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CHEMICAL IONIZATION MASS SPECTROMETRY II.[1]

DIFFERENTIATION OF PRIMARY, SECONDARY, AND TERTIARY AMINES

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In chemical ionization (CI) mass spectrometry the sample molecule under investigation is ionized in the gas phase by an ion-molecule reaction rather than by the conventional electron impact process.[2] As part of a research effort to explore the utility of CI mass spectrometry in the structure elucidation of organic compounds, we have recently studied the gas phase reactions of the ammonium ion, NH_4^+, with a variety of organic species. In this report we describe a relatively simple procedure for differentiating between primary, secondary, and tertiary amines using this reagent ion and its deuterated analog, ND_4^+.

When ammonia is bombarded with high energy electrons (500eV) at a pressure of 0.5 torr, abundant ions are produced at m/e values corresponding to NH_4^+ (m/e 18), $(NH_3)_2H^+$ (m/e 35), and $(NH_3)_3H^+$ (m/e 52).[3] Electron bombardment of

$$NH_3 + e^- \longrightarrow NH_3^{+\cdot} + 2e^-$$

$$NH_3^{+\cdot} + NH_3 \longrightarrow NH_4^+ + NH_3^{\cdot}$$

$$NH_4^+ + NH_3 \longrightarrow (NH_3)_2H^+$$

d_3-ammonia affords a similar set of ions corresponding to ND_4^+ (m/e 22), $(ND_3)_2D^+$ (m/e 42), and $(ND_3)_3D^+$ (m/e 62).

Each of the above ions functions as a Bronsted acid toward simple aliphatic and aromatic amines. Thus, when a sample of 2,6-dimethylaniline (1) is vaporized into the ion source containing ammonia at 0.5 torr, the spectrum shown in Figure 1 results.* Peaks derived from 1 occur at m/e 122 (M+1) and 139 ($M+NH_4^+$). No fragment ions are produced. When d_3-ammonia is used as the reagent gas, the latter two ions appear in the spectrum at m/e 125 (d_2-1 + D^+) and 145 (d_2-1 + ND_4^+). Thus, each of the hydrogen atoms attached to the nitrogen atom in the primary amine are exchanged for deuterium, and D^+ or ND_4^+ then adds to the resulting deuterated derivative.

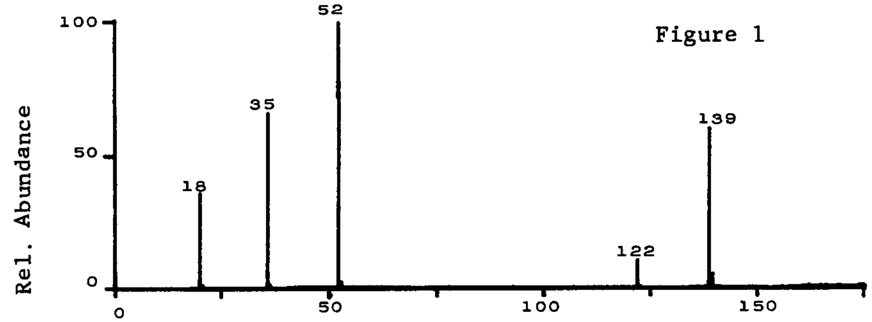
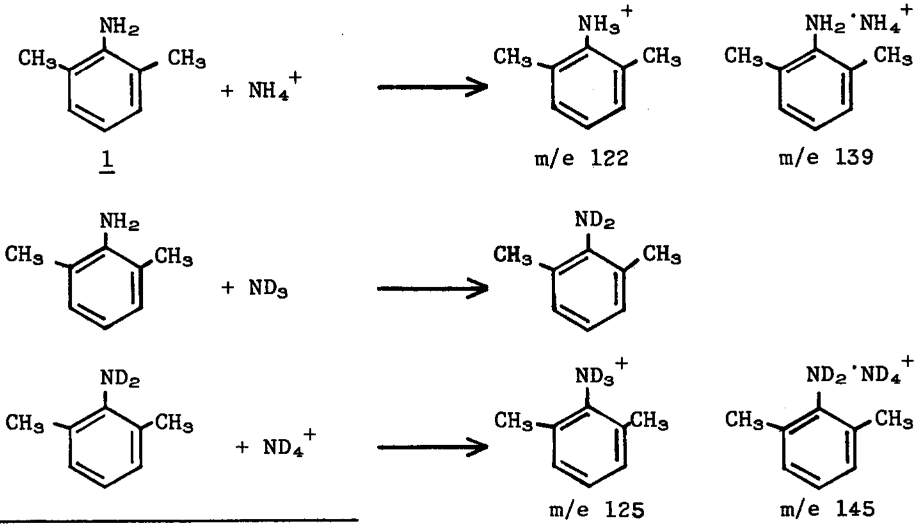


Figure 1



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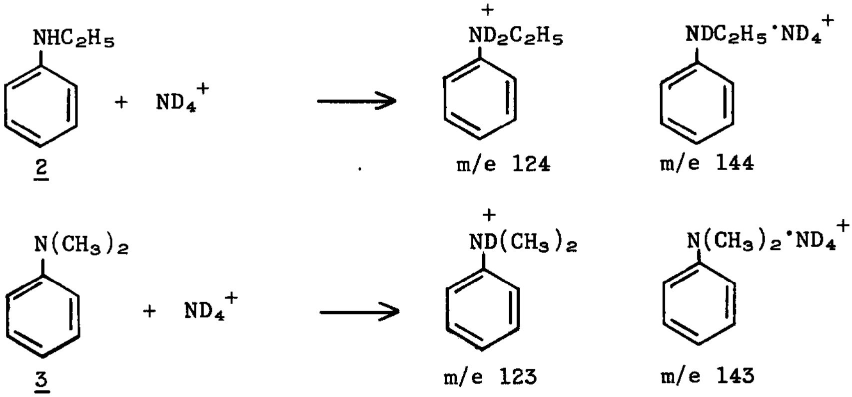
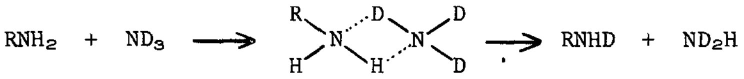
* All mass spectra were obtained at a resolution of 5000 and source temperature of 150-200° using an AEI MS-902 mass spectrometer. This instrument is equipped with a dual CI/EI ion source manufactured by Scientific Research Instrument Corporation, Baltimore, Md.

The CI spectrum of the isomeric secondary amine, N-ethyl aniline (2), also exhibits peaks at m/e 122 and 139 when ammonia is employed as the reagent gas. With d_3-ammonia, however, the same ions appear at m/e 124 and 144 since there is only one exchangeable hydrogen in 2. The tertiary amine, N,N-dimethylaniline (3), has no exchangeable hydrogens and affords spectra containing ions at m/e 122 and 139 with ammonia and 123 and 143 with d_3-ammonia as reagent gases. Thus, as a result of rapid isotopic exchange in the CI source, it is possible to differentiate simple primary, secondary, and tertiary amines (using μg quantities of sample) by obtaining two CI mass spectra, one with NH_4^+ and the other with ND_4^+ as reagent ions. No exception to this generalization has been found in any of the more than two dozen simple amines that have been examined to date.



In the d_3-ammonia CI spectrum of β-aminoethanol abundant ions appear at m/e 66 and 86 indicating that all three hydrogens bonded to oxygen and nitrogen are exchanged for deuterium in the ion source. Since M+1 and $M+NH_4^+$ ions are not observed in the ammonia CI mass spectrum of simple alcohols, the exchange reactions discussed above probably involve a hydrogen-bonded intermediate such as 4 rather than a multistep protonation-deprotonation sequence.



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Additional studies are planned using other deuterated reagents such as D_2O, CH_3OD, $(CD_3)_2CO$, CD_3NO_2 and D_2.

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