ABSTRACT

A mass spectrometer of the type Atlas CH-4 is used in combination with deconvoluted first differential (DFD) technique in order to investigate the ionization efficiency (IE) curves for molecular ions $[C_2H_7N]^{+\cdot}$, $[C_4H_{11}N]^{+\cdot}$ and $[C_6H_{15}N]^{+\cdot}$ as well as $[CH_4N]^+$, $[C_2H_6N]^+$ and $[C_3H_8N]^+$ fragment ions produced from the three molecules, namely ethylamine, diethylamine and triethylamine. All the studied IE curves are measured for about 3.5 eV above threshold.

The relative intensities of the prominent ions in the mass spectra of the three amine molecules are reported at 70 and 14 eV. The effect of branching groups on the intensity of different fragment ions is discussed. Metastable peaks associated with formation and fragmentation of the studied fragment ions are also reported, and the kinetic energy released ($T_{0.5}$) values associated with these processes are determined.

The values of ionization energies at threshold are measured at 8.95±0.07, 8.15±0.08 and 7.63±0.07 eV for ethylamine, diethylamine and triethylamine, respectively, and are explained as due to removal of one of lone pair electrons of the nitrogen atom. Also, higher molecular energy levels have been detected in the ionization energy (IE) curves of the molecular ions of the three molecules and some of these levels are compared with other works. Appearance energies (AE,s) of the studied fragment ions are measured and reported at threshold and possible fragmentation processes for the formation of these ions have been suggested.

Modified Neglect of Diatomic Overlap (MNDO) calculations have been carried out on the three precursors to calculate the charge distribution on different atoms in order to interpret some of the fragmentation mechanisms.

Thermodynamical threshold ($\Delta E_{th.}$) values are calculated and used together with AE data as well as kinetic energy released ($T_{0.5}$) values in order to shed some light on the structure of the studied fragment ions

The results may indicate that at threshold $[CH_4N]^+$ (m/z = 30) fragment ions obtained from ethylamine are formed with methaniminium $[CH_2NH_2]^+$ structure whereas the ions are formed from diethylamine and triethylamine with methylnitrinium $[CH_3NH]^+$ structure. The $[C_2H_6N]^+$ (m/z =44) ions generated from ethylamine and diethylamine at threshold are formed with ethaniminium structure whereas the ion formed from triethylamine with β-aminoethyl structure. The $[C_3H_8N]^+$ (m/z = 58) fragment ions formed from the diethylamine and triethylamine at threshold with ethylmethaniminium $[CH_3CH_2NH{=}CH_2]^+$ structure.

Finally, the kinetic energy release ($T_{0.5}$) values associated with fragmentation of metastable $[CH_4N]^+$, $[C_2H_6N]^+$ and $[C_3H_8N]^+$ fragment ions allow the following conclusions: (i) The metastable $[CH_4N]^+$ ions generated from the precursors appear to undergo loss of H_2 from a common structure. (ii) The metastable $[C_2H_6N]^+$ ions generated from the precursors appear to undergo loss of C_2H_2 from a common structure or mixture of structures. (iii) The metastable $[C_3H_8N]^+$ ions generated from diethylamine and triethylamine appear to undergo loss of C_2H_4 from a common structure or mixture of structures.