FORMATION OF THE PROTONATED METHANE ION, CH_5^+,
IN THE MASS SPECTRUM OF 2-METHOXYETHANOL

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ABSTRACT

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by Kermit Rainsford Way, Jr.

A doublet had been observed at m/e = 17 in the mass spectrum of 2-methoxyethanol. It was suspected that one of these peaks was due to CH_5^+ although the ion had never before been seen in a methane-free system. This study endeavored to identify the ion and to learn something about its formation.

Measurement of the exact mass of the ion showed that the ion was CH_5^+. This was confirmed by high resolution spectra which resolved the multiplet at m/e = 17 in samples of 2-methoxyethanol which contained small amounts of ammonia or methane-d_1.

Pressure dependence studies indicated that this ion is being formed by a unimolecular process rather than by an ion-molecule reaction.

Isotopic labeling was done to determine from which part of the molecule the ion was formed. The mass spectrum of 2-methoxy-^{13}C-ethanol indicated that the carbon came from the methyl group, while mass spectra of 2-methoxyethanol-1,1-d_2 and 2-methoxyethanol-d do not indicate involvement of the labeled hydrogens. It was concluded that the ion is formed from the methyl group and both hydrogens in the C-2 position in the compound.

A mechanism involving cleavage between the C-1 and C-2 carbons followed by further fragmentation of the $C_2H_5O^+$ ion (which is the base peak in the spectrum) to yield CH_5^+ was proposed:

$$[CH_3OC_2H_4OH]^+ \longrightarrow [CH_3OCH_2]^+ + \text{other fragments}$$

$$[CH_3OCH_2]^+ \longrightarrow CH_5^+ + CO.$$

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By

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INTRODUCTION

I. Historical Background

Early History

The ion CH_5^+ has been observed readily in the mass spectrometer and has also been postulated in radiation chemistry mechanisms. In every case reported, the ion has been formed by an ion-molecule reaction in which methane, either the molecule or one of the ions therefrom, constituted at least one of the reactants.

The first observation of this ion which has been reported was by Eltenton (1,2) in 1940. The ion was rediscovered in the period 1940-1946 by Nier (3). However, at the time neither of these discoveries was published.

The first published report of the CH_5^+ ion appeared in 1952 when Tal'roze and Lyubimova (4,5) noted its appearance in the mass spectrum of methane at increased pressure. Shortly thereafter, Stevenson and Schlissler (2,6) (unaware of Tal'roze's work) referred to Eltenton's unpublished results in a communication on ion-molecule reaction rates.

Alekseevskii, Tal'roze and Shelyapkin (7) confirmed the identity of CH_5^+ by resolving the multiplet at $m/e = 17$ using high resolution techniques. Field, Franklin and Lampe (8) also confirmed the appearance of this ion during a study of the high pressure mass spectrum of methane.

Mass Spectrometric Systems

In addition to the formation of CH_5^+ in the electron impact spectrum of methane by the reaction

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$$

there have been several other systems in which this ion has been observed.

Wagner, Wadsworth, and Stevenson (9) compared the cross section of formation of $CH_3D_2^+$ and CD_4H^+ in the mass spectrum of mixed CH_4 and CD_4. They found that the cross section of formation for $CH_3D_2^+$ was only one-sixtieth of that predicted if the H and D were randomly arranged. Therefore, they concluded that the activated complex was loosely bound $(CH_4 \cdot CD_4)^+$ rather than tightly bound $C_2H_4D_4^+$. Derwish et al. (10) saw evidence that the $m/e = 19$ peak in the spectrum of this mixture may be due to CD_3H^+ from the reaction of $CD_3^+ + CH_4$. If this is true in whole or in part, it would add more support to the loosely bound complex.

In a very high pressure study (300 μ), Field, Franklin and Munson (11) report some evidence for the reactions

$$CH_3^+ + CH_4 \longrightarrow [C_2H_7]^+$$

$$[C_2H_7]^+ + CH_4 \longrightarrow CH_5^+ + C_2H_6$$

in addition to the usual production of CH_5^+ in the methane spectrum. They also note the decomposition of CH_5^+ by collision with CH_4 in the analyzer tube.

Several studies have been conducted of systems in which a methane molecule or ion reacts with something other than another methane. Munson, Field and Franklin (12) have done a study of the systems CH_4

and H_2, CH_4 and D_2, and CD_4 and H_2. They conclude that the CH_5^+-type ions can be formed by the reaction of CH_4^+ with either H_2 or of CH_4 with H_3^+. It will be noted that the latter is a termolecular reaction since the formation of H_3^+ is bimolecular. They also found that the reaction of CH_4^+ with D_2 produced CH_4D^+ but very little $CH_3D_2^+$ indicating that the activated complex for this reaction was loosely bound, similar to Wagner <u>et al.</u>'s findings for the $(CH_4 \cdot CD_4)^+$ complex. Previous to this there had been some disagreement as to whether or not the reaction

$$CH_4^+ + H_2 \longrightarrow CH_5^+ + H$$

(or the corresponding reaction with either reactant deuterated) took place. Tal'roze and Frankevitch (13) reported the reaction but Lampe and Field (14,15) had been unable to observe it.

Lampe and Field (14) have also found the ion CD_4H^+ in the mass spectrum of mixtures of CD_4 with CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, CH_3Cl, NH_3, H_2S and HCl.

Mass spectrometry using photoionization rather than ionization by electron impact is comparatively rare. However, CH_5^+ was observed by Cook and coworkers (16) during a study of photoionization-induced ion-molecule reactions.

Quantitative Studies

There are several review articles available on the mass spectrometry of ion-molecule reactions (17,18,19,20,21) of which perhaps the best introduction to the subject is the one by Stevenson (19). It is not our present purpose to explore ion-molecule reactions in detail.

However, all of the mass spectrometric studies of the CH_5^+ ion have been ion-molecule studies. Therefore, a large amount of the data relating to this ion is in the form of reaction cross sections and rate constants. These data have been collected in Table I. In such studies the neutral product(s) must be inferred although sometimes their nature is obvious. Also, it is not known whether the ion or atom is transferred in some cases such as reaction 1. In this table we have used brackets around both reactants with the charge outside the brackets in cases where it was not determined which species was ionic and which was neutral. In the reference column, the year is also included for convenience in examining the data. The voltage gradient indicated in the Comments column is the reported gradient in the ionization region, i.e. the draw-out potential. The entry "thermal" indicates that the data apply to ions possessing only thermal velocities. Table II contains a similar tabulation of values for the enthalpy of formation of CH_5^+ and the proton affinity of methane.

A few studies have been conducted which do not lend themselves to tabular presentation. Cassuto (32) has studied thermal effects on the formation of ions and concludes that there is no activation energy (± 0.2 kcal./mole) for the reaction

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 .$$

This is in agreement with Tal'roze's (13) postulate that a reaction involving a significant activation energy barrier would be undetectable. Melton and Hamill (33) have done careful appearance potential work on the same reaction and concluded that the CH_4^+ is in the ground state. Finally, vonKoch (34) observed the reaction

Table I. Data on ion-molecule reactions involving the CH_5^+ ion.

No.	Reaction	Cross Section σ (cm^2) x 10^{16}*	Rate Constant k x 10^{10}* (cm^3/sec. molec.)	Reference	Comments
1	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$		11.6	22(1959)	At 370°K with ions containing thermal energy only.
2	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$		10.7	23(1965)	10 v/cm
			17.0		Ions of thermal energy only.
3	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	5.6	2.2	8(1957)	100 v/cm
		15	4.8		60 v/cm
		27	7.0		40 v/cm
		45	8.4		20 v/cm
		61	8.5		10 v/cm
		66	8.5		8 v/cm
		68	8.0		6 v/cm
		71			4 v/cm
		55	5.0		2 v/cm
			8.93		10 v/cm from another part of same paper.
		221	2.8×10^{-9}		298°K, thermal
			1.3×10^{-9}		Theor.
4	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	39	5.8	24(1956)	10 v/cm; experimental
		34			10 v/cm; theoretical
		58	6.2		Thermal; calculated by author's formula.
			11.2		Thermal; calculated by Eyring's formula.
5	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$		11.1	25(1964)	By pulse technique.
6	$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$		13.8	2(1955)	One of first papers.

Table I. (Cont.)

No.	Reaction	Cross Section σ (cm^2) x 10^{16*}	Rate Constant k x 10^{10*} (cm^3/sec. molec.)	Reference	Comments
7	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	60.6	8.50	26(1958)	10 v/cm; in CH_4-HCl system
8	$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$	63.4	7.94		10 v/cm; in CD_4-HCl system
9	$CH_4^+ + HCl \rightarrow CH_5^+ + Cl$	33	4.6		10 v/cm
10	$CD_4^+ + HCl \rightarrow CD_4H^+ + Cl$	41	5.1		10 v/cm
11	$CD_4^+ + HCl \rightarrow CD_4H^+ + Cl$	96	8.0		extrapolated to zero field strength
12	$CD_4^+ + H_2S \rightarrow CD_4H^+ + HS$	12	1.5		10 v/cm
13	$CD_4^+ + CH_4 \rightarrow CD_4H^+ + CH_3$		$1.00 \times k_{CH_4}$	14(1957)	$k_{CH_4} \equiv$ rate constant for reaction 13.
14	$CD_4^+ + C_2H_6 \rightarrow CD_4H^+ + C_2H_5$		$0.11 \times k_{CH_4}$		
15	$CD_4^+ + C_3H_8 \rightarrow CD_4H^+ + C_3H_7$		$0.05_6 \times k_{CH_4}$		
16	$CD_4^+ + iso\text{-}C_4H_{10} \rightarrow CD_4H^+ + C_4H_9$		$0.04_6 \times k_{CH_4}$		
17	$CD_4^+ + CH_3Cl \rightarrow CD_4H^+ + CH_2Cl$		$0.04_1 \times k_{CH_4}$		
18	$CD_4^+ + NH_3 \rightarrow CD_4H^+ + NH_2$		$0.08_8 \times k_{CH_4}$		
19	$CD_4^+ + H_2S \rightarrow CD_4H^+ + HS$		$0.17 \times k_{CH_4}$		
20	$CD_4^+ + HCl \rightarrow CD_4H^+ + Cl$		$0.56 \times k_{CH_4}$		
21	$CD_4^+ + H_2 \rightarrow CD_4H^+ + H$	$(\sigma_{21} + 0.53\sigma_{22}) \leq 2 \times 10^{-17}$		15(1959)	Reactions unobserved
22	$H_2^+ + CD_4 \rightarrow CD_4H^+ + H$				
23	$CH_4^+ + D_2 \rightarrow CH_4D^+ + D$	$(\sigma_{23} + 0.56\sigma_{24}) \leq 2 \times 10^{-17}$			Reactions unobserved
24	$D_2^+ + CH_4 \rightarrow CH_4D^+ + D$				

Table I. (Cont.)

No.	Reaction	Cross Section $\sigma(cm^2) \times 10^{16*}$	Rate Constant $k \times 10^{10*}$ (cm^3/sec. molec.)	Refer-ence	Comments
25	$[CH_4+CD_4]^+ \rightarrow CH_3D_2^+$	$\leq(0.10 \pm .05) x \sigma_{CH_5^+}$		9(1958)	$\sigma_{CH_5^+} \equiv$ cross section for the formation of CH_5^+ ion;all reactions take place in the same system.
26	$[CH_4+CD_4]^+ \rightarrow CD_4H^+$	$(0.91 \pm .03) x \sigma_{CH_5^+}$			
27	$CD_4^+ + CD_4 \rightarrow CD_5^+$	$(0.85 \pm .03) x \sigma_{CH_5^+}$			
28	$CH_4^+ + D_2 \rightarrow CH_4D^+$	$< 1 \times 10^{-17}$	2.5×10^{-12}	12(1963)	
29	$CH_4^+ + H_2 \rightarrow CH_5^+$		$0\text{-}7 \times 10^{-12}$		
30	$CH_4^+ + D_2 \rightarrow CH_3D_2^+$		$\leq 1 \times 10^{-13}$		
31	$CH_5^+ + CH_4 \rightarrow CH_4^+ + H$	2		11(1963)	At 2000v in analyzer tube
32	$CH_5^+ + CH_4 \rightarrow$	1.6		27(1962)	12.6 v/cm;products not specifically given but text indicates they are probably polymeric ions.

*Unless another multiplier is indicated.

Table II. Heat of formation of the CH_5^+ ion and proton affinity of methane.

No.	Heat of Formation ΔH_f (CH_5^+) (kcal/mole)	Proton Affinity $P(CH_4)$ (kcal/mole)	Reference	Comments
1	$218 < \Delta H_f \leq 234$	$113 < P < 129$	15(1959)	
2		$114 < P < 129$	13,28(1958)	Contradicts No. 3.
3	233-234	113	14(1957)	Contradicted by No. 2; $\Delta H_f(CD_4H^+)$
4		167	29(1962)	By calculation
5		> 115	2(1955)	One of first papers
6		173	30(1959)	By calculation
7		161	31(1959)	By calculation

$$CH_4^+ + CD_4 \longrightarrow CD_2H^+ + D_2 + CH_3$$

in a charge exchange study. He feels this indicates all of the bonds in CH_5^+ are of equal strength.

Miscellaneous Reports

Other workers (10,35) have noted the CH_5^+ ion in passing, although the object of their study was something else. In addition, the reaction

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$$

has been used as a reference reaction in studies of hydrogen abstraction by cyanides (36), hydride transfer (37), and ion-molecule reactions in methanol and ethanol (38). Two studies (22,25) used the same reaction to test their pulse method of studying ion-molecule reactions in the mass spectrometer, and Field and Lampe (26) used the deuterium analog of this reaction in their study of the methane-hydrogen sulfide system to determine the partial pressure of methane-d_4 when they felt their samples were not thoroughly mixed.

Radiation Chemistry

Knowledge of the CH_5^+ ion has also had an influence upon radiation chemistry. Tunitskiĭ and Kupriyanov (39) studied the mass spectrum of methane with the intention to apply this knowledge to radiation chemistry processes. They found that the ions CH_5^+ and $C_2H_5^+$ were an order of magnitude more abundant than any other secondary ions in the spectrum.

Wexler and Jesse (27) studied consecutive ion-molecule reactions in the mass spectrometer also with the intent of applying this knowledge to the radiolysis of methane. They found CH_5^+ to be very reactive and suggested the reaction

$$CH_5^+ + CH_4 \longrightarrow C_2H_5^+$$

although they admitted it to be endothermic. Ausloos and coworkers (40) consider the fate of the CH_5^+ ion to be rather in doubt. They (41) find evidence that the reaction of CH_5^+ with CH_4 may be quenched either by the products or by impurities in the system. Munson, Franklin and Field (42) support Ausloos' findings that this reaction is probably negligible in the radiolysis of methane.

Several workers (43,44,45) have postulated various mechanisms that include the ion CH_5^+ (and usually also CH_4T^+) in the exchange of T_2 with CH_4. It should be mentioned though, that a study by Munson, Field and Franklin (12) offers some contrary evidence. The latter feel CH_3^+ rather than CH_5^+ is involved.

Meisels, Hamill and Williams (46) irradiated the krypton-methane-iodine system and suggested that the CH_5^+ ion breaks up to form H_2 and CH_3^+. The latter is detected as CH_3I. In a later paper (47) on the krypton-methane system they conclude that CH_5^+ is neutralized to form CH_3 and possibly some CH_2 radicals:

$$CH_5^+ + e^- \longrightarrow CH_3 + H_2 \qquad \text{and}$$

$$CH_5^+ + e^- \longrightarrow CH_2 + H_2 + H.$$

Ausloos and Lias (48) feel that they have established proton (or deuteron) transfer, during gamma ray irradiation, by the reaction

$$H_3^+ + CH_4 \longrightarrow CH_5^+ + H_2 .$$

The latter product is detected by transfer of a proton (or deuteron) to C_3H_8. In a later paper (49) they indicate that CH_5^+ is one of the most likely bimolecular products in the radiolysis and photolysis of methane. They feel however, that the CH_5^+ is neutralized to form CH_4 and H rather than CH_3 and H_2.

Rearrangements

A number of books (50,51,52,53) in recent years have been concerned, in whole or in part, with fragmentation mechanisms in mass spectrometry. The emphasis, however, has been to explain the major peaks in the spectrum without being concerned with minor ones (51). At the same time small peaks at $m/e = 17$ and 18 may be ignored because samples generally contain water impurity (54). These are perhaps the reasons CH_5^+ has not been noted as a rearrangement peak in mass spectra.

For a thorough discussion of fragmentation mechanisms, one is referred to the references above. We shall only attempt to mention a few points as they apply to the present work. The most important feature both of ether spectra and of alcohol spectra is β cleavage.[1] (The same bond is β with respect to both groups in 2-methoxyethanol.) Beyond this, and the fragmentation characteristic of the hydrocarbon portion of the molecule, most of the spectrum is characterized by rearrangements.

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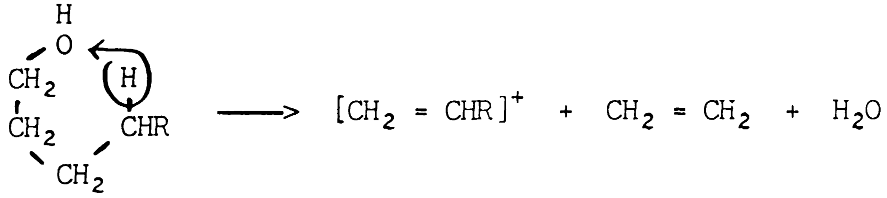
[1] α cleavage is cleavage of the bond between the functional group and the rest of the molecule. β cleavage is cleavage of the bond between the atoms which are α and β with respect to the functional group, etc.

One of the rearrangements for oxygen-containing compounds which is more commonly proposed by Budzikiewicz et al. (52) is the rearrangement of hydrogen through a five or six member ring. In such a rearrangement, a δ (or γ) hydrogen is transferred to the oxygen.



McLafferty (55) has proposed four member rings in which hydrogen is transferred from the β carbon to a heteroatom, such as O in OH, to eliminate H_2O. In a later book (53) he states that the four membered ring is not well established, however, he expands upon proposed mechanisms involving such rings.

These four membered rings are also accepted by other authors (51,52) such as in explaining Momigny's (56) work on deutero-labeled ethanol. However, a recent paper by Meyerson and Leitch (57) on the mass spectra of hexanol with various positions labeled with deuterium found most (91%) of the water eliminated to result from a six member intermediate ring (1,4-elimination) and the remainder from smaller rings which they feel is 1,3-elimination. Benz and Biemann (58) also felt that the 1,2 mechanism was not well supported as a general mechanism and studied the mass spectra of a series of deutero labeled alcohols. They find that the six member ring is by far the most important.

It seems that five or six membered transition states are the most likely to be formed when such are possible. However, in other ions where this is not possible, a smaller ring can also transfer hydrogen across the molecule.

In addition to transfer of a single hydrogen there are instances where transfer of two or more hydrogens occurs. Beynon (50) mentions examples such as the $C_2H_5O_2^+$ ion at m/e = 61 from α-methylpropyl ethanoate, the H_3O^+ ion from 2-propanol, and the NH_4^+ ion from many nitrogen containing compounds. In fact, the NH_4^+ peak in the spectrum of trimethyl hydrazine is cited as being 11 per cent of the base peak in the spectrum.

II. Objectives of the Present Study

We noted the presence of a doublet at m/e = 17 in the mass spectrum of 2-methoxyethanol. One peak was assumed to be OH^+ from water impurity and/or the hydroxyl group in the compound. The other peak was thought to be CH_5^+ since ammonia was believed to be absent (also it is doubtful that our instrument could resolve OH^+-NH_3^+) and the peak was much too intense to be an isotopic variation of either O^+ or CH_4^+ at m/e = 16.

Our study attempted to verify that the ion, CH_5^+ was present in the mass spectrum of 2-methoxyethanol, to determine whether or not this was being formed by an ion-molecule reaction, and (particularly if it were not an ion-molecule reaction product) to determine by isotopic labeling how the ion is formed.

EXPERIMENTAL

I. Instruments

Most of this study was conducted on a Consolidated Electrodynamics Corporation mass spectrometer, Model 21-103C. This model instrument is described elsewhere (59). The samples were admitted through the gas inlet with a normal reservoir pressure of about 70 to 80 microns. The usual ionizing electron beam was 10 microamps at 70 volts; the instrument was operated with the narrow collector slit (0.18 mm), high sensitivity and focused. A magnet current of about 0.234 amps allowed the range m/e = 12 through m/e = 80 to be covered in one scan.

A tungsten filament was used for all experiments except those involving the isotopically labeled 2-methoxyethanol. For these, a different Isatron (ion source) with a rhenium filament was used. Additional spectra were taken of peaks of interest while operating non-focused with increased ionizing and magnet currents to improve the resolution.

The high resolution spectra were obtained for us on a double-focussing Hitachi mass spectrometer, model RMU-6D, through the courtesy of the Perkin-Elmer Corporation.

II. Chemicals

2-Methoxyethanol, $CH_3OC_2H_4OH$, unlabeled

The unlabeled 2-methoxyethanol was Fisher Certified Reagent dried at least twelve hours over anhydrous calcium sulfate (non-indicating "Drierite"). This was analyzed with a gas chromatograph containing a hydrogen flame detector. Analyses were made using a Silicone column at 90-95° and a PDEAS, HMDS treated 60/80 Chrom. W. Column (phenyldiethanolamine on hexamethyldisilazane treated white diatomaceous earth from Wilkens Instrument and Research, Inc.) at 125° C. No impurities were detected using sensitivities capable of detecting impurities in the order of one part per thousand.

2-Methoxy-^{13}C-ethanol, $^{13}CH_3OC_2H_4OH$

2-Methoxyethanol with a labeled methyl group was prepared using a Williamson synthesis (60).

$$^{13}CH_3I + NaOC_2H_4OH \longrightarrow {}^{13}CH_3OC_2H_4OH$$

The amount of each reactant was modified to reduce side products such as 1,2-dimethoxyethane and yet favor complete use of the iodomethane-^{13}C. A solution was prepared by dissolving 1.5 g of sodium in 25 ml of cooled 1,2-dihydroxyethane (redistilled, b.p. 94-96°C at 11 mm Hg). To 8 ml of this solution was added about 0.50 g of iodomethane-^{13}C (57-63.8% C-13 from Merck, Sharp and Dohme of Canada, Ltd.). This was allowed to react about five hours, a little water was added to react with the remaining organosodium salt, and a crude distillation was done using semi-micro apparatus. The fraction boiling 103-128°C was further purified by preparative gas chromatography using a Carbowax 20M column (from Wilkens Instrument and Research, Inc.) at 126-130°C.

The gas chromatographic separation was done in several small batches. An infrared spectrum of the product of one such run was taken on a Beckman infrared spectrophotometer, Model IR-8. This spectrum was compared with similar spectra taken of unlabeled 2-methoxyethanol from a commercial source (Fisher Certified Reagent) and from a preparation equivalent to the labeled preparation except that ordinary iodomethane was used. The only difference between these three spectra was a possible shift of the 1120 cm^{-1} ether vibration by about 6 cm^{-1} in the labeled compound. This may be an isotope effect or it may be of instrumental nature since such a small shift is near the detection limit of the instrument. There seems though to be little doubt of the identity of the compound.

A portion of the same labeled compound used for the mass spectra was analyzed by gas chromatography similarly to the preparative runs. Impurities (as detected by a thermal conductivity cell) appear to be less than one part in one thousand. Anhydrous calcium sulfate was added as a drying agent to the sample vial from which the compound was introduced into the mass spectrometer. The material was determined mass spectrometrically to be about 56 percent labeled.

2-Methoxyethanol-1,1-d_2, $CH_3OCH_2CD_2OH$

2-Methoxyethanol with deuterium labelling on the C-1 carbon was prepared by a three step synthesis:

$$CH_3OC_2H_4OH \xrightarrow{HNO_3} CH_3OCH_2COOH$$

$$CH_3OCH_2COOH \xrightarrow{C_2H_5OH} CH_3OCH_2COOC_2H_5$$

$$CH_3OCH_2COOC_2H_5 \xrightarrow{LiAlD_4} CH_3OCH_2CD_2OH$$

The oxidation with nitric acid followed a well known organic method (61). The esterification also followed a conventional method (62) but was modified by the substitution of 4-methylbenzenesulfonic acid for sulfuric acid and by omitting the washings but separating the product with two distillations. The reduction of the ethyl ester with lithium aluminum deuteride (63) (from Metal Hydrides, Inc.) was done under helium atmosphere using solvent ether which had been distilled from lithium aluminum hydride directly into the reaction vessel and separatory funnel.

The product (b.p. 120-123°C) was determined mass spectrometrically to be at least 97 percent dideuterated and was dried with anhydrous calcium sulfate shortly before being used.

2-Methoxyethanol-d, $CH_3OC_2H_4OD$

2-Methoxyethanol with deuterated hydroxyl was obtained from Drs. G. J. Papenmeier and W. H. Reusch and had been prepared by exchange of unlabeled $CH_3OC_2H_4OH$ with D_2O. It was dried by repeated trap to trap distillation between traps containing fresh anhydrous calcium sulfate and was analyzed mass spectrometrically to be about 20 percent deuterated.

Ammonia, NH_3

The ammonia was Matheson anhydrous ammonia dried over sodium.

Methane-d, CH_3D

The mondeuterated methane was from Merck and Co., Ltd. and was used as received.

III. Method of Exact Mass Measurement

An exact measurement of the mass of the ion at m/e = 17 was made by measuring the accelerating voltages needed to focus peaks m/e = 15, 16, 17, 18, and 19 on the collector slit. This was done by measuring the voltage across a voltage divider circuit (consisting of fixed resistors) in the instrument with a millivolt potentiometer (Leeds and Northrup Catalog No. 8691). The voltage measured was nominally one four thousandth the actual accelerating voltage.

In a magnetic mass spectrometer the accelerating voltage is related to the mass of the ion by

$$m/e = k/V,$$

where the proportionality constant, k, includes the strength of the magnetic field, etc. The values of k were determined from the measured voltages for the peaks at m/e = 15, 16, 18, and 19. From the average of these values and the voltage for the peak at m/e = 17, the exact mass was calculated. All of the measurements were repeated for each trial. The results are shown later.

RESULTS

I. Identification of the Ion

The identification of the ion at m/e = 17 was based both upon measurement of the mass of the ion and upon the resolved peaks in high resolution spectra containing intentional impurities. The results of the mass measurements performed as described earlier are shown in Table III, together with the calculated mass of some ions of the same nominal mass based on the atomic weights given by Beynon and Williams (64) and considering the mass of the electron.

A high resolution spectrum of 2-methoxyethanol containing a small amount of ammonia is shown in Figure 1. It is quite apparent that there is another peak present besides OH^+ and those from ammonia. If this other peak is CH_5^+, the NH_3^+ peak would be expected to fall about 65 percent of the distance from the OH^+ peak to the CH_5^+ peak. Inspection of the figure shows this to be the case.

A similar high resolution spectrum of 2-methoxyethanol containing some methane-d_1 is shown in Figure 2. The mass separation of the CH_3D^+ and the CH_5^+ peaks is one part in eleven thousand. This is approximately equal to the expected resolution of the mass spectrometer used. The figure shows a partially resolved peak on the high mass side of CH_3D^+. This is where it is expected.

Several other combinations of carbon and hydrogen isotopes also have a mass of 17. Of these, the most likely is $^{13}CH_4^+$. Since the natural abundance of ^{13}C is 1.1% of ^{12}C, the $^{13}CH_4^+$ peak must be about

Table III. Determination of the exact mass of the m/e = 17 peak.

Trial	Mass Found	Ion	Calculated Mass
1	17.0435	OH^+	17.0022
2	17.0377	NH_3^+	17.0260
3	17.0434	$^{13}CH_4^+$	17.0341
4	17.0441	CH_3D^+	17.0370
5	17.0337	CH_5^+	17.0386
Average	17.0405 (± 0.0038)*		

*Average Deviation.

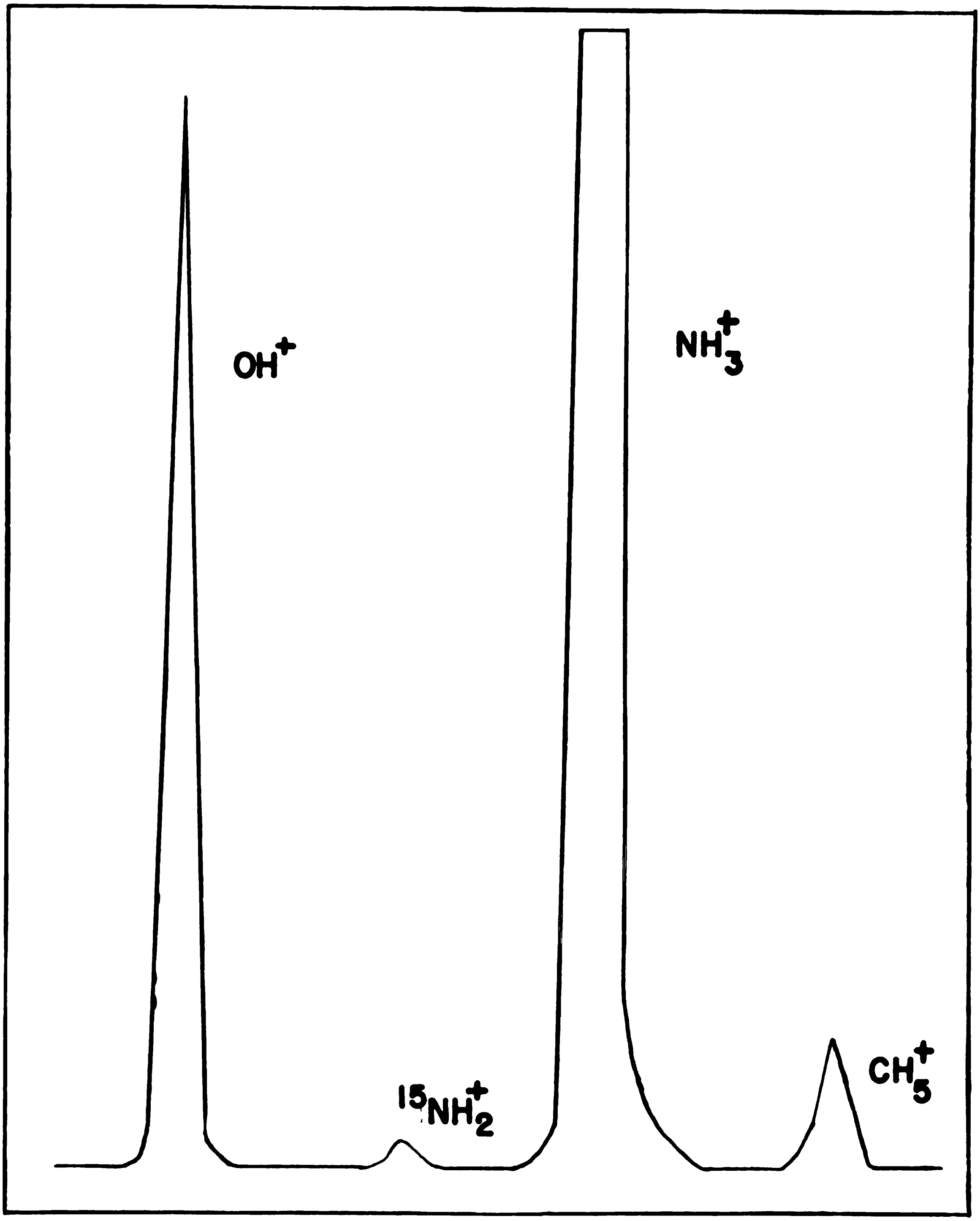


Figure 1. High resolution spectrum of the multiplet at m/e = 17 in 2-methoxyethanol with added ammonia.

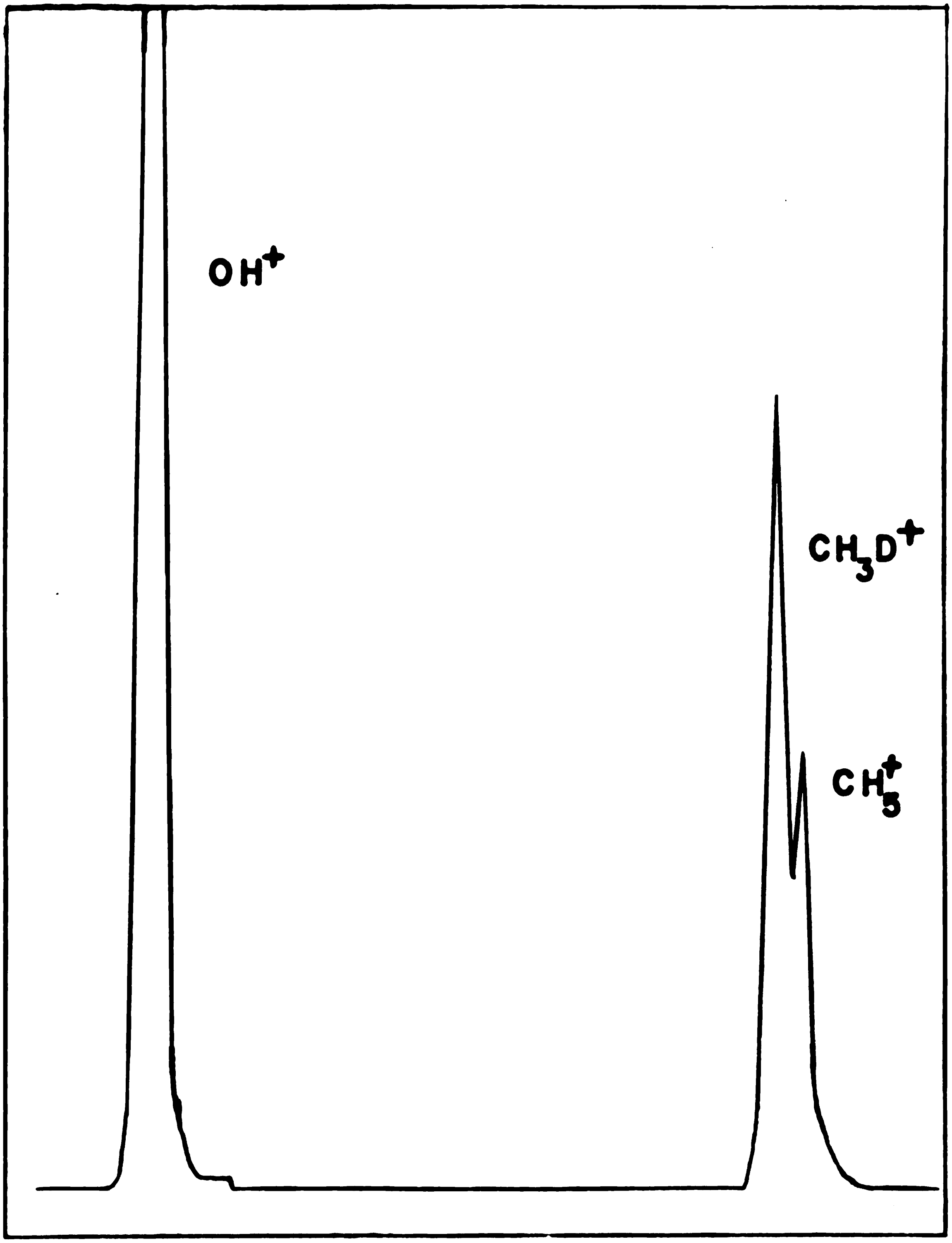


Figure 2. High resolution spectrum of the multiplet at m/e = 17 in 2-methoxyethanol with a small amount of added methane-d.

one percent of the $^{12}CH_4^+$ peak at m/e = 16. Actually the m/e = 17 peak is about eighty percent of the $^{12}CH_4^+$ peak. Other isotopic variations such as ^{17}O or deuterated ions would be expected to be even less abundant. Therefore, we feel that the ion in question is CH_5^+.

II. Pressure Dependence Studies

Studies were made of the intensity of the CH_5^+ ion as the sample reservoir pressure (which is proportional to the pressure in the ion source) was varied. Figures 3 and 4 show these data for two runs (separated by four months time) plotted as peak intensity vs. pressure and as peak intensity vs. (pressure)^2. It is easily seen that a linear pressure dependence for the formation of this ion exists. This means that the ion, CH_5^+ is not being formed by an ion-molecule reaction (which requires dependence on the square of the pressure) and is, to our knowledge, the first time it has been so seen.

III. Isotopic Studies

Since the CH_5^+ ion in the 2-methoxyethanol spectrum is apparently formed by an intramolecular process, we desired to know from which part of the molecule this ion is formed. Spectra were taken of 2-methoxyethanol with the atoms in various positions isotopically labeled. The pertinent portions of these spectra are shown in Figures 5, 6, 7, and 8.

Figure 5 (operating conditions: nonfocused, slow scan, 85 μa ionizing current, P_{inlet} = 60 microns) shows very definitely that a $^{13}CH_5^+$ peak is present at m/e = 18 in 2-methoxy-^{13}C-ethanol. This is

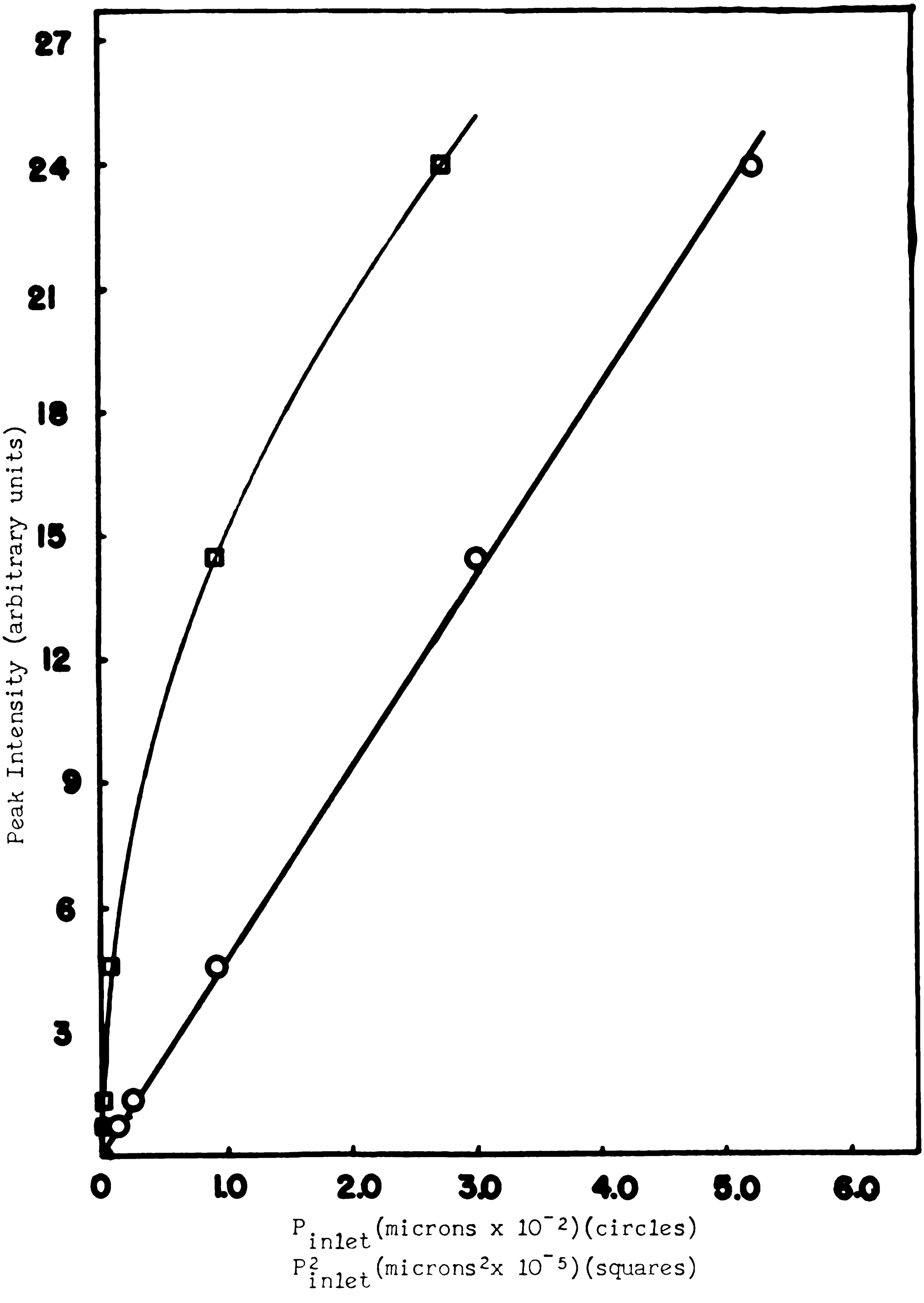


Figure 3. Intensity of the m/e = 17 peak as a function of pressure.

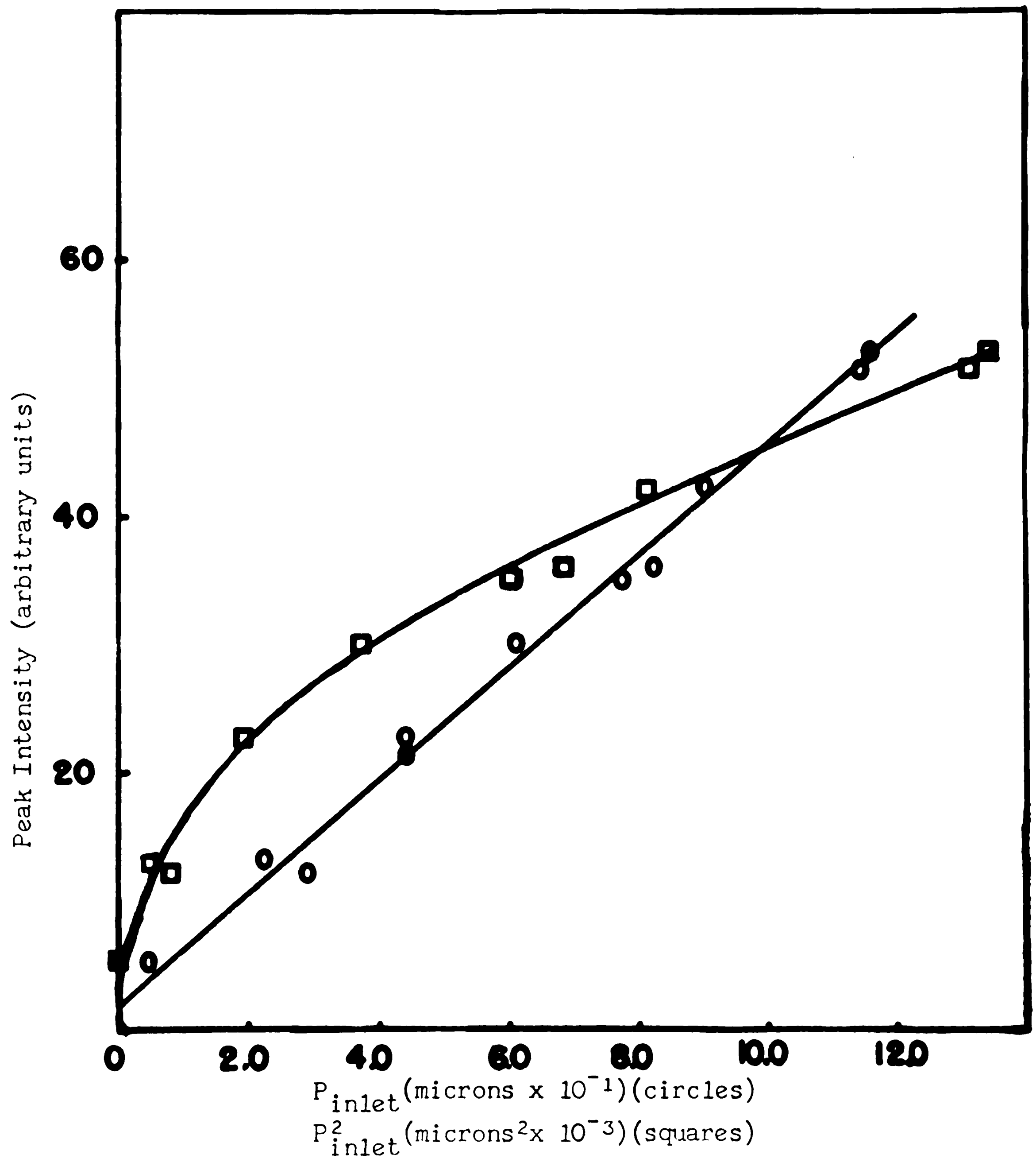


Figure 4. Intensity of the m/e = 17 peak as a function of pressure.

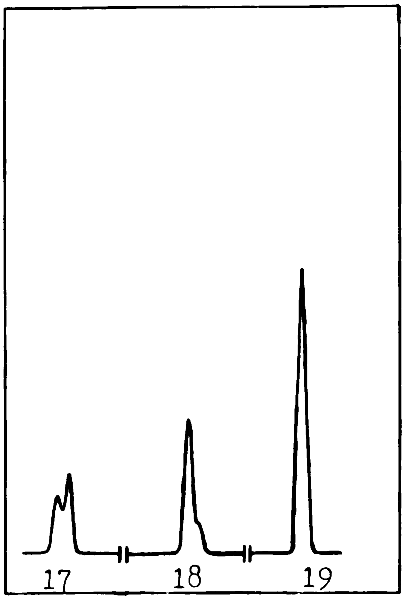


Fig. 5. Peaks at m/e = 17, 18, and 19 in 2-methoxy-^{13}C-ethanol.

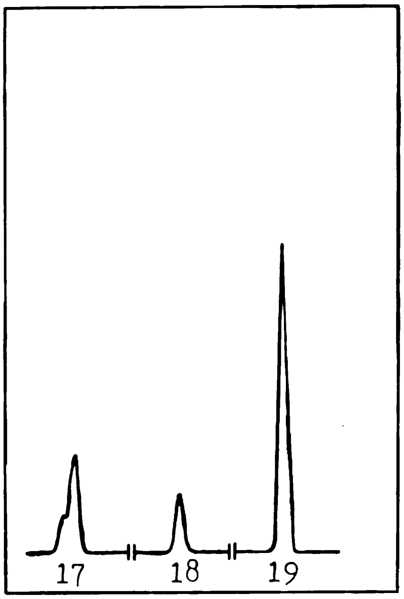


Fig. 6. Peaks at m/e = 17, 18, and 19 in unlabeled 2-methoxyethanol.

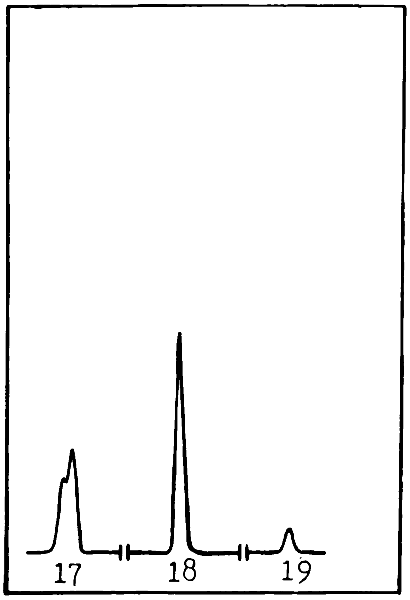


Fig. 7. Peaks at m/e = 17, 18, and 19 in 2-methoxyethanol-1,1-d_2.

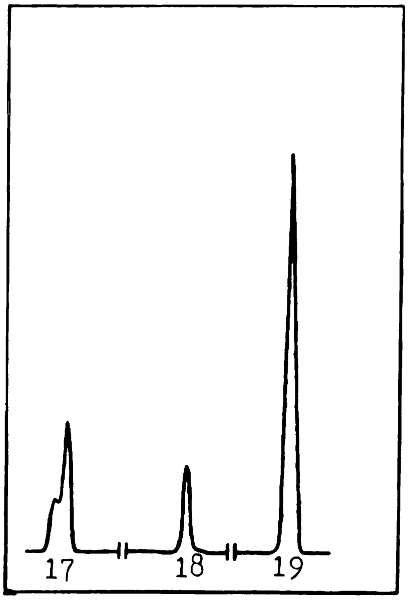


Fig. 8. Peaks at m/e = 17, 18, and 19 in 2-methoxyethanol-d.

not seen in the unlabeled compound, Figure 6 (operating conditons: same except P_{inlet} = 64 microns). The large size of the higher mass side of the m/e = 17 doublet is the sum of $^{13}CH_4^+$ and $^{12}CH_5^+$.

Figure 7 (operating conditions: focused, slow scan, 10 μa ionizing current, P_{inlet} = 54 microns) of 2-methoxyethanol-1,1-d_2 shows no significant difference in the CH_5^+ peak from the unlabeled compound in Figure 6. Due to the very high percentage of deuterium (over 97 percent) one would expect the CH_5^+ peak to become very small as well as a second peak at m/e = 18 or 19 to appear if one or both of the hydrogens on the C-1 carbon were involved. The peaks due to water impurity do, of course, vary between samples; also the m/e = 19 peak is diminished.

Figure 8 (operating conditions: nonfocused, slow scan, 85 μa ionizing current, P_{inlet} = 83 microns) of 2-methoxyethanol-d also shows no significant difference from Figure 6. Although the percentage of labeling is much smaller than in the other compounds (about 20 percent) it is still large enough that the CH_4D^+ ion, if present, would be plainly visible.

CONCLUSION AND DISCUSSION

This study indicates that the ion CH_5^+ can be observed in systems which do not include methane and that it is present in the mass spectrum of pure 2-methoxyethanol. Further, the ion is formed by a mechanism which is unimolecular. (Calculation shows that with rate constants in the order of 10^{-9} cm^3 $molecule^{-1}$ sec^{-1} and the usual pressure in the ionization region, a bimolecular reaction will have a half-life in the order of milliseconds while unimolecular fragmentation processes have half-lives in the order of microseconds. Therefore this could not be a rate limiting, unimolecular step followed by a fast bimolecular step.) Isotopic labeling indicates that the ion is formed from the methoxy- carbon and the five hydrogens around the ether oxygen.

As noted earlier, much of the discussion of alcohol and ether spectra is based on β cleavage and rearrangements through five or six member rings. Such a ring mechanism would lead to the formation of the CH_5^+ ion from the hydrogens on C-1 rather than from C-2 as found in the present study.

One would, however, expect from the fragmentation mechanisms of both ethers and alcohols that the C-C bond in the parent ion would break most easily. This is confirmed by the intense base peak at $m/e = 45$. (The spectra of methoxy-^{13}C-ethanol and methoxyethanol-1,1-d_2 further support this assignment.) It is possible that the ion CH_5^+ is formed by a rearrangement and fragmentation of the ion $C_2H_5O^+$:

$$[CH_3OC_2H_4OH]^+ \longrightarrow [CH_3OCH_2]^+ + \text{other fragments}$$

$$[CH_3OCH_2]^+ \longrightarrow CH_5^+ + CO$$

Such a mechanism would be energetically favored by the formation of the molecule CO. However, it is only a supposition. A search for a metastable ion at m/e = 6.4 would support this proposition. A scan which was made of the low mass region showed nothing from m/e = 4 through m/e = 10. However, the detection of a metastable peak places a requirement upon the rate as well as the mechanism, its absence does not preclude the proposed mechanism.

A preliminary, uncalibrated set of appearance potential measurements is shown in Appendix 2. The values of 0.4 volts for m/e = 45 and 5.1 volts for m/e = 17 do not contradict the proposed mechanism since a precursor ion should have an appearance potential lower than its fragments. Such data do limit the possible choices of precursor ions.

Some other features relating to highly rearranged ions were also noted in this study. The H_3O^+ ion, which was also found to be unimolecular (see Appendix 3) shifted in large part to m/e = 20 and 21 in the spectrum of 2-methoxyethanol-1,1-d_2. This indicates some mechanism other than a five or six membered ring is operating. The CH_5O^+ ion at m/e = 33 in methyl ethers is believed (54) to be a rearrangement although this portion of the spectrum was not covered in our pressure dependence work. This peak is also at least partially shifted to m/e = 34 and 35 in the spectrum of the dideuterated compound. Here, though, the data are insufficient to propose a mechanism.

POSSIBLE FURTHER STUDIES

A search could be made for a metastable ion at m/e = 6.4 by taking spectra at various ionizing voltages. The appearance of such a peak which shifts to m/e = 7.0 for 2-methoxy-^{13}C-ethanol or to m/e = 7.7 for 2-methoxyethanol-2,2-d_2 but is not affected by isotopic labeling at C-1 or at the hydroxyl would give considerable support to the proposed mechanism. In addition to varying the ionization voltage, one could increase the sensitivity of the mass spectrometer by using a vibrating reed electrometer or an electron multiplier for ion detection. One might also adapt scan averaging techniques (such as has recently been introduced by Varian Associates, Palo Alto, California for NMR Spectroscopy) to mass spectrometry to detect a very broad low intensity, metastable peak.

Another investigation which might be more fruitful than the search for metastable peaks would be the examination of the peaks at m/e = 17 in other compounds, particularly methyl ethers such as methoxyethane and 1,2-dimethoxyethane. Perhaps CH_5^+ ions being formed from these compounds have heretofore been overlooked as OH^+ or have been covered by OH^+ from water impurity.

A study which might prove very interesting is the study of the intensity of highly rearranged ions such as CH_5^+ with ionization energy. Chupka (65) has suggested that an ion such as our rearrangement CH_5^+ ion should be very persistent in low ionization voltage spectra. This is because it would take longer for an ion to fragment if it is at lower energy and such additional time would be favorable toward a highly rearranged ion. It is interesting to note in Appendix 3 that the ions H_2O^+ and H_3O^+ are also formed by unimolecular mechanisms. While it is conceivable that the H_2O^+ peak is due to a constant percentage of impurity in the sample, the H_3O^+ ion must be another rearrangement ion. Appendix 2 indicates that this also may be quite persistent at low ionizing voltages.

With an instrument of higher resolution, one could learn much more about the fragmentation of this compound from the spectrum of isotopically labeled molecules. For instance, if one were trying to determine which carbon is used to form the CO^+ ion in the present study he would be in difficulty. First, it is not known what percentage of the peak is CO^+, what percentage is $C_2H_4^+$ and what percentage is due to other contributions such as $^{12}C^{13}CH_4$. More important however, the peak at m/e = 29 is so much larger than the peak at m/e = 28 that the addition of $^{13}CO^+$ to the unresolved peak would add an insignificant increment to its size. Using sufficiently high resolution, one could see the peak due to each of these ions and the problem would cease to exist.

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APPENDICES

APPENDIX 1

Mass Spectrum of 2-Methoxyethanol

m/e	Normalized Intensity	Probable Identity	m/e	Normalized Intensity	Probable Identity
1*	2.56	H^+	42	1.74	$C_2H_2O^+$
2*	0.19	H_2^+	43	8.64	$C_2H_3O^+$
12	0.42	C^+	44	1.51	$C_2H_4O^+$
13	1.07	CH^+	45	100	$C_2H_5O^+$
14	3.77	CH_2^+	~45	metastable	?
15	27.5	CH_3^+	46	3.88	i (&$C_2H_6O^+$)
16	0.680	CH_4^+	47	5.46	$C_2H_7O^+$
17	0.560	CH_5^+(&OH^+)	48	0.13	i
18	~0.7	H_2O^+	49	0.017	i
19	1.81	H_3O^+	55	0.041	$C_3H_3O^+$
~19	metastable	?	56	0.042	$C_3H_4O^+$(or $C_2O_2^+$)
24	0.036	C_2^+	57	0.169	$C_3H_5O^+$(or $C_2O_2H^+$)
25	0.214	C_2H^+	58	2.50	C_3H_6O(or $C_2H_2O_2^+$)
26	1.69	$C_2H_2^+$	~58	metastable	?
27	6.72	$C_2H_3^+$	59	0.232	C_3H_7O(or $C_2H_3O_2^+$)
28	2.32	CO^+ &/or $C_2H_4^+$	60	0.14	$C_2H_4O_2^+$
29	26.5	CHO^+(& $C_2H_5^+$?)	61	0.114	$C_2H_5O_2^+$
~29	metastable	?	69	0.044	$C_3HO_2^+$
30	1.94	CH_2O^+	70	0.022	$C_3H_2O_2^+$
31	23.4	CH_3O^+	72	0.135	$C_3H_4O_2^+$
32	0.73	i & O_2^+	73	0.039	$C_3H_5O_2^+$
33	0.94	CH_5O^+	74	0.031	$C_3H_6O_2^+$
36	0.015	C_3^+	75	0.165	$C_3H_7O_2^+$
37	0.166	C_3H^+	76	5.40	parent
39	0.076	$C_3H_3^+$	77	0.202	i
40	0.048	C_2O^+ or $C_3H_4^+$	78	0.027	i
41	0.348	C_2HO^+			

*m/e = 1 thru 11 based on only one copy of the spectrum.

APPENDIX 2

Preliminary Determination of Appearance Potentials for Selected Ions in the Mass Spectrum of 2-Methoxyethanol

These appearance potentials are the result of a single, uncalibrated determination and should only be considered approximate. Due to the complete lack of calibration (the values reflect the reading of the "ionizing voltage" meter on the instrument) they should be considered merely as ordinal numbers. Some discrepancies due presumably to scatter are obvious.

The criteria for selection of ions was to report those ions between m/e = 12 and m/e = 76 which, a) at 40 volts produced a deflection of at least 10 percent of full scale on the most sensitive galvanometer (m/e = 17 produced 37 per cent), b) at 10 volts produced a deflection of at least 1 percent of the deflection at 40 volts, and c) at 10 volts produced a deflection of a least 1 percent of full scale on the most sensitive galvanometer (m/e = 17 produced 9.6 percent).

m/e	Volts	m/e	Volts
15	7.5	33	4.2
16	8.0	41	4.6
17	5.1	42	10.5
18	inconclusive	43	5.6
19	6.7	44	5.3
26	15.2	45	0.4
27	9.3	46	0.2
28	4.7	47	< 0
29	6.2	58	0.7
30	9.2	59	2.0
31	5.0	76	0.0
32	6.2		

APPENDIX 3

Pressure Dependence of Some Ions in the Mass Spectrum of 2-Methoxyethanol.

Below are reported some pressure dependence data taken at the same time as the data used to plot Figure 3. The peak intensites reported are in arbitrary units. Also reported is a determination of the CH_5^+ ion in the methane spectrum to illustrate a second order pressure dependence. The latter would be expected to show considerable scatter since making the correction for $^{13}CH_4^+$ involves finding a small difference between two large numbers.

	2-Methoxyethanol							Methane	
Pressure (microns)	m/e = 13 (CH^+)	m/e = 14 (CH_2^+)	m/e = 15 (CH_3^+)	m/e = 16 (CH_4^+)	m/e = 17 (CH_5^+)	m/e = 18 (H_2O^+)	m/e = 19 (H_3O^+)	Pressure (microns)	m/e = 17 (CH_5^+)
12.13	129	444	3170	43.6	58.6	34.9	205	7.581	2.2
25.36	272	918	....	96.6	128	65.9	422	46.02	3.0
93.20	863	3220	(~22,500)	354	457	225	1510	92.71	9.9
301.7	2890	....	70,000	1140	1440	653	4660	268.5	76
524.1	5150	16450	102,000	2000	2400	1080	7680	488.6	206
Order[1]	0.99	0.96	0.92	1.02	1.00	0.91	0.97	Order[1]	1.8

[1] By log-log plot.

APPENDIX 4

Infrared Spectrum of 2-Methoxyethanol

Frequency (cm^{-1})	Peak
740	medium
770	medium broad
830	strong
880	strong
960	weak
1010	strong
1050	very strong
1120	very strong
1190	strong with shoulder
1220	medium
1360	strong
1400	medium
1450	strong with shoulder
2710	weak
2810	strong
2880	very strong
2920	very strong
2990	strong
3460	broad strong
3600	medium