

THE RADIOLYSIS AND MASS SPECTROMETRY OF SEVERAL DEUTERATED ETHANOLS

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Received June 19, 1957

Five isotopic species of liquid ethanol have been irradiated with cobalt-60 γ -rays— $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CD}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OD}$ and $\text{CD}_3\text{CD}_2\text{OD}$. From the rates of hydrogen production ($G(\text{H}_2)$), observed in these radiolyses, (1) $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH} + \text{H}$, it is concluded that hydrogen production proceeds *via* a primary radical process wherein the hydrogen atoms originate almost exclusively from the CH_2 -group (process 1). From measurements of the deuterium content of the radiolytic hydrogen, it is concluded that the ensuing abstraction reaction occurs principally on the $-\text{OH}$ hydrogen (80–90%) by process 2 with a small amount occurring at the CH_3 -group (10–20%) by process 3. (2) $\text{H} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{H}_2$; (3) $\text{H} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2$. Examination of the mass spectra of these deuterated ethanols demonstrates that the formation of hydrogen atoms from electron impact on very tenuous ethanol gas proceeds by a similar mechanism.

Introduction

The formation of acetaldehyde and 2,3-dihydroxybutane during the radiolysis of ethanol with ionizing radiation has been generally attributed to a particular sensitivity of this molecule at the $-\text{CH}_2$ -position.³ In addition, the formation of these two products has suggested the possibility that hydrogen may be formed in part by a radical mechanism and in part by a molecular mechanism.

A critical examination of these possibilities has now been carried out by means of an isotopic tracer technique which consisted in the preparation and irradiation of the species: $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CD}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OD}$ and $\text{CD}_3\text{CD}_2\text{OD}$, as described in the following sections.

Experimental

1. Preparation of Isotopically Labeled Substances. $\text{CH}_3\text{CH}_2\text{OD}$; **Ethanol-1- d_1** .—A slurry of 53 g. (0.5 mole) of sodium carbonate (vacuum dried at 110°), 89 g. (0.50 mole) of freshly vacuum distilled ethyl oxalate and 5 ml. (0.25 mole) of D_2O was heated at 150° until the vigorous evolution of gas had ceased (about two hours). The product ethanol- d_1 was distilled continuously during this time, at a head temperature of 68 – 77° . The crude product had only a very small peak at 3350 cm^{-1} , indicating excellent isotopic purity. It was redistilled through a thoroughly dried Widmer column and collected in a thoroughly dried flask. From the size of the peak at 3350 cm^{-1} observed in this product, it was estimated that less than 5% ethanol was present. A comparison of its nuclear magnetic resonance spectrum with that of ethanol showed the complete disappearance of one of the hydrogen lines.

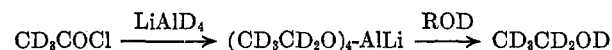
$\text{CH}_3\text{CD}_2\text{OH}$; **Ethanol-2- d_2** .—To a chilled (0°) solution of 3 g. of LiAlD_4 (50% excess) in 50 ml. of diethylene glycol (DEC) was added over a period of 45 minutes a solution of 5 g. of freshly distilled acetic anhydride in 25 ml. of DEC. The reaction mixture was stirred overnight at room temperature, and then heated to 100° for one hour. Butyl carbitol (50 ml.) was then added to decompose the complex, and the mixture stirred several hours. The ethanol-2- d_2 was then distilled under high vacuum into a liquid nitrogen-cooled trap, and redistilled onto Drierite. Vapor Fractionator (Perkin-Elmer) analysis of this product showed it to be ethanol containing only a trace of water and no other contaminants. Infrared analysis of this material indicated excellent isotopic purity⁴; this was confirmed by examination of the nuclear magnetic resonance spectrum. A similar reduction of acetyl chloride with LiAlD_4 produced ethanol-

2- d_2 containing about 5% ethyl-1- d_1 acetate⁵ which was very difficult to remove.

Since it was found by separate experiments that 5 mole % of ethyl acetate reduced the hydrogen yield in ethanol from 3.66 to 3.03 (probably *via* trapping of the hydrogen atoms by the carbonyl group), it was evident that ethyl acetate was one contaminant which could not be tolerated for these radiolyses.

$\text{CD}_3\text{CH}_2\text{OH}$; **Ethanol-3- d_3** .—Malonic acid (30 g.) was equilibrated three times with 30-ml. portions of D_2O ⁶; the heavy water was removed completely after each equilibration by vacuum distillation. The final product (calculated to contain 97.5% deuterium) was vacuum dried and decomposed as above. The deuterated acetic acid so obtained (18.15 g.) was mixed with 53 ml. of phthaloyl chloride⁷; the mixture was heated at 60 – 180° over a period of two hours. The yield of deuteroacetyl chloride was 16.02 g. (69%) yield. A portion of this acid chloride (6.3 ml.) was reduced with a slurry of 3 g. of lithium aluminum hydride in 75 ml. of diethyl carbitol as above. Only a small forerun of ethyl acetate was obtained in the vacuum line fractionation, and the deutero alcohol was dried over Drierite and distilled directly into evacuated ampules for irradiation. Examination of the infrared spectra of this product indicated isotopic purity in excess of 95%.

$\text{CD}_3\text{CD}_2\text{OD}$; **Ethanol- d_6** .—An attempt was made to prepare this material *via* the reaction sequence



but the product contained 25–30% of perdeuteroethyl acetate which could not be reduced below 5% by either vacuum line fractionation or hydrolysis with sodium + D_2O . The sample of perdeuteroethanol employed for the radiolysis was therefore obtained from Tracerlab, Inc. Vapor Fractionator analysis showed that this material was chemically pure and dry; infrared analysis showed that it was isotopically pure within the limits of detection of the apparatus.

2. Irradiation of Isotopically Labeled Substances.—The isotopically labeled materials were degassed by refluxing at 10^{-4} mm. and distilled into evacuated ampules prepared from appropriate lengths of 14 mm. tubing. The ampules

(5) An interesting sequence of reactivities was observed during the course of these preparative experiments. The reduction of either CH_3COCl or CD_3COCl with LiAlH_4 proceeded readily and the product was an ethanol free of any ester. The reduction of acetyl chloride with LiAlD_4 resulted in a product containing more than 5% of ethyl-1- d_1 acetate, and the reduction of CD_3COCl with LiAlD_4 produced a product containing about 25–30% of perdeuteroethyl acetate. The perdeuteroethyl acetate was hydrolyzed only very slowly by heating with metallic sodium and a few drops of D_2O . These observations suggest⁸ that the reduction of acid chlorides proceeds through an intermediate ester formation and that the reduction of such deuterated ester intermediates by LiAlD_4 is quite slow; and that the kinetics of reductions by LiAlD_4 and the kinetics of hydrolysis of deuterated esters should provide interesting information about the isotope effect of deuterium substitution at positions adjacent to reactive centers.

(6) J. O. Halford and L. C. Anderson, *J. Am. Chem. Soc.*, **58**, 736 (1936).

(7) J. D. Cox and H. S. Turner, *J. Chem. Soc.*, 3176 (1950).

(1) Atomics International, P. O. Box 309, Canoga Park, California.

(2) A preliminary account of this work appeared in *J. Am. Chem. Soc.*, **79**, 751 (1957).

(3) Cf., for example, W. McDonnell and A. S. Newton, *J. Am. Chem. Soc.*, **76**, 4651 (1954).

(4) A detailed analysis of the infrared spectra of these five ethanols will be reported in a subsequent publication by H. W. Morgan and J. G. Burr, Jr.

containing the substances (about 1–2 g.) were irradiated in a cobalt-60 source at an intensity of $8.0\text{--}8.5 \times 10^{17}$ e.v./g. water-minute. The radiation dosages received by the substances were computed from the time of irradiation and the electron density relative to water (1.015 for ethanol). Experiments were carried out which showed that there was negligible radiation-induced exchange (or back reaction) between the organic substrate and the molecular hydrogen formed in the reaction.⁸ In addition, the infrared spectra of irradiated ethanol-*d*₁ was taken (after distillation to remove products of low volatility) and found identical with the unirradiated substance. This demonstrates that there was no randomization or relocation of the label during the irradiations.

3. Recovery and Analysis of Radiation Products.—The ampules containing the irradiated material were placed in a holder on a vacuum line and the system evacuated. The ampules were broken under vacuum, and the gases removed by Toeplering through a trap at -78° , one at -196° and through a palladium valve at 430° . The two traps removed all products except hydrogen, methane and carbon monoxide. The palladium valve passed only the hydrogen. The quantity of hydrogen so obtained was measured in a gas buret attached to the Toepler pump. The hydrogen samples were pumped into evacuated ampules which were closed with vacuum stopcocks. Deuterium contents of these samples were measured on a mass spectrometer.

All materials were irradiated at least in duplicate, and all deuterium analyses were at least in duplicate. The mass spectra of the alcohols were observed on a modified G.E. mass spectrometer. The spectrum of $\text{CH}_3\text{CH}_2\text{OD}$ could not be obtained because of the extensive exchange which occurred on the surfaces of the instrument, and which invalidated the data.

Results

The data obtained by these experiments are shown in the following tables. Table I displays the rate of hydrogen (= hydrogen + deuterium) production as $G(\text{H}_2)$ —i.e., molecules of hydrogen produced per 100 e.v. of energy absorbed by the sample. The total dosages were about 5×10^{20} e.v. per gram; and thus were on the linear portion of the yield curve for hydrogen produced by radiolysis of ethanol.⁹ Also listed in this table are the deuterium contents of the samples of hydrogen thus obtained. As noted (footnote *d*), the deuterium content of the hydrogen produced from perdeuteroethanol was low and this taken in conjunction with the results of calibrating samples occasionally submitted along with the samples of radiolysis hydrogen suggests that all of these deuterium analyses are 4–6% low.

Table II displays the mass patterns of three of these alcohols.

TABLE I

Substance	$G(\text{H}_2)^a$	% Deuterium in radiolytic hydrogen ^b
$\text{CH}_3\text{CH}_2\text{OH}$	3.66 ± 0.26	...
$\text{CD}_3\text{CH}_2\text{OH}$	$3.90 \pm .15$	4.27
$\text{CH}_3\text{CD}_2\text{OH}$	2.81^c	42.0
$\text{CH}_3\text{CH}_2\text{OD}$	$3.67 \pm .08$	34.2
$\text{OD}_3\text{CD}_2\text{OD}$	$2.98 \pm .04$	93–95 ^d

^a These are the averages and average deviations obtained from two or three independent irradiations. ^b Mass spectrometer analysis. ^c Single experiment. ^d This low value suggests, as mentioned in the text, that all of the deuterium analyses are 4–6% low.

Discussion

Significance of the $G(\text{H}_2)$ Values.—From the

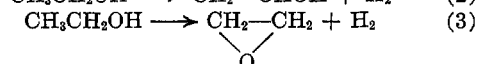
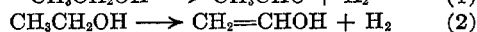
(8) J. G. Burr, Jr., *J. Chem. Phys.*, **25**, 587 (1956).

(9) A. S. Newton and W. McDonnell, *J. Am. Chem. Soc.*, **78**, 4554 (1956).

TABLE II

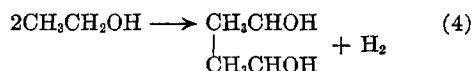
Mass no.	⁴⁶ $\text{CH}_3\text{CH}_2\text{OH}$	⁴⁹ $\text{CD}_3\text{CH}_2\text{OH}$	⁴⁸ $\text{CH}_3\text{CD}_2\text{OH}$
50		4.75	
49		100.00	7.18
48		248.80	100.00
47	2.74	46.00	12.50
46	100.00	98.4	100.0
45	205.0	49.25	15.45
44	9.37	28.75	18.40
43	37.80	12.12	17.15
42	12.30	4.94	4.55
41	3.65	2.06	3.68
40	1.60	1.56	1.46
39			2.36
38			3.05
37			
36			
35			
34			65.9
33		4.13	455.0
32	1.04	78.00	71.80
31	457.0	625.0	75.00
30	24.80	119.0	104.5
29	80.8	154.5	79.2
28	87.4	100.0	68.8
27	87.2	32.9	25.70
26	24.9	12.0	8.90
25	5.49	3.06	2.27
24	1.51	1.81	
23			
22			
21		10.5	
20		19.5	6.57
19	18.95	4.94	5.90
18	5.84	24.25	4.55
17	2.74	18.45	26.8
16	2.96	19.50	14.80
15	29.75	11.8	15.20
14	16.10	9.56	7.23
13	5.48	2.44	3.09
12	2.42	3.25	2.82
4		1.13	
3		3.31	2.45
2	6.52	5.56	3.36
1	0.46	4.75	4.09

data in Table I, it may be concluded that $G(\text{H}_2)$ is lowered from the value observed in ethanol (3.66) to that observed in perdeuteroethanol (2.98) only by deuterium substitution in the $-\text{CH}_2-$ group; $G(\text{H}_2)$ is unaffected by deuterium substitution in either the CH_3- or the $-\text{OH}$ groups. Therefore, the following types of molecular process can be excluded from consideration as major contributors to the radiolytic formation of hydrogen from ethanol



on the grounds that the rate of hydrogen formation by any of these processes should be equally affected by deuterium substitution in either of at least two of the groupings in ethanol. A fourth possible molecular process (4) must be considered since the

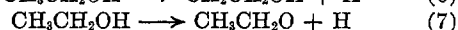
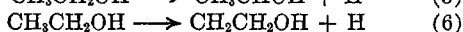
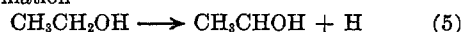
rate of hydrogen formation by this process would be affected, in accordance with the data, by deuterium substitution only in the $-\text{CH}_2-$ group.



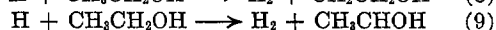
The implication thus far from the data is that the primary process leading to hydrogen formation is either a radical process (5) in which only deuterium atoms are produced from the $-\text{CD}_2-$ group of $\text{CH}_3\text{CD}_2\text{OH}$, or process 4 which would produce pure D_2 from $\text{CH}_3\text{CD}_2\text{OH}$. If, in the former case, the D atoms abstracted only from the CH_3 or $-\text{OH}$ groups, then the maximum H content of the gas would be 50%. Any abstraction from the $-\text{CD}_2-$ group would decrease the H content of the hydrogen, and, of course, the maximum H content of gas produced by process 4 would be zero. One would therefore expect that the operation of process 5 followed by random abstraction, or the operation of any mixture of processes 4 and 5 in the radiolysis of $\text{CH}_3\text{CD}_2\text{OH}$ would produce hydrogen with an H content of less than 50%. The observed H content of this gas was 58%, and therefore any substantial contribution by either the molecular process 4 or by hydrogen abstraction from the $-\text{CD}_2-$ need not be considered seriously.

Significance of the Deuterium Content of the Radiolytic Hydrogen.—One is then left with a partial mechanism which consists of a pure radical process where the H atoms originate from the $-\text{CH}_2-$ and abstract from either the CH_3- or the $-\text{OH}$ group. This mechanism can now be substantiated further by consideration of the other data in Table I and the following sets of processes

H atom formation



H atom abstraction



The logic outlined in the previous paragraphs means that of the processes 1–7, only process 5 need be considered as the primary chemical process. Therefore, the observed deuterium content of the radiolytic hydrogen from the various species must be explained by some combination of process 5 with processes 8, 9 and 10. Process 9 may be eliminated as described above. From the various combinations of 5, 8 and 10, an excellent semi-quantitative fit to the data is found by considering (5) and (10) as the only major contributors to the formation of hydrogen from ethanol—*i.e.*, hydrogen is formed in the radiolysis of ethanol principally by initial hydrogen atom formation from the $-\text{CH}_2-$ group of the molecule followed by hydrogen abstraction from the $-\text{OH}$ group.

The preciseness of this fit can be shown by the following analysis. If the deuterium analyses in Table I are assumed to be uniformly 5% low, as mentioned earlier (probably by a systematic error in the mass spectrometer operation) and the following mechanistic assumptions are made: (a)

the primary chemical process is pure radical process—*i.e.*, leads only to the formation of hydrogen atoms, but no molecular hydrogen (process 5); (b) hydrogen atom abstraction from the CH_3- and $-\text{OH}$ groups occurs in the following proportions: 82% from the $-\text{OH}$ group (process 10), 18% from the CH_3 group (process 8), then the following data fit is observed.

TABLE III

Species	% Deuterium in the radiolytic hydrogen	
	Predicted	Found
$\text{CD}_3\text{CH}_2\text{OH}$	9	9
$\text{CH}_3\text{CD}_2\text{OH}$	50	47
$\text{CH}_3\text{CH}_2\text{OD}$	41	39

There can be little question that the mechanism of hydrogen formation is primarily radical, that the hydrogen atoms originate principally from the $-\text{CH}_2-$ group and abstract principally from the $-\text{OH}$ group; however, the accuracy of the data obtained in this investigation is such that the mechanism illustrated in Table II is only semi-quantitative. One cannot exclude, by the present data, small contributions of hydrogen atoms from the CH_3- or $-\text{OH}$ groups or assign precisely the relative rates of abstraction from these three hydrogen groups in the ethanol molecule. A knowledge of the relative amounts of H_2 , HD and D_2 species present in the radiolytic hydrogen would have been of great assistance in evaluating the relative rates of the abstraction processes; although care is being taken to obtain such data from the subsequent similar investigations now in process, unfortunately such data was prohibited in this investigation by the process chosen for purification of the radiolytic hydrogen gas.

The mechanism for hydrogen production stated in the above paragraphs is also supported by consideration of the relative amounts of other radiolysis products¹; this is discussed in a subsequent section.

The Isotope Effect.—The conclusions reached in the above sections must be evaluated in the light of the known difference in reaction rates between C–H and C–D bond-breaking. It will be found that the above conclusions are reinforced by consideration of the isotope effect, and that some additional information about the nature of the radiolysis is available from the sizes of the observed isotope effects.

The primary process demonstrated above is the rate-determining cleavage of a C–H bond, followed by a rapid hydrogen abstraction reaction. The values of $k_{\text{H}}/k_{\text{D}}$ which have been observed for a number of rate-determining C–H bond cleavages which occur near room temperature *via* ionic mechanisms range from 6–10¹⁰; this ratio is known to decrease with increasing reaction temperature to a theoretical minimum value of 1.4¹⁰. The value of this ratio in the radiolytic processes under study here can be evaluated from the relative rates of hydrogen formation from ethanol and perdeuteroethanol or $\text{CH}_3\text{CD}_2\text{OH}$ (if it is assumed that the rates of formation of molecular hydrogen are determined by the rates of hydrogen atom forma-

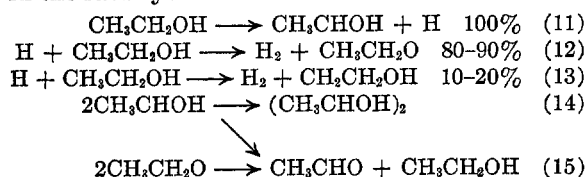
(10) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

tion—*i.e.*, a pure radical process) and is found to be about 1.3. This suggests that the rate-determining process in this radiolysis is one of high equivalent temperature. One way of phrasing this is to say that the primary disengagement of hydrogen atoms must occur from a molecule of high energy content—*i.e.*, an excited or ionized species. This may be regarded as constituting one of the first experimental confirmations of the widely held assumption that radiation-induced bond rupture in organic molecules occurs *via* excited or ionized species.

Secondly, a preferential bond rupture of the C-D bond in $\text{CH}_3\text{CD}_2\text{OH}$ is observed despite the greater number of C-H bonds in that molecule and despite the considerably greater ease with which those bonds would be broken. Thus preference for the rupture of the bonds in the $-\text{CH}_2-$ group of ethanol itself must be even greater than that observed for the deuterated molecule.

The abstraction reactions discussed above are also subject to an isotope selectivity. Hydrogen atoms are abstracted more easily than deuterium atoms. No data are available for hydrogen abstraction by hydrogen atoms themselves, but the data for the relative abstraction rates of H and D by other radicals¹⁰ suggest that the relative rates of abstraction of H or D by hydrogen atoms should be about 1.2–1.4 ($k_{\text{H}}/k_{\text{D}}$). Thus the preferential abstraction of D from $\text{CH}_3\text{CH}_2\text{OD}$ happens despite the greater ease with which abstraction of H would occur, and thus this process must also be even more favored in the radiolysis of ethanol itself.

Proposed Mechanism for the Radiolysis of Ethanol.—In the light of the above considerations, the following mechanism may be rather confidently proposed for the formation of the major products in the radiolysis of ethanol



Since the mechanism found for the formation of hydrogen predicts that 90–95% of the simultaneously formed organic radicals will be either CH_3CHOH or $\text{CH}_3\text{CH}_2\text{O}$, one would expect that the radiolysis products, other than hydrogen, should be principally 2,3-dihydroxybutane and acetaldehyde. Furthermore, since acetaldehyde can be formed from either of the two organic radicals, and the glycol from only one, one would also expect that more acetaldehyde than glycol should be formed. In confirmation of this, McDonnell and Newton¹ have found that acetaldehyde, 2,3-dihydroxybutane and hydrogen are by far the principal products of the radiolysis, and that acetaldehyde and the glycol are formed in the ratio of 2.2/1.05.

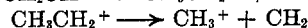
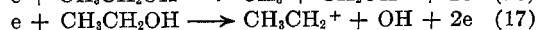
Correlation of the Radiolysis Mechanism with the Mechanism of Gas Phase Electron Impact.—It is illuminating to examine the mass spectra of

these deuterated ethanols in the light of the liquid phase radiolysis mechanism discussed above. An examination of mass pattern (Table II) of ethanol itself shows that loss of one hydrogen atom (the radical process) from the parent ion is a much more probable process than simultaneous loss of two hydrogen atoms (the molecular process). The relative sizes of the m/e 48 and 47 in the spectrum of $\text{CD}_3\text{CH}_2\text{OH}$ show that the radical process is here also much preferred, and that furthermore hydrogen is lost rather than deuterium. On the other hand, the sizes of the m/e 47 and 46 peaks in the spectrum of $\text{CH}_3\text{CD}_2\text{OH}$ shows clearly that the radical process is again the preferred one—and that the atom lost is deuterium rather than hydrogen, despite the opposition offered to this preference by the isotope effect (*vide supra*).¹¹ These observations, and the conclusions drawn therefrom, are in good agreement with the data of Momigny¹² who measured the spectra of $\text{CH}_3\text{CD}_2\text{OH}$, and with the spectra of $\text{C}_2\text{H}_5\text{CD}_2\text{OH}$ as reported by Harley and Wiberley¹³; as well as with the pioneering observations of Friedman and Turkevich¹⁴ on the mass spectra of the deuterated propyl alcohols.

It is apparent that the mechanisms for the formation of hydrogen atoms by the action of electrons upon every tenuous ethanol gas (10^{-5} mm.) is identical with the mechanisms of formation of hydrogen atoms by the action of electrons upon liquid ethanol. The significance of this correlation together with other examples of similar correlations are discussed in one of the following articles.

Acknowledgments.—The author wishes to acknowledge particularly the assistance of Dr. T. J. Sworski, of the Oak Ridge National Laboratory, who not only made many helpful suggestions about interpretation but also suggested several critical experiments. Thanks are also owing to Dr. D. E. McKenzie of Atomics International, and Dr. J. A. Ghormley of Oak Ridge National Laboratory, for many illuminating discussions, and to Dr. F. W. McLafferty, of Dow Chemical Company, for bringing several key references to my attention.

(11) Evidence about the nature of other processes occurring in the mass spectrometer may be gained from examination of other parts of these mass spectra. From the fact that the CH_3OH^+ and CD_3OH^+ ions are produced from these molecules without evidence of hydrogen rearrangement whereas appearance of the CH_3^+ ions is accompanied by extensive hydrogen rearrangement, it is apparent that these two groups of ions are produced by different processes. In particular, it seems probable that the CH_3^+ ions may result from the disruption of a very short lived state of the CH_3CH_2^+ ion, since extensive and rapid hydrogen rearrangement would be expected to occur in the ethyl ion and evidently does not occur in the $\text{CH}_3\text{CH}_2\text{OH}^+$ ion. Evidence from these two spectra



concerning the hydrogen rearrangement agree well with that obtained by Momigny¹² from the mass spectrum of $\text{CH}_3\text{CD}_2\text{OH}$.

(12) J. Momigny, *Bull. soc. roy. Sci. Liege*, **24**, 111 (1955).

(13) J. H. Harley and S. E. Wiberley, "Instrumental Analysis," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 348.

(14) L. Friedman and J. Turkevich, *J. Am. Chem. Soc.*, **74**, 1686 (1952).