

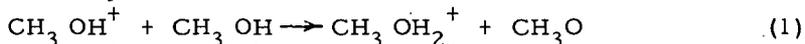
Ion-Molecule Reactions in Methanol and Ethanol

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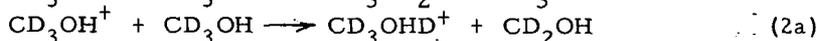
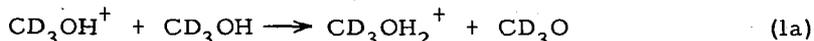
INTRODUCTION

The very large cross section observed for proton transfer ion-molecule reactions in alcohol has prompted a number of workers to investigate these systems in some detail. Theard and Hamill investigated the dependence of the cross section for proton transfer on the field strength in the ion source for 70 volt electrons (1), while Moran and Hamill have shown that the total cross section for these reactions changes significantly with the energy of the ionizing electrons. (2) Recently extensive studies on ethanol and methanol by the method of charge exchange have been reported by Lindholm et al. (3, 4, 5) In addition, these workers determined relative cross sections for the two possible proton transfer reactions between the parent methanol ion and methanol molecules

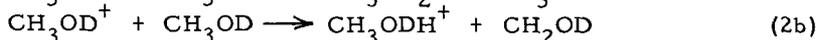
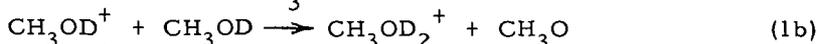


The use of the isotopically labeled methanol (CD_3OH) established the mechanism of formation of the product ion.

In Lindholm's apparatus the secondary ion beam is extracted in a direction perpendicular to the direction of the primary ion beam. This procedure is certainly suitable for the study of dissociative charge transfer but severe discrimination occurs against the extraction of secondary ions formed by processes involving momentum transfer. This discrimination is sufficient to preclude the observation of ion-molecule interactions in which entities other than the isotopes of hydrogen are transferred. Furthermore, in the reactions



the observed relative rate constants will be greater than for the equivalent reactions in methanol because of both this discrimination and the deuterium isotope effect. An indication of the magnitude of these effects can be obtained from the parallel reactions with CH_3OD



which have also been reported by Lindholm and Wilmenius. (5)

An examination of recorded appearance potential data for methanol reveals that at least one volt separates the onset of the parent ion and the process of next lowest energy (6). Consequently a study of proton transfer in the electron energy region below the onset of the CH_2OH^+ ion should yield information on the required

(1) Visiting Research Associate

cross sections. Once these are known a study of proton transfer as a function of electron energy should allow the elucidation of additional proton transfer reactions in the methanol system. These results, using the older techniques of ion molecule studies, are essentially free of momentum discrimination effects.

Until now the proton transfer reaction in ethanol has been assumed to involve the parent ion exclusively (7). By analogy with methanol it appeared that this reaction might also occur with the $\text{CH}_3\text{CH}_2\text{OH}^+$ ion. Accordingly an examination of the possible proton transfer reactions in ethanol was also undertaken.

Experimental

The instrument used in this study, a modified Consolidated Model 21-103C, has been described recently (8). The Bendix model M.306 electron multiplier was replaced by a Consolidated electron multiplier while the Wien filter was retained.

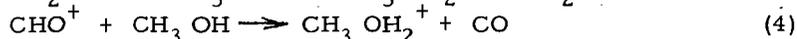
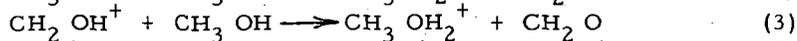
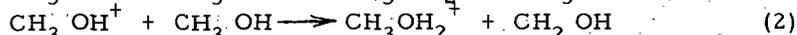
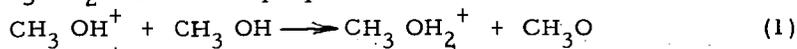
Appearance potentials were measured in the following manner: Magnetic scanning was used to bring the ions of interest to focus at 500 volts. Electric fields in the ionization region were reduced by operating the electron trap at 10 volts and both ion repellers at 4.5 volts. In order to compare the appearance potentials of two ions the sensitivity of the ion detector was adjusted so that the apparent abundances of both ions were the same at 50 electron volts. The appearance potential of an ion was arbitrarily taken to be the electron energy at which the ion current had fallen to 0.3 per cent of its value at 50 electron volts. Because of the similarity in shape of the curves being compared this technique was considered to be satisfactory. Furthermore, the difference in appearance potential between any two ions studied was constant irrespective of whether of the onset was chosen as the energy where the ion current had reached 0.1, 0.2 or 0.3 per cent of its value at 50 volts. In subsequent sections of this paper we are concerned only with the difference in energy for the onset of several processes. Accordingly we have used an uncorrected electron energy scale.

To facilitate the determination of appearance potentials, the ionization efficiency curves were displayed directly on an Electro Instrument Inc. model 300 X-Y recorder. Since the ion source of the mass spectrometer is always at acceleration potential (relative to ground) a signal from the helipot used to control the electron energy could not be fed directly to the recorder. Accordingly the output of the electron energy helipot was transmitted mechanically by means of an insulating shaft to a second helipot. A constant one volt signal was placed across this second potentiometer causing an electrical signal proportional to the electron energy to be developed between one end of the helipot and the moving contact. This signal was transmitted to the recorder and, suitably attenuated, was applied to the x-axis.

The relationship between reservoir pressure and ion source concentration was determined after the method described by Stevenson and Schissler, (9) using the ionization cross section of argon and the dimensions of the source. In this calibration reservoir pressures were read directly from the micromanometer provided with the instrument. In the methanol investigation reservoir pressures greater than 584 microns were sometimes employed. Since this pressure is the upper limit of reading of the micromanometer range all ion source concentrations corresponding to higher reservoir pressures than this were measured directly in the source by the method of total ionization. To convert total ion current to units of concentration it is only necessary to know the ionization cross section of methanol relative to argon. This was determined at lower ion source concentrations where the reservoir pressures of the gases could be measured.

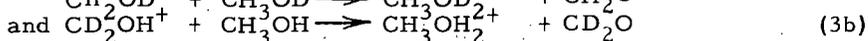
Formation of $\text{CH}_3\text{CH}_2\text{OH}_2^+$

The CH_3OH_2^+ ion has been observed in the high pressure mass spectrum of methanol, (1, 2, 9, 10) in the mass spectrum of mixtures of methanol and water (11) and in the experiments of Lindholm et al. (3-5) Mechanisms for the formation of CH_3OH_2^+ have been proposed as follows:



Using isotopically substituted methanols Theard and Hamill (1) found the appearance potentials for mechanisms (1) and (2) to be the same within experimental error.

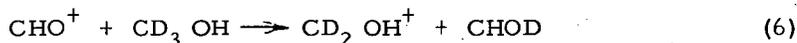
The importance of reaction (3) involving proton transfer from the hydroxyl position has been demonstrated by Lindholm and Wilmenius (5), who observed the reactions



in their tandem instrument. They also postulated mechanism (4) followed by the subsequent dissociation of some of the product ion (2)

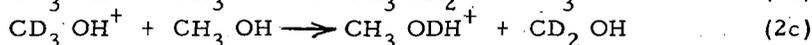
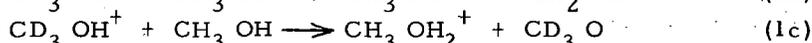
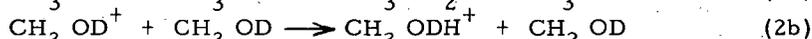
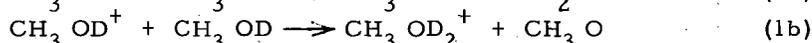
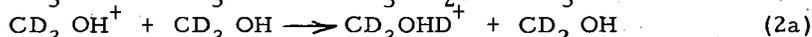
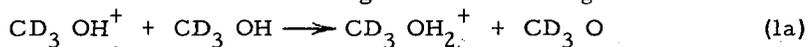


However, in a later publication (3) the same authors appear to favor the following hydride ion transfer reaction



over reaction (4).

In order to determine the relative cross sections of reactions (1) and (2) Lindholm and Wilmenius investigated the following reactions



In these three sets of reactions the ratios of product ion by mechanism (1) to product ion by mechanism (2) were 2:3, 1:3 and 2:3 respectively.

We have studied proton transfer using the techniques outlined by Lampe, Franklin and Field. (12) Since in our ion source secondary ions formed along the path of the primary ion beam are extracted in the same direction as the primary ion beam, discrimination because of momentum transfer should be minimized.

Figure 1 shows a plot of $\frac{\text{CD}_3\text{OH}_2^+}{\text{CD}_3\text{ODH}^+}$

against nominal electron energy over an eight volt range near threshold in the high pressure mass spectrum of CD_3OH . The curve has three distinct regions; A.

and C. In the low energy region one can detect only those secondary ions which have the parent ion as their precursor. As the electron energy is increased the curve breaks steadily upward along B. This is interpreted as the appearance of $CD_3OH_2^+$ ions from reaction of CD_2OH^+ with CD_3OH analogous to reaction (3). Eventually an electron energy is reached above which the ratio of product of CD_3CHD^+ relative to the rate of production of $CD_3OH_2^+$ is again constant. The establishment of this plateau C demonstrates that the only two ions which contribute significantly to proton transfer in this region of electron energy are CD_3OH^+ and CD_2OH^+ . It may be noted that this second plateau occurs in the same region of nominal ionizing voltage where the ionization efficiency curves for CH_2OH^+ and CH_3OH^+ from methanol are parallel.

The mean ratio in the plateau region A is about 0.92:1 whereas the ratio in the second plateau region is approximately 1.75:1. A parallel set of measurements using CH_3OD resulted in a value of 0.71 for the ratio $\frac{CH_3OD_2^+}{CH_3ODH^+}$ in plateau region A.

Under the source conditions employed it is apparent that the ratio of product from reaction (1) to product from reaction (2) must lie between 0.92:1 and 0.71:1. In order to estimate the true ratio one may proceed as follows: Let α be the ratio of the probability of transferring H^+ to that of transferring D^+ from any position on the molecule. Further let β be the ratio of the probability of collecting an ion to which H^+ been transferred to that of collecting an ion to which D^+ has been transferred. Clearly β is a measure of the momentum discrimination against D^+ transfer. If R is the true ratio for the transfer then

$$R = \frac{0.92}{\alpha\beta} \quad \text{from reactions 1a and 2a.}$$

$$R = 0.71 \alpha \beta \quad \text{from reactions 1b and 2b.}$$

Hence, $\beta = 1.14$ and a value of $R = 0.81$ may be deduced from our measurements.

Similar treatment of the results of Lindholm and Wilmenius gives $\beta' = 1.4$ and $R = .475$. If we assume α to be the same in both sets of results one obtains $\beta' = 1.24$. This leads to the expected result that discrimination against momentum transfer is considerably greater in the collision chamber used by Lindholm and Wilmenius.

It is not clear why the values of R calculated from our results and those of Lindholm and Wilmenius should be so different. One experimental uncertainty is the energy of the impacting ion beam. Since it is well known that cross sections for ion-molecule reactions are strongly dependent on the velocities of the primary ions, the measured ratio may depend on the ion velocity. Lindholm and Wilmenius report their measurements for ions of about 5 e.v. impacting energy. Our results in Figure 1 are reported for a repeller value of 4.5 volts. The geometry of the C. E. C. 103 ion source is such that the maximum energy an ion can acquire before arriving at the ion exit slit is about half the repeller voltage. This maximum energy of about 2.3 volts is somewhat lower than the energy of the ions used by Lindholm. However, we found no significant change in the measured ratio when the field strength was varied from 4 to 40 volts/cm. From our results we therefore, conclude that the relative probability of proton transfer from the two positions is independent of ion energy over this range.

From the results of Theard and Hamill (4) in their study with CD_3OH it is clear that the ratio $\frac{CD_3OH_2^+}{CD_3ODH^+}$ at an electron impacting energy of 70 volts remained

unchanged as the field strength was varied from 12 to 80 volts/cm. Since this ratio reflects the contribution of several independent proton transfer processes it can be assumed that the ratio of the reaction rates of any two of these processes is independent of field strength.

Once the ratio of proton transfer from reactions (1) and (2) is established the relative importance of processes such as (3) and (4) at higher electron energies can be determined. As shown in Table 1 the ratio $\frac{CD_3ODH^+}{CD_3OH^+}$ is independent of

electron energy for some seven volts above the ionization potential. Combining this result with the fact that the ratio $\frac{CD_3OH_2^+}{CD_3OHD^+}$ from reactions involving the parent

ion is 0.92:1 it is possible to calculate the amount of $CD_3OH_2^+$ formed by reactions involving ions other than the parent ion. Also shown in Table 1 is the ratio $\frac{\Delta CD_3OH_2^+}{CD_2OH^+}$ where $\Delta CD_3OH_2^+$ represents the increase in $CD_3OH_2^+$ due to ions

other than the parent. Because $\frac{\Delta CD_3OH_2^+}{CD_2OH^+}$ is constant for at least 10 volts above the onset of CD_2OH^+ we conclude that CD_2OH^+ is the only ion apart from the parent ion which contributes significantly to the formation of $CD_3OH_2^+$ in this energy range. The increase at 14 volts indicates the onset of additional deuteron transfer processes.

As would be expected, the formation of $CH_3OH_2^+$ from methanol by processes not involving the parent ion is reflected in the appearance potential curve of the secondary ion. We have already mentioned the appearance potentials were obtained by comparing the ionization efficiency curves for two ions after arbitrarily making their sensitivities equal at 50 electron volts. However, this procedure is only satisfactory when each of the ions is formed by only one process. When more than one process contributes to the formation of a given ion this fact must be considered. This is illustrated in Figure 2. In 2a we compare the ionization efficiency curves of CH_3OH^+ with $CH_3OH_2^+$ by adjusting the ion detector to indicate equal sensitivities for both ions at 50 electron volts. It can be seen that the apparent onset of $CH_3OH_2^+$ is higher than the onset of CH_3OH^+ .

In Figure 2b we again compare the ionization efficiency curve of $CH_3OH_2^+$ with that of CH_3OH^+ . In this case we have taken into account the observation that only 46% of the $CH_3OH_2^+$ ions are formed from the parent ion when making the sensitivity adjustment at 50 electron volts. When this is done it can be seen that both ions have the same apparent onset. The upward break in the $CH_3OH_2^+$ curve corresponds to the formation of significant amounts of $CH_3OH_2^+$ from CH_2OH^+ .

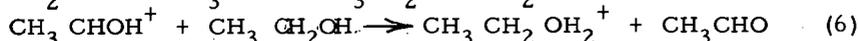
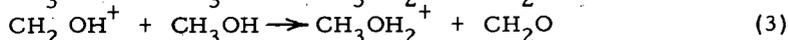
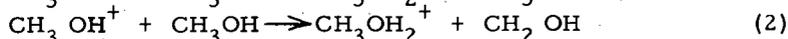
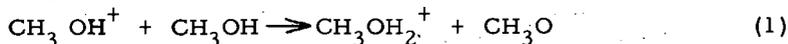
Formation of $C_2H_5OH_2^+$ in Ethanol

Several workers have observed the formation of $C_2H_5OH_2^+$ in the high pressure mass spectrum of ethanol. Tal'roze compared the appearance potential curves of $C_2H_5OH_2^+$ and $C_2H_5OH^+$ and concluded that $C_2H_5OH^+$ was a precursor for the formation of $C_2H_5OH_2^+$. (7) No other ions have previously been associated with the formation of $C_2H_5OH_2^+$.

In Figure 3 we show our ionization efficiency curves for the ions CH_3CHOH^+ , $\text{CH}_3\text{CH}_2\text{OH}^+$ and $\text{CH}_3\text{CH}_2\text{OH}_2^+$. From these results it is clear that CH_3CHOH^+ is the only important precursor for the formation of $\text{CH}_3\text{CH}_2\text{OH}_2^+$ for at least ten volts above the onset of $\text{CH}_3\text{CH}_2\text{OH}^+$. Furthermore, the same cross section is obtained for this reaction in the energy range of Figure 3 and at 70 ev. In sharp contrast to methanol the ethanol molecular ion plays no significant part in the formation of $\text{CH}_3\text{CH}_2\text{OH}_2^+$. This difference between the two molecules does not seem explicable in terms of the energetics of the corresponding reactions. Tal'roze and Frankevich have established lower limits and tentative upper limits to the proton affinities of the alcohols as 177-183 kcal/mole for methanol and 185-202 kcal/mole for ethanol. (11) From the work of D'or and Collin (12) and tabulated heats of formation in Field and Franklin (6) one can estimate the proton affinity of the methanol radical CH_2OH as 153 kcal/mole and of the ethanol radical CH_3CHOH as 159 kcal/mole. We are unable to suggest an alternate explanation.

Rate Constants for Proton Transfer Reactions

Having established the relative rates of proton transfer in the case of methanol and having shown that CH_3CHOH^+ , not $\text{CH}_3\text{CH}_2\text{OH}^+$, is the precursor for $\text{CH}_3\text{CH}_2\text{OH}_2^+$ formation it is possible to determine the rate constants for the following reactions



Consistent with recently tabulated values (13) we have determined rate constants and reaction cross sections at an ion repeller field of 10 volts/cm. Rate constants for all these reactions were observed to rise sharply at low field strength and to decrease at higher values, as is normally observed for ion-molecule reactions involving complex molecules. However, no attempt to extrapolate these results to zero field strength in order to obtain rate constants for thermal ions has been made.

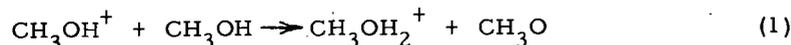
For any given secondary reaction, a plot of the ratio of secondary ions to the sum of precursor ions and secondary ions against ion source concentration is a straight line. As shown by Lampe and Field the slope S of this line can be expressed as

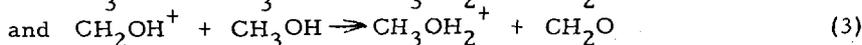
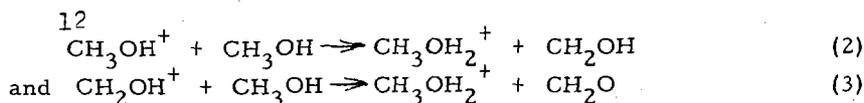
$$S = k\tau \quad (a)$$

$$S = l\sigma \quad (b)$$

Where k is the specific reaction rate, τ is the source residence time of the primary ion, l is the path length from the point of formation of the primary ions to the ion exit slit and σ is the reaction cross section. (14)

Reported in Table 2 are the reaction cross sections and rate constants for the reactions discussed. Also shown are results for methane from this study compared with earlier work. In this compilation we have corrected for the observation that 71% of the proton transfer product ion at a nominal electron impacting energy of 15 electron volts is produced by the parent ion. Since at this energy the remaining 29% of proton transfer product can be attributed to the CH_2OH^+ ion, the rate constants for

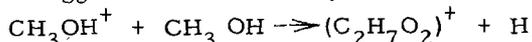




can be calculated by measuring the amount of proton transfer product at 15 volts and using the observed relative rates of reactions (1) and (2).

Ions with higher mass-to-charge ratios than those involving proton transfer

During this study we observed ions in the high pressure mass spectra of methanol and ethanol that had masses greater than those corresponding to proton transfer. In methanol the ions 73, 72, 63 and 45 were all observed. Of these only the 63 ion consistently exhibited a square law dependence on pressure. We are not sure of the mechanism of formation of these ions, but it is clear that 73 and 72 cannot be formed by second order ion molecule reactions involving only pure methanol. The appearance potential for 63 agrees well with that for CH_3OH^+ which suggests it is formed by the reaction.



In any event the abundance of these ions is less than 0.5 per cent of those produced by proton transfer.

In the high pressure mass spectrum of ethanol ions of mass-to-charge ratio 77 and 73 were both observed to follow a square law dependence with pressure. The relative abundance of these ions was less than 0.5 per cent of the secondary ions produced by proton transfer.

References

1. Theard, L. P. and Hamill, W. H., J. Amer. Chem. Soc. 84, 1134, (1962).
2. Moran, T. F. and Hamill, W. H., J. Chem. Phys. 39, 1413, (1963).
3. von Koch, H. and Lindholm, E., Arkiv For Fysik 19, 123, (1961).
4. Wilmenius, P. and Lindholm, E., Arkiv For Fysik 21, 97, (1962).
5. Lindholm, E. and Wilmenius, P., Arkiv For Kimi 20, 255, (1963).
6. Field, F. H. and Franklin, J. F., "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press Inc., New York (1957).
7. Tal'roze, V. L., Pure and Appl. Chem. 5, 455, (1962).
8. Futrell, J. H. and Tiernan, T. O., J. Chem. Phys. 39, 2539, (1963).
9. Schissler, D. O. and Stevenson, D. P., J. Chem. Phys. 24, 926, (1956).
10. Stevenson, D. P., J. Phys. Chem. 61, 1453, (1957).
11. Tal'roze, V. L. and Frankevich, J., J. Amer. Chem. Soc. 80, 2344, (1958).
12. D'Or, L. and Collin, J., Bull. Roy. Soc. Liege 22, 285, (1956).
13. Lampe, F. W., Franklin, J. L. and Field, F. H., "Progress in Reaction Kinetics", G. Porter Ed. Pergamon Press 1961, pages 67 ff.
14. Lampe, F. W. and Field, F. H., Tetrahedron 7, 189, (1959).

TABLE 1

Nominal Energy E.V.	$\frac{CD_3ODH^+}{CD_3OH^+}$	$\frac{CD_3OH_2^+}{CD_2OH^+}$
5.6	.15	
6.0	.15	
6.4	.15	
6.8	.16	
7.2	.16	0
7.6	.16	0
8.0	.16	.08
8.4	.16	.12
8.8	.16	.14
9.2	.16	.14
9.6	.16	.13
10.0	.16	.14
10.4	.16	.13
10.8	.16	.14
12.0	.16	.14
13.0	.16	.14
14.0	.17	.14
15.0	.18	.132

TABLE 2

Reaction	σ , cm ² molecule ⁻¹ x 10 ¹⁶	k, cm ³ sec ⁻¹ molecule ⁻¹ x 10 ¹⁰
CH ₃ OH ⁺ + CH ₃ OH → CH ₃ OH ₂ ⁺ + CH ₃ O	79	11.0
CH ₃ OH ⁺ + CH ₃ OH → CH ₃ OH ₂ ⁺ + CH ₂ OH	97	13.5
CH ₂ OH ⁺ + CH ₃ OH → CH ₃ OH ₂ ⁺ + CH ₂ O	48	6.8
CH ₃ CHOH ⁺ + CH ₃ CH ₂ OH → CH ₃ CH ₂ OH ₂ ⁺ + CH ₃ CHO	531	60
CH ₄ ⁺ + CH ₄ ⁺ → CH ₅ ⁺ + CH ₃	{ 54	10.7
	{ 61 (a)	8.5 (a)

(a) Field, F. H., Franklin, J. L. and Lampe, F. W., J. Amer. Chem. Soc. 79, 2419, (1957)

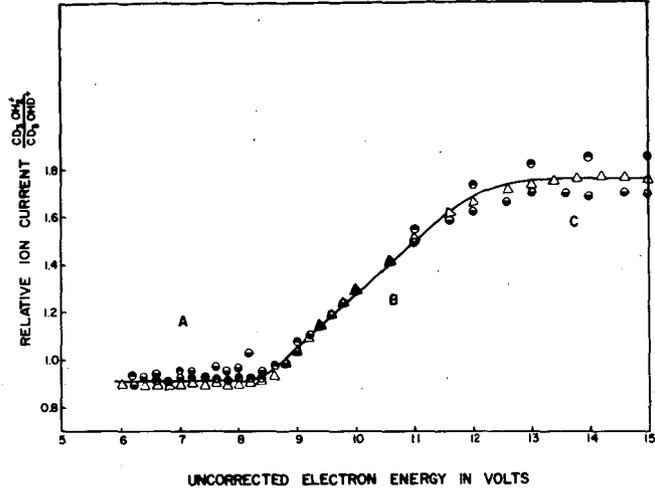


FIGURE 1 $\frac{CD_3OH_2^+}{CD_3OHD^+}$ current versus uncorrected electron energy (3 expts. at 3 different pressures in 3 different sources).

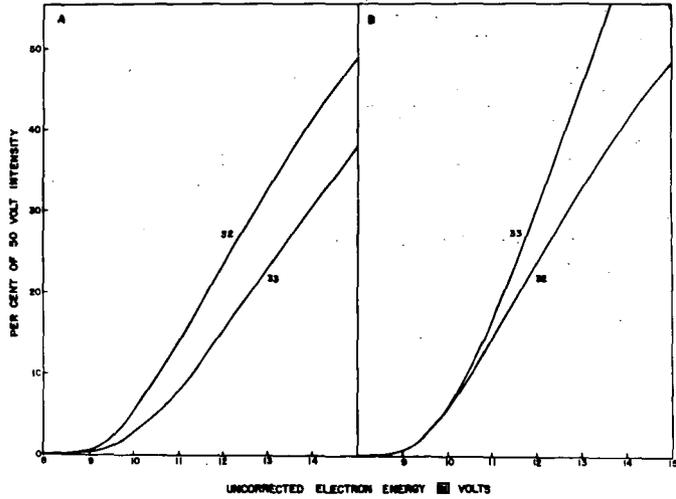
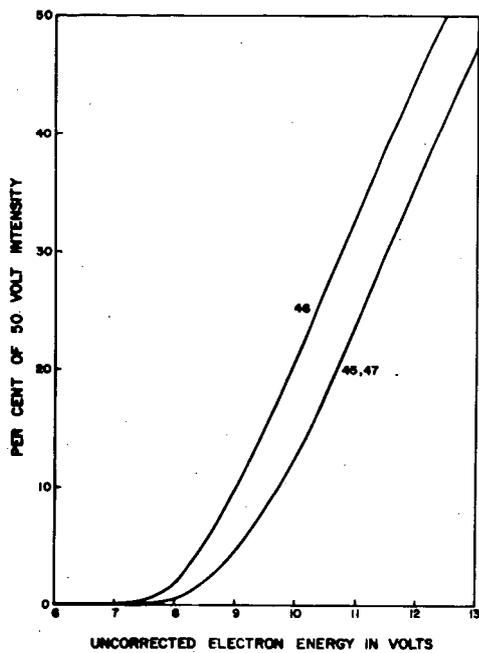


FIGURE 2 Uncorrected ionization efficiency curves for m/e 32 and 33 from methanol normalized to 50 volts and same curves corrected for $CH_3OH_2^+$ from CH_2OH^+ , respectively.



Normalized ionization efficiency curves for m/e 45, 46, and 47 from ethanol.

FIGURE 3