



Structural Identification of $C_2H_5O^+$ and $C_3H_7O^+$ ions obtained from Polyethylene Glycols and Polyethylene Glycol Dialkyl Ethers and other Sources using Chemical ionization and Fourier Transformation ion Cyclotron Mass Spectrometry

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Abstract

Sample ion/sample molecule reactions often occur under high pressure CI and low pressure FT/ICR conditions with large sample size of polar compounds, and are useful in obtaining molecular weight information. In this paper, FT/ICR/MS was used to study ion-molecule reactions of $C_2H_5O^+$ ions made from three different sources. The ions were reacted with PEG oligomers so as to differentiate among the structures of the m/z 45 ions. Time dependence studies of product ions from these reactions were also made. $C_2H_5O^+$ ions produced from ethylene oxide and from PEG oligomers reacted essentially by proton transfer and gave similar spectra which are different from those of $C_2H_5O^+$ ions made from dimethyl ether. The suggested structure could be any of II–IV. The reactions of the isomeric $C_2H_5O^+$ ions from dimethyl ether with PEG oligomers show a methyl cation transfer as a product ion, $(M+13)^+$ ions, suggesting a $CH_3-O=CH_2^+$ structure as shown in structure I. The two isomers reacted mostly by proton transfer with minor amounts of methyl cation transfer which points to structure IX. The $C_3H_7O^+$ ions from the ion-molecule reaction of acetone and vinyl methyl ether react mostly by proton transfer could have the structure of X or XI.

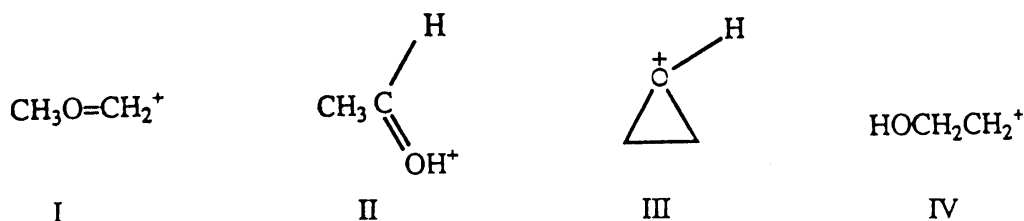
Keywords: FT/ICR, ion-molecule reactions, mass spectrometry, polyethylene glycol dialkyl ethers, structural identification.

Introduction

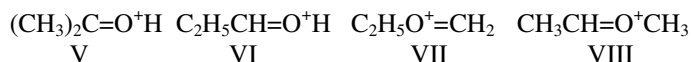
Chemical ionization (CI) technique is a very useful analytical technique based on ion-molecule reaction and has been used to obtain structural information and other thermochemical properties of many compounds¹. Ion-molecule reaction has also been used to study the reactivity's of different functional groups with the same reagent ions and to derivatize functional groups for additional structural information². Various mass spectrometric methods such as GC/CIMS, FT/ICRMS and Ion-Trap/MS have been used to study ion-molecule reactions²⁻¹¹.

Sample ion/sample molecule reactions have been shown to occur by many pathways that include proton and hydrogen ion transfer, alkyl cation transfer, charge transfer, negative or hydride ion transfer, condensation and association transfers, and displacement or elimination reactions, to produce different product ions^{2,12}. As shown earlier in our previous paper¹², the CH_4/CI of PEGs and PEG dimethyl ethers consist mostly of MH^+ , $(C_2H_4O)_nH^+$, $(H(OC_2H_4)_nOH)H_2^+$, and $CH_3(OC_2H_4)_n^+$ ions and small amount of $C_2H_5OC_2H_4^+$ ions. The relative abundances of the MH^+ ions and some of the products ions vary across the chromatographic peaks which implies that the formation of the MH^+ ions and the other product ions occurs not only by direct proton transfer from the reagent ion to the neutral compound, but also by sample ion/sample molecule reactions with the

neutral sample molecules. Studies of the reaction profiles of the product ions allow us to know which sample ion is taking part in forming the product ions. In the previous paper¹³, sample ion at m/z 45 and m/z 59 were identified as the major sample ions taking part in the ion-molecule reactions of PEG and PEGDME oligomers respectively. Experiments to identify the structure of isomeric ion at mass 45 have been done by observing different chemical reactivity's of each isomer^{2,15,16} and also by metastable or CID techniques¹⁷. Structures including those shown in I to IV, have been suggested for $C_2H_5O^+$ ions^{2,14,15}. The $C_2H_5O^+$ ions made from ethers were assigned the structure $CH_3O=CH_2^+$ (I)^{2,14,16} and have been found to undergo H⁻ abstraction, methyl cation transfer²², and formation of $(M+13)^+$ adduct ions (with alkyl ethers²). The protonated ethylene oxide (III) reacts exclusively by proton transfer with alcohols¹⁵. Metastable decomposition studies have also shown that structures II and IV isomerizes to structure III (protonated ethylene oxide)² and react predominantly by proton transfer¹⁵. The ion at m/z 45 is the dominant ion in the mass spectra of all PEG oligomers and is also abundant in the mass spectra of PEG dimethyl ethers. The reaction profile of this ion (m/z 45) obtained in the CH_4/CI and FT/ICR mass spectra of the PEG oligomers were shown to decrease with increasing extent of conversion or time of reaction^{1,13}. In the earlier papers including ours, it was assumed that the ion at m/z 45 may be protonated ethylene oxide and it reacted predominantly by proton transfer^{12-13,15}.



Isomeric $\text{C}_3\text{H}_7\text{O}^+$ ions (m/z 59) from alcohols, ethers, and acetone have been studied by metastable^{17, 18} CA^{19} , and MIKE²⁰ mass spectrometry. Structures represented in V - VIII are some of the stable isomeric structures of $\text{C}_3\text{H}_7\text{O}^+$ ions identified by these techniques. $\text{C}_3\text{H}_7\text{O}^+$ ions produced by electron impact in the spectrum of t-butyl alcohol^{21,22} and in high pressure experiments with acetone^{23,24} were reported to have the structure of protonated acetone (V).



The present experiments were undertaken to study the reactions of isomeric ions at m/z 45 obtained from PEGs, ethylene oxide and dimethyl ether and isomeric ions at m/z 59 from PEGDME, acetone, vinyl ether and mixture of ethylene oxide and methyl iodide and propose their structures. The mass spectra were obtained with an FTICR spectrometer and used to suggest possible structures for the isomeric ions at m/z 45 and 59.

Material and Methods

FT/ICR data were obtained with an Extrel 2000 FT/MS mass spectrometer at 300°K and sample pressure of 2.0×10^{-8} Torr (gauge pressure). Electron ionization (EI) and CH_4 CI methods were used to obtain the isomeric ions at 45 and 59 in the source of an FT/ICR mass spectrometer. Ion ejection techniques (Chirp, SWIFT) were used to isolate $\text{C}_2\text{H}_5\text{O}^+$ (m/z 45) and $\text{C}_3\text{H}_7\text{O}^+$ ions (m/z 59) in the analyzer cell. These ions were pulsed into the source cell and allowed to react with neutral PEG and PEGDME oligomers respectively. $\text{C}_2\text{H}_5\text{O}^+$ ions (m/z 45) were obtained from PEG, ethylene oxide and dimethyl ether and reacted with the neutral PEG and PEGDME oligomers in the source of the FT/ICR mass spectrometer. The pressure of the PEG and PEGDME used in these experiments was $\sim 2 \times 10^{-8}$ Torr (gauge pressure) and the reaction time was one second.

The $\text{C}_3\text{H}_7\text{O}^+$ ions were obtained from acetone, ethylene oxide/methyl iodide mixture, and vinyl methyl by electron ionization (EI) and CH_4 CI in analyzer cell of the FT/ICR mass spectrometer. Ion ejection techniques (Chirp, SWIFT) were also used to isolate the ions and subsequently pulsed into the source cell. These ions (m/z 59) were allowed to react with neutral PEGDME's. Product ions from these reactions were monitored and analyzed for structural determination.

Results and Discussion

Structural Identification of Isomeric Ion $\text{C}_2\text{H}_5\text{O}^+$ (m/z 45):

The relative abundances of ions obtained from the reactions of $\text{C}_2\text{H}_5\text{O}^+$ from three different sources with triethylene glycol are shown in figures 1a - c. Figure 1c also shows the mass spectrum obtained by the reactions of $\text{C}_2\text{H}_5\text{O}^+$ (from reaction of dimethyl ether) with triethylene glycol. The ion presumably has the structure $\text{CH}_3\text{-O}=\text{CH}_2^+$ (I) and is expected to undergo methyl cation transfer. The mass spectrum contains the methyl cation transfer ion at m/z 163, (M+13), and other ions at m/z 77, 87, 103 and 131. Appearance of (M+13)⁺ ion support the proposed structure I. This mass spectrum is different from the mass spectra obtained by the reaction of $\text{C}_2\text{H}_5\text{O}^+$ ions obtained from triethylene glycol (EI) and ethylene oxide, with triethylene glycol and shown in figures 1a and 1b respectively. These spectra (figure 1a and 1b) do not contain (M+13)⁺ ions or the ions at m/z 77, 87, 103, and 131.

These differences indicate that the structure of mass 45 from dimethyl ether (I) is not the same as those obtained from PEG and ethylene oxide (II-IV). The product distribution from reaction of $\text{C}_2\text{H}_5\text{O}^+$ from the PEG oligomers and ethylene oxide are essentially the same, it is reasonable to assume that this ion ($\text{C}_2\text{H}_5\text{O}^+$) have protonated ethylene oxide structure (III). The initial step in the reaction of the ion of mass 45 with alkyl ethers has been reported to form (M+45)⁺ ions¹⁴. It was, therefore, tempting to assume that the reaction of m/z 45 obtained from the PEG oligomers and ethylene oxide would also go through a similar intermediate. Ions of mass 45 were made from the PEG oligomers and ethylene oxide and reacted with PEG oligomers. The FT/ICR MS was set to eject ions at mass (M+45)⁺ and the mass spectra acquired. The ion ejection did not have any effect on the formation of the MH^+ ions. It may be assumed that the (M+C₂H₅O)⁺ ions was not formed or its life time was too short to be detected. Therefore, MH^+ ions is assumed to be predominantly formed by direct proton transfer from the $\text{C}_2\text{H}_5\text{O}^+$ ions indicating its structure to be any of the hybridized protonated ethylene oxide (II-IV).

Structural Identification of Isomeric $\text{C}_3\text{H}_7\text{O}^+$ Ions: Structures V-VII have been suggested for isomeric $\text{C}_3\text{H}_7\text{O}^+$ ions (m/z 59)¹⁷⁻²⁴ and we suggest other structures such as IX, and XI for the same ion. The mass spectra obtained from reactions of isomeric m/z 59 ions with ethylene glycol dimethyl ether, EGDME, are shown in figures 2a-d.



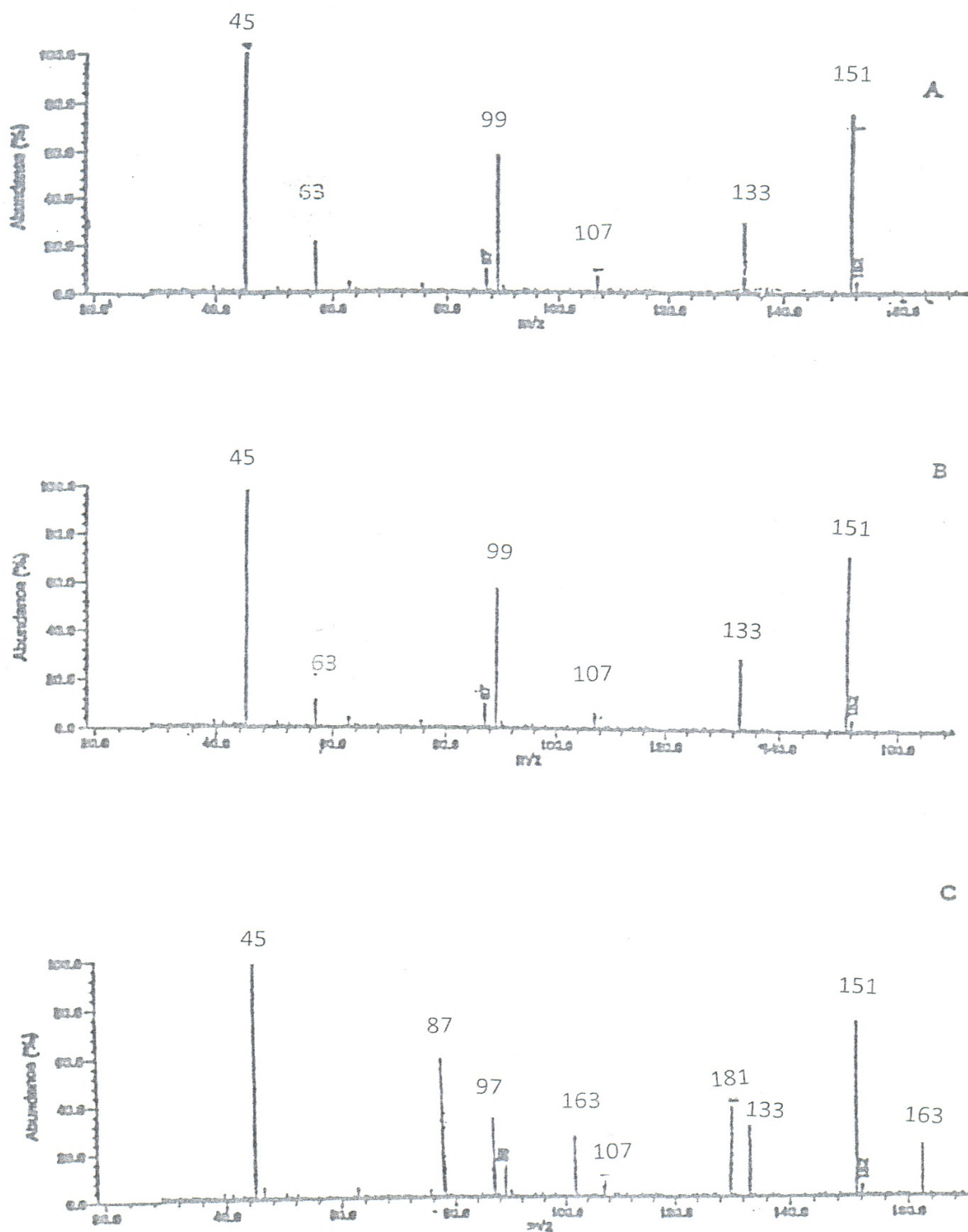


Figure-1
FT/ICR Mass Spectra of Triethylene Glycol (MW =150) Obtained from the Reaction of m/z 45 Obtained from (a) Triethylene Glycol (CI) (b) Ethylene Oxide (c) Dimethyl Ether with TEG

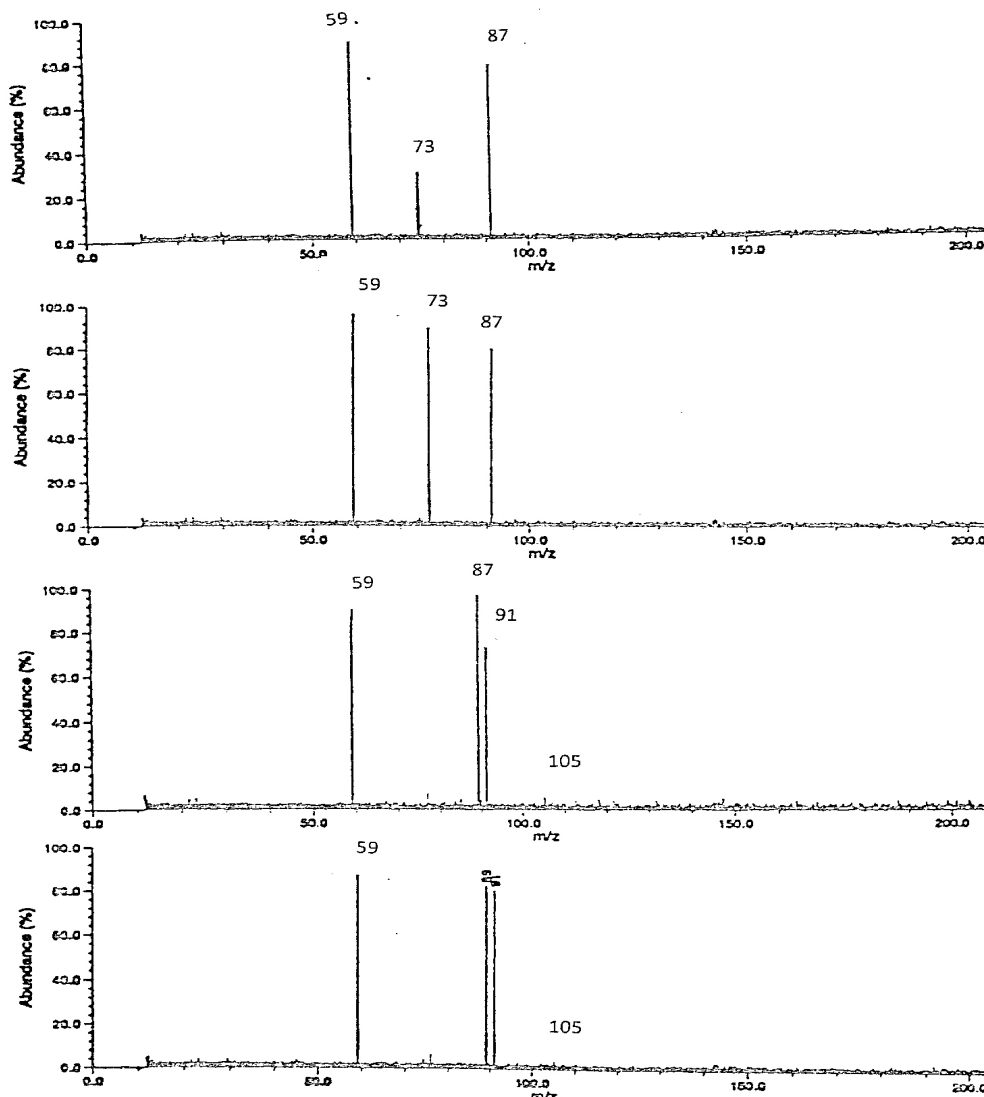
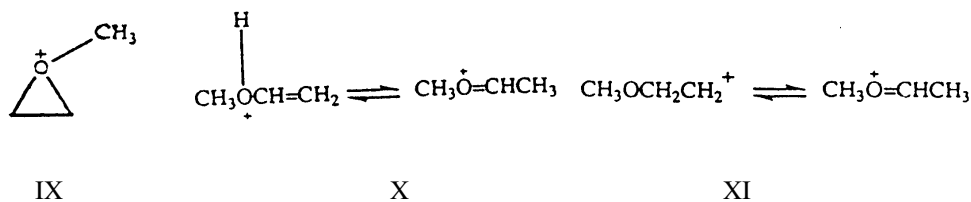


Figure-2

FT/ICR Mass Spectra Obtained from the Reaction of Ethylene Glycol Dimethyl Ether with $C_3H_7O^+$ Ions Obtained by (a) Ion-Molecule Reaction of Acetone (b) Ion-Molecule reaction of Vinyl Methyl Ether (c) EI of Ethylene Glycol Dimethyl Ether (d) Ion -Molecule reaction of Ethylene Oxide/Methyl Iodide mixture. ($P = 2.0 \times 10^{-8}$, $T = 300^\circ K$)



The $C_3H_7O^+$ ion used in our experiment were obtained from PEGDME, ethylene oxide/methyl iodide, acetone, and vinyl methyl ether and is assumed to be represented by structures V, VII, IX, X and XI respectively. These ions were reacted with neutral PEGDME's and their spectra compare to those obtained from PEGDME's (obtained by EI or CI with FTICR). Previously reported ionic reactions of protonated acetone (V,

$C_3H_7O^+$) include dehydration reaction^{21, 22} and formation of protonated acetone dimer ions³¹. Spectra obtained from the reaction of protonated acetone, V; with EGDME is shown in Figure 2a. The major reaction observed is proton transfer to give MH^+ (m/z 91) and m/z 73, ($M-H_2O$)⁺, which is similar to what was earlier observed in the literature²². There is no methyl cation transfer, ($M+15$)⁺, with this ion as shown in figures 2b

and 2c. Other ions such as m/z 75, perhaps $(MH-CH_4)^+$, and 89 $(M-H)^+$ which are present in the mass spectra obtained with isomeric m/z 59 from other sources, are not present in this spectra.

The structure represented by X is assumed to be the structure of m/z 59 from vinyl methyl ether and its mass spectra is shown in figure 2b. The structure is similar to the structure of ion of mass 45 obtained from dimethyl ether ($CH_3O=CH_2^+$, I); therefore, it is expected that it reacts by H⁺ abstraction, methyl cation transfer, and perhaps by forming $(M+27)^+$ adduct ion similar to the formation of the $(M+13)^+$ ¹⁴ ion. The dominant reaction observed is still proton transfer to form MH^+ ion. The spectra however, contain ion at m/z 75, $(MH-CH_4)^+$, which is more abundant than in the mass spectra obtained with other isomeric ions. $(M+15)^+$ at m/z 105 ion is observed in this spectrum suggesting a methyl ion transfer which therefore, supports the suggested structure, X. There were no $(M+27)^+$ adduct ion ions in the spectrum. The mass spectra obtained with the reaction of EGDME with isomeric $C_3H_7O^+$ ions made from EI of EGDME and by ion-molecule reaction of the mixture of ethylene oxide/methyl iodide is shown in Figs. 2c and 2d respectively. The fragment ions in both spectra are the same but their relative abundances are different from each other. The dominant reaction is also proton transfer reaction. The structure suggested for the $C_3H_7O^+$ ions from this two sources is the methylated ethylene oxide, IX, which we assume isomerizes to one of the structures shown in VII, X or XI. The methoxy hydrogen in the isomeric structure shown in X is very labile. Evidence of its migration was shown in the decomposition reaction of the deuterated analog observed with MIKE spectroscopy²⁰. This hydrogen may have participated in the protonation process observed in the reaction of the hydrogen analog with EGDME. Both spectra contain detectable amount of ion at m/z 105 $(M+15)^+$ which are absent in those of higher oligomers ($n = 2 - 4$, may be due to steric hindrances as n increases). This ion (m/z 105) can only occur as a result of methyl cation transfer to EGDME. The ratio of the $(M+15)^+/MH^+$ ion is $\sim 1:13$ and $\sim 1:40$ respectively (from the two sources) which indicates that the energy requirement for the protonation reaction to occur (probably involving this hydrogen) is lower than the energy required for methyl cation transfer. The appearance of the ion at m/z 105 suggest that the structure of the $C_3H_7O^+$ ions obtained from EGDME and ethylene oxide/methyl iodide mixture are different from the ones obtained from acetone and vinyl methyl ether.

The ionic products from the reactions of all the isomeric ions of mass 59 with higher oligomers are more complex than obtained with EGDME. The mass spectra obtained in the reaction of these ions with triethylene glycol dimethyl ether, TEGDME, are shown in Figures 3a -d. Figure 3a also shows the mass spectrum obtained from the reaction of protonated acetone, (suggested structure V), with TEGDME. The mass spectrum contain essentially MH^+ ions and fragment ions resulting from its decomposition: m/z 147 $(MH-CH_3OH)^+$, m/z 103 $(MH-$

$HOC_2H_4OH)^+$, and $(CH_3OC_2H_4OCH_3)H^+$ at m/z 277. This supports the suggested structure V, which is different from isomeric ions from other sources (figures 3b-d).

The mass spectrum obtained from the reaction of TEGDME with the ion of mass 59 from vinyl methyl ether (suggested structure X) is shown in figure 3b. The spectrum is different those made from other isomeric ion of mass 59. There are fragment ions at m/z 71, 75, and 88 which are not present in those of figures 3a, 3c, and 3d. The ion at m/z 71 suggest a reaction by ethyl cation transfer to form $(M+27)^+$ ion followed by a loss of diethylene glycol dimethyl ether, $(M+27-DEGDME)^+$.

This points to the fact that m/z 59 from vinyl methyl ether have the structure X. The mass spectra in Figs.3c and 3d are the spectra obtained from the reaction of m/z 59 ions made by EI of TEGDME and the ion-molecule reaction of ethylene oxide/methyl iodide mixture, with TEGDME respectively. The fragment ions in both spectra are the similar but their relative abundances are different from each other. The predominant reaction is proton transfer which suggests that $C_3H_7O^+$ ion made from both sources have similar structures; possibly, methylated ethylene oxide (IX) that can isomerizes to VII or XI.

Conclusion

The dominant fragment ion in the CH_4/CI mass spectra of all PEG and PEGDME's are the ion at m/z 45 ($C_2H_5O^+$) and m/z 59 ($C_3H_7O^+$) respectively. These ions react to form product ions which enable us to differentiate between the structures of the isomeric sample ions taking part in the ion-molecule reactions. Isomeric $C_2H_5O^+$ and $C_3H_7O^+$ ions made from different sources were reacted with PEG and PEGDME oligomers. The $C_2H_5O^+$ ions made from PEG's and ethylene oxide gave similar spectra and to that obtained by CH_4/CI . The major ion in these spectra is the MH^+ ions indicating a predominantly proton transfer reaction suggesting structures II to IV. The reactions of isomeric $C_3H_7O^+$ ions made from PEGDME and ethylene oxide/methyl iodide mixture with PEGDME's gave similar products. The two isomers reacted mostly by proton transfer with minor amounts of methyl cation transfer supporting the structure shown in IX. The $C_3H_7O^+$ ion from acetone and vinyl methyl ether react mainly by proton transfer which supports the structure shown in X and XI.

However, the ion at m/z 71 (figure 3b) points to a possible formation of transient ethyl cation transfer intermediate with the m/z 59 ion from vinyl methyl ether suggesting structure X.

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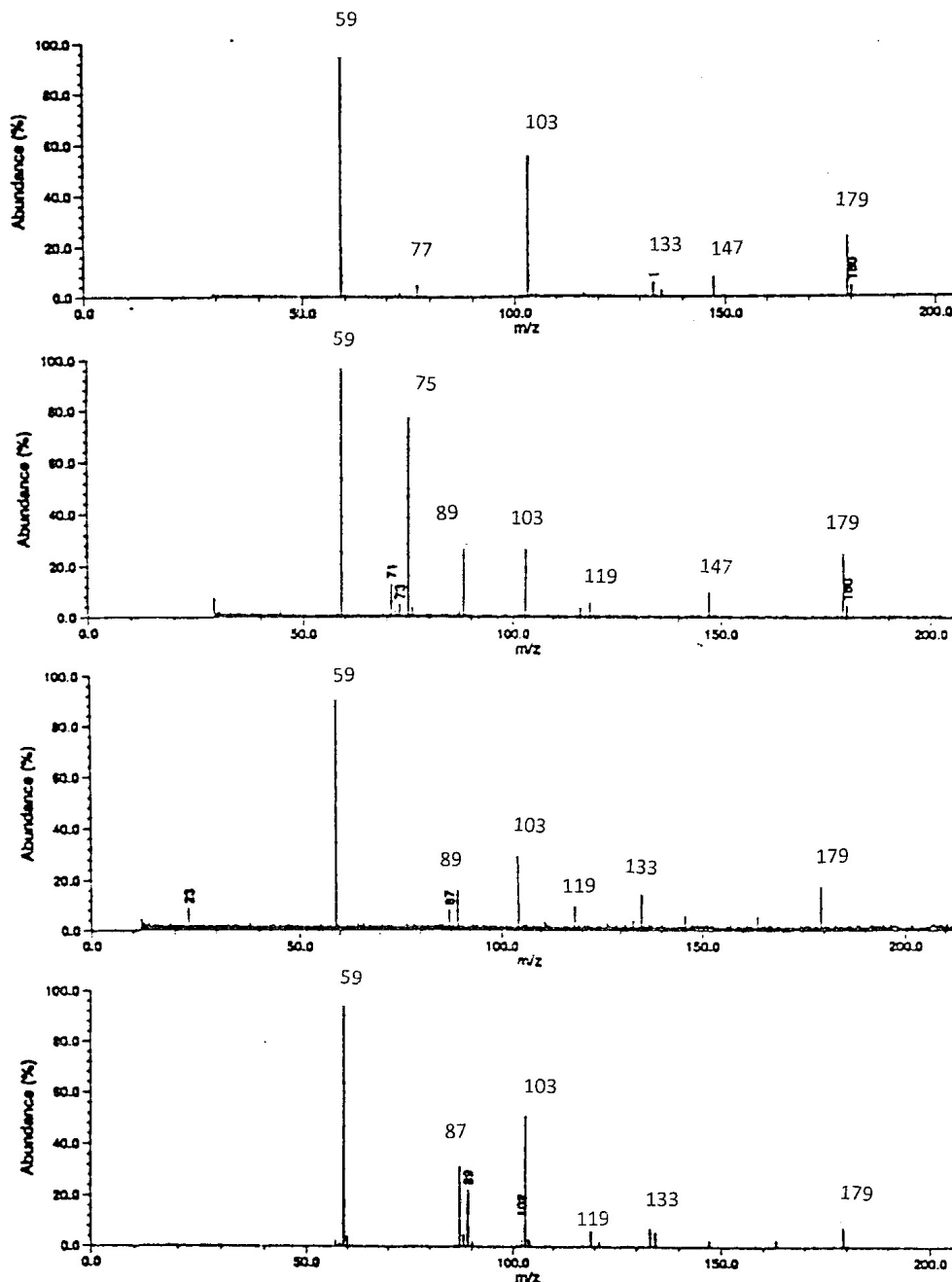


Figure-3

Mass Spectra of Triethylene Glycol Dimethyl Ether obtained by its reaction with $C_3H_7O^+$ ions obtained by (a) Ion-Molecule Reaction of Acetone (b) Ion-Molecule Reaction of Vinyl Methyl Ether (c) EI of Triethylene Glycol Dimethyl Ether (d) Ion-Molecule Reaction of Ethylene Oxide/Methyl Iodide. ($P = 2 \times 10^{-8}$ Torr., $T = 300^\circ C$)

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