

Full Length Research Paper

# Sample ion/sample molecule reactions in gas chromatography/chemical ionization mass spectrometry of polyethylene glycols and polyethylene glycols dimethyl ethers

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Sample ion/sample molecule (SISM) reactions frequently occur under chemical ionization (CI) conditions with large sample size polar compounds, and are useful in forming  $MH^+$  ions for molecular weight determination. Studies about the variation of chemical ionization spectra with sample size were made in this report using gas chromatography/mass spectrometry, GC/MS, to observe the relative abundances of the major ions in the spectra of each sample as the sample size varies across the chromatographic peak. A plot of the fraction of total ionization of each major ion against the extent of conversion of the reagent ions to product ions indicated the reactivity of each major ion and those of the products of SISM reactions. The result also revealed that the relative abundances of the  $MH^+$  ion in the methyl chemical ionization ( $CH_4$  CI) mass spectra of polyethylene glycols (PEG) and polyethylene glycol dimethyl ethers (PEGDME) increased dramatically with increasing sample size because of SISM reactions. The dominant fragment ion of all PEG and PEGDME oligomers are the ion at  $m/z$  45 ( $C_2H_5O^+$ ) and  $m/z$  59 ( $C_3H_7O^+$ ) respectively. These ions reacted to form product ions such as  $MH^+$  and  $(C_2H_4O)_nH^+$  ions whose abundances increased with extent of conversion. Ions formed by 1,3 hydrogen rearrangements,  $H(OC_2H_4)_nOH_2^+$ , were also present in these spectra and their relative abundances also increased with increasing extent of conversion.

**Key words:** Gas chromatography, mass spectrometry, polyethylene glycol ethers, sample ion/sample molecule.

## INTRODUCTION

The mass spectrometer provides a wealth of information for a very small quantity of sample relative to many other analytical tools and is a good technique for determining structures, molecular weights of compounds, and detection and risk assessment of pollutants in the environment.

The potential of mass spectrometry as an analytical research tool is tremendous and its range covers small organic compounds ( $MW \leq 100$ ) to large molecules ( $MW \geq 10,000$ ). Coupled techniques such as gas chromatography mass spectrometry (GC/MS), have

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increased the scope of quantitative and qualitative information that can be obtained from a sample. New developments in various spheres of sciences have produced many commercial products and as well increased risk to human health and environmental pollution. For example, packaging materials such as Bisphenol and paraffin's have been found to migrate into food materials and reacts with food components such as proteins (Petersen et al., 2007; Simal-Gándara et al., 2009, 2000; Biedermann and Grob, 1998). Pesticides such as chlorpyrifos and penconazole residues have been found in wines (Batta et al., 2005; Rial et al., 2002) and large biopolymers such as epoxy resins are used in art conservation (Peris-Vicente et al., 2009) and as sensors (Airoudj et al., 2009) in many chemical applications. Identification and characterization of these chemicals require fast and accurate analytical techniques and instrumentation such as chemical ionization (CI). The CI technique is based on ion-molecule reactions and its usefulness depends on the types of reactions and also on the rates of the reactions (Harrison, 1992). Ion-molecule reactions can occur by charge transfer (Lindholm, 1972; Allgood et al., 1990), proton transfer (Field and Munson, 1966; Cairns et al., 1989), negative-ion transfer (Field and Lampe, 1958; Park et al., 1985) and by condensation reactions (Abramson and Futrell, 1968; Orlando et al., 1988), and it generally occurs when the reactions are thermoneutral or exothermic. These reactions have been used to obtain structural information and other thermochemical properties of many compounds. Different reagent gases, such as  $\text{CH}_4$ ,  $(\text{CH}_3)_4\text{Si}$ ,  $\text{NH}_3$  and  $\text{CH}_4/\text{NH}_3$ , have been used for selectivity in chemical analysis (Rudewicz and Munson, 1986b; Hogg and Nagabhusan, 1972). For example,  $\text{NH}_3$  and  $\text{CH}_4/\text{NH}_3$  mixtures were used as selective reagent gases in the study of the complex mixtures of polyethylene glycols (PEG) mono alkyl ethers (Rudewicz and Munson, 1986a; Stephanou, 1984). The spectra obtained with  $\text{NH}_3$  consist essentially of  $(\text{M}+\text{NH}_4)^+$  ions and those obtained with  $\text{CH}_4/\text{NH}_3$  mixture contain essentially  $(\text{M}+\text{NH}_4)^+$  ions with small amounts of  $(\text{MH})^+$  ions. Ion-molecule reactions have also been used to study the reactivity of different functional groups with the same reagent ions and to derivatize functional groups for additional structural information (Onigbinde et al., 2012a). Different mass spectrometric methods such as GC/CIMS, FT/ICRMS and Ion-Trap/MS have been used to study ion-molecule reactions that include sample ion/sample molecule reactions (Eitchmann and Broadbelt, 1993; Lin et al., 1993).

Sample ion/sample molecule reactions are the reactions between sample ions and the neutral sample. Lee et al. (1983) observed that the relative intensities of  $\text{MH}^+$  ions of crown ethers increased with increasing sample pressure in the source of an ion cyclotron resonance (ICR) mass spectrometer. This observation was explained by proton transfer reactions of sample ions at  $m/z$  45 with sample molecules. He suggested that

sample ion/sample molecule reactions can occur in the source of mass spectrometers under CI conditions, especially with polar compounds. High pressure CI and low pressure ICR experiments have also been used to show the occurrence of sample ion/sample molecule reactions of di-alkyl ethers and alcohols with trimethylsilyl ions (Blair et al., 1980; Clemens and Munson, 1985; Trenerry and Bowie, 1979; Orlando and Munson, 1986). It has been observed that the  $\text{CH}_4/\text{CI}$  of PEGs and PEGMAEs consist mostly of  $\text{MH}^+$ ,  $(\text{C}_2\text{H}_4\text{O})_n\text{H}^+$ ,  $(\text{H}(\text{OC}_2\text{H}_4)_n\text{OH})\text{H}_2^+$ , and  $\text{CH}_3(\text{OC}_2\text{H}_4)_n^+$  ions and small amount of  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4^+$  ions (Onigbinde et al., 2012b). The relative abundances of the  $\text{MH}^+$  ions and some of the products ions vary across the chromatographic peaks. These observations imply that the formation of the  $\text{MH}^+$  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. In this paper, sample ion/sample molecule reactions occurring in the CI mass spectra of the PEG oligomers and polyethylene glycol dimethyl ethers (PEGDME's) as functions of the extent of conversion of the reagent ions to products ions will be studied.

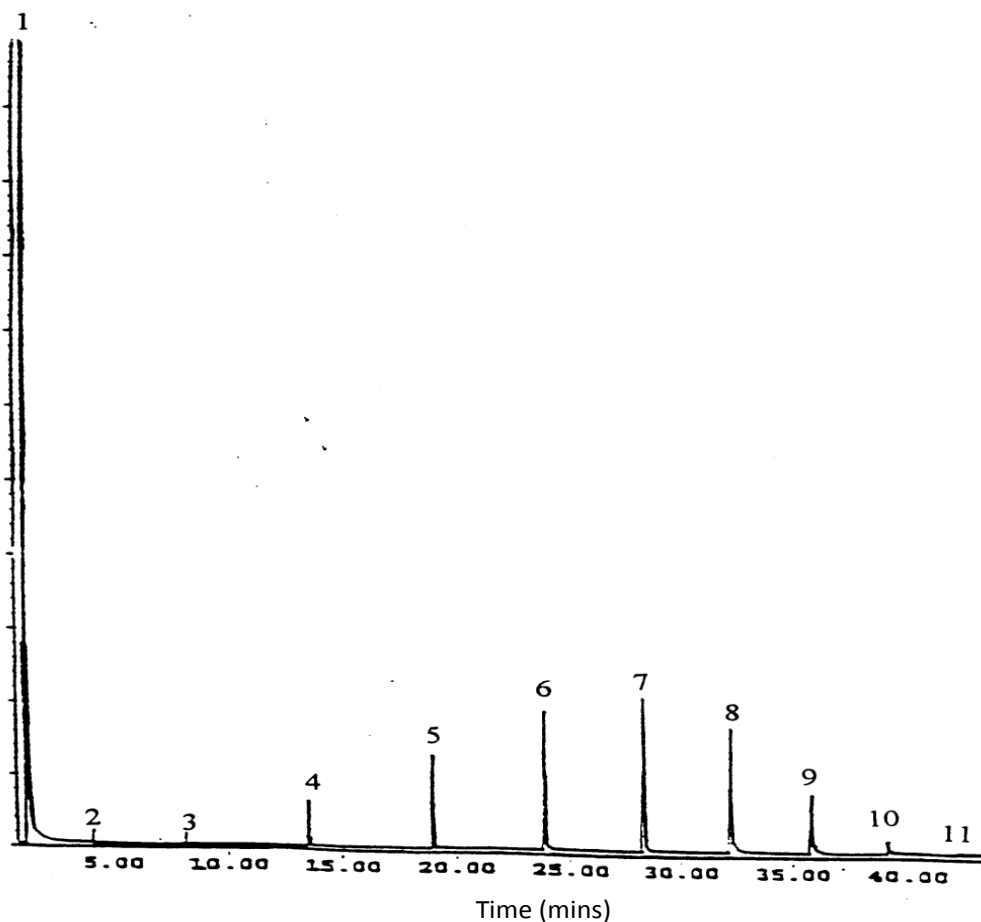
## MATERIALS AND METHODS

### Gas chromatography

Chromatographic conditions varied according to the mixtures being analyzed. Solutions of known concentrations ( $\sim 10$ – $4$  M) of the lower oligomers ( $n = 1$ – $6$ ) in ethanol were separated with  $30 \text{ m} \times 0.25 \text{ mm}$  cross-linked methyl silicone capillary columns (Alltech SE-30, SE-54) using a temperature program of  $\sim 35$  to  $250^\circ\text{C}$  at  $5^\circ\text{C} \text{ min}^{-1}$  and an injection port temperature of  $250^\circ\text{C}$ . Solutions of PEG (Aldrich), PEG 200 (Aldrich), PEG 400 (Aldrich) and PEGDME oligomers were also separated on these columns under similar conditions. PEG oligomers up to  $n = 11$  (Figure 1) could be detected in PEG 400 with a final column temperature of  $330^\circ\text{C}$  and an injection port temperature of  $300^\circ\text{C}$ . It was necessary to maintain the source of the mass spectrometer at a higher temperature ( $\sim 280^\circ\text{C}$ ) when analyzing the higher oligomers. The chromatograms of solutions of the pure oligomers showed no significant impurities. Examination of the spectra across the chromatographic peaks gave no indication of significant impurities eluting with the PEG and PEGDME oligomers from PEG 200 or PEG 400. The chromatographic peaks for all of the oligomers were sharp but with slight tailing that often occurs in chromatography of alcohols. Splitless injections of  $0.05$  to  $0.5 \mu\text{l}$  of solutions were used. PEGDME's were synthesized in this laboratory (Johnstone and Rose, 1969).

### Chemical ionization (CI)

Some CI mass spectra of PEG oligomers and PEGDME were obtained with a VG MM16 mass spectrometer (single-focusing) attached to a Varian Model 3700 gas chromatograph. Data were collected with an IBM-XT computer, interfaced to the mass spectrometer with Technivent interface software. Different scan rates and ranges were used for different mixtures. Perfluorotributylamine was used for tuning and calibration. The



**Figure 1.** GC/CI Chromatogram of PEG 400 Obtained With MSD 5972. (1) Solvent (2) Diethylene glycol (3) Triethylene glycol (4) Tetraethylene glycol (5) Pentaethylene glycol (6) Hexaethylene glycol (7) Heptaethylene glycol (8) Octaethylene glycol (9) Nonaethylene glycol (10) Decaethylene glycol (11) Undecaethylene glycol. (MSD 5972; 120, 1 min; 120 - 300°C @ 10°C/min, 19 min; 300°C, 25 min, 70 eV, Alltech SE30, SE54, 30 m × 0.25 mm × 0.33 μm cross-linked methyl phenyl silicone).

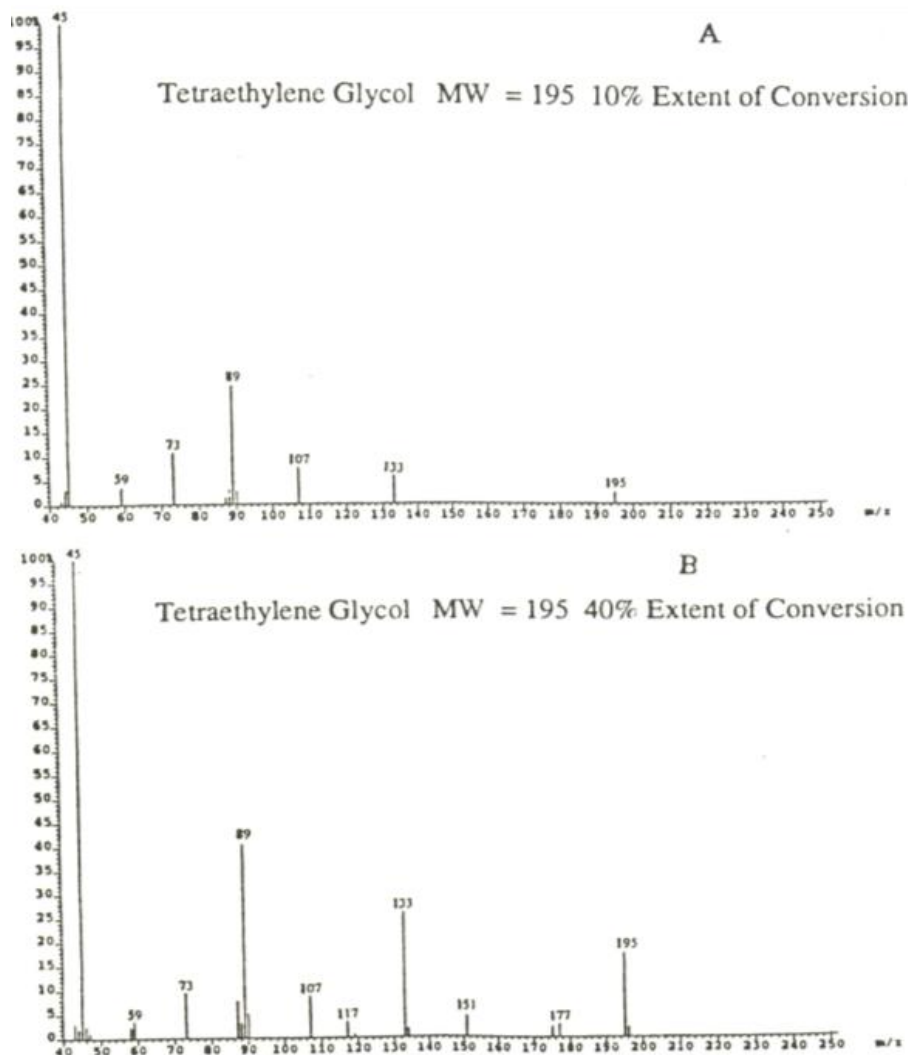
source temperature was 250°C (uncalibrated). The pressures were measured with a capacitance manometer (MKS Instruments, Burlington, MA, USA) connected directly to the source of the mass spectrometer by a gas tube through the inlet for the direct insertion probe. The reagent gas pressures (CH<sub>4</sub>) were ~ 0.3 torr. Other CI mass spectra were obtained with the AutoSpecQ mass spectrometer attached to an HP 5980 Series II gas chromatograph. The pressures of the reagent gas (CH<sub>4</sub>) were not measured with this instrument but are comparable to the one used for CI experiments in commercial mass spectrometers. The ratio of the major ions in the methane reagent gas for the two instruments is similar:  $m/z$  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. There is only a small amount of water, or H<sub>3</sub>O<sup>+</sup>, in each reagent gas. All experiments were done in the splitless injection mode with no solvent delay times. The source temperature was 250°C and the transfer line temperature was 280°C (uncalibrated). The CH<sub>4</sub>CI mass spectra were obtained at different points across the chromatographic peaks to show the variation in spectra with sample

concentration in the source of the mass spectrometer. The CH<sub>4</sub>CI mass spectra are the average of 10 to 15 spectra after background subtraction. Experiments were also performed at reduced electron multiplier voltages to obtain the spectrum of each reagent gas for each set of GC/CIMS experiments. The total sample ion current (TIC) was obtained by summing the ion currents of all sample ions in each spectrum. The total sample ion current was recorded over the mass range of all samples (30 to 600 μ). The baseline of each peak was determined by the computer and all calculations were done using the standard software package on the MS systems.

## RESULTS AND DISCUSSION

### Sample ion/sample molecule reactions in CH<sub>4</sub>/CI of polyethylene glycols

The CH<sub>4</sub>CI spectra of PEG oligomers (PEG) were described in an earlier paper (Onigbinde et al., 2012b).



**Figure 2.** CH<sub>4</sub>/Cl mass spectra of tetraethylene glycol at (A) 10%, (B) 40% extent of conversion.

The major ions in these spectra are MH<sup>+</sup>, H(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub><sup>+</sup> at m/z 45, 89, 133 and m/z 63, 107, 151, .... (H(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH<sub>2</sub><sup>+</sup>). Because of the rapid changes in the concentrations of samples across the chromatogram, there are significant changes in the relative abundances of fragment ions at different points along the peak, or at different extents of conversion of the reagent ions to products.

The extent of conversion,  $\Sigma I_i(\text{Sample})/\Sigma I_i(\text{Total})$ , is a qualitative measure of sample concentration. With the reaction



as a model, then

$$d[\text{CH}_5^+]/dt = -\kappa_T[\text{CH}_5^+]$$

and

$$[\text{CH}_5^+]/[\text{CH}_5^+]_0 = \exp^{-\kappa_T[\text{M}]\tau}$$

and

$$\frac{[\Sigma \text{P}_i^+]/[\text{CH}_5^+]_0}{[\Sigma \text{P}_i^+]/[\text{CH}_5^+]_0} = \frac{\Sigma I_i(\text{Sample})/\Sigma I_i(\text{Total})}{\Sigma I_i(\text{Sample})/\Sigma I_i(\text{Total})} = 1 - \exp^{-\kappa_T[\text{M}]\tau} \approx \kappa_T[\text{M}]\tau.$$

For small extents of conversion, the extent of conversion is proportional to the sample concentration, [M], at constant ionic reaction time. The extent of conversion increases as [M] increases, although the two are not linearly related for large extents of conversion.

Figure 2 shows the CH<sub>4</sub>/Cl mass spectra of tetraethylene glycol obtained at a small (~10%) and relatively large extents of conversion (~40%). The spectra

show different relative abundances of ions at the different extents of conversion (different sample pressure). The relative abundance of  $MH^+$  obviously increases and the relative abundance of  $C_2H_5O^+$  decreases for each compound with increasing extent of conversion. These differences in the relative abundances of the sample ions at different extent of conversion (sample size) are due to sample ion/sample molecule reactions. Plots of the relative abundances of the major ions in the  $CH_4$  CI mass spectra of ethylene glycol vs. extent of conversion are shown in Figure 2. The decrease in the relative abundance of ions at  $m/z$  45 and the increase in the relative abundance of ions at  $m/z$  63 mean that the fragment ions at  $m/z$  45, presumably protonated ethylene oxide, react with neutral ethylene glycol to form the  $MH^+$  ions at  $m/z$  63.

There is no obvious variation in the low relative abundance of ions at  $m/z$  63. The protonated dimer,  $(EG)2H^+$  at  $m/z$  125, is also observed at low abundances. Obviously, this ion is formed by sample ion/sample molecule reaction between  $MH^+$  and M. The relative abundances of these ions extrapolated to zero extent of conversion represent the "true" CI spectrum of ethylene glycol: that is, the ionic products of reactions of only  $CH_5^+$  and  $C_2H_5^+$  with ethylene glycol. The extrapolated intercepts are not easy to determine precisely, but there is only very small amount of  $MH^+$  formed by proton transfer whose concentration increases with increasing sample size or extent of conversion.

The dominant reactions of  $CH_5^+$  and  $C_2H_5^+$  are dissociative proton transfer to give  $C_2H_5O^+$ . There appears to be a downward curvature in the plot of the relative abundance of the ion at  $m/z$  45, but the data also give a reasonable fit to a straight line. Linear extrapolations of these curves give  $m/z$  45 as 87% and  $m/z$  63 as 6% of the ionic products from the reaction of  $CH_5^+$  and  $C_2H_5^+$ . Figure 4 shows similar plots for the variations of the abundances of sample ions with increasing sample size for diethylene glycol and tetraethylene glycol. Similar observations can be made for these curves:  $C_2H_5O^+$  ions decrease and  $MH^+$  ions increase in relative abundances as the extent of conversion (or sample concentration) increases from a very small value at very small extents of conversion. Proton transfer occurs from the dominant fragment ion,  $C_2H_5O^+$ , to the PEG oligomers, as was the case for ethylene glycol.

The protonated dimer,  $(DEG)2H^+$  at  $m/z$  213, was formed with diethylene glycol at the highest concentrations. However, no protonated dimer is observed under comparable conditions with tetraethylene glycol or with higher glycols (not shown). This difference in behavior is similar to that observed by Morton and Beauchamp (1972) for the compounds,  $CH_3O(CH_2)_nOCH_3$ , for which it was observed that ion-molecule reactions gave  $M2H^+$  ions for short chains, but not for long chains under comparable ICR conditions.

This difference in behavior was attributed to internal hydrogen bonding for the longer chain species. We also assume the same for tetraethylene glycol and the higher PEG oligomers, as well.

The relative abundances of  $MH^+$  ions in the  $CH_4$ CI mass spectra of diethylene glycol and tetraethylene glycol are small. It is difficult to obtain a precise number for these quantities from an extrapolation to zero extent of conversion; however, there is no obvious increase in relative abundances of  $MH^+$  ions in the  $CH_4$ CI spectra with increasing molecular weight of the PEG oligomer. The data suggest that there is a smaller relative abundance of  $MH^+$  ions for tetraethylene glycol than for the others. The stability of  $MH^+$  ions does not appear to increase with the increasing number of vibrational degrees of freedom (increasing molecular weight).

Figure 4A shows a small increase in the relative abundance of the ions at  $m/z$  89,  $(C_2H_4O)2H^+$ , with increasing sample concentration for diethylene glycol. This small increase indicates a reaction of  $C_2H_5O^+$  with diethylene glycol to give  $(C_2H_4O)2H^+$ . There is no significant change in the relative abundance of the ions at  $m/z$  73,  $(M + C_2H_5 - HOCH_2CH_2OH)^+$ . Figure 4A also shows a significant increase in the relative abundance of the minor ion at  $m/z$  133,  $(C_2H_4O)3H^+$ , with increasing sample concentration.

Figure 4B shows a maximum in the relative abundance of the ions at  $m/z$  89 with increasing concentration of tetraethylene glycol. This observation suggests that this ion is formed by dissociative proton transfer from  $C_2H_5O^+$  and adduct formation with tetraethylene glycol, both resulting to  $MH^+$ . The reaction profiles in Figures 3 and 4 suggest that the primary reaction of  $CH_4$  reagent ions,  $CH_5^+$  and  $C_2H_5^+$ , with PEG oligomers include: (a) formation of an excited intermediate protonated PEG which dissociates into  $(C_2H_4O)H^+$  ions (dominant fragmentation); (b) formation of hydrogen rearrangement products,  $(HOC_2H_4OH)H^+$ ; (c) formation of small amounts of  $MH^+$ , and (d) dissociative ethyl addition. It also shows that the reaction of ions at  $m/z$  45 with neutral PEG occur either by proton transfer or by the formation of an intermediate  $(M+45)^+$  adduct similar to those observed in the ion-molecule reactions of dimethyl ethers (Eitchmann and Broadbelt, 1993). There is no collision stabilization of the  $(M+C_2H_5)^+*$  intermediates; consequently, it is likely that the enhancement of the  $MH^+$  with increasing sample size results from these ion-molecule reactions and not collision stabilization of the excited  $MH^+$  intermediate.

#### Sample ion/sample molecule reaction in $CH_4$ /CI MS of PEG dimethyl ethers

Figure 5 compares the  $CH_4$ /CI spectra of tetraethylene glycol dimethyl ether at small (~10%) and large (~40%) extent of conversion of reagent ions to product ions. The

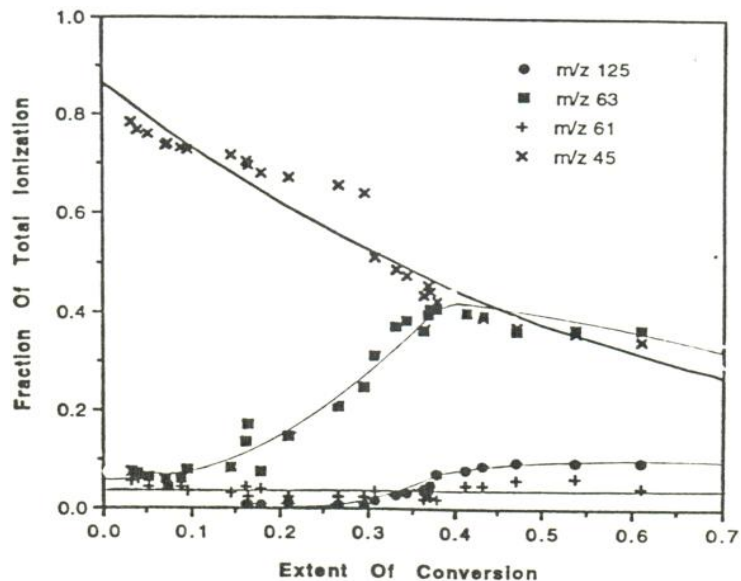


Figure 3. CH<sub>4</sub>Cl reaction profile of ethylene glycol vs extent of conversion.

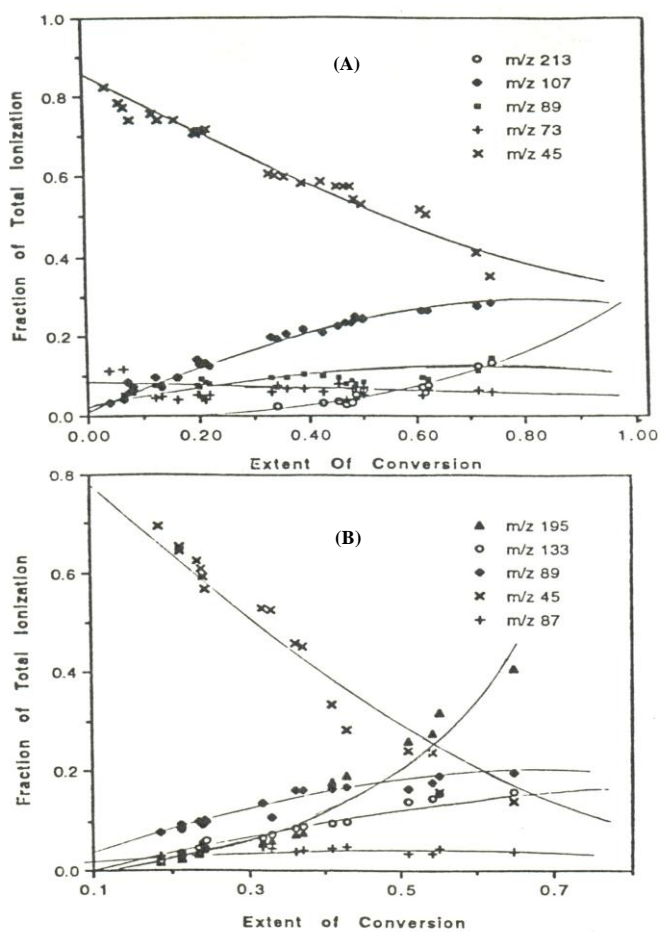
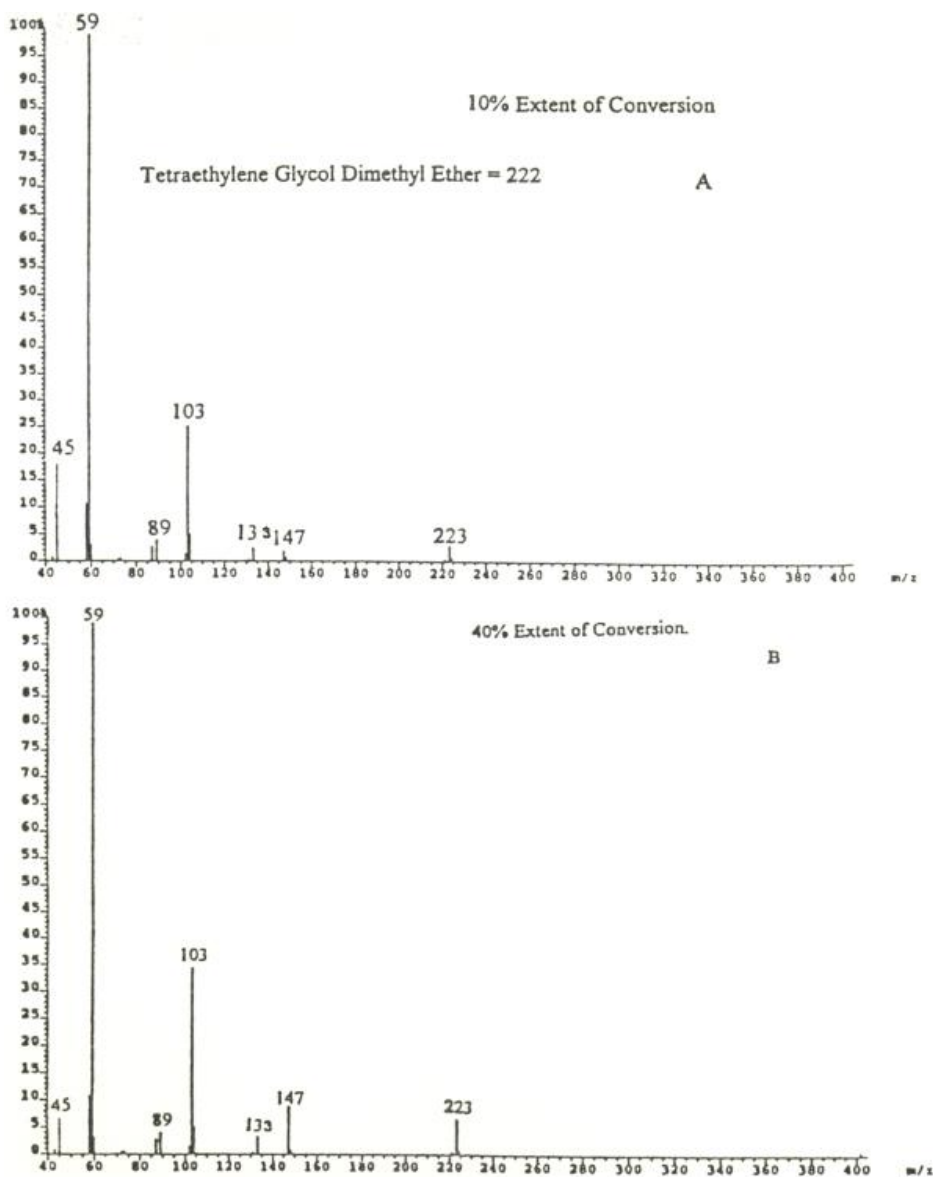


Figure 4. CH<sub>4</sub>Cl reaction profile of (A) Diethylene glycol (B) Tetraethylene glycol vs extent of conversion.



**Figure 5.**  $\text{CH}_4/\text{Cl}$  mass spectra of tetraethylene glycol dimethyl ether (A) 10%, (B) 40% extent of conversion.

major ions in the  $\text{CH}_4/\text{Cl}$  spectra of PEG dimethyl ethers, PEGDME, are  $\text{CH}_3(\text{OC}_2\text{H}_4)_n^+$  ( $m/z$  59, 103, 147,...) with less abundant ions at  $\text{CH}_3(\text{OC}_2\text{H}_4)_n+\text{O}=\text{CH}_2$  ( $m/z$  45, 89, 133,...), and small and variable amounts of  $\text{MH}^+$  ions. The relative intensities of  $\text{MH}^+$  ions, like the  $\text{MH}^+$  ions of the PEG oligomers, increase with increasing extent of conversion due to sample ion/sample molecule reactions. The reaction profiles of the major ions in the  $\text{CH}_4/\text{Cl}$  spectra of ethylene glycol dimethyl ether are shown in Figures 6 and 7. One can see that the major ions from the reactions of  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  with ethylene glycol dimethyl ether are  $\text{C}_2\text{H}_5\text{O}^+$  at  $m/z$  45 and  $\text{C}_3\text{H}_7\text{O}^+$  at  $m/z$  59 each at (~45% at zero extent of conversion).

There are also small amounts of  $\text{MH}^+$  ions (~3%) and  $(\text{M}-\text{H})^+$  ions at  $m/z$  89 (~3%) at zero extent of conversion. The reaction profiles show that ions at  $m/z$  45 react rapidly and are accompanied by an increase in the abundances of the ions at  $m/z$  59 with a smaller increase in abundances of the ions at  $m/z$  91. The approximately constant value of ~7% for the relative abundances of ions at  $m/z$  45 for extent of conversion greater than 30% suggests two structures for  $\text{C}_2\text{H}_5\text{O}^+$  ions: one reactive and one unreactive with ethylene glycol. The ions at  $m/z$  59 show a maximum in fraction of sample ionization with increasing extent of conversion. There is a continuous increase in the abundance of the  $\text{MH}^+$  ions with

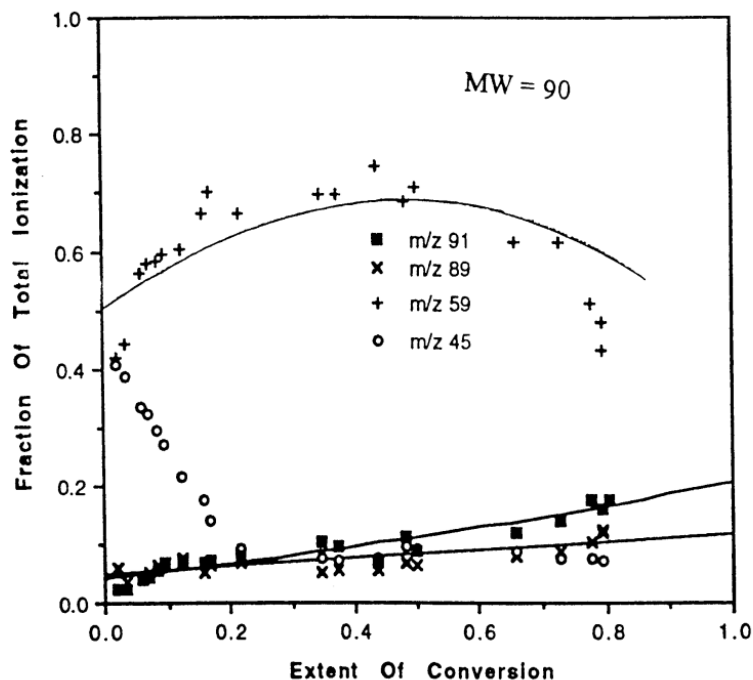
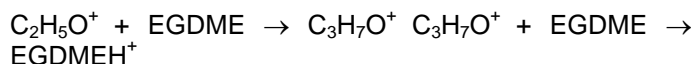


Figure 6.  $\text{CH}_4/\text{CI}$  reaction profile of ethylene glycol dimethyl ether (MW = 90).

increasing extent of conversion. The reaction sequence shown below is indicative of these observations



The  $m/z$  45 ion is more abundant in the spectra of EGDME than in the spectra of higher oligomers (~10 to 15% at zero extent of conversion) and its contribution to the formation of ion at  $m/z$  59 is more pronounced in ethylene glycol dimethyl ether than in those of higher oligomers. The reactions in the other oligomers are primarily proton transfer from the dominant  $\text{C}_3\text{H}_7\text{O}^+$  ion at  $m/z$  59 to form  $\text{MH}^+$  ions. The relative abundances of  $\text{MH}^+$  ions at zero concentrations are very small or zero for all of these oligomers.

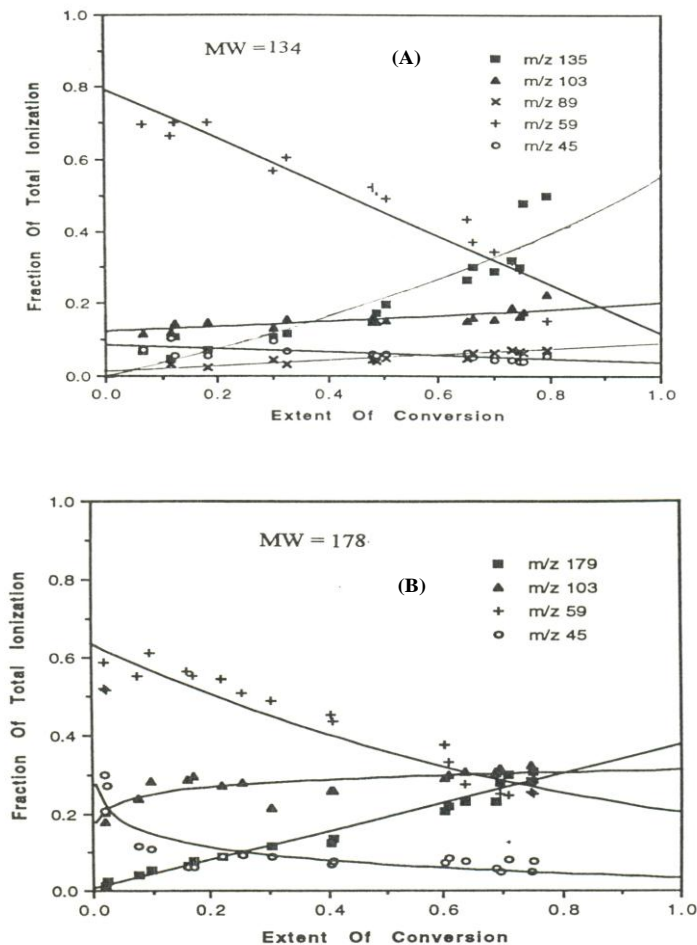
There are two likely structures for the ions at  $m/z$  45,  $\text{CH}_3\text{O}=\text{CH}_2^+$  and  $\text{C}_2\text{H}_4\text{OH}^+$ .  $\text{C}_2\text{H}_4\text{OH}^+$  ions can likely be formed from the higher PEG dimethyl ethers through rearrangement decompositions while  $\text{CH}_3\text{O}=\text{CH}_2^+$  ions can be formed by protonation and cleavage of a C-C bond (Eitchmann and Broadbelt, 1993; Beauchamp and Dunbar, 1970; Blair and Harrison, 1973). Each ICR reports have shown that the  $\text{CH}_3\text{O}=\text{CH}_2^+$  ions reacted by forming  $(M + 45)^+$  adduct ions with PEG oligomers which subsequently decomposed to  $(M+13)^+$  ions (Onigbinde et al., 2012a) by losing a molecule of methanol and by H- and/or methyl cation transfer (Onigbinde et al., 2012b; Morton and Beauchamp, 1972). For ethylene glycol

dimethyl ether in Figure 7, the dominant product of reaction of  $\text{C}_2\text{H}_5\text{O}^+$  is  $\text{C}_3\text{H}_7\text{O}^+$  at  $m/z$  59: neither  $(M+13)^+$  nor  $(M+15)^+$  ions are observed as products under these high pressure CI conditions. However, only a small amount of H- abstraction occur giving rise to the  $m/z$  89 ion.

## Conclusion

Sample ion/sample molecule reactions occur frequently under CI conditions with polar compounds, particularly with large sample size and are useful in forming  $\text{MH}^+$  ions for molecular weight determination. The relative abundances of the  $\text{MH}^+$  in the  $\text{CH}_4/\text{CI}$  mass spectra of PEG and PEGDMEs increased dramatically with increasing sample size because of these sample ion/sample molecule reactions. These sample ion/sample molecule reactions will not be noticed unless studies are made about the variation of chemical ionization spectra with sample size. Such studies were made with GC/MS by observing the relative abundances of the major ions in the spectra of each sample as the sample size varies across the chromatographic peak. A plot of the fraction of total ionization of each major ion against the extent of conversion of the reagent ions to product ions will indicate the reactivity of each major ion and also the products of sample ion/sample molecule reactions. Ions whose relative abundances decrease with increasing





**Figure 7.** CH<sub>4</sub>/Cl reaction profile of (A) Diethylene (MW = 134), (B) Triethylene glycol dimethyl ether (MW = 178).

extent of conversion are clearly reacting to form those ions whose relative abundances increase with increasing extent of reaction.

The CH<sub>4</sub>/Cl mass spectra of PEG and PEGDME's contain structurally useful fragment ions and MH<sup>+</sup> ions. The dominant fragment ion in the CH<sub>4</sub>/Cl mass spectra of all PEG's is the ion at m/z 45 (C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>). This ion reacts to form product ions such as MH<sup>+</sup> and (C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>H<sup>+</sup> ions whose abundances increase with extent of conversion. Ions formed by 1,3 hydrogen rearrangements (H(OC<sub>2</sub>H<sub>4</sub>)OH)H<sup>+</sup> are also present in these spectra and their relative abundances also increase with increasing extent of conversion. The dominant ion in the spectra of the PEGDME's is the ion at m/z 59 and it reacts in a similar fashion to the ion at m/z 45 of the PEG's.

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