that the reaction proceeds via an α-distonic intermediate as shown in eq 24; the fragmentation of neither the α,α-dideuteriated nor the α'-deuterated analogues results in deuterium incorporation in the m/z 58 product ion.
Excited Stares; Chapter

Table I. MIKE Spectra of N- and C-Alkyl 5-Distonic Ions

| Ion | m/z | 11 | 100 | 88 | 86 | 74 | 73 | 72 | 60 | 59 | 58 | 48 | 47 | 46 | 45 | 44 | 31 | 30 | 18 | 17 | 15 |
|-----|-----|----|-----|-----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 3 5NH2C6H5 | 59 | 11 | 100 | 90 |
| 4
| 5NH2C6H5 | 75 | 25 | 100 |
| 5 5NH2C6H5 | 89 | 25 | 100 |
| 6 5NH2C6H5 | 110 | 25 | 100 |
| 7 5NH2C6H5 | 117 | 25 | 100 |
| 8a 5NH2C6H5 | 131 | 25 | 100 |
| 9 5NH2C6H5 | 87 | 100 |
| 10 | 89 | 100 |
| 11 | 101 | 100 |
| 12 | 7a | 100 |
| 13 | 59 | 100 |
| 14 | 59 | 100 |
| 15 | 59 | 100 |
| 16 | 59 | 100 |
| 17 | 73 | 100 |
| 18 | 73 | 100 |
| 19 | 73 | 100 |
| 20 | 73 | 100 |

Table II. CID Spectra of 5-Distonic Ions and C-Alkyl 5-Distonic Ions

| Ion | m/z | 45 | 44 | 43 | 42 | 41 | 40 | 39 | 38 | 37 | 36 | 35 | 34 | 33 | 32 | 31 | 30 | 29 | 28 | 27 | 16 | 15 |
|-----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 13 | 5NH2C6H5 | 59 | 10 | 100 | 70 | 10 | 6 | 5 | 25 | 5 | 20 | 15 | 8 | 175 | (15) | 5 |
| 14 | 5NH2C6H5 | 59 | 3 | 14 | 6 | 100 | 55 | 9 | 5 | 5 | 4 | 10 | 11 | 5 | 110 | 9 | 5 |
| 15 | 5NH2C6H5 | 59 | 10 | 44 | 96 | 13 | 68 | 15 | 7 | 100 | 800 | 19 | 57 | 37 | 19 | 63 | 22 | 10 |
| 16b | 5NH2C6H5 | 59 | 11 | 43 | 84 | 11 | 65 | 13 | 7 | 100 | 1400 | 24 | 63 | 37 | 19 | 49 | 15 | 8 |
| 17 | 5NH2C6H5 | 59 | 12 | 43 | 56 | 11 | 65 | 13 | 7 | 100 | 1400 | 24 | 63 | 37 | 19 | 49 | 15 | 8 |
| 18b | 5NH2C6H5 | 59 | 12 | 43 | 56 | 11 | 65 | 13 | 7 | 100 | 1400 | 24 | 63 | 37 | 19 | 49 | 15 | 8 |

Conclusions

Distant ions are charged radicals. The characteristic reactions of distant amine radical cations all involve the radical site directly, and the isomerization and fragmentation processes observed are closely related to well-described reactions of neutral radicals.

This applies in particular to the reactions involving C=N cleavage immediately adjacent to the radical site in o- and β-distant ions, and to the intramolecular hydrogen atom abstraction with five-membered or larger cyclic transition states. Further, 1,2-migration of a protonated amino group to a neighboring radical site has been established as a novel and general radical rearrangement, in many ways analogous to the well-known 1,2-migration of halogen atoms in β-substituted haloalkyl radicals. It may play a part in counterion H⁺-induced rearrangements, and we expect that it will be observed also in other radical reactions in the condensed phase.

It has been suggested that some putative distant ions should be considered, instead, as ion–molecule complexes, bonded primarily by electrostatic interactions. Our results do not support this view for distant amine ions. Consensus seems not to have been reached with regard to the predictions that can be derived from models involving intermediate ion–molecule complexes, nor have unambiguous criteria to establish the intermediacy of such complexes been proposed. However, neither the existence of an appreciable barrier to 1,2-NH₃ migration in 14 nor the specific γ-hydrogen transfer in 15 would seem compatible with description of β-distonic ions as alkene radical cations loosely bonded to amines. This is in agreement with computational results for ion 2, which predict a "normal" C=N bond length (1.53 Å) and a substantial barrier to the 1,2-NH₃ migration (120 kJ/mol).

The heat of formation calculated for 2 lies considerably below that estimated for a [C₆H₄• + NH₃]+ complex bonded only by electrostatic interactions between alkene and ammonia. Finally, our results show that only distant amine ions with long alkyl substituents isomerize below the threshold for decomposition to the corresponding amine molecular ions. Isomerization is reversible, and the low-energy fragmentations of many amine molecular ions in fact turn out to be reactions of the distonic amine radical cations all involve the radical site directly, and the isomerization and fragmentation processes observed are closely related to well-described reactions of neutral radicals.
Secondary Hydrogen Isotope Effects on Simple Cleavage Reactions in the Gas Phase: The α-Cleavage of Tertiary Amine Cation Radicals

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Abstract: Intramolecular secondary hydrogen isotope effects on the α-cleavage reaction of 14 unsymmetrically deuterium labeled tertiary amine cation radicals have been determined in order to probe the variation of the isotope effect with the distance to the rupturing carbon–carbon bond, with the structural basis of the radical lost, and with the internal energy of the reactant. The low-energy molecular ions exhibit normal isotope effects (i.e., predominant loss of the unlabeled alkyl radical), which are highest for β-labeled ions (1.30 per deuterium) and decrease with increasing distance between the isotope label and the point of rupture; significant effects are observed even for deuterium substitution four bonds removed (1.04 per deuterium for t-labeled ions). The isotope effects are relatively small and normal for molecular ions with high internal energy, with one exception: the secondary isotope effect on the fast (ion-source) reactions of the δ-labeled N-methyldipentylamine is inverse (0.98 per deuterium). The structure of the alkyl radical lost seems not to have a pronounced influence on the secondary isotope effects.

Isotope effects are often encountered in studies of the reactions of gaseous positive ions. Structural and mechanistic information has in most instances been derived from the observation of primary hydrogen isotope effects; conclusions have, in some cases, been based on the (implicit) premise that secondary isotope effects are generally relatively small and can be neglected. This may often not be a valid assumption, given that appreciable secondary isotope effects are observed even for deuterium substitution four bonds removed (1.04 per deuterium for t-labeled ions). Intramolecular secondary isotope effects have been described for loss of methyl radicals from the molecular ions of alkylbenzenes,5,6 for elimination of methane from the propane and 2-methylpropane cation radicals,10 and for elimination of 2-methylbutyrate ions in the gas phase.14 Isotope labeling influences the rates of the reactions of cation radicals, in many cases through a combination of primary and secondary isotope effects. Mechanistic conclusions often depend on the ability to distinguish between the relative contributions from primary and secondary effects, but a quantitative distinction can be difficult; even qualitative estimates can be difficult to make, in the absence of systematic experimental studies of secondary hydrogen isotope effects. We have therefore investigated the influence of deuterium substitution on simple cleavage reactions of cation radicals, to determine the variation of secondary hydrogen isotope effects with the distance to the bond cleavage, with the structure of the alkyl radical lost, and with the internal energy

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