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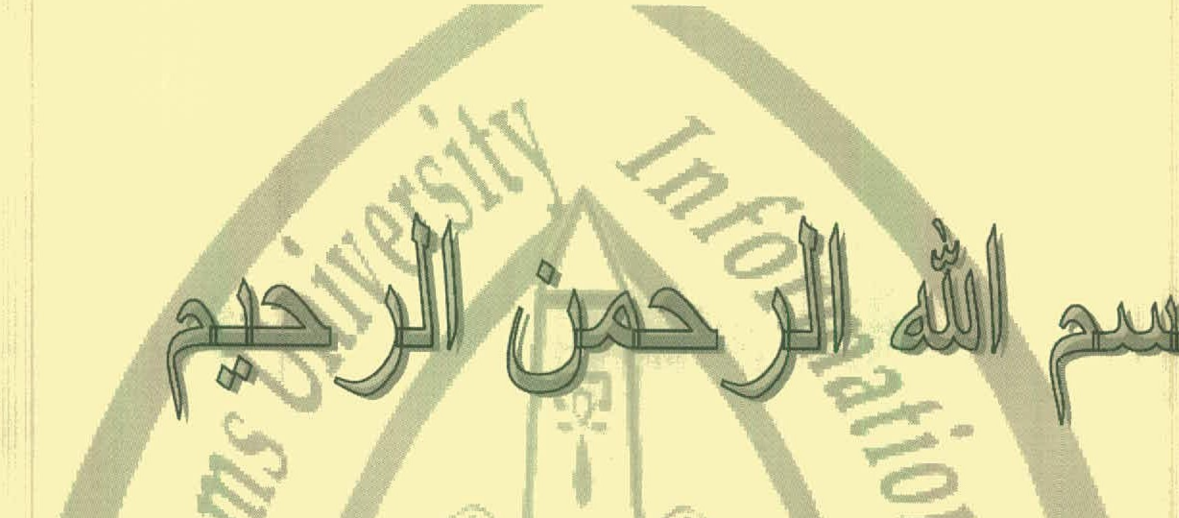

بعض الوثائق
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INVESTIGATION OF IONIZATION AND FRAGMENTATION OF CHLOROANISOLE ISOMERS USING ELECTRON IMPACT MASS SPECTROMETRY AND SEMI-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS

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ABSTRACT

An electron impact mass spectrometry is used in combination with deconvoluted first differential (DFD) technique in order to determine ionization energy values at threshold as well as higher energy states for the molecular ions $[C_7H_7OCl]^{+\cdot}$ of chloroanisole isomers. Appearance energy values at threshold only are also measured for $[C_6H_4OCl]^+$, $[C_6H_5Cl]^+$, $[C_7H_7O]^+$, $[C_5H_4Cl]^+$ and $[C_3H_2Cl]^+$ fragment ions produced from the three precursor molecular ions.

The relative intensities of the prominent ions in the mass spectra of the three isomers are reported at 70 and 15 eV (nominal) for ionizing electron energy and are discussed in terms of the relative position of the two substituents (-Cl and OCH_3) on the benzene ring. Also, the metastable peaks associated with formation and fragmentation of the prominent fragment ions are recorded and the kinetic energy release ($T_{0.5}$) values associated with these processes are determined.

The values of ionization energy at threshold are measured at 8.46 ±0.06, 8.82±0.05 and 8.37±0.05 eV for o-, m- and p-chloroanisole isomers, respectively, and are explained as due to ionization of $1e_{1g}$ electrons from π_3 (B_2 component) orbitals of the corresponding chloroanisole isomers. Higher energy levels have been detected in the ionization efficiency curves of the molecular ions of the three isomers and some of these levels are tentatively explained by the author. Appearance energy values at threshold for $[C_6H_4OCl]^+$ fragment ions are measured at 11.85±0.09, 11.90±0.12 and 11.79±0.09 eV, for $[C_6H_5Cl]^+$ fragment ions at 11.37±0.06, 11.63±0.07 and 11.63±0.07 eV, for $[C_7H_7O]^+$ fragment ions at 10.44±0.05, 10.32±0.05 and

10.57±0.06 eV, for $[C_5H_4Cl]^+$ fragment ions at 13.88±0.09, 13.33±0.08 and 13.67±0.11 and for $[C_3H_2Cl]^+$ fragment ions at 17.72±0.10, 17.53±0.08 and 17.84±0.08 eV for ions produced from o-, m- and p-chloroanisole isomers, respectively. It is worthwhile to mention that appearance energy values for nine out of fifteen studied fragment ions are reported for the first time.

The heat of formation, charge distribution and bond orders of the molecular chloroanisole isomers are calculated using the semiempirical molecular orbital calculation MNDO method. The MNDO method is used also to suggest the structural geometry of the molecular ions of chloroanisole as well as some of the studied fragment ions.

The possible fragmentation processes for the formation of the studied fragment ions have been suggested and thermodynamical threshold values (ΔE_{th}) for these processes (except for $[C_3H_2Cl]^+$ fragment ions) are calculated. The present results may indicate that $[C_6H_4OCl]^+$ ions are formed from the three precursors at threshold having a chlorophenoxide structure, $[C_6H_5Cl]^+$ ions are formed from the three precursors at threshold having a chlorobenzene structure, $[C_7H_7O]^+$ ions are formed from the three precursors at threshold having a phenoxymethylene structure while $[C_5H_4Cl]^+$ ions are formed with one or mixture of linear structures. However the present results obtained for $[C_3H_2Cl]^+$ ions do not allow the suggestion of any structure(s) for the ions formed from the three precursors with reasonable certainty.

Finally, the kinetic energy release ($T_{0.5}$) values associated with the fragmentation of metastable $[C_7H_7O]^+$ suggest that the decomposing $[C_7H_7O]^+$ ions from o-, m- and p-chloroanisoles, have the same structure or mixture of structures at 70 eV, while the decomposing $[C_3H_2Cl]^+$ ions produced from o- and m-chloroanisoles have the same structure that is different from that obtained from p-chloroanisole at 70 eV.

CHAPTER 1

INTRODUCTION AND AIM OF THE WORK

1.1. Introduction :-

Mass spectrometry is one of the most successful and powerful tools in analytical chemistry, in particular for the identification and structural analysis of organic compounds. The basis of the success of an analytical application of mass spectrometry is the observation of the fragmentation of ionized and energized species in the gas phase, the essence of a mass spectrometric structural analysis is the requirement that the fragmentations obey the rules of the reaction mechanisms developed for other types of organic reactions. The correlation between the structure of a compound and its mass spectrum was a strong stimulus for the idea of studying organic reactivity by mass spectrometry(1).

Fragmentations are generally thought to be formed from a series of competing and consecutive unimolecular fragmentation reactions starting from molecular ion. Accordingly, the resultant mass spectrum is defined by the relative rates of these fragmentation reactions. The interpretation of mass spectra of organic molecules depends largely on a rationalization(2) of the observed experimental results, but one can not emphasis too much the fact that the available evidence for many of the postulated mechanisms and ion structures is still tenuous at best. Actual determination of the structures of ions produced from the mass spectrometer is still an extremely difficult task.

The electron impact mass spectra of isomeric molecules show some differences in the relative abundance of the ions. Some isomeric systems can not be distinguished by electron impact mass spectra because of the similarity(2) of the relative intensities of the fragments. Therefore, it is difficult to make a correlation between structure and mass spectra only. Since the energy necessary for ionization and fragmentation of organic molecules is dependent upon structure, it could be possible to use energetic data as a source of information for structural elucidation of isomeric molecules.

For the evaluation of critical energies 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(IE) and appearance energy(AE) is the energy spread of electrons(3) obtained from the heated filament and this effect can be overcome by using a suitable deconvolution method.

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 ions.

Fragmentation of metastable ions are observed in mass spectrometers over a time interval 10^{-6} - 10^{-5} sec. after formation of the ions in the ion source and so the metastable ions will have rate constants lying with a limited range, around 10^{5} sec.$^{-1}$. It has been estimated that for polyatomic organic ions these rate constants typically correspond to a range of internal energies of the ion lying in the order of a fraction of an electron volt above the critical energy for the reaction. Thus, when reactions of metastable ions are studied, a narrow range of ion interval energies is automatically selected. Therefore they can be expected to contain more accessible information than normal mass spectra.

The first semiquantitative relationship between metastable peak intensities and the structure of a fragmenting ion was proposed in 1966 by Shannon and McLafferty(4) following a related study by Rosenstock et.al.(5). The so called metastable abundance ratio test was based on the premise that when two (or more) competing fragmentations from the same ion give reasonably intense metastable peaks, then the ratio of their abundance may be used as a criterion for ion structure. It has had some success but suffers from severe limitations, mostly connected with the fact that the properties of metastable ions depend on both structure and internal energy(6), factors which have been difficult to separate.

From the examination of metastable peak shapes, a valuable wealth of physicochemical information can be obtained, rather than, for example, only measuring relative peak heights. The shape of the metastable peak can be regarded as a close reflection to the conversion of the internal energy of the precursor ions into translational energy released ($T_{0.5}$) calculated from the peak width at half height of the signal provides a simple and reliable method for establishing the identity or non identity of ions generated from different sources(7).

If experimental data is not available, the heat of formation may be deduced from MO calculations; and its theoretical calculation if reliable, is highly desirable. Thus the energetic data can be directly compared