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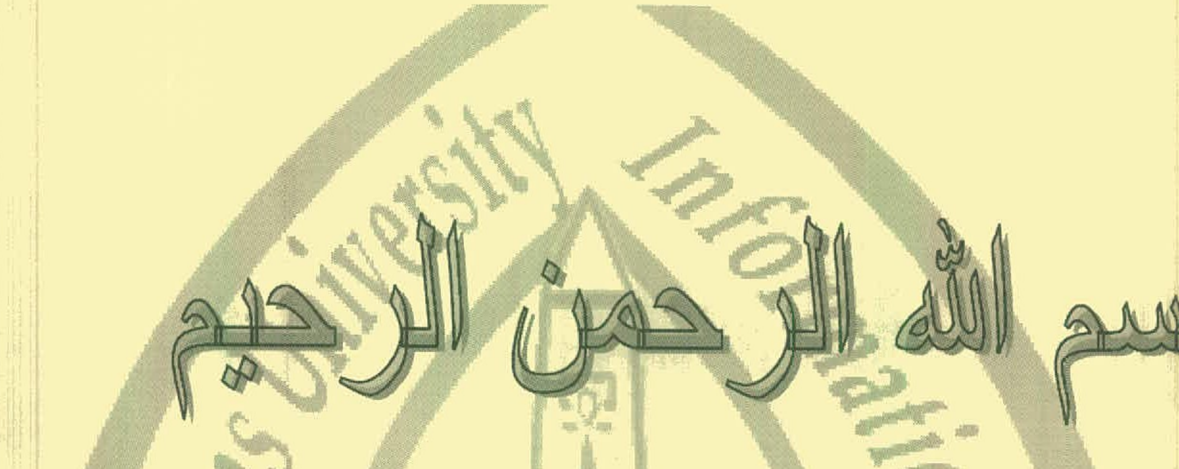

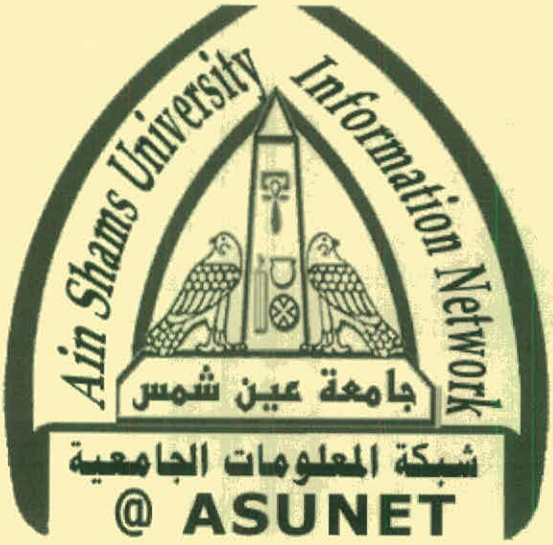

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

شبكة المعلومات الجامعية

جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
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يجب أن

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ZAGAZIG UNIVERSITY
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FACULTY OF SCIENCE
PHYSICS DEPARTMENT

MASS SPECTROMETRIC STUDY OF IONIZATION AND FRAGMENTATION OF ETHYLAMINE, DIETHYLAMINE AND TRIETHYLAMINE USING ELECTRON IMPACT TECHNIQUE.

BY

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THESIS

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2001

الله

بسم الله الرحمن الرحيم

قالوا سبحانك لا علم لنا إلا ما
علمتنا إنك أنت العليم الحكيم .

صدق الله العظيم
البقرة - ٣٢ -

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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 (ΔE_{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 ions 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 conclusion (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.

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.