



Gas Chromatography / Chemical Ionization Mass Spectrometry of Polyethylene Glycol Monoalkyl Ethers

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Abstract

The CH₄/CI mass spectra of polyethylene glycol monoalkyl ethers, C_xH_{2x+1}(C₂H₄O)_nOH, contain MH⁺ and fragment ions that can be used to identify each oligomer. The relative abundances of the MH⁺ ions are low, variable, and increase with increasing sample size across the chromatographic peaks and not with increasing value of x or n; hence, a major portion of these ions is formed by sample ion/sample molecule reactions. The base peaks in CH₄/CI are variable and are determined by the ethylene oxide moiety (x ≤ 3). Those of higher mass oligomers (x ≥ 4, n ≥ 3) are MH⁺ ions and ions formed by hydrogen rearrangement decompositions of the MH⁺ ions ((HOC₂H₄OH)_nH⁺, n = 1, 2.) Isobutane CI (i-C₄H₁₀/CI) spectra are pressure dependent. The pressure in the source of our mass spectrometer is not known but it is described by the ratio of ionic abundances of m/z 43 and 57: P(0.15) = I(43/57) = 0.15 (high pressure), and P(0.05) = I(43/57) = 0.05 (higher pressure). The spectra obtained at the lower pressure (P=0.15), show less fragmentation to that observed with CH₄/CI. Those at higher pressure, P(0.05), contain essentially MH⁺ ion. The base peak at both pressures is the MH⁺ ions. Estimates of the heat of formation of some of the CH₄ CI proton transfer reactions were made from the thermochemistry of some of the decomposition reactions using n-butyl ether oligomer as a model compound.

Keywords: Chemical ionization, gas chromatography, mass spectrometry, polyethylene glycol mono alkyl ethers, heat of formation.

Introduction

Polyethylene glycol mono alkyl ethers, (PEGMAE), C_xH_{2x+1}(C₂H₄O)_nOH, have been used in making cleaning formulations, agriculture chemicals^{1,2} pharmaceuticals, alkaline batteries, coating agents, and textile fibres^{3,4}. PEGMAE and ethylene glycol derivatives are found in environmental samples and usually undergo microbial degradation to produce toxic substances that are dangerous to the environment⁵. The EI mass spectra of low mass PEGMAE, like those of similar hydrocarbons, alcohols, and ethers, show low abundance of molecular ions (x ≤ 3, n = 1 - 4) while the higher members (x ≥ 4, for all n) do not contain molecular ions⁶. Since the EI mass spectra of PEGMAE (x ≥ 4) do not show detectable molecular ions and contain mostly low mass fragment ions, soft ionization techniques such as field desorption ionization FD⁷, thermospray, liquid chromatography/mass spectrometry (LC/MS)⁸, fast atom bombardment (FAB)^{9,10}, flow injection analysis/mass spectrometry¹¹, and tandem mass spectrometry¹¹ were used to obtain molecular weight and structural information of some PEGMAE (x ≥ C₁₀). In this study, methane chemical ionization (CH₄ CI), and iso-butane chemical ionization (i-C₄H₁₀ CI) mass spectra of PEGMAE (C₁-C₁₂) were obtained and used to obtain the qualitative, quantitative and molecular weight information of some of these PEGMAE's. Also, the heats of formation of the proton transfer reactions that occur under CH₄ CI conditions were measured.

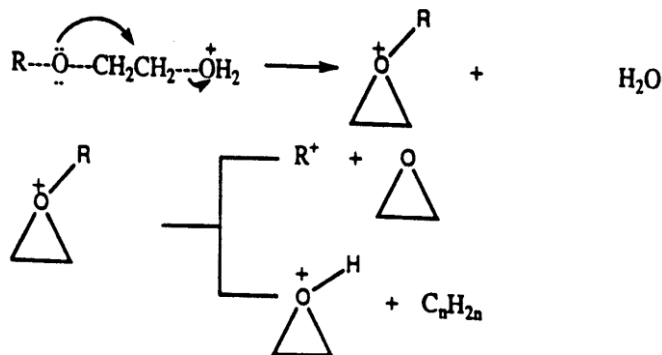
Material and Methods

Chemical ionization (CI) mass spectra were obtained using a VG MM-16/Varian Model 3700 gas chromatograph mass spectrometer and a VG AutoSpecQ mass spectrometer. Perfluorotributylamine, PFTBA, was used for tuning and calibration. Different scan rates were set for different mass ranges. Methane and isobutane gases were used as reagent gases to obtain CI mass spectra of the compounds. The ratios of the major ions in the methane reagent gas are: m/z 29/17 = 1, 19/17 = 0.02, 41/17 = 0.03 and 43/17 = 0.02 with the VG MM-16 and m/z 29/17 = 0.65, 19/17 = 0.02, 41/17 = 0.11 and 43/17 = 0.04 with the VG AutoSpecQ mass spectrometer respectively. There is only a small amount of water, or H₃O⁺, in each reagent gas. Isobutane (i-C₄H₁₀) CI experiments were obtained with the VG AutoSpecQ mass spectrometer at the following pressures: P(0.75) = I(43/57) = 0.75 (high pressure), P(0.15) = I(43/57) = 0.15 (higher pressure) and P(0.02) = I(43/57) = 0.02 (highest pressure). All experiments were done in the split less injection mode with no solvent delay times. The injection port, transfer line, and the source temperatures were set at 250 °C, 280 °C, and 200 °C respectively. 0.05 - 0.5 μL sample sizes were used for these experiments. Helium is the carrier gas at a flow rate of 1 mL/min and separations were generally achieved using 30m x 0.25mm x 0.33 μm cross-linked methyl silicone capillary columns (Alltech SE30, SE54). A temperature program of ~35-230 °C at 5 °C/min, an initial hold time of one minute at 35 °C,

and a final hold up time of 10 minutes at 230 °C, was employed to achieve complete separation of some mixtures containing low molecular weight glycols ethers (n = 1-3). The total sample ion current (TIC) was obtained by summing the ion currents of all sample ions in each spectrum. The TIC was recorded over the mass range of all samples (30 - 600μ). Averages of 10 - 15 spectra were obtained across each chromatographic peak.

Results and Discussion

Methane Chemical Ionization (CH₄/CI) of Ethylene Glycol Monoalkyl Ethers (EGMAE): Result in figure-1 shows the CH₄ CI mass spectra of ethylene glycol monobutyl ether and ethylene glycol monododecyl ether. Both spectra show the MH⁺ ion and contain less decomposition than their EI spectra¹. However, the MH⁺ ions are not the base peak in these spectra. The relative abundance of MH⁺ ion varies across the chromatographic peak (sample size dependent) and may be produced to some extent by sample ion/sample molecule reactions. There are small amounts of the (M-H)⁺ ion in each spectrum and its abundances increases slightly with increasing chain length (~0.3 – 1.6 % TIC). Most of the fragment ions in each spectrum appear in the low mass region consisting mostly of alkyl, alkenyl, and oxygen containing ions. The C_xH_{2x+1}⁺, C_xH_{2x}⁺, ions were 60% and 84% of TIC respectively. Ethylene oxide units are the base peak in the CH₄ CI mass spectrum of the PEG oligomers¹, while those of EGMAE (except the methyl and ethyl analog) is the ion at m/z 63, (HOC₂H₄OH)⁺. This ion is formed by hydrogen re-arrangement reaction with the loss of neutral alkene and constitutes ~ 37 and 15% of the TIC respectively (scheme 1). m/z 45 is formed by anchimeric assisted charge-site reaction as observed with PEG oligomers¹, (~19%, 7%TIC) but its abundances is less than that observed with ethylene glycol (~94%)¹. The decrease in abundance is explained in terms of increase in alternative decomposition pathways with increasing hydrocarbon chain length. For example, the C₁₀H₂₁⁺ ion at mass 141 is less abundant (~3%) than the analogous butyl ion in the mass spectrum of the monobutyl ether (m/z 57, ~16%) because of probable decompositions into lower mass ions.



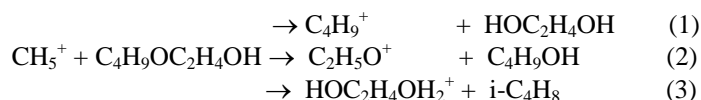
Scheme-1
Formation of HOC₂H₄OH₂⁺ Ions by Hydrogen Rearrangement Reactions

Result in figure 2 compares the CH₄ CI spectra of tetraethylene glycol dodecyl ether (m/z 362) obtained from scans at different positions across the chromatographic peak. Figure-2A shows a spectrum obtained at the leading edge of the peak with a relatively small sample size (as indicated by the extent of conversion of reagent ions to product ions (~0.05)). The mass spectrum is scanned from high mass to low mass, so the concentration of the sample increases significantly between the time when m/z 363 is detected and the time when m/z 45 is detected. Consequently, this spectrum is distorted and the abundances of ions at m/z 45 (and other low mass ions) are larger than they should be, compared with a spectrum obtained at constant sample pressure. Figure- 2B shows a spectrum obtained on the descending side of the peak and at a larger sample concentration (as indicated by an extent of conversion of reagent to sample ions (~ 0.25), for which the concentration of sample is larger when m/z 363 is detected than when m/z 45 is detected. Consequently, this spectrum is distorted by an enhancement in the abundances of ions at m/z 363 and other high mass ions. Also, if one takes the abundance of MH⁺ as % of TIC for ethylene glycol ethers, there is no indication of increased stabilization of MH⁺ ions with increasing alkyl chain length or molecular weight: 6% (C₄H₉OC₂H₄OH₂⁺), 3%(C₁₀H₂₁OC₂H₄OH₂⁺), ~4% (C₁₂H₂₅OC₂H₄OH₂⁺) and one cannot be precise about the extent of MH⁺ ions formed by proton transfer from CH₅⁺ and C₂H₅⁺.

The changing abundances of the MH⁺ ions as the pressure of the compounds at different positions of the chromatographic peaks increases may be partially due to by sample ion/sample molecule reactions. This observation is similar to that made for the MH⁺ ions of PEG oligomers¹. The spectra obtain with VG AutospecQ is similar to those of the VG MM16 mass spectrometer.

(MH-H₂O)⁺ ions are also present in all spectra and it is the base peak in the spectrum of the methyl ether of EGMAE (m/z 59, 47% TIC) but its abundances decrease with increasing length of the alkyl chain: ethyl (m/z 73 = 10%); butyl (m/z 101 = 2%); hexyl (m/z 129 = 0.3%); mono-decyl (m/z 185 = 0.03%); and dodecyl (m/z 213 = 0.01%). This reaction may require anchimeric assistance from the ether oxygen to give a cyclic, alky or protonated ion and would certainly be restricted by long alkyl side chains which explain the decrease in abundance with increasing size of the alky chain.

Thermochemistry: Many of the necessary thermochemical data for the observed reactions are not available. However, estimates can be made from the thermochemistry of some of the decomposition reactions (table-1). If one uses the n-butyl ether as a model compound, then, three of the major decomposition reactions may occur as shown below.



If one uses the data for heats of formation of the species from table 1, then, one may estimate that reaction i. is 22 kcal exothermic, ii. is 32 kcal exothermic; and iii. is 55 kcal exothermic. It is likely that this order of heat of reaction will hold for all of the higher EGMAE. Although there is some uncertainty in these values for the heats of reactions, the most abundant product ion is formed in the most exothermic reaction. The relative order of the heats of reactions are the same if $C_2H_5^+$ is the reactant ion, rather than CH_5^+ , but the exothermicity of each reaction is reduced by ~32 kcal.

Table- 1
Heats of Formation of Decomposition Species

Species	H_f^0 (g, 298 K), kcal/mol
CH_5^+	217.9 ^c
$C_4H_9OC_2H_4OH$	-104.9 ^{a,b}
$C_4H_9^+$	203 ^c
EG	-94.3 ^a
EOH^+	165 ^a
C_4H_9OH	-66.5 ^c
$HOC_2H_4OH_2^+$	76.2 ^c
i- C_4H_8	-0.2 ^c

^a $\Delta H_f^0(CH_3OC_2H_4OH) = 90.07 + 3(-4.95 \text{ kcal/mol}/CH_2)$; ^dD. R. Stull et al.^{11,12}. ^bS.W. Benson¹². ^cS. G. Lias. et al.¹³; $PA(HOC_2H_4OH) = 195.1 \text{ kcal/mol}$.

One notes, however, that the same order of heats of reaction is observed for the ethyl ether analog, for which protonated ethylene oxide at m/z 45 is present at about four times the abundance of protonated ethylene glycol at m/z 63. The loss of water from protonated ethylene glycol to form protonated

ethylene oxide is ~ 30 kcal/mol endothermic. If significant amounts of the excess energy are retained in the protonated ethylene glycol ions (~55 kcal/mol exothermic), then subsequent decomposition of $HOCH_2CH_2OH_2^+$ formed by dissociative proton transfer from CH_5^+ may occur.

The CH_4/CI mass spectra of PEG decyl and dodecyl ethers are simple and similar to those of EGMAE's. The relative abundances of their MH^+ ions are sample size dependent and increased from ~3- 9% for n=1-3. Large fraction of their spectra consist of MH^+ , $(C_2H_4O)_nH^+$, $C_xH_{2x+1}^+$, $C_xH_{2x-1}^+$, $H(OC_2H_4)_nOH_2^+$.

There are significant differences between the CH_4/CI mass spectra of the mono and dodecyl PEG ethers reported by Stephanou et al.¹⁴ and the ones obtained in this laboratory. Stephanou¹⁴ reported formation of adducts ($MC_2H_5^+$, $MC_3H_5^+$) and the base peaks as the MH^+ ions for all the PEGMAE he studied. In our experiment, there were no adduct ions and the base peak are the $H(OC_2H_4)_nOH_2^+$ ions (n = 1 - 3). Only tetraethylene glycol dodecyl ether has its base peak as the MH^+ ion which suggests a possible change in structure to something similar to that of 12-crown-4 ether, with the hydroxyl tucked inside the crown-like ring or perhaps a third body stabilization due to changing sample concentration in the source of the mass spectrometer. The loss of water from MH^+ varies from ~5% to less than 0.1% of the TIC as n increases, which may support the 12-crown-4 ether structure of the tetramer.

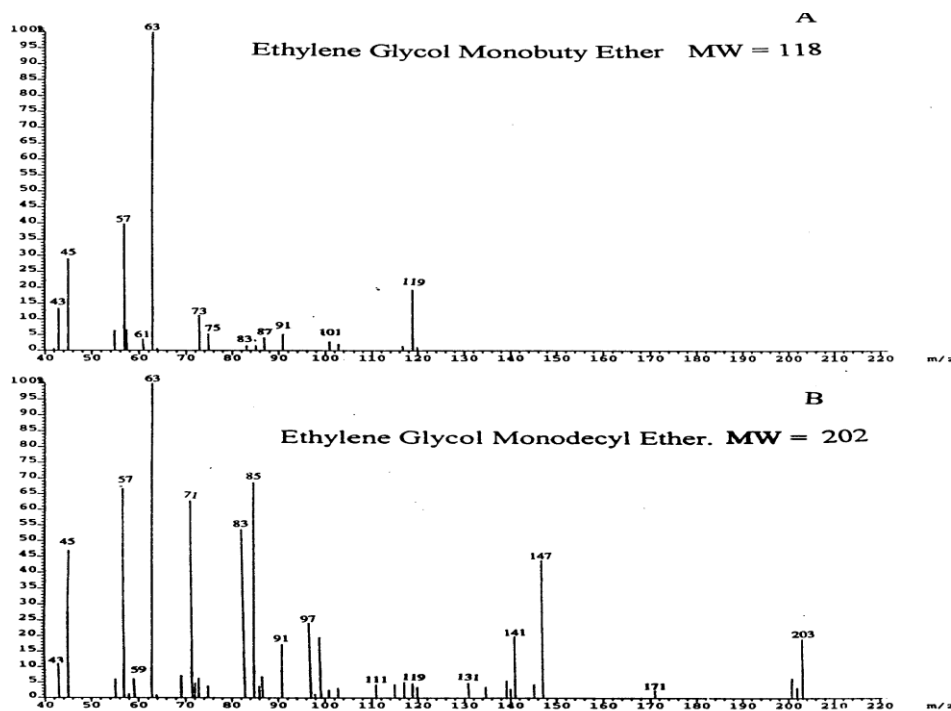


Figure-1
 CH_4/CI Mass Spectra of (A) Ethylene Glycol Monobutyl Ether (B) Ethylene Glycol Monodecyl Ether

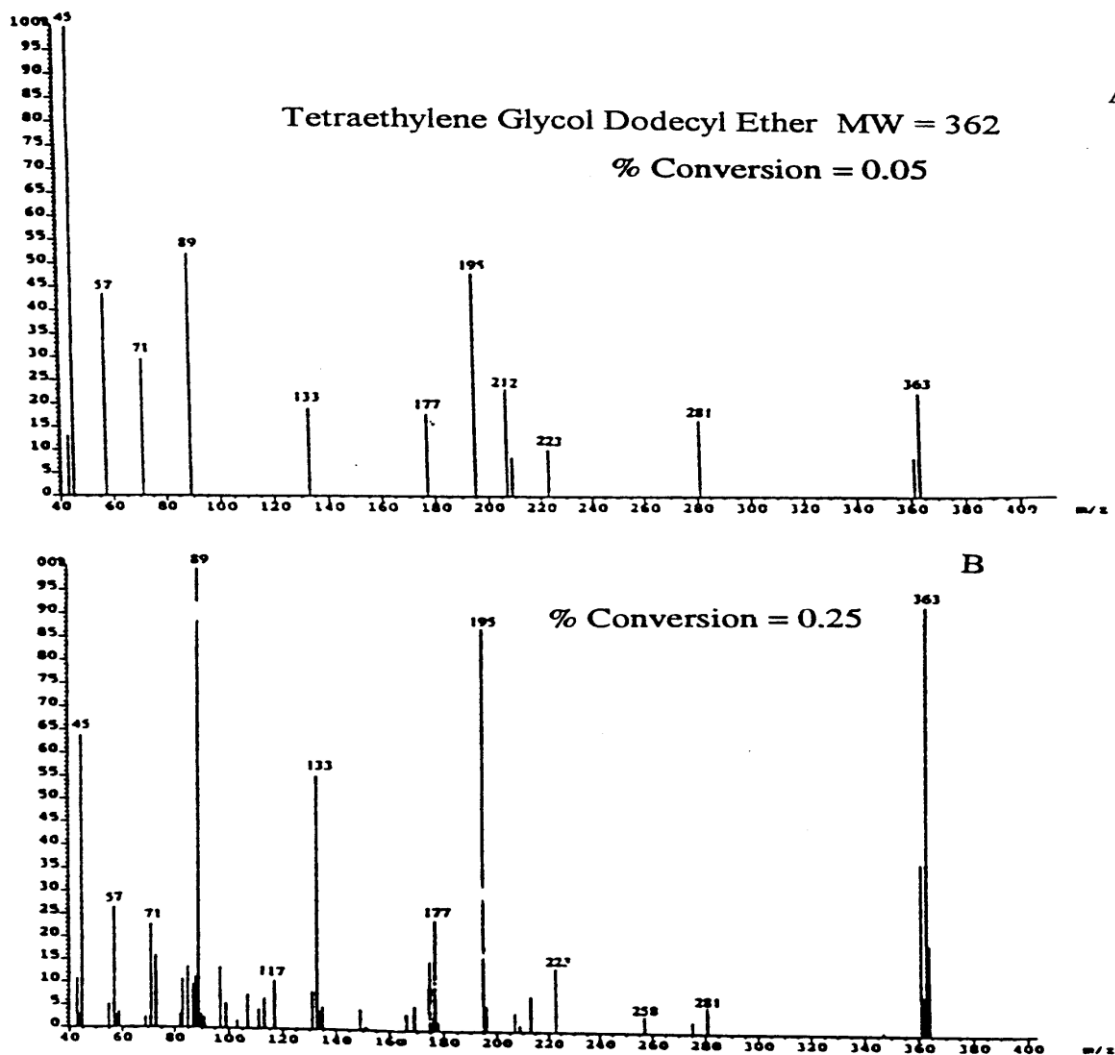


Figure-2

Variation of the Relative Abundances of Ions Tetraethylene Glycol Dodecyl Ether (A) Leading Scan (B) Descending Scan

Isobutane CI Mass Spectra of Ethylene Glycol Monoalkyl Ethers: Figure 3 compares $i\text{-C}_4\text{H}_{10}$ CI mass spectra of ethylene glycol dodecyl ether at two different pressures. The pressures are not known, but both pressures are relatively high because the C_4H_9^+ is the dominant reactant ion at both pressures. The $\text{C}_3\text{H}_7^+/\text{C}_4\text{H}_9^+$ ratio, $I(43)/I(57) = 0.15$ is considered the high pressure and $I(43)/I(57) = 0.05$ as the higher pressure. C_3H_7^+ and C_4H_9^+ are the major ions of the isobutane reagent gas and both ions can act as a Brønsted and Lewis acid but are weaker than the CH_5^+ and C_2H_5^+ ions from the CH_4 CI conditions. Consequently, the $i\text{-C}_4\text{H}_{10}$ and CH_4 CI mass spectra of EGMAE's are similar but with less fragmentation. As noted previously for the PEG oligomers¹, the $i\text{-C}_4\text{H}_{10}$ CI mass spectra of PEGMAE are dependent on the pressure of the reagent gas. Since the amounts of $s\text{-C}_3\text{H}_7^+$ decreases with increasing pressure, it is likely that the fragment ions result from reactions of $s\text{-C}_3\text{H}_7^+$ with the PEG ethers not from the reactions of $t\text{-C}_4\text{H}_9^+$. Some additional collision stabilization of MH^+ may

occur at the higher pressures which help to reduce decomposition reactions. Figure- 3A ($P = 0.15$) consists mostly of MH^+ ions at m/z 231 (base peak), $\text{HOC}_2\text{H}_4\text{OH}_2^+$ (m/z 63), alkyl ions at m/z 169, 141, etc, and $\text{C}_2\text{H}_4\text{OH}_2^+$ at m/z 45. The ion at m/z 195 is the protonated tetraethylene glycol which is an impurity from previous experiments. There are no $(\text{M-OH})^+$ ions at this pressure. The mass spectrum obtained at the higher pressure, $P = 0.05$, figure 3B, consists essentially of the MH^+ ions (~76% of TIC) with a very small amount of fragmentation. This is true for all EGMAE's. The relative abundances of MH^+ ions decrease from ~94% to ~76% of TIC with increasing size of the alkyl group. It was reported that the base peaks in the $i\text{-C}_4\text{H}_9$ mass spectra of linear alcohols ($x = 1 - 4$) are the MH^+ ions and are the alkyl ions for those with $x \geq 5$ ¹⁵. However, the base peak of the corresponding EGMAE's observed in this work is the MH^+ ion. These differences between the higher alcohols and higher ethylene glycol derivatives suggest protonation at ether oxygen or stabilization by internal hydrogen bonding.

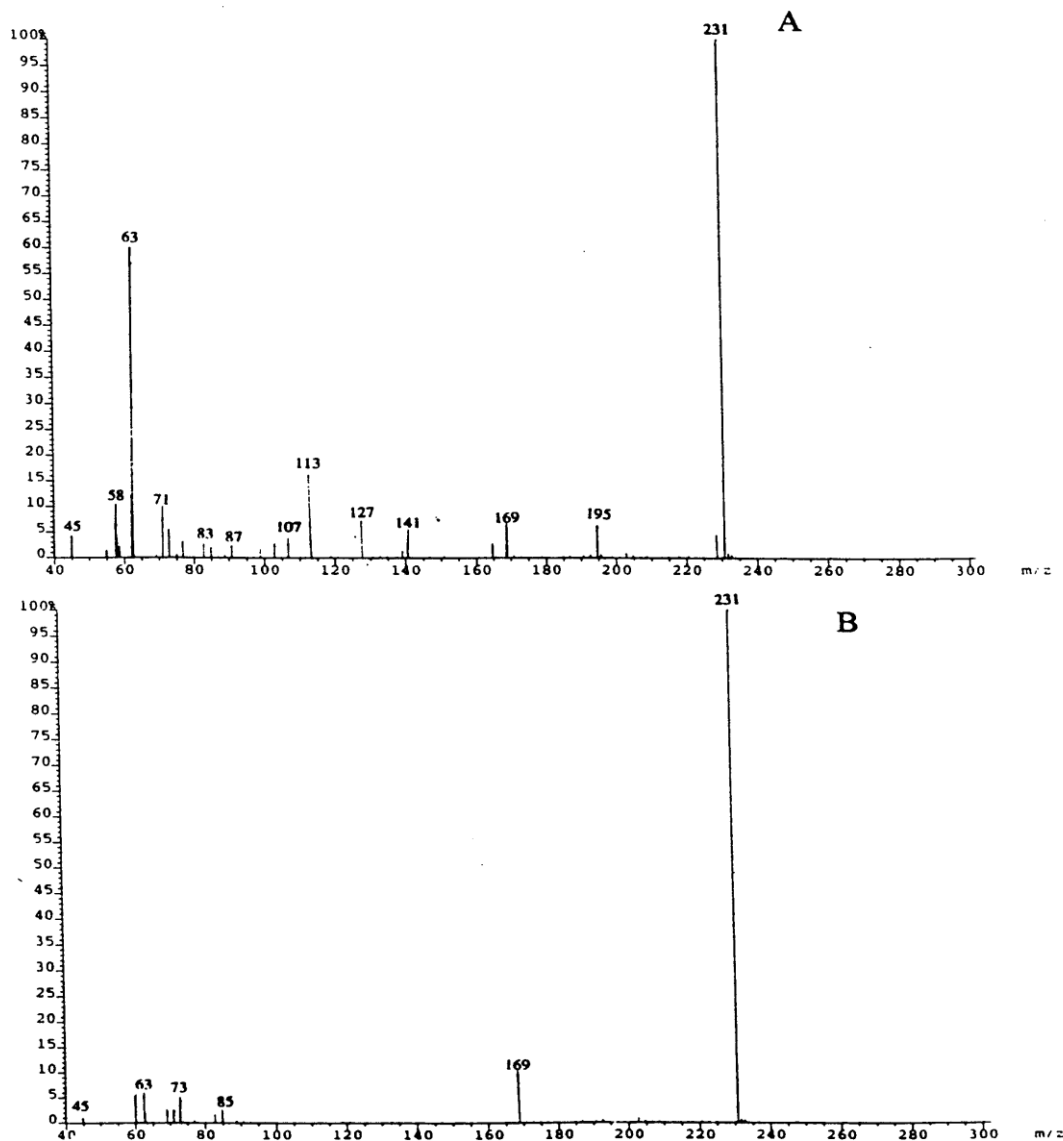


Figure-3
 $i\text{-C}_4\text{H}_{10}$ CI Mass Spectra of Ethylene Glycol Dodecyl Ether obtained at (A) $I(43)/I(57) = 0.15$ (B) $I(43)/I(57) = 0.05$

In general, the mass spectrum obtained at the lower pressure, $P = 0.15$, for all PEGDME consist of MH^+ , alkyl ions, PEGH^+ , $(\text{OC}_2\text{H}_4)_{1-4}\text{H}^+$, $\text{C}_x\text{H}_{2x+1}^+$, $\text{H}(\text{O}_4\text{H}_2^+\text{C}_2\text{H}_4)_{1-4}\text{OH}_2^+$, and $\text{C}_x\text{H}_{2x+1}\text{O}^+$ ions, while the higher pressure, $P = 0.05$ spectrum contains essentially MH^+ ion (~ 97 , no $(\text{MH}-\text{H}_2\text{O})^+$ and protonated dimer ions.

Conclusion

The EI spectra of PEGMAE do not give MW information and few are found in the mass spectral data base. The base peaks are variable and depend on the hydrocarbon portion ($n \leq 2$, $x \geq 3$) and the ethylene moiety ($n \geq 3$). The CH_4/CI spectra give MW information and also fragments that give structural information.

The base peaks under CH_4 CI are $\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}_2^+$ ($n = 1-3$), or MH^+ for $n \geq 4$. The $i\text{-C}_4\text{H}_{10}$ CI is pressure dependent. The spectra at the lower pressure are similar to those of CH_4 CI spectra but the extent of fragmentation is less. The spectra at higher pressure contain essentially MH^+ ($i\text{-C}_4\text{H}_{10}$) CI. $i\text{-C}_4\text{H}_{10}$ gas will be a better reagent gases than CH_4 for quantification. The thermochemical data for some of the dominant cleavages were determined for the CH_4 CI reactions.

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