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Products of Ionization by Electron Impact in Methyl and Ethyl Alcohol

CHARLES S. CUMMINGS, II* AND WALKER BLEAKNEY
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

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Fourteen different ions were observed in methyl alcohol and twenty-five in ethyl alcohol. The appearance potentials of many of these were measured and the manner of dissociation in several cases was definitely established. The ionization potentials of the two molecules were found to be 10.8 volts for methyl and 11.3 volts for ethyl alcohol. In all cases subject to unambiguous interpretation that reaction occurred which required the least dissociation energy. The concept of localized charge on the oxygen atom in certain complex ions is supported by the results.

INTRODUCTION

SOME careful investigations have been made in the last few years of the products of ionization resulting from electron collisions in several of the simpler hydrocarbons. Methane was studied by L. G. Smith,[1] acetylene by Tate, P. T. Smith and Vaughan,[2] ethylene by Kusch, Hustrulid and Tate[3] and Delfosse and Hipple,[4] ethane by Hipple,[5] propane, propylene and allene by Delfosse and Bleakney.[6] It is the purpose of this paper to describe some results on methyl and ethyl alcohol, two close relatives of methane and ethane.

The apparatus used in this investigation was a mass-spectrograph which has been only briefly described. A more detailed report on this instrument will appear elsewhere. For the present it will be sufficient to say that this instrument is a demountable, all-metal design which may be baked at elevated temperatures to insure good vacuum conditions. The analyzer is of the familiar 180° type. In principle the apparatus is exactly the same as that in which most of the work in this field has been done. The yield of ions produced by electrons of controllable speed is studied as a function of this speed to determine the minimum energy required to produce an ion of a given type. The details of this procedure may be found in the references already cited.

The method of admitting the gas into the ionization chamber consisted in adjusting the pressure of the alcohol vapor behind a glass capillary leak. The vapor flowed continuously through the leak into the mass spectrograph and out through the pumps. There was some differential of pressure between the ionization chamber and the analyzer maintained by the pumps. It was found that the best stock chemicals were pure enough for the purposes in hand.

The first question which must be studied in an investigation of this kind is whether the ions actually observed are the result of single electron collisions. Several other processes may conceivably occur such as chemical reaction with residual impurities in the apparatus or with the walls, dissociation on the electron emitting filament, ionization through multiple collision or other changes suffered after the first electron impact. In the results to be described we are convinced that, with the possible exception of the mass 28 and mass 12 peaks in methyl alcohol, none of these disturbing processes played an important role. Experiments showed the results to be independent of pressure, electron current and filament temperature under the conditions of operation, and the values of the appearance potentials themselves indicate, as has been amply demonstrated in previous work, that we were observing the effect of single impacts.

It is convenient to represent the appearance potential of an ion as the sum of three quantities: (1) a dissociation energy, (2) an ionization energy, (3) the kinetic and excitational energy carried off by the products of the dissociation.

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* Now at the Remington Arms Company, Bridgeport, Connecticut.

[1] L. G. Smith, Phys. Rev. **51**, 4 (1937).

[2] Tate, Smith and Vaughan, Phys. Rev. **48**, 523 (1935).

[3] Kusch, Hustrulid and Tate, Phys. Rev. **52**, 843 (1937).

[4] J. Delfosse and J. A. Hipple, Phys. Rev. **54**, 1060 (1938).

[5] J. A. Hipple, Phys. Rev. **53**, 530 (1938).

[6] J. Delfosse and W. Bleakney, Phys. Rev. **56**, 256 (1939).

This can be expressed algebraically as:

$$A(\mathrm{X}^+) = P(\mathrm{X}) + I(\mathrm{X}) + W(\mathrm{X}^+),$$

where: $A(\mathrm{X}^+) \equiv$ Appearance potential of the ion X^+; $I(\mathrm{X}) \equiv$ Ionization potential of molecule X; $W(\mathrm{X}^+) \equiv$ Excess energy (kinetic or excitational) appearing in the production of the ion X^+ from the parent molecule; $P(\mathrm{X}) \equiv$ Energy to produce neutral X from a parent molecule, all products being in their lowest state. In giving values for $P(\mathrm{X})$ the products as well as X must be stated.

TABLE I. *Heats of dissociation (ev). In all cases where source references are not given, values have been recalculated from data of Bichowsky and Rossini.*[8]

$D(H_2)$	4.48[7]	$D(CH_3)$	10.6[1]	$D(HCHO)$	13.68
$D(OH)$	4.31[7]	$D(C_2H_2)$	12.97	$D(CH_3OH)$	19.01
$D(CH)$	3.47[7]	$D(C_2H_4)$	19.31	$D(C_2H_5OH)$	29.27
$D(CH_4)$	15.16	$D(C_2H_6)$	25.17	$D(CH_3CHO)$	24.23
$D(H_2O)$	9.49[7]	$D(CH_2)$	7.0[1]		

With the present type of instrument there is no way of measuring the kinetic energy of the reaction nor of determining in what excited states the products are left. Hence, when we subtract the calculated dissociation energy from the appearance potential, we obtain a figure that is really $I(\mathrm{X}) + W(\mathrm{X}^+)$, i.e., an upper limit to the ionization potential. In most cases other evidence shows that $W(\mathrm{X}^+)$ is a small quantity.

The calculation of the dissociation energy, and hence the determination of the ionization potential and process of formation, involves thermochemical data. The difficulty here is that practically all the molecules studied so far contain carbon, so that the heat of sublimation of carbon is involved in the thermochemical equations. This quantity is still subject to some uncertainty which is carried over into the calculated heats of dissociation. In this work we have adopted the value $L(C) = 5.413$ electron volts as given by Herzberg.[7]

Table I lists the calculated heats of dissociation used in the analysis of the data. The values of the heats of formation involved in the calculations were taken from Bichowsky and Rossini.[8] Although the reactions induced by electron impact correspond thermochemically to reactions taking place at absolute zero, the correction of the heats of formation to their values at this temperature can be neglected.[1]

EXPERIMENTAL RESULTS

Methyl alcohol

The methyl alcohol vapor was obtained from a bulb that contained several cubic centimeters of liquid alcohol at room temperature. The maximum available pressure behind the leak was the vapor pressure of the alcohol at room temperature. This was, however, more than adequate. After passing through the capillary leak into the mass spectrograph the vapor was subjected to electron bombardment under various conditions of pressure and electron energy and the product ions studied. A summary of the results and their interpretation is given in Tables II and III.

Table IV lists the energies of various combinations of one carbon, one oxygen and four hydrogen atoms with respect to the combination CH_3OH as zero.

Mass 32.—The appearance potential of the ion corresponding to this mass was $A(\mathrm{X}^+) = 10.8 \pm 0.2$ volts. This could have been only the molecular ion. Hence the reaction is uniquely determined:

$$CH_3OH \rightarrow CH_3OH^+ + e$$
$$I(CH_3OH) = A(CH_3OH^+) = 10.8 \text{ volts.}$$

TABLE II. *Observed relative abundances for electron energy of 70 volts. No negative ions observed.*

MASS	ION†	ETHYL ALCOHOL	METHYL ALCOHOL	MASS	ION†	ETHYL ALCOHOL	METHYL ALCOHOL
46	$C_2H_5OH^+$	100.0		27	$C_2H_3^+$	272.0	
45	$C_2H_4OH^+$	242.0		26	$C_2H_2^+$	110.0	
44	CH_3CHO^+	20.0		25	C_2H^+	23.5	
43	CH_3CO^+	56.4		24	C_2^+	4.8	
42	CH_2CO^+	24.4		19	H_3O^+	30.9	trace
41	$CHCO^+$	8.7		17	OH^+	3.9	0.5
40	C_2O^+	1.7		16	$CH_4^+ + O^+$	9.6	2.5
32	CH_3OH^+	11.3	100.0	15	CH_3^+	74.8	64.5
31	CH_2OH^+	986.0	176.0	14	CH_2^+	43.8	10.8
30	$HCHO^+$	56.5	16.1	13	CH^+	17.0	5.2
29	HCO^+	293.0*	134.7	12	C^+	18.7	6.0
29	$C_2H_5^+$			2	H_2^+	30.4	2.0
28	$C_2H_4^+$	390.0**		1	H^+	4.7	5.1
28	CO^+		81.5				

† For the purposes of this table, the designation of the ion is intended to indicate its components and not its structure.

* Either or both HCO^+ and $C_2H_5^+$.

** Appearance potential due to $C_2H_4^+$. Total peak may, however, contain a large fraction of CO^+.

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[7] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc., 1939).

[8] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

According to Mulliken[9] the oxygen atom in CH_3OH (and also in C_2H_5OH) possesses four nonbonding orbitals, two of which are practically free from mixing and have the lowest ionization potentials of any of the electrons in the molecule. This implies that two of the electrons belong almost exclusively to the oxygen atom itself and are not very much involved in determining the structure of the molecule. Aside from the fact that their ease of removal should be somewhat modified by the fact that they are, after all, part of a molecular system they may be expected to behave very much as though they were outer electrons of a free oxygen atom.

Let us assume that it was one of these electrons that was removed and that the ionization potential of the molecule is the (modified) ionization potential of the oxygen atom and remains constant as long as the structure of the molecule is not radically altered. On this basis we shall assume 10.8 volts to be the energy necessary to remove one of these nonbonding electrons from the oxygen atom in the methyl alcohol molecule. This assumption will be justified by the following results.

Mass 31.—The appearance potential of the ion corresponding to this mass was $A(X^+) = 11.8 \pm 0.1$ volts. If we assume that the hydrogen atom came from the oxygen, the bond energy (dissociation energy) being roughly 4.6 volts,[10] we have the reaction:

$$CH_3OH \rightarrow CH_3O^+ + H + e,$$

which leads to the equation $I(CH_3O) \leqq 7.2$ volts, a rather unlikely figure. If it is assumed that the ion results from the breaking of a C—H bond without further change, the situation is equally bad.

TABLE III. *Summary of results and interpretations.*

	Appearance Potential		Reaction	
Ion	Ethyl Alcohol	Methyl Alcohol	$C_2H_5OH \rightarrow$	$CH_3OH \rightarrow$
$C_2H_5OH^+$	11.3 ± 0.2		$C_2H_5OH^+$	
CH_3CHOH^+	11.0 ± 0.1		$CH_3CHOH^+ + H + e$	
CH_3CHO^+	11.4 ± 0.3		$CH_3CHO^+ + H_2 + e$	
CH_3OH^+		10.8 ± 0.2		CH_3OH^+
CH_2OH^+	11.3 ± 0.2	11.8 ± 0.1	$CH_2OH^+ + CH_3 + e$	$CH_2OH^+ + H + e$
$HCHO^+$	12.8 ± 0.2	12.4 ± 0.1	$HCHO^+ + CH_4 + e$	$HCHO^+ + H_2 + e$
$C_2H_4^+$	11.3 ± 0.2		$C_2H_4^+ + H_2O + e$	
$C_2H_3^+$	14.5 ± 0.2		$C_2H_3^+ + H_2O + H + e$	
$C_2H_2^+$	14.1 ± 0.2		$C_2H_2^+ + H_2O + H_2 + e$	
H_3O^+	14.4 ± 0.3	?		
HCO^+		14.2 ± 0.2		
CH_3^+	15.5 ± 0.3	14.0 ± 0.5		
CH_2^+	16.5 ± 0.5	15.4 ± 0.5		

TABLE IV. *Energies of various combinations of one carbon, one oxygen and four hydrogen atoms with respect to* CH_3OH *as zero. Concerning the accuracy of the various values the following remarks can be made: (1) This value is accurate to within the accuracy of the heat of sublimation of carbon and the heat of formation of methyl alcohol. (2) This is quite rough. It was estimated on the basis of the assumption that the* CH *bonds are, roughly, the same as the corresponding bonds in methane. That is, for the energy to remove this hydrogen atom, the difference between* $D(CH_4)$ *and* $D(CH_3)$ *was used. (3) This was calculated on the basis of the strength of the* O—H *link in alcohol as given by Sidgwick.*[10] *(4) Accurate to within the accuracy of the heat of sublimation of carbon and the heat of formation of formaldehyde. (5) Same as (4) plus* $D(H_2)$*. (6) Estimated in same manner as (2) and hence quite rough. (7) Same as (6) plus* $D(H_2)$.

(1) $C+O+4H$	19.01 ev	(5) $HCHO+H_2$	0.85 ev
(2) CH_2OH+H	4.56	(6) $HCOH+2H$	8.16
(3) H_3CO+H	4.60	(7) $HCOH+H_2$	3.68
(4) $HCHO+2H$	5.33	(8) CH_3OH	0.00

There is, however, another alternative. It must be remembered that O^+ is trivalent and that the C—O— in the molecule can become $C{=}O^+$— in the ion, assuming, of course, the localization of the charge on the oxygen atom as discussed above. This allows us to postulate the reaction:

$$CH_3OH \rightarrow CH_2OH^+ + H + e,$$

where the bond between C and O is now double and is quite consistent with the postulate that the electron removed in the ionization process came from the oxygen atom. Further, the change from single to double bond gives us back some of the energy ordinarily required to break a C—H bond. Using the figure 10.8 volts for the (modified) ionization potential of the oxygen atom as justified in the discussion of mass 32 and basing our calculation on the above reaction, we should be able to estimate the appearance potential of the mass 31 ion and get some idea concerning the reasonableness of our assumptions.

For the difference between the C—O and C=O bonds we shall use the value 3.65 volts.[10] For the energy to break the C—H bond we shall use the value 4.56 volts (Table IV). We then have:

$$A(X^+)_{\text{est}} = 10.8 + 4.56 - 3.65 = 11.7 \text{ volts.}$$

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[9] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935).

[10] N. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, 1933).

This is to be compared with the experimental value of 11.8 volts. The agreement is much better than the accuracy of the data would lead one to expect and for this reason should not be taken too seriously. However, it definitely favors our postulated reaction and the idea of the "independence" and localization of the nonbonding orbital. It may seem remarkable that all this readjustment in the structure of the molecule takes place during the time of a single electron collision, but throughout this investigation the evidence allows no other conclusion. Such phenomena have been suggested before in the case of cyanogen[11] and benzene.[12]

Mass 30.—The appearance potential of the ion corresponding to this mass was $A(X^+)=12.4 \pm 0.1$ volts. Depending upon whether the two hydrogen atoms are considered to have come from the carbon or one from the carbon and one from the oxygen we have a choice of the following four reactions:

$$\begin{aligned}&(1)\ CH_3OH\rightarrow HCHO^+ + 2H + e\\&(2)\ CH_3OH\rightarrow HCHO^+ + H_2 + e\\&(3)\ CH_3OH\rightarrow HCOH^+ + 2H + e\\&(4)\ CH_3OH\rightarrow HCOH^+ + H_2 + e.\end{aligned}$$

The ionized molecule in the first two reactions is of course the formaldehyde molecule. On the basis of the energies given in Table I the following values for the upper limit of the ionization potential are obtained: (1) 7.1 volts, (2) 11.5 volts, (3) 4.3 volts, (4) 8.8 volts. Of these, reaction (2) is the most reasonable. However, to assist in determining the actual reaction, formaldehyde was admitted to the apparatus and its ionization potential measured directly. For this the value 11.4±0.2 volts was obtained. This indicates strongly that reaction 2 was the one that actually occurred. Jewitt[13] has obtained the value 11.3±0.5 volts for the directly measured value of the ionization potential of the formaldehyde molecule. This is in very good agreement with the values reported here.

Mass 19.—This ion was present in sufficient quantity to be detected, but not to allow its appearance potential to be measured. The ion must be identified as H_3O^+. This is in accord with the concept of a trivalent O^+.

Mass 28 and mass 12.—The ions corresponding to these masses must have been CO^+ and C^+, respectively. Changing the gas pressure or the filament temperature over a limited range gave no indication that this was true, but their appearance potentials indicate very strongly that these ions were to some extent produced from free CO due to thermal decomposition of the alcohol on the filament. This is seen from the fact that the observed appearance potentials were 14.0 and 22.6 volts, respectively. For the appearance potentials of CO^+ and C^+ from CO Vaughan[14] gives 13.9 and 22.5 volts, respectively. The agreement is too close to be ignored.

Ethyl alcohol

Vapor of absolute ethyl alcohol was admitted to the apparatus and studied in the same manner as the methyl alcohol discussed above. Time did not permit quite such a thorough investigation of ethyl alcohol. Not all of the appearance potentials were measured, nor of those which were determined was the accuracy as good as in the case of methyl alcohol. However, the most important measurements were made with sufficient accuracy for all those reactions which offered some hope of a unique identification. The results obtained in the case of this molecule are summarized in Tables II and III. The energies of the most important combinations of two carbon, one oxygen and six hydrogen atoms referred to the molecule C_2H_5OH as zero are listed in Table V.

Mass 46.—The appearance potential of this ion was 11.3±0.2 volts. Since this must correspond to the molecular ion we have the unique reaction

$$C_2H_5OH\rightarrow C_2H_5OH^+ + e.$$

This gives $I(C_2H_5OH)=A(C_2H_5OH^+)=11.3$ volts. Following the argument put forth in the discussion of the methyl alcohol molecule we shall assume that ionization represents the removal of a nonbonding electron from the oxygen atom in the molecule and that 11.3 volts is its ionization potential. This is 0.5 volt higher

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[11] Bleakney, Condon and Smith, J. Phys. Chem. **41**, 197 (1937).

[12] Hustrulid, Kusch and Tate, Phys. Rev. **54**, 1037 (1938).

[13] T. N. Jewitt, Phys. Rev. **46**, 616 (1934).

[14] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

TABLE V. *Energies of various combinations of two carbon, one oxygen and six hydrogen atoms with respect to* C_2H_5OH *as zero. In addition to the uncertainty in the heat of sublimation of carbon the numbered items in this table depend on the following quantities: (1) Heat of formation of ethyl alcohol. (2) Heat of formation of acetaldehyde. (3) Same as (1) plus* $D(H_2)$. *(4) Heat of formation of ethane. (5) Heats of formation of formaldehyde and methane. (6) Heats of formation of ethylene and water. (7) The error here lies chiefly in the value assumed for the strength of the first* C – H *bond in ethylene. It was obtained by interpolation between the heats of dissociation of acetylene and ethylene. (8) Same as (7) plus* $D(H_2)$. *(9) Same as (7) plus* $D(OH)$. *(10) Same as (9) plus* $D(H_2)$. *(11) Same as (7) plus* $D(H_2O)$. *(12) Heats of dissociation of acetylene, water and hydrogen.*

(1)	$2C+O+6H$	29.27 ev
(2)	$CH_3CHO+2H$	5.04
(3)	CH_3CHO+H_2	0.56
(4)	C_2H_6+O	4.10
(5)	$HCHO+CH_4$	0.43
(6)	$C_2H_4+H_2O$	0.47
(7)	C_2H_3+O+3H	13.10
(8)	$C_2H_3+O+H_2+H$	8.62
(9)	$C_2H_3+OH+2H$	8.79
(10)	$C_2H_3+OH+H_2$	4.31
(11)	$C_2H_3+H_2O+H$	3.61
(12)	$C_2H_2+H_2O+H_2$	2.33
(13)	C_2H_5OH	0.00

than the corresponding potential in methyl alcohol.

Mass 45.—The ion corresponding to this mass appeared at 11.0±0.1 volts. For the production of this ion we shall assume a reaction analogous to that deduced for the production of mass 31 in methyl alcohol:

$$C_2H_5OH \rightarrow CH_3CHOH^+ + H + e.$$

In a similar manner we should be able to predict an appearance potential for this ion. For the energy to remove the hydrogen atom we shall use the value 2.90 volts assumed to be the strength of the first C – H bond in ethane.[5] For the difference between the C – O and C = O bonds in ethyl alcohol we have the value 3.61 volts.[10] For the ionization potential of the oxygen atom we shall use the value 11.3 volts found for the molecular ion. We then have

$$A(X^+)_{est} = 11.3 + 2.9 - 3.6 = 10.6 \text{ volts}.$$

This is to be compared with the experimental value 11.0 volts and, in view of the roughness of the assumed values for the various bond strengths, can be considered fairly good agreement. Any other mechanism leads to quite unreasonable results.

Mass 44.—The appearance potential of this ion was 11.4±0.3 volts. This is about 3 volts below $I(CO_2)$. The most reasonable assumption is that this peak represents the acetaldehyde ion produced according to one of the reactions:

$$C_2H_5OH \rightarrow CH_3CHO^+ + 2H + e$$
$$C_2H_5OH \rightarrow CH_3CHO^+ + H_2 + e.$$

The first gives us $I(CH_3CHO) \leq 6.4$ volts and the second ≤ 10.7 volts. The latter is a very reasonable value and is in good accord with the values obtained for methyl and ethyl alcohol and formaldehyde as is to be expected from the Mulliken picture.

Mass 31.—The appearance potential of this ion was 11.3±0.2 volts. This was by far the most abundant ion. A straightforward and unique explanation of the nature of this ion and the reaction involved in its production cannot be made. However, on the basis of some not unreasonable assumptions a rather interesting case can be made. Let us assume that the ion is the same as the ion that we have concluded corresponded to mass 31 in methyl alcohol and that the reaction involved is

$$C_2H_5OH \rightarrow CH_2OH^+ + CH_3 + e.$$

On this basis let us try to estimate its appearance potential. Recognizing the fact that the ions are not produced in "steps" we can, nevertheless, for the sake of energy considerations, break this reaction down into the following chain:

(a) $C_2H_5OH \rightarrow CH_3OH + CH_2$
(b) $CH_3OH + CH_2 \rightarrow CH_2OH^+ + CH_2 + H + e$
(c) $CH_2OH^+ + CH_2 + H + e \rightarrow CH_2OH^+ + CH_3 + e.$

The appearance potential will then be the algebraic sum of the energies involved in the three steps. From Table V the energy required for (a) is 3.26 volts. From our data on methyl alcohol the energy required for (b) is 11.8 volts. According to Smith[1] the energy required for (c) is −3.6 volts. Hence:

$$A(X^+) = 11.8 + 3.3 - 3.6 = 11.5 \text{ volts}.$$

This is in very close agreement with the experimental value 11.3 volts. It is scarcely necessary to add, however, that this result simply makes the postulates plausible and is in no sense proof. Some alternative process may exist that will give just as good agreement, although it is not obvious just what it would be. The low appearance potential demands some way in which energy can be saved as in the formation of the double bond. Any process not based on this concept seems most unlikely.

Mass 30.—This ion appeared at 12.8±0.2 volts. For this mass we have not only a choice of several reactions to produce one ion but also a choice of two ions, namely $C_2H_6^+$ and $HCHO^+$. For the first we have $C_2H_5OH \rightarrow C_2H_6^+ + O + e$. This gives $I(C_2H_6) \leq 8.7$ volts, much lower than the directly measured value 11.6 volts found by Hipple.[5] The only reasonable alternative is that the ion is $HCHO^+$. The only reaction consistent with the value 11.4 volts for the directly measured ionization potential of HCHO is

$$C_2H_5OH \rightarrow HCHO^+ + CH_4 + e.$$

This gives $I(HCHO) \leq 12.4$ volts, and requires an excess energy of about 1 volt.

Mass 28.—The appearance potential of this ion was 11.3±0.2 volts. On the basis of mass this could have been due to either CO^+ or $C_2H_4^+$. The first is at once ruled out, since the directly measured ionization potential of CO is 13.9 volts.[12] The ion must have been $C_2H_4^+$ produced by the reaction

$$C_2H_5OH \rightarrow C_2H_4^+ + H_2O + e.$$

This gives $I(C_2H_4) \leq 10.8$ volts in complete agreement with the directly measured value 10.80 volts.[3]

Mass 27.—The appearance potential of the ion corresponding to this mass was 14.5±0.2 volts. This could have been only the $C_2H_3^+$ ion. The processes by which the ion could have been formed are limited to the following:

(1) $C_2H_5OH \rightarrow C_2H_3^+ + O + 3H + e$
(2) $C_2H_5OH \rightarrow C_2H_3^+ + O + H_2 + H + e$
(3) $C_2H_5OH \rightarrow C_2H_3^+ + OH + 2H + e$
(4) $C_2H_5OH \rightarrow C_2H_3^+ + OH + H_2 + e$
(5) $C_2H_5OH \rightarrow C_2H_3^+ + H_2O + H + e$.

Corresponding to these reactions we have the following upper limits for $I(C_2H_3)$: (1) 1.4 volts, (2) 5.9 volts, (3) 5.7 volts, (4) 10.2 volts, (5) 10.9 volts. The value obtained on the basis of reaction (5) is in very good agreement with the 11.0 volts given by Kusch, Hustrulid and Tate.[3] (The value 11.0 volts given by them was not changed by a recalculation on the basis of the thermochemical data used in the present paper.)

Mass 26.—The appearance potential of the ion corresponding to this mass was 14.1±0.2 volts. This peak must have been due to the acetylene ion $C_2H_2^+$. The only reaction leading to a reasonable ionization potential is:

$$C_2H_5OH \rightarrow C_2H_2^+ + H_2O + H_2 + e.$$

This gives $I(C_2H_2) \leq 11.8$ volts. The directly measured value is 11.2 volts.[2] The extra 0.6 volt can be very reasonably accounted for as excess energy.

Mass 19.—This peak must be identified with H_3O^+. Its appearance potential was 14.4±0.3 volts. Because of the great number of possible configurations involved and our lack of accurate data concerning the energies of most of them, no inference can be made as to the reaction responsible for the production of this ion.

CONCLUSION

The work reported here can be summarized briefly in the following way.

Ions were produced from methyl and ethyl alcohol by electron impact and their abundances and appearance potentials measured. In all cases subject to analysis the reactions giving the most reasonable interpretations were those requiring the lowest dissociation energy. The concept of "localized" ionization and the nonmixing of the nonbonding orbitals is supported by the results obtained from these substances. In fact, unless this picture is adopted we are led to unreasonably low ionization potentials and very unsatisfactory interpretations of the results.

In conclusion we should like to express our appreciation to Mr. Ralph Osborne for construction of the apparatus and to the Research Corporation for financial assistance.