



The Rate of Reactions of Isomeric $C_2H_5O^+$ and $C_3H_7O^+$ Ions with Polyethylene Glycols and Polyethylene Glycols Ethers with Fourier Transformation/Ion Cyclotron Resonance Mass Spectrometry (FT/ICRMS)

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Abstract

Sample ion/sample molecule reactions occur with polar compounds under chemical ionization conditions and have been used to determine thermochemical parameters that include rate of reactions. In this paper, the bimolecular rates of reaction of the isomeric $C_2H_5O^+$ and $C_3H_7O^+$ ions at m/z 45 and m/z 59 with PEG's and PEGDMES were studied using the FT/ICR mass spectrometer. The bimolecular rate constants of the reactions of the isomeric $C_2H_5O^+$ ions with PEG oligomers were measured and were found to increase with increasing molecular weight or polarizability of the PEG oligomers. The rate constants for reactions of $C_2H_5O^+$ from PEG and ethylene oxide were very similar for all the PEG oligomers and were relatively close to the calculated ADO values. The rate constants for reaction of $C_2H_5O^+$ ions from dimethyl ether with ethylene glycol and diethylene glycol were significantly lower than the rate constants from the reaction with the other isomers. Similarly, the bimolecular rate constants of the reaction of the $C_3H_7O^+$ ions were measured and found to increase with increasing molecular weight of the PEGDME oligomers. The experimental rate constants are greater than their Langevin values.

Keywords: FT/ICR, ion molecule, mass spectrometry, polyethylene glycol monoalkyl ethers, rate constant.

Introduction

Chemical ionization (CI) technique is based on ion-molecule reactions which can be thermoneutral or exothermic. Its usefulness depends on the types of reactions and also on the rates of the reactions¹. Ion-molecule reactions occur by charge transfer^{2,3}, proton transfer^{4,5}, negative-ion transfer^{6,7}, and by condensation reactions^{8,9} and have been used to obtain structural information and other thermochemical properties of many compounds¹. Different reagent gases, such as CH_4 ⁴, $(CH_3)_4Si$ ³, NH_3 and CH_4/NH_3 ^{10,11} have been used for selectivity in chemical analysis^{12,13}, studying the reactivity's of different functional groups and to derivatize functional groups for additional structural information¹⁴.

Different mass spectrometric methods such as GC/CIMS, FT/ICRMS and Ion-Trap/MS have been used to study ion-molecule reactions^{10,11,14-16} and the occurrence of sample ion/sample molecule reactions of dialkyl ethers and alcohols with trimethylsilyl ions^{9,17-20}. As shown in our previous papers^{21,22}, sample ion/sample molecule reactions contributed to the formation of MH^+ and other product ions in CI experiments. In this study, the bimolecular rates of reaction of the ion-molecule reactions of the isomeric sample ions at m/z 45 and m/z 59 with PEG's and PEGDMES will be studied using the FT/ICR mass spectrometer.

Material and Methods

FT/ICR data were obtained with an Extrel 2000 FT/MS mass. Ions at m/z 45 were made from three sources: (1) EI/CI of PEG; (2) ion-molecule reactions of ethylene oxide, and (3) EI/ion-molecule reactions of dimethyl ethers. $C_3H_7O^+$ ions were made from: i. EI/CI of PEGDME's, ii. ion-molecule reactions of ethylene oxide/methyl iodide mixture, iii. ion-molecule reaction of acetone; iv ion-molecule reaction of vinyl methyl ether. All experiments were done at a source temperature of 27°C (300 K). A 100 μ s pulse (70 eV) was used in ionizing the samples (EI/CI), followed by a 100 μ s delay before ion ejection (Chirp, 15ms). A voltage of ~2 volts was used to trap the ions. Various delay times (0.01 - 2sec) were employed to allow the ions to react with the neutral sample and a 5 ms time were allowed for detection.

Results and Discussion

The time dependence studies of the reactions of neutral ethylene glycol with $C_2H_5O^+$ from three different sources are shown in figure 1. The $C_2H_5O^+$ (m/z 45) is the principal reacting sample ions observed in the CI experiments with PEG's. This is also true for the low pressure ICR experiments. Isomeric $C_2H_5O^+$ ions obtained from PEGs and ethylene oxide reacted primarily by dissociative proton transfer (figures 1a and b) to give MH^+ ions which dissociate into other ions at m/z 87 and 89. These

sequential reactions are established by the observed increase in the ratios of $I(87)/I(63)$ and $I(89)/I(63)$ with time and the constant value for the ratio, $I(87)/I(89)$ also with time. Since the pressures of PEG's are essentially the same for these experiments, the similarities in the extents of conversion indicate that the rate constants for the reactions are similar. Figure 1c shows the reactions of the $C_2H_5O^+$ produced from dimethyl ether with ethylene glycol. The products are clearly different from those shown in figures 1a and 1b. The $C_2H_5O^+$ ions from dimethyl ether gave predominantly $(M+13)^+$ ion at m/z 75 with a smaller amount of MH^+ at m/z 63. Since the

pressure of ethylene glycol in this experiment is essentially the same as the pressure in the experiments in figures 1a and 1b, the smaller extent of conversion indicates that the $C_2H_5O^+$ ions from dimethyl ether react more slowly than the $C_2H_5O^+$ ions from ethylene glycol or from ethylene oxide. These observations support the earlier contentions that the $C_2H_5O^+$ ions from ethylene glycol have the structure of protonated ethylene oxide and are different from the isomeric ion $(CH_3-O=CH_2^+)$ ion from dimethyl ether²². No $(M+45)^+$ adduct ions were observed in any of these experiments, even though $(M+45)^+$ ions were reported by other authors¹⁴.

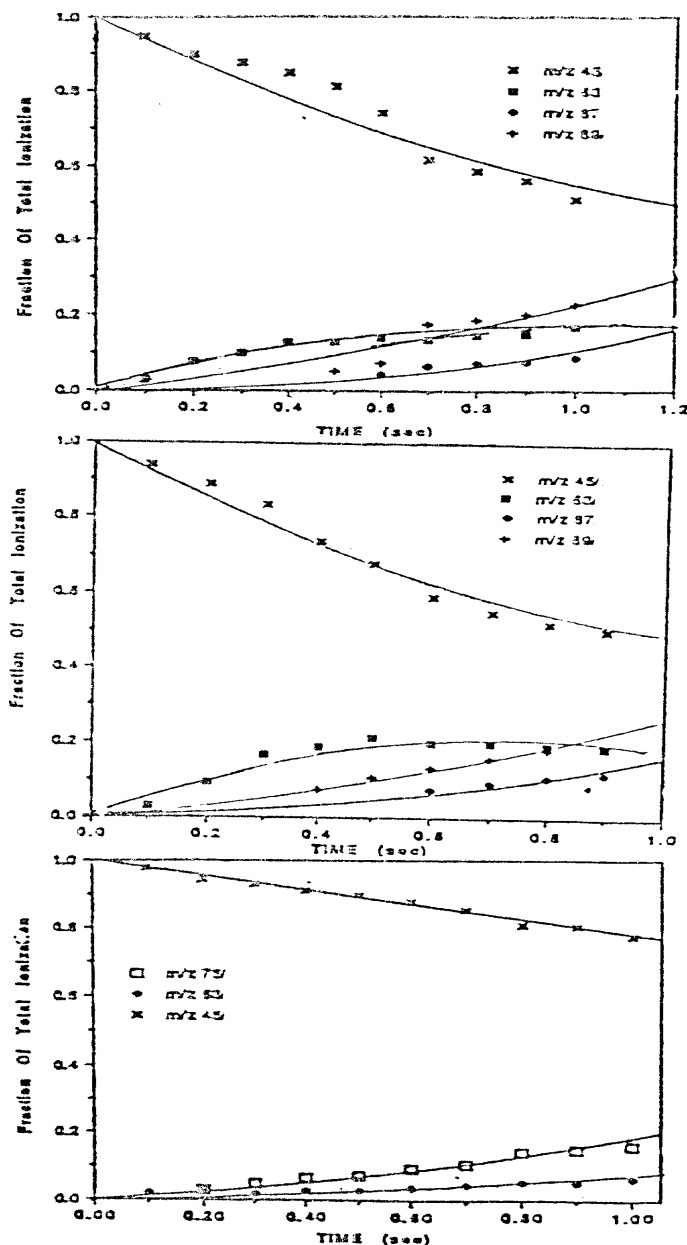


Figure-1

Time Dependence Studies of Ethylene Glycol with Isomeric $C_2H_5O^+$ ions obtained from (a) EI of Ethylene Glycol (b) Ion-Molecule Reaction of Ethylene Oxide (c) Ion-Molecule Reaction of Dimethyl Ether. ($P = 2.0 \times 10^{-8}$, $T = 300^\circ K$)

Figures 2a and 2b shows the reactions of $C_2H_5O^+$ produced from EI of diethylene glycol (DEG) and from ion-molecule reactions of ethylene oxide with DEG. The products of the reactions, distributions, and the extents of reaction (for the same reaction time interval and sample pressure) are similar. Figure 2c shows the reactions of $C_2H_5O^+$ ions from dimethyl ether with DEG. The reaction products are different and the extents of reaction (for the same reaction times interval and sample pressure) are different. The ratio of $I(M+13)^+/I(MH^+)$ is smaller for the reactions of this isomeric ion ($CH_3-O=CH_2^+$) with DEG than with ethylene glycol. The conclusion from these experiments is that the $C_2H_5O^+$ ions from EI of PEG's and the from protonated ethylene oxide ions have a common structure that is different

from the isomeric ion ($CH_3-O=CH_2^+$) from dimethyl ether²². Similar experiments were performed with some of the higher PEG oligomers.

One can calculate the rate constants for the reaction of $C_2H_5O^+$ with these PEG oligomers using standard methods. A plot of $\ln\{I(45)\}/\Sigma I_i$ vs. reaction times will give a straight line whose slope is $-k[PEG]$. The pressure of the PEG oligomers could not be measured directly because of possible adsorption losses between the source and the ionization gauge and because the conversion factor from ionization gauge reading to pressure is not directly known.

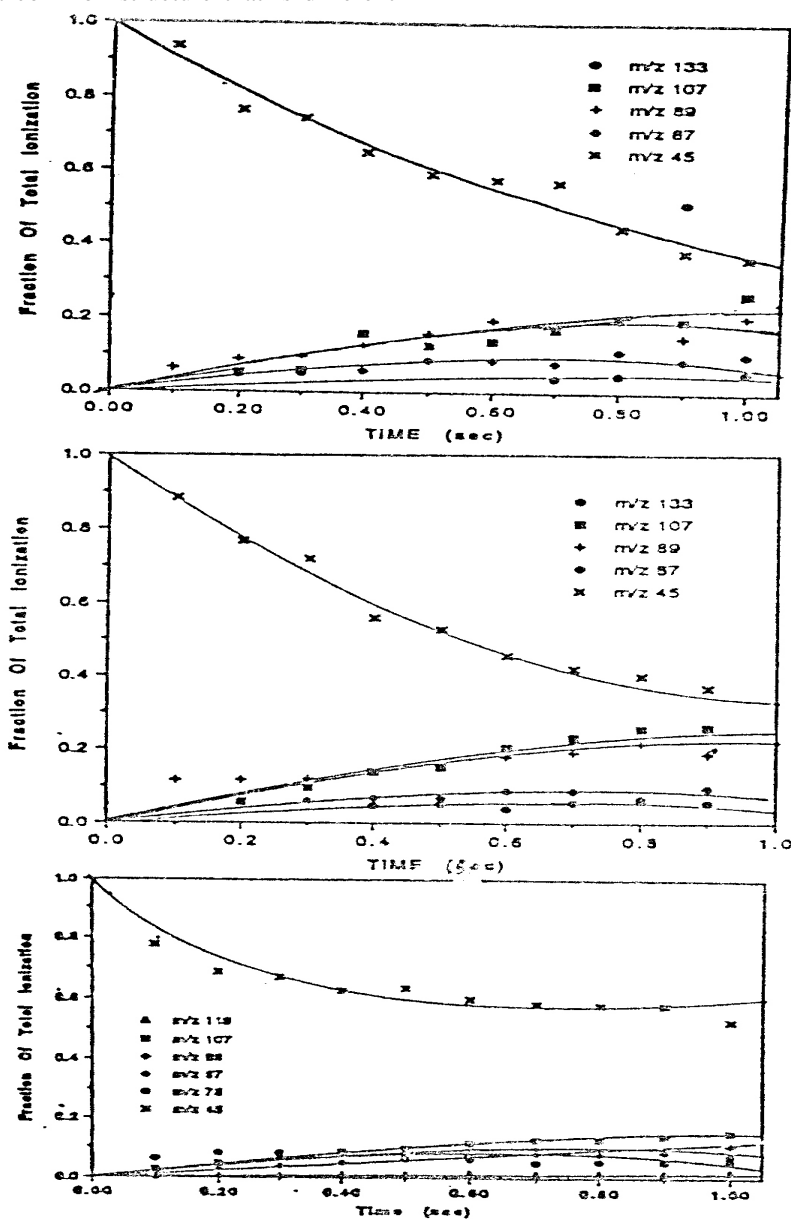


Figure-2

Time Dependence Studies of Diethylene Glycol reaction with Isomeric $C_2H_5O^+$ ions obtained from (a) EI of Diethylene Glycol (b) Ion-Molecule Reaction of Ethylene Oxide (c) Ion-Molecule Reaction of Dimethyl Ether. ($P = 2.0 \times 10^{-8}$, $T = 300^\circ K$)

However, an indirect method of determining the pressures and bimolecular rate constants has been developed²³. The appropriate equation is shown below:

$$k = (-\text{slope}) \alpha \beta / \Sigma I_i$$

k = the bimolecular rate constant; the slope is obtained from the experimental data; α = the polarizability of the sample, β = instrumental constant; and ΣI_i = the sum of all ions from the sample under 70 eV ionization.

The value of β was obtained from the known rate constants for the reaction of CH_3CO^+ with acetone ($\beta = 2.06 \pm 0.11 \times 10^{-6}$) and for the reaction of CH_2OH^+ with methanol ($\beta = 3.19 \pm 0.21 \times 10^{-6}$) at five different pressures of acetone and methanol ranging from 2×10^{-8} - 1.2×10^{-7} torr. The average value of $\beta = 2.63 \pm 0.31 \times 10^{-6}$ was used in our calculations. The polarizability, α , for each PEG was calculated according to the method of Miller and Savchik²⁴.

A summary of the rate of reactions of $\text{C}_2\text{H}_5\text{O}^+$ with some PEG oligomers is given in table 1. The reported values are averages of three determinations. The standard deviations are given as a measure of the reproducibility of the determinations. There is an additional uncertainty associated with the uncertainty in the instrument constant measured above. Also included in this table are the rate constants for these reactions, calculated according to Langevin and ADO models^{1,25}.

The experimental rate constants for the reactions of $\text{C}_2\text{H}_5\text{O}^+$ produced by EI of the PEG oligomers and from

protonated ethylene oxide and reacted with diethylene glycols are indistinguishable and are significantly larger than the rate constants of the isomeric $\text{C}_2\text{H}_5\text{O}^+$ ($\text{CH}_3\text{-O=CH}_2^+$) from dimethyl ether. Similar trend is observed for the higher oligomers. The Langevin model does not include the dipole moment of the neutral molecule, and it is apparent that its values are smaller than the experimental rate constants. The experimental rate constants are somewhat lower than the values calculated from the ADO theory for ethylene glycol and diethylene glycol. For the higher PEG oligomers, the ADO and the experimental values are probably not distinguishable. The $\text{C}_3\text{H}_7\text{O}^+$ (m/z 59) ion is the principal reacting sample ions observed in the CI experiments with PEGDME's. The $\text{C}_3\text{H}_7\text{O}^+$ ions were obtained from four different sources: EI of the dimethyl ether of the PEG oligomer, ion-molecule reactions of $\text{CH}_3\text{I}/\text{C}_2\text{H}_4\text{O}$ mixture, ion-molecule reactions of acetone, and from vinyl methyl ether. Isomeric $\text{C}_3\text{H}_7\text{O}^+$ ions obtained from PEG's, and ethylene oxide reacted primarily by dissociative proton transfer and minor alkyl cation transfer while the isomeric ion from acetone and vinyl methyl ether reacted mainly by proton transfer.

Table 2 contains rate constant data for the reactions of isomeric $\text{C}_3\text{H}_7\text{O}^+$ ions with the PEGDME. The values were obtained by procedures essentially the same as those outlined above for the determination of the rate constants of the isomeric $\text{C}_2\text{H}_5\text{O}^+$ ions. The uncertainties given are the standard deviations from triplicate experiments.

Table-1
Bimolecular Rate Constants for the Reaction of Isomeric $\text{C}_2\text{H}_5\text{O}^+$ Ions with PEGs

Compound	MW	μ^a	α^b	D^c	κ_{ETO}^c	κ_{PEG}^d	κ_{DME}^e	κ_L^f	κ_{ADO}^g
Ethylene Glycol	62.1	26.1	5.61	2.27	20 ± 1	22 ± 2	13 ± 2	14	28
Diethylene Glycol	106.2	31.6	9.87	2.69	26 ± 2	26 ± 3	17 ± 1	17	31
Triethylene Glycol	150.2	34.8	14.1	2.99	32 ± 1	30 ± 1	28 ± 3	19	33
Tetraethylene Glycol	194.1	36.7	18.4	3.25	33 ± 2	34 ± 2	33 ± 2	21	35
Pentaethylene Glycol	238.1	37.9	22.7	3.42	35 ± 2	36 ± 2	34 ± 1	23	38
Hexaethylene Glycol	282.2	38.9	29.9	3.46	39 ± 1	37 ± 4	36 ± 2	26	41

$\kappa = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $P[\text{PEG}] = \sim 2 \times 10^{-8}$ (Gauge Pressure); $T = 300^0\text{K}$; All values of κ are averages of three experiments. μ^a = Reduced Mass; α^b = Polarizability (according to ref 24); D^c = Dipole Moment (Values Taken From Reference 26). κ_{ETO}^c = Bimolecular Rate Constants calculated for the reaction of $\text{C}_2\text{H}_5\text{O}^+$ from Ethylene oxide. κ_{PEG}^d = Bimolecular Rate Constants calculated for the reaction of $\text{C}_2\text{H}_5\text{O}^+$ from PEGs. κ_{DME}^e = Bimolecular Rate Constants calculated for the reaction of $\text{C}_2\text{H}_5\text{O}^+$ from Dimethyl Ether. κ_L^f = Langevin rate constant = $2\pi\epsilon(\alpha/\mu)^{1/2}$. κ_{ADO}^g = Average dipole orientation rate constant²⁷.

Table-2
Rate Constants for the Reaction of Isomeric $\text{C}_3\text{H}_7\text{O}^+$ Ions with Polyethylene Glycol Dialkyl Ethers

Compound	MW	μ^a	α^b	${}^2\kappa_{\text{PEGDME}}^d$	$\kappa_{\text{ETO/MI}}^e$	κ_{ACE}^f	κ_{VME}^g	κ_L^h
Ethylene Glycol Dimethyl Ether	90.2	35.64	9.24	26 ± 2	25 ± 3	27 ± 2	22 ± 1	15
Diethylene Glycol Dimethyl Ether	134.2	40.96	13.51	30 ± 3	31 ± 2	35 ± 4	26 ± 2	17
Triethylene Glycol Dimethyl Ether	178.1	44.31	17.77	34 ± 1	33 ± 3	38 ± 2	24 ± 3	19
Tetraethylene Glycol Dimethyl Ether	222.2	46.61	22.0	39 ± 4	38 ± 3	41 ± 4	37 ± 2	21

$\kappa = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, μ^a = Reduced Mass; α^b = Polarizability (calculated according to reference 24); D^c = Dipole Moment (Values Taken From Reference 26). ${}^2\kappa_{\text{PEGDME}}^d$ = Bimolecular Rate constants calculated for reaction of $\text{C}_3\text{H}_7\text{O}^+$ from polyethylene glycol dimethyl ether. $\kappa_{\text{ETO/MI}}^e$ = Bimolecular Rate constants calculated for the reaction of $\text{C}_3\text{H}_7\text{O}^+$ from ethylene oxide/methyl iodide mixture. κ_{ACE}^f = Bimolecular Rate Constants calculated for the reaction of $\text{C}_3\text{H}_7\text{O}^+$ from Acetone. κ_{VME}^g = Bimolecular Rate Constants calculated for the reaction of $\text{C}_3\text{H}_7\text{O}^+$ from vinyl methyl ether. All values of ${}^2\kappa$ are averages of three experiments. κ_L^h = Langevin rate constants = $2\pi\epsilon(\alpha/\mu)^{1/2}$.

The rate constants for the reactions of the $C_3H_7O^+$ ions from a single source increases with increasing number of ethylene oxide units in a manner similar to that shown for the PEG oligomers in Table 1 and are consistently larger than the Langevin values for all isomeric ions. Since the dipole moments for the neutral PEGDME's were not available, calculations of the ADO rate constants could not be made for comparison. The values of the rate constants for the reaction of $C_3H_7O^+$ from different sources with PEGDME'S are obviously not distinguishable.

Conclusion

Sample ion/sample molecule reactions occur frequently under CI conditions especially with polar compounds. The dominant fragment ion in the CI mass spectra of all PEG oligomers is the ion at m/z 45 ($C_2H_5O^+$). This ion reacts to form product ions such as MH^+ and $(C_2H_4O)_nH^+$ ions whose abundances increase with extent of conversion. FT/ICR/MS was used to obtain $C_2H_5O^+$ ions from three sources and reacted with neutral PEG's. The $C_2H_5O^+$ ions made by EI (CI) of PEG's and from ethylene oxide reacted predominantly by proton transfer while the isomeric ion from dimethyl ethers reacted mostly by methyl cation transfer. Similarly, $C_3H_7O^+$ ions were made from four different sources and reacted with PEGDME's. The $C_3H_7O^+$ ions from PEG's, ethylene oxide/methyl iodide mixture reacted mostly by proton transfer with minor amounts of methyl cation transfer while those of acetone and vinyl methyl ether reacted mostly by proton transfer. The bimolecular rate constants of the reactions of the isomeric $C_2H_5O^+$ ions with PEG oligomers were measured and were found to increase with increasing molecular weight or polarizability of the PEG oligomers. The rate constants for reactions of $C_2H_5O^+$ from PEG and from ethylene oxide are very similar for all the PEG oligomers and were relatively close to the calculated ADO values. The rate constants for reaction of $C_2H_5O^+$ ions from dimethyl ether with ethylene glycol and DEG were significantly lower than the rate constants from the reaction with the other isomers. The rate constants for the reaction of $C_2H_5O^+$ (dimethyl ether) with the higher oligomers were approximately the same as the calculated ADO values. The bimolecular rate constants of the reaction of the $C_3H_7O^+$ ions were measured and also found to increase with increasing molecular weight of the PEG oligomers. However, the experimental bimolecular rate constants are greater than their Langevin values.

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