CHAPTER (1)

INTRODUCTION AND AIM OF THE WORK

1.1 Introduction

Mass spectrometry is one of the most successful and powerful tool for identification and structural analysis of organic compounds. The basis of the success of an analytical application of mass spectrometry is still the observation of the fragmentation of ionized and energized species in the gas phase. The essence of mass spectrometric structure analysis is the requirement that the fragmentation obey the rules of the reaction mechanisms developed for other types of organic reactions(1).

In mass spectrometry the fragmentation of molecular ions consists of a series of competitive and consecutive fragmentation. The structure elucidation needs some information about the path along which particular fragment ions are formed and also how many fragmentation steps are involved in their formation. Information concerning some individual steps involved can be gleaned from the observation of metastable peaks(2).

For the evaluation of critical energies (ε_o) and heats of formation (ΔH_f) of gaseous ions commercially available electron impact (EI) mass spectrometers may be used. One of the significant sources of errors in the measurements of ionization energy and appearance energy is the energy spread of electrons obtained from the heated filament and this effect can be overcome by using a suitable deconvolution methods(3-6).

Amine spectra(7) tend to be more complex since it is possible to have three-side chain on nitrogen atom. The nitrogen in amines strongly influences the fragmentation pattern observed for this class of compounds. This is due to the low electrophilic character of nitrogen in molecular ion; the nitrogen readily shares its odd electron during homolytic fission of adjacent bonds(8). A very important fragmentation process is cleavage at the bond β to nitrogen atom, with positive charge remaining on the nitrogen-containing fragment.

Inspection of the published work done on the mass spectra, ionization and fragmentation as well as structure elucidation of fragment ions obtained from ethylamine, diethylamine and triethylamine show that:-

1. The values of the ionization energy for the ethylamine, diethylamine and triethylamine at threshold were reported by many authors ; Collin(9,10), Morrison and Nicholson(11) and Melton and Hamill(12)using electron impact technique, Watanabe and Mottle(13) using Photoionization technique. The measurement of molecular ionization energies based on photoelectron spectroscopy for some aliphatic amine has been studied by some authors(14) . The first ionization energies and higher energy levels for ethylamine, diethylamine and triethylamine were measured by Al-Joboury and Turner(14a) pioneering in this field.

2- The appearance energies at threshold for $[CH_4N]^+$, $[C_2H_6N]^+$ and $[C_3H_8N]^+$ (obtained from diethylamine) ions produced from the precursors were measured by Lossing et al.(15) using an energy-resolved electron beam , Collin and Franskin et al(9,16,17) using electron impact technique for $[CH_4N]^+$and $[C_2H_6N]^+$ ions. Also, the AE at threshold for $[CH_4N]^+$ion produced from ethylamine was reported by Chupka(18) using photoionization technique, while, the $[C_2H_6N]^+$ ion produced from ethylamine and diethylamine was reported by Solka and Russell(19).

3- Lossing et al(15) had determined the gas-phase heats of formation (ΔH_f) of $[CH_2NH_2]^+$, $[CH_3CHNH_2]^+$, $[CH_3NHCH_2]^+$, $[CH_3CH_2CHNH_2]^+$ and $[CH_3CH_2NHCH_2]^+$ from their AE,s in ionic dissociations using energy-resolved electron beam.

1.2 Aim of the Work :

The aim of the present thesis is to use electron impact mass spectrometric technique in order to investigate ethylamine, diethylamine and triethylamine molecules from the following points of view:-

1. To record the mass spectra of the three molecules at 70 and 14 eV and to study the effect of branching ethyl group on the relative intensities of the common fragment ions obtained from the three molecules as well as to record the metastable peaks associated with the different fragmentation processes and to calculate the kinetic energy released ($T_{0.5}$) values associated with these peaks.

2. To investigate the ionization efficiency curves (IE) for molecular ions as well as $[CH_4N]^+$, $[C_2H_6N]^+$ and $[C_3H_8N]^+$ fragment ions produced from ethylamine, diethylamine and triethylamine using Deconvolution First Differential (DFD) technique. The investigation includes the determination of ionization and appearance energies at threshold as well as the higher energy levels in the IE curves of molecular ions.

3. To suggest the different fragmentation processes which are responsible for the formation of different fragment ions at threshold and to study the energetics of these processes. Further more, to use appearance energy values together with thremochemical calculations and kinetic energy released ($T_{0.5}$) values associated with metastable peaks in order to obtain some information about the structure of the studies fragment ions.

4. To use MNDO procedure to calculate the charge distribution on different atoms for neutral molecules and molecular ions in order to define the site of electron rupture and to interpret some fragmentation mechanisms.