(corresponding to $\lambda_{\max}=1450$A). Apparently little data exist on the work function of oxidized copper; the work function of clean copper is 4.4 v[18] and, by analogy with the work on oxidation of Pt and Ag[19] which produced almost a doubling of the work function, a value for copper of 8.5 volts seems possible and reasonable.

Attempts made to show the difference between fairly clean and oxidized copper by a rough vacuum technique which was, however, as good as that often used in the preparation of satisfactory counters,[10] were made, and the results showed that copper cleaned as well as possible in our apparatus had apparently a higher work function and was therefore probably better oxidized in the physical, but not chemical sense, than the grossly oxidized cathodes we prepared. It is intended to carry out further experiments with a greatly improved vacuum technique, but this deficiency of knowledge does not seriously affect the main conclusions of this paper, i.e., that counters working very satisfactorily in normal self-quenching arrangements show considerable discharge spread which is mainly due to the cathode photo-emission effect. The results of Figs. 6, 7, and 8 will therefore not be accurately reproducible; the data of Fig. 12 should have more fundamental significance.

ACKNOWLEDGMENTS

The authors wish to thank Mr. F. R. Perry for his interest in and encouragement of the work, Sir Arthur P. M. Fleming, C.B.E., D.Eng., Director of Research and Education, and Mr. B. G. Churcher, M.Sc., M.I.E.E., Manager of Research Department, Metropolitan-Vickers Electrical Company, Ltd., for permission to publish this paper.

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[18] A. L. Hughes and L. A. Du Bridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932), p. 75.

[19] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Teddington, England, 1935), pp. 148–151.

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The Ionization and Dissociation of Formic Acid Monomer by Electron Impact*

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In HCOOH vapor in a mass spectrometer, low velocity electrons have produced the ionized molecule, one negative and twelve positive fragment ions. For the negative ion and six positive ions the mode of production has not been established. The other fragment ions originate in the reactions requiring the least dissociation energy for the production of the corresponding radicals, although for one of these a more energetic reaction seems preferred at high electron energies. One of the ions of doubtful origin also probably originates in a reaction involving more than the minimum degree of dissociation. The first appearance potential of four ions with established reactions, of one ion of doubtful origin, and probably of another of doubtful origin, as well as the second appearance potential of CO_2^+, all indicate that the corresponding reactions involve no more than 1.0 volt excess energy. Both HCO^+ and $COOH^+$ utilize the trivalency of O^+ in their structure. $HCOOH^+$, $COOH^+$, and HCO^+ seem to have a second appearance potential close to the first. To explain this, and to make the electron impact and spectroscopic ionization potentials of the molecule compatible, it is assumed that a *trans*-form of HCOOH exists. Estimates of its abundance relative to the known *cis*-form give for the energy difference between the two forms the probable limits 1.2–3.0 kcal/mole.

I. INTRODUCTION

In the electron-impact studies of the more than forty molecules already reported in the literature,†† the most useful information has been obtained by application of the mass spectrometer to the determination of appearance

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* The data on which this paper is based were obtained prior to November, 1941; but circumstances beyond our control have delayed preparation of the paper. A preliminary presentation of data was made at a recent A.P.S. meeting (see Phys. Rev. **71**, 139(A), 1947).

** This work is a summary of Part II of a thesis presented to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Now at the Research Laboratories of the American Cyanamid Company, Stamford, Connecticut.

†† See. H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931) for a review of work to that date, and J. A. Hipple, J. App. Phys. **13**, 551 (1942) for more recent references.

potentials of ions, that is, the minimum energies required for the production of ions in particular modes of dissociation of molecules. Since this is also true in the study of formic acid monomer, it seems desirable to review the fundamental considerations, although they have been presented more extensively elsewhere.

An appearance potential $A(X^+)$, of an ion, X^+, may be regarded as the sum:

$$A(X^+)=I(X)+P(X)+W(X),$$

where, following the usual notation,[1,2] $I(X)$ is the ionization potential of the radical, X; $P(X)$ is the energy required to dissociate the parent molecule into neutral fragments in their lowest states in the mode of dissociation giving rise to the radical; and $W(X)$ is the total excitational and mutual kinetic energy of the products of dissociation. $W(X)$ includes, in appropriate cases, electron affinities (with a negative sign) and ionization potentials of radicals other than X receiving charges in the process being considered. It is clear from the expression for an appearance potential that analysis of electron impact data is greatly dependent upon a knowledge of the energy relationships in the numerous possible reactions. Much of this can be gained from thermochemical data and from known or estimated ionization potentials and electron affinities. When this knowledge, used in conjunction with the measured appearance potential of an ion, is adequate to establish in what reaction the ion was produced, other data may be derived. Ionization potentials of molecules themselves, which can be determined uniquely and usually within closer limits than derived data, are likely to be subject to five or ten times the error of similar quantities obtained by accurate analysis of band spectra. Derived ionization potentials of radicals will generally be subject to even greater error, and derived thermodynamic data will be quite inaccurate on chemical standards; but when the quantities have been, or can be, determined only in this way, the values are of interest.

II. EXPERIMENTAL

Apparatus

The mass spectrometer used in the study of formic acid monomer was designed particularly to achieve high resolving power for other purposes and was only incidentally applied to the present problem. Since the instrument will be fully described elsewhere, only a brief description will be presented here for the purpose of giving significance to the conditions of operation prevailing during the experiments on formic acid monomer.

Crossed electric and magnetic fields were used to perform the m/e analysis as in the mass spectrometer described by Bleakney and Hipple,[3] who have discussed the properties of this arrangement. Differences in mechanical design, necessitated by the larger size of our instrument, are unimportant so far as the present work is concerned. The ion orbit was a prolate cycloid with $b=262$ mm, $\theta=89.5°$ (in the notation of ref. 3), and the ratio of ion-accelerating voltage to analyzing-electric field = 8.8 cm. A magnetic field of about 2230 gauss was used, except that for observation of H^+ and H_2^+ it was reduced to about 540 gauss. For the electron-impact experiments the entrance- and exit-slit widths were 0.05 mm and 3.18 mm, respectively, so that the resolving power was only 81. Such low resolution was used intentionally to obtain broad, square-topped peaks, in order to facilitate the making of relative abundance and appearance potential measurements; and it was entirely adequate. Even at the highest sample pressures used the scattering was so slight that at $M/e=46$ the ion beam contributed less than 0.05 percent of its peak intensity to an ion beam one mass unit removed.

In order to minimize errors due to differential retardation of the electrons in the ionization chamber, no voltage was impressed between the ionization chamber and the first ion slit during appearance-potential measurements. As a check on the performance of the instrument a preliminary measurement was made of the difference between the ionization potentials of neon and argon very early in the work. It was found to be

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[1] L. G. Smith, Phys. Rev. **51**, 263 (1937).

[2] C. S. Cummings II and Walker Bleakney, Phys. Rev. **58**, 787 (1940).

[3] W. Bleakney and J. A. Hipple, Jr., Phys. Rev. **53**, 521 (1938).

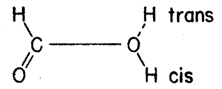
6.0±0.15 volts, in comparison with the spectroscopic value 5.78 volts.[4] In view of the fact that this determination was not made under the more favorable conditions prevailing during the experiments on HCOOH, this was taken to mean only that, at least for ions with mass-to-charge ratios near that of the calibrating gas (argon, $M/e=40$), no appreciable instrumental errors existed.

The Sample

Kahlbaum formic acid was treated in a manner similar to that found effective by Coolidge.[5] The final vapor pressure at 20°C was 32.5±0.2 mm, which, on the basis of Coolidge's data, indicates that water was not present in an amount greater than 1 percent. The sample was stored at solid CO_2 temperature except when part of it was extracted for experiments; and part of the sample was sublimed in vacuum before each extraction. The handling of the sample and the fact that Bonner and Hofstadter[6] found no perceptible decomposition of formic acid held for 36 hours at 150°C, both give assurance that no appreciable amount of impurity was present.

The sample was admitted to the mass spectrometer through a capillary leak using a gas handling system similar to that described by Smith, Lozier, Smith, and Bleakney,[7] except that no liquid air trap was used between the leak and the mass spectrometer. Pressures of formic acid between 10 and 20 mm were used on the high pressure side of the leak for appearance-potential

TABLE I. Ions produced in HCOOH by impact of 65-volt electrons.



M/e	Ion	65 volt Relative Abundance	Appearance Potential (volts)	PROBABLE REACTION	CALCULATED MINIMUM ENERGY (volts)	Deduced Ionization Potential or Additional Energy Required (volts)
46	$HCOOH^+$	100.00	11.0±0.1 11.6±0.2	HCOOH (trans?) → $HCOOH^+$ " (cis ?) → "	I(HCOOH) (trans?) " (cis?)	I(HCOOH) (trans?) $\leqq$ 11.0±0.1 " (cis ?) $\leqq$ 11.6±0.2
45	$COOH^+$	67.8	12.1±0.1 12.9±0.2	HCOOH (trans?) → $H\text{-}O\text{-}C{\equiv}O^+ + H$ " (cis?) → " "	I(HCOOH) (trans?) + 1.5 = 12.5 roughly " (cis?) + 1.5 = 13.1 "	
44	CO_2^+	9.8	14.2±0.1 18. ±1.0	$HCOOH \rightarrow CO_2^+ + H_2$ " $\rightarrow CO_2^+ + 2H$	$I(CO_2) - .25 = 13.5$ " + 4.2 = 17.9	W(X) = 0.7±0.1 W(X) = 0.1± 1.0
34	$H_2O_2^+$	0.06	11.6±0.4	Probably impurity	$I(H_2O_2)$	$I(H_2O_2) \leqq 11.6 \pm 0.4$ probably high
33	HO_2^+	0.01	17.0±0.5	$H_2O_2 \rightarrow HO^+ + H$ from imp.	$I(H_2O_2) + 5.2 = 16.8 \pm 0.4$	
30		2.64	14.1±0.3	probably isotopic HCO^+, corresponding to higher appearance potential		
29	HCO^+	185.	12.8±0.2 13.2±0.3	HCOOH (trans?) → $HC{\equiv}O^+ + OH$ " (cis?) → " "	I(HCOOH) (trans?) + 2.3 = 13.3 roughly " (cis?) + 2.3 = 13.9 roughly	
28	CO^+	16.7	14.6±0.3	$HCOOH \rightarrow CO^+ + H_2O$	I(CO) + 0.18 = 14.1±0.2	W(X) = 0.5±0.5
18	H_2O^+	28.4	13.1±0.1	" $\rightarrow H_2O^+ + CO$	$I(H_2O) + 0.18 = 12.77 \pm 0.05$	W(X) = 0.3± .15
17	OH^+	8.3	19.2±0.2	indeterminate, see text		
16	O^+	3.5	21.0±0.6	" " "		
14	CH_2^+	.22	24.7±0.5	$HCOOH \rightarrow CH_2^+ + 2O$	$I(CH_2) + 11.8 \leqq 23.8 \pm 0.2$	W(X) $\geqq$ 0.9±0.7
13	CH^+	3.0	25.4±0.5 27.4±0.6	indeterminate, see text " " "		
12	C^+	2.3	23.9±0.2 29.5±1.0	" " " " " "		
2	H_2^+	.03	16.0±0.3	$HCOOH \rightarrow H_2^+ + CO_2$	$I(H_2) - .25 = 15.1$	W(X) = 0.9±0.3
1	H^+	.4	19.0±0.4	Indeterminate, see text		
−17	OH^-	.03	15±5	indeterminate		

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[4] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., 1932).
[5] A. S. Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).
[6] L. G. Bonner and R. Hofstadter, J. Chem. Phys. **6**, 531 (1938).
[7] P. T. Smith, W. W. Lozier, L. G. Smith, and W. Bleakney, Rev. Sci. Inst. **8**, 51 (1937).

measurements and slightly higher pressures for some of the relative-abundance measurements. The pressure in the ionization chamber was not determined directly; but it probably was much lower than 10^{-4} mm Hg and certainly was not above 10^{-3} mm Hg. Assuming a pressure of 10^{-3} mm Hg and a temperature not lower than 293°K in the ionization chamber, and using Coolidge's[5] equation for the dissociation constant, it is calculated that not more than 0.06 percent of the sample subjected to electron impact was in dimer form. Owing to the conservativeness of the assumptions, it is probable that the amount was even less.

Precautions Against Secondary Effects

In order to insure that the interpretation of the data would not be complicated by a high probability of secondary effects, such as having individual molecules struck by more than one electron or having individual electrons strike more than one molecule, the relative abundances of the ions were measured as a function of pressure and electron current, each variable being changed by a factor of three, encompassing the range of conditions actually used. There were found no systematic changes in relative abundances attributable to a significant probability of occurrence of the phenomena mentioned.

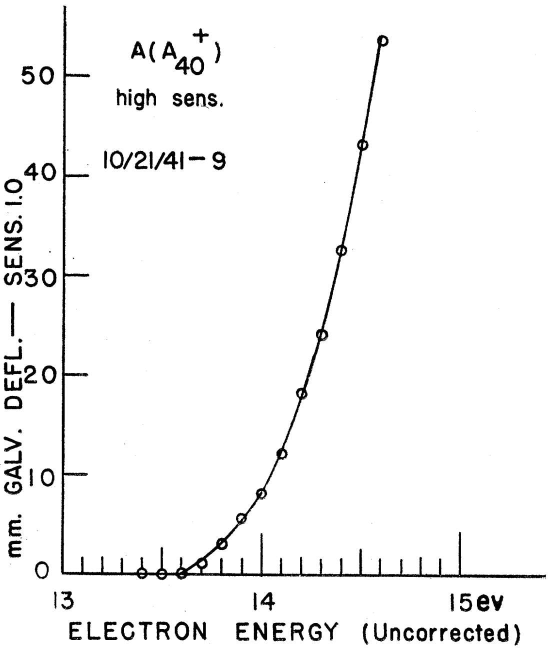

FIG. 1. Representative appearance-potential curve for the calibrating gas, argon, on high sensitivity as used for calibration.

Appearance Potential Measurements

A Barth[8] type amplifier, employing a 10^{10} ohm grid shunt, and having a sensitivity of 1.08×10^5 mm/volt was used to measure the ion currents at electron energy intervals of 0.1 volt for the more abundant ions and at larger intervals for the less abundant ions. The zero of the amplifier was read before and after each ion current reading in order to eliminate distortion of the appearance-potential curves by amplifier drift. The voltage scale for the electrons was corrected by the difference between the known[4] and observed ionization potential of argon, which was admitted to the mass spectrometer along with the HCOOH so that the correction could be determined for each set of observations. Representative appearance-potential curves are shown

TABLE II. Energies relative to HCOOH of possible states of aggregation of 2H, 2O, and C.

Arbitrary designation i	State of aggregation	Expression for energy, E_i	E_i, e.v.
a	HCOOH	———	0.00
b	$C+2H+2O$	$Q_f(HCOOH)+L(C)+D(O_2)+D(H_2)$	18.82
c	$CH+H+2O$	$E_b-D(CH)$	15.35
d	CH_2+2O	$E_b-D(CH_2)$	11.82
e	H_2+O_2+C	$E_b-D(O_2)-D(H_2)$	9.26
f	$2H+O_2+C$	$E_b-D(O_2)$	13.74
g	H_2+2O+C	$E_b-D(H_2)$	14.34
h	CO_2+H_2	$Q_f(HCOOH)-Q_f(CO_2)$	−.25
i	CO_2+2H	$E_h+D(H_2)$	4.23
j	H_2O+CO	$Q_f(HCOOH)-Q_f(CO)-Q_f(H_2O)$	.18
k	$OH+H+CO$	$E_j+E(H_2O\rightarrow OH+H)$	5.36
l	$2H+O+CO$	$E_k+D(OH)$	9.67
m	$H+OH+C+O$	$E_b-D(OH)$	14.51
n	H_2+CO+O	$E_k+D(OH)-D(H_2)$	5.19
o	H_2O+C+O	$E_b-D(H_2O)$	9.33
p	$CH+OH+O$	$E_b-D(OH)-D(CH)$	11.04
q	$2OH+C$	$E_b-2D(OH)$	10.20
r	O_2+CH+H	$E_b-D(O_2)-D(CH)$	10.27
t	CH_2+O_2	$E_b-D(O_2)-D(CH_2)$	6.74
u	$HOOH+C$	$Q_f(HCOOH)+L(C)-Q_f(HOOH)$	7.80
v_1	$HCHO+O$	$Q_f(HCOOH)+\frac{1}{2}D(O_2)-Q_f(HCHO)$	5.14
v_2	$HCOH+O$	approx. $Q_f(HCOOH)+\frac{1}{2}D(O_2)-Q_f(CH_3OH)+E(CH_3OH\rightarrow HCOH+H_2)$	8.0 (roughly)
w_1	$HCO+H+O$	$E_{v1}+E(HCHO\rightarrow HCO+H)$	9.62
w_2	$HCO+OH$	$E_{w1}-D(OH)$	5.31
w_3	$COH+O+H$	$E_{v2}+D(CH)$ (roughly)	11.5 (roughly)
w_4	$COH+OH$	$E_{w3}-D(OH)$	7.2 (roughly)
x_1	HO_2+C+H	$E_u+E(H_2O_2\rightarrow H+HO_2)$ approx. $E_u+E(H_2O\rightarrow HO+H)$	12.98
x_2	HO_2+CH	$E_{x1}-D(CH)$	9.51
y	$HCOO+H$	approx. $B(O-H)$ alcohols	4.6
z	$H+COOH$	$E(HCHO\rightarrow HCO+H)$	4.48

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[8] G. Barth, Zeits. f. Physik **87**, 399 (1934); D. B. Penick, Rev. Sci. Inst. 6, 115 (1935).

TABLE III. Values of thermodynamic quantities used in calculating energies of states in Table II.

Quantity or reaction†	Energy in e.v.	Reference
Q_f(HCOOH)	3.85	a
Q_f(H_2O_2)	1.46	a
Q_f(CO_2)	4.10	a
Q_f(CO)	1.16	a
Q_f(H_2O)	2.51	a
Q_f(HCHO)	1.25	a
Q_f(CH_3OH)	2.10	a
D(O_2)	5.08	10
D(H_2)	4.48	10
D(CH)	3.47	10
D(H_2O)	9.49	10
D(CO)	9.14	10*
D(CH_2)	7.0	1
D(OH)	4.31	10
L(C)	5.41	10*
$CH_3OH \rightarrow HCOH + H_2$	3.7	1, 2
$H_2CO \rightarrow HCO + H$	4.48	11
$H_2O \rightarrow OH + H$	5.18	10
B(C=O) formaldehyde	6.16	b
B(O—O)	1.51	b
B(C=O)—B(C—O)	3.6	2
B(O—H) alcohols	4.6	c

† Q_f( ) = heat of formation of compound indicated; D( ) = heat of dissociation of compound or radical indicated; B( ) = bond energy; L(C) = heat of sublimation of carbon.

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

[b] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

[c] N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, Ithaca, New York, 1933).

* H. D. Hagstrum (Phys. Rev. **71**, 376 (1947)) has recently suggested an interpretation of the band spectrum of CO which is consistent with the value $D(CO) = 9.6$ volts. If this should be correct, use of Herzberg's cycle (reference 10, p. 521) would yield the value $L(C) = 5.87$ volts. The energies of states $b, c, d, e, f, g, m, o, p, q, r, t, u, x_1$, and x_2 in Table II would thus have to be increased by 0.46 volts· This would in no way affect decisions concerning what processes are responsible for the ions observed from HCOOH; and it would affect detailed conclusions in only one process, namely that giving rise to CH_2^+. We would then obtain for this process $W(X) = 0.4 \pm 0.7$ volts, which is insignificantly more desirable than the value shown in Table I.

in Figs. 1 to 8 inclusive, in which the appropriate corrections have not been applied to the voltage scale.

The uncorrected first appearance potential of an ion was taken to be the observed electron energy at which the first perceptible ion current was detected, and the second one that at which the first perceptible "break" occurred in the appearance-potential curve.[9]

A "break" in an appearance-potential curve is a point separating a region of lower slope from one of higher slope. When the two regions are separated by a transition region, the "break" is taken to be at the beginning of the transition region. Depending on the nature of the processes involved and the conditions under which an appearance potential curve is recorded, a "break" may or may not be very pronounced. A "break" may arise from three sources, in general. First, it may result from instrumental factors such as a sudden increase in electron current. Second, it may be due to the natural trend of the appearance-potential curve for a single process, which in turn depends on the shapes and relative positions of the potential functions of the states involved. Third, it may be the nocsequence of the onset of a new process of production of the ions in question. Only in the last case should we regard the "break" as a second appearance potential. It is not difficult to take into account the instrumental factors. Thus, in the case of an abrupt change in slope, the decision concerning its significance as a second appearance potential can usually be made with confidence. When the "break" is not well defined, however, the decision cannot be made with such confidence, and

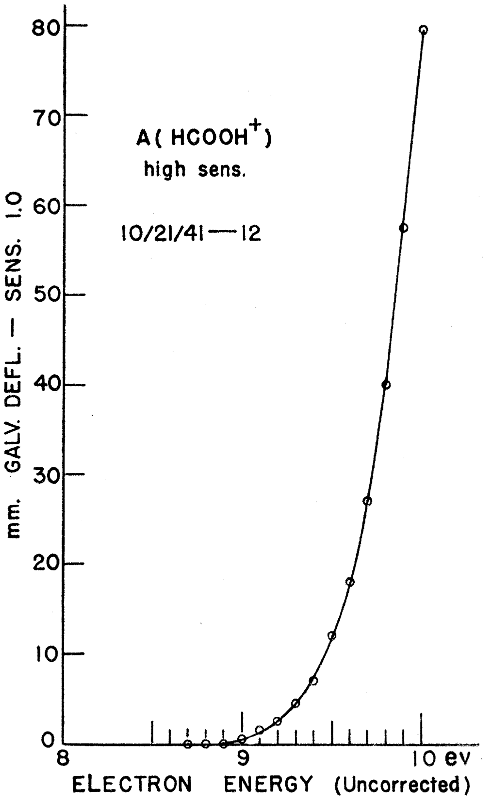

FIG. 2. Representative appearance-potential curve for $HCOOH^+$ on high sensitivity, used to determine the first ionization potential.

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[9] This is the usual method of using appearance-potential curves. A different method has recently been used by R. H. Vought, Phys. Rev. **71**, 93 (1947). For a discussion of the two methods see the following paper.

the personal factor may be important even in the detection of the "break." Thus, it is possible to conclude that a second appearance potential exists when only the natural trend of the ion-production efficiency of a single process is represented, or to overlook the onset of a second process when it actually occurs. In doubtful instances further experimentation may aid in reaching a conclusion; but in some cases the reasonableness of the assignment of a second appearance potential will rest solely on the reasonableness of the conclusions to which it leads, and the conclusions must then be recognized as having resulted from somewhat indecisive evidence.

The appearance potentials of ions produced in formic acid monomer by electron impact are listed in Table I, along with their relative abundances for 65-volt electrons. Except for the less abundant ions, an effort was made to adjust conditions so that each appearance potential was determined from curves in which the onset of production of ions related to the appearance potential had about the same degree of sharpness that characterized the onset of ionization in argon. The extent to which such conditions were realized had a major influence on the estimated error for the separate determinations. The listed errors are meant to refer only to the estimated precision of locating on an individual appearance-potential curve, the electron energy corresponding to the onset of ionization for a particular process, and they include the similar estimated error for the calibrating gas. Since the onset of ionization for the calibrating gas was very sharp (see Fig. 1), and since less sharp onset of ionization for any other ion corresponds to lower initial slope of the appearance-potential curve, thereby decreasing the estimated precision of locating the critical points, it is believed that the estimated error includes in it most of the potential error due to electron-energy distribution; for there would be essentially no such error if all the curves had the same initial high slope. All the first appearance potentials of ions from HCOOH for which corresponding reactions are listed in Table I are the result of at least three separate determinations (except that there were only two in the case of CH_2^+), and in all these cases, the estimated error is both greater than the maximum deviation from the mean and about twice as great as the average magnitude of the deviation from the mean.

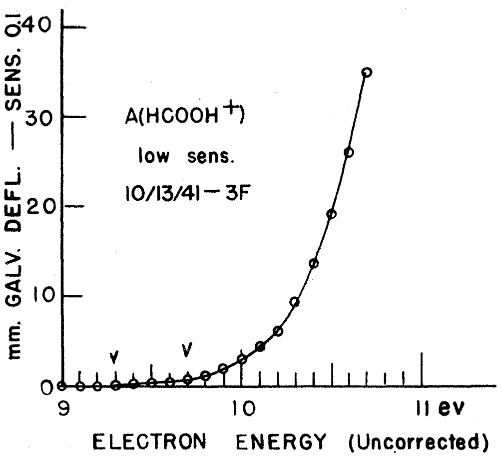

FIG. 3. Representative appearance-potential curve for $HCOOH^+$ on low sensitivity, used to determine the second ionization potential.

III. DISCUSSION

In order to arrive at the interpretations of the appearance potentials indicated in Table I extensive use was made of the calculated energies (relative to HCOOH=0) of the various possible states of aggregation of 2H, 2O, and C. Table II lists the states in the order in which their energies were calculated. and gives the expressions for the energies to indicate how they were calculated. The arbitrary designations of the states are simply for convenience in writing the expressions for the energies. The values of the various thermodynamical quantities employed in reducing the energy expressions to the numerical values shown in Table II are given in Table III along with references to the sources. Quantities originally given in kcal./mol have been converted by means of the factor, 23.05 kcal./mol = 1 electron-volt.[10] Heats of formation have not been corrected to absolute zero, since an examination of some such corrections made by Burton[11] indicated that they would be of the order of magnitude of the minimum experimental uncertainties. Other data besides those appearing in

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[10] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. I, *Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), p. 4.

[11] M. Burton, J. Chem. Phys. 6, 818 (1938).

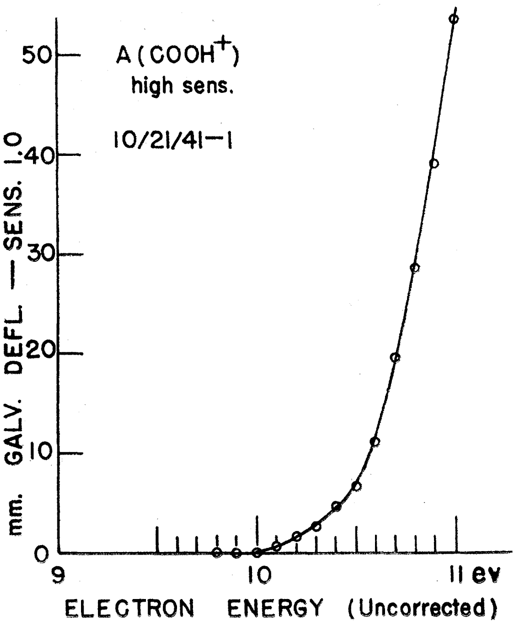


FIG. 4. Representative appearance-potential curve for $COOH^+$ on high sensitivity, used to determine the first appearance potential.

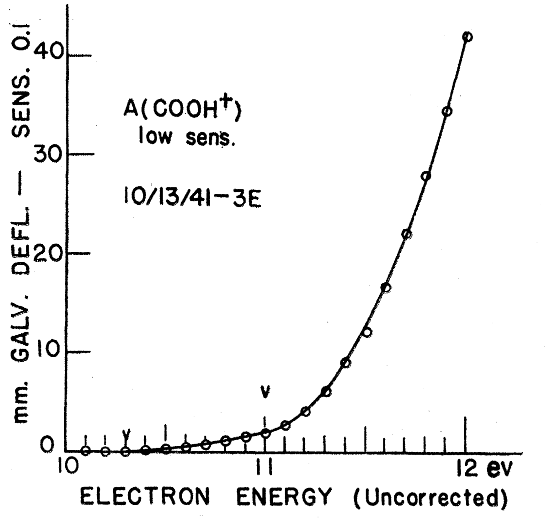


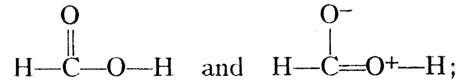
FIG. 5. Representative appearance-potential curve for $COOH^+$ on low sensitivity, used to determine the second appearance potential.

the tables will be required for a full discussion of the production of the ions, but they will be introduced in the treatment of the ions individually.

$M/e=46$

Appearance potential curves taken on high and low sensitivity, respectively (e.g. see Figs. 2 and 3), permitted the determination of two ionization potentials of HCOOH, namely at 11.0±0.1 and 11.6±0.2 volts. Price and Evans[12] from the ultraviolet absorption spectrum, have obtained the value 11.29 volts for the ionization potential of formic acid monomer, and have associated that value with the removal of one of the essentially non-bonding $2p$ electrons of the carboxyl oxygen. Although they do not state their experimental error, it is reasonable to assume that it is not more than a few hundredths of a volt at most.[13] Thus, there is, between the value of Price and Evans and the lower value of the present work, a discrepancy of 0.2 v. beyond the estimated experimental error of the electron impact data.

It is unlikely (although not impossible) that the electron impact data are so much in error—particularly in the indicated direction, since ionization potentials obtained by electron impact are more likely to be on the high side. Moreover, if we assume that a large error does exist and that our first ionization potential is to be identified with the spectroscopic value, then the possible explanations of the second ionization potential are not very appealing. For example, we might assume it to be due to ionization of the hydroxyl oxygen, which would probably have a higher ionization potential than the carboxyl oxygen as a result of resonance[6,14,15,16] between the structures:



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \quad \text{and} \quad H-\overset{\overset{\displaystyle O^-}{|}}{C}=O^+-H;$$

but it would be difficult to explain the greater probability of ionization of the hydroxyl oxygen. (It is apparent from Fig. 3, that the mode of ionization corresponding to the second appearance potential is the more probable when the

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[12] W. C. Price and W. M. Evans, Proc. Roy. Soc. A162, 110 (1937).

[13] For the ionization potential of formaldehyde obtained in a similar manner Price gives ±0.01 volts as the error; J. Chem. Phys. 3, 256 (1937).

[14] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

[15] R. J. B. Marsden and L. E. Sutton, J. Chem. Soc. (London) 1383 (1936).

[16] L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933).

electrons have enough energy to excite either mode.) Of course, we cannot categorically exclude the possibility that the second appearance potential is spurious, arising from the, effects discussed in the third paragraph of *Appearance Potential Measurements.* However, the possibility that instrumental effects are responsible is extremely unlikely; and it will soon be seen that a second appearance potential so near the first occurred only in the case of three types of ions and that one explanation seems plausible for all three.

If we discard the assumption that a large error exists in the measurement of the first ionization potential, and if we consider, rather, that our second ionization potential is to be identified with the spectroscopic value, there is a discrepancy of only 0.1 volt beyond the estimated experimental error, and it is in an understandable direction. However, we must account for the lower ionization potential at 11.0±0.1 volts. This seems readily done by assuming, as Coop, Davidson, and Sutton have suggested as a possible explanation of their dipole moment data,[17] that there exist two forms of HCOOH, one with the hydroxyl hydrogen *cis* to the carbonyl oxygen, and the other with it *trans*. Marsden and Sutton[15] have stated that the *cis*-form*** of the carboxylic esters should be the more stable; and we would expect the same to be true for HCOOH. In fact, Williams[18] has found the infra-red spectrum of HCOOH to be compatible with the *cis*-form; but, in conversation with one of us, has stated that his data do not preclude the possibility of existence of a *trans*-form in low concentration. The *trans*-form, then, should appear in lower concentration than the *cis*, if at all. Moreover, the ionization potential of the carbonyl oxygen should be lower in the *trans*-form than in the *cis*; for, in the latter, the greater proximity of the hydroxyl hydrogen provides a greater attractive force on the $2p$ electrons of the carboxyl oxygen. These considerations are consistent with Fig. 3, in which it is evident that the lower ionization potential is associated with the production of ions in low abundance relative to the ions associated with the higher ionization potential. The implication of the apparent relative abundance of *cis*- and *trans*-forms will be presented at the end of the paper, since the estimate of the abundance will involve other ions as well as HCOOH.

Before deciding that the assumption of a *trans*-form of HCOOH is plausible, it seems necessary at least to correlate the structure of the molecule with the difference between the ionization potentials 11.0±0.1 volts and 11.6 ±0.2 volts which we would assume to apply to the $2p$ electrons of the carbonyl oxygen in the *trans*- and *cis*-forms, respectively. Let us assume the potential field for these electrons to be divided into two parts: V_2 due to the hydroxyl hydrogen, and V_1 due to the rest of the molecule

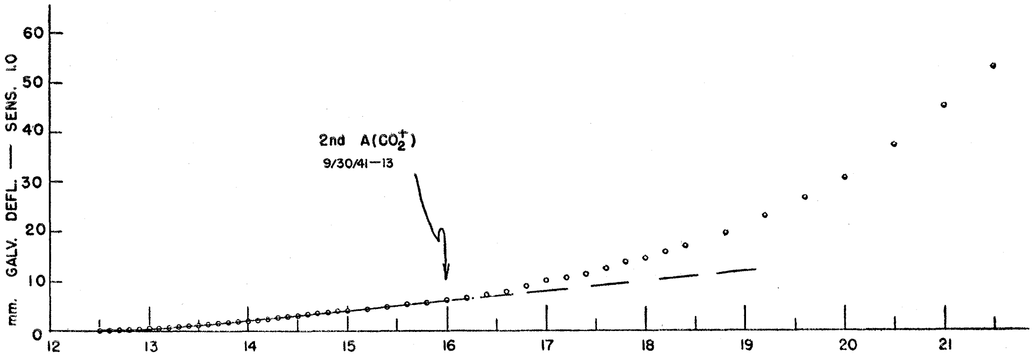

FIG. 6. Appearance potential-curve for CO_2^+ on low sensitivity, used to determine the second appearance potential.

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[17] I. E. Coop, N. R. Davidson, and L. E. Sutton, J. Chem. Phys. 6, 905 (1938).

*** They use "*trans*"; but they have labelled the forms in the opposite sense, referring them to the alkyl radical on the carbon atom.

[18] V. Z. Williams, J. Chem. Phys. 15, 232 (1947).

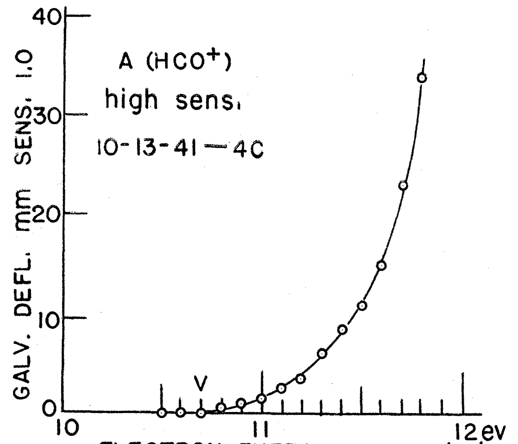

FIG. 7. Representative appearance-potential curve for HCO^+ on high sensitivity, used to determine the first appearance potential.

Let us assume further that the *trans*-form differs from the *cis*-form described by Williams[18] only in that the hydroxyl hydrogen is rotated 180° around the C—O bond as axis. To a first approximation, V_1 will be the same for both forms, and we need consider only the field due to the hydroxyl hydrogen in computing the difference in ionization potentials of the two forms. If the hydroxyl hydrogen is considered to have an effective charge e_h'(esu), we may approximate the difference ΔIP between the ionization potentials by the difference between the coulomb interaction energies (between the hydroxyl hydrogen and a $2p$ electron of the carbonyl oxygen) for the two forms; or:

$$\Delta IP = -e_h' e \left\{ \frac{1}{r_{cis}} - \frac{1}{r_{trans}} \right\},$$

where $e = -4.80 \times 10^{-10}$ esu, and where r_{cis} and r_{trans} are the distance between the hydroxyl hydrogen and the $2p$ electron in the *cis*- and *trans*-forms. If we accept the corresponding interatomic distances as reasonable approximations, we have for r_{cis} and r_{trans} the values 2.39×10^{-8} cm and 3.08×10^{-8} cm, respectively. These lead to:

$$\Delta IP = e_h' \times 4.47 \times 10^{-3} \text{ ergs}.$$

We obtain a more convenient form by expressing ΔIP in electron-volts and the residual charge, e_h, in terms of fractions of a positive electronic charge. We then have:

$$\Delta IP = e_h \times 1.34 \text{ ev}.$$

The observed difference in ionization potentials (0.6±0.3 ev) then leads to $e_h = 0.45 \pm 0.23$ positive electron unit. This should correspond to the value assigned from dipole moment data, which, according to Sidgwick (reference c, Table III), is 0.31 positive electron unit. Thus, the observed ΔIP is not of the wrong order of magnitude to be interpreted in terms of *cis*- and *trans*-forms of HCOOH.

For the rest of the discussion, then, it will be assumed that 11.0±0.1 volts is the ionization potential corresponding to the removal of a $2p$ electron from the carbonyl oxygen in molecules of the *trans*-form, and that 11.6±0.2 volts is the corresponding value for molecules of the *cis*-form. This assumption will not affect the selection of probable dissociation processes; but it will be useful in interpreting double appearance potentials in the case of some other ions.

$M/e = 45$

The ion corresponding to the removal of a hydrogen atom from HCOOH has appearance potentials at 12.1±0.1 volts and 12.9±0.2 volts, determined from appearance-potential curves similar to those shown in Figs. 4 and 5. The difference between the appearance potentials is essentially the same as found for $HCOOH^+$.

If we assume that this ion is formed simply by the rupture of the C—H or O—H bond, accompanied by ionization of the radical, the calculated appearance potential (referring to

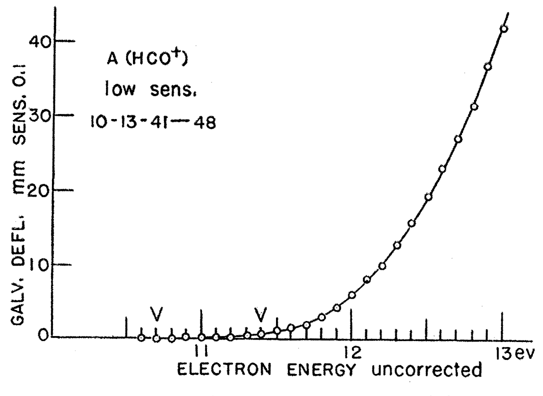

FIG. 8. Representative appearance-potential curve for HCO^+ on low sensitivity, used to determine the second appearance potential.

states of aggregation y and z) is:

either (for y)

$$4.6+I(\mathrm{HCOO})+W(X)=A(\mathrm{HCOO^+}),$$

or (for z)

$$4.5+I(\mathrm{COOH})+W(X)=A(\mathrm{COOH^+}).$$

From the observed appearance potentials we then calculate:

$$I_1(\mathrm{HCOO})\leqq 7.5\pm 0.1\text{ v};$$
$$I_2(\mathrm{HCOO})\leqq 8.3\pm 0.2\text{ v}$$

and

$$I_1(\mathrm{COOH})\leqq 7.6\pm 0.1\text{ v};$$
$$I_2(\mathrm{COOH})\leqq 8.4\pm 0.2\text{ v},$$

which are unreasonably low.

We find much more plausible energy relationships if we assume a process similar to that found convenient by Cummings and Bleakney[2] in explaining some of the appearance potentials in methyl and ethyl alcohol. If the ionization of the radical takes place at the carbonyl oxygen, the ion can have the form $\mathrm{H-O-C\equiv O^+}$ (utilizing the trivalency of $\mathrm{O^+}$), which would require for its production an energy less than that for state z by the difference between the triple and double bond energies. We have taken for this difference: $D(\mathrm{CO})-B(\mathrm{C=O})$, or 3.0 v. The calculated appearance potential is, then:

$$1.5+I(\mathrm{COOH})+W(X)=A(\mathrm{COOH^+}),$$

which by use of the observed appearance potentials gives

$$I_1(\mathrm{COOH})\leqq 10.6\pm 0.1\text{ v};\quad I_2\leqq 11.4\pm 0.2\text{ v}.$$

Considering the crudeness of the approximation used in obtaining the dissociation energy, these values are in good agreement with the values for the ionization potential of the carbonyl oxygen (assumed) in the molecule, and it seems plausible to assume that the two appearance potentials in the present case arise from the *trans*- and *cis*-forms of HCOOH just as we did in the case of the molecular ion.

Since the utilization of the trivalency of $\mathrm{O^+}$ is necessary to explain the low appearance potential of the ion of $M/e=45$, it must be the $\mathrm{C-H}$ hydrogen which is rejected in the dissociation; otherwise there would not be enough free valencies on the carbon atom to permit the formation of the triple bond with the oxygen. The trivalency of $\mathrm{O^+}$ could be used in the alternate form of the ion in which the ionization occurs at the hydroxyl oxygen: $\mathrm{H-O^+=C=O}$, and consideration of appearance potentials alone does not permit excluding this possibility. However, since, as was pointed out earlier, the ionization potential of the hydroxyl oxygen is probably higher than that of the carbonyl oxygen, the ionization probably takes place at the carbonyl oxygen. In addition, if it is the hydroxyl oxygen which is ionized in the ion now under discussion, the occurrence of two appearance potentials is not easily explained. Finally, it will be seen later that independent arguments lead to the conclusion that it is probably the carbonyl oxygen which is ionized in the case of the ion of $M/e=29$.

$M/e=44$

Curves taken on high sensitivity yielded the value 14.3 ± 0.1 v for the first appearance potential of $\mathrm{CO_2^+}$; and curves taken on low sensitivity, such as that shown in Fig. 6, gave the value 18 ± 1.0 v for the second appearance potential. $\mathrm{CO_2^+}$ can be produced from HCOOH only in the two reactions indicated in Table I; and the assignment of the first appearance potential must be correct, for it corresponds to an electron energy too low to cause a higher degree of dissociation than is indicated. If the second appearance potential is real, as it seems to be, it can be associated only with the other possible reaction. If the appearance potential curve has been properly interpreted, it seems that the reaction giving the higher degree of dissociation is the more probable one at high electron energies.

In calculating the energies required for the two reactions, $I(\mathrm{CO_2})$ was taken to be 13.73 ± 0.01 v as given by Price and Simpson.[19] It should be noted that $W(X)$ is small for both reactions.

$M/e=34$: and $M/e=33$

As is indicated in Table I, these ions appeared in very low abundance relative to the molecular ion, $M/e=46$, and are attributed to a slight

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[19] W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A169**, 501 (1939).

impurity of H_2O_2 in the sample. The complete reasoning on which this conclusion is based is rather extended; and, since the final conclusion contributes nothing concerning the molecule being studied, it seems hardly worth while taking space for the argument.

$M/e=32$

These ions had the same appearance potential in background and sample; and no increment to the background peak could be observed when the sample was admitted. Since the background at $M/e=32$ was only 0.25 percent of the intensity of the peak at $M/e=46$ in the sample, it is evident that very few, if any, O_2^+ ions were formed from HCOOH. If it is assumed that the background ions are O_2^+, we deduce the value $I(O_2)=13.2\pm0.6$ v, which is to be compared with 12.3 ± 0.1 v given by Hagstrum and Tate.[20] The discrepancy of 0.2 v beyond the combined experimental errors may probably be taken as indicative of the specific error introduced by comparing an appearance-potential curve of very low slope (as was the case for $M/e=32$) with one of very high slope (as was the case for the calibrating gas).

$M/e=30$

Owing to the isotope effect, there should be ions of $M/e=30$ in the amount of 1.16 percent of mass 29 (or 2.15 percent of mass 46) plus 0.2 percent of mass 28 (or 0.03 percent of mass 46), making a total of 2.18 percent of mass 46.[a] The observed number, 2.64 percent of HCOOH, was slightly greater. The difference might be due to an abnormal distribution of isotopes or to a few H_2CO^+ ions. The calculated appearance potential in the process (cf. state v_1):

$$\mathrm{HCOOH}+A(\mathrm{H_2CO^+})\rightarrow \mathrm{H_2CO^+}+\mathrm{C}+W(X)+e$$

is 15.97 volts (using Price's value[14] for $I(H_2CO)$), which is higher than the observed 14.1 ± 0.3 v. It will presently be seen that ions of $M/e=29$ are produced with two appearance potentials, the lower of which is associated with the production of ions in rather small quantities. The appearance potentials of the mass 30 ions, then, is certainly to be identified with the higher appearance potential (13.2 ± 0.3 v) of the mass 29 ions. There is a discrepancy of 0.3 volt beyond the combined limits of error of measurement. This is the same order of magnitude as the discrepancy found in the case of the mass 32 ions, which is not surprising considering the fact that the appearance-potential curves for 30 and 32 had nearly the same low slope.

$M/e=29$

Ions of $M/e=29$ were the most abundant of the ions produced from HCOOH by electron impact. Figures 7 and 8 are characteristic of those taken at high and low sensitivities to determine, respectively, a lower appearance potential at 12.8 ± 0.2 v and a higher appearance potential at 13.2 ± 0.3 v. The difference is essentially the same as found in the case of mass 46 and mass 45.

Of the modes of straightforward dissociation of HCOOH giving rise to a radical of mass 29, the one yielding the final state of aggregation w_2 requires the least energy. The calculated appearance potential of HCO^+ in the corresponding reaction,

$$\mathrm{HCOOH}+A(\mathrm{HCO^+})\rightarrow \mathrm{HCO^+}+\mathrm{OH}+W(X)+e,$$

is $I(HCO)+5.3$ v. Using the two observed appearance potentials we obtain $I_1(HCO)\leqq7.5\pm0.2$ v and $I_2(HCO)\leqq7.9\pm0.3$ v. These seem too low, since we expect $I(HCO)$ to be nearly the same as $I(HCOOH)$, for which we have obtained the values 11.0 ± 0.1 v and 11.6 ± 0.2 v ascribed, respectively, to the (presumed) *trans*- and (known) *cis*-forms of HCOOH. The energy relationships are much better if we assume, in the reaction above, that the HCO^+ ion has the structure $H-C\equiv O^+$. In this case the dissociation energy is reduced by about 3.9 volts as in the analagous situation considered for mass 45; and we obtain

$$I_1(\mathrm{HCO})\leqq10.5\pm0.2\text{ v}$$

and

$$I_2(\mathrm{HCO})\leqq10.9\pm0.3\text{ v}.$$

These are in good agreement with the values

$$I_1(\mathrm{COOH})\leqq10.6\pm0.1\text{ v}$$

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[20] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1934).

[a] On the basis of relative abundances of C, H, O, isotopes as given by G. T. Seaborg, Rev. Mod. Phys. **16**, 1 (1944).

and

$$I_2(\mathrm{COOH}) \leqq 11.4 \pm 0.2 \text{ v}$$

obtained in the discussion of mass 45; and, considering the uncertainty in the approximation used for difference in energy between $-\mathrm{C{=}O^+}$ and $-\mathrm{C{\equiv}O^+}$, they are in reasonable agreement with the values obtained for $I(\mathrm{HCOOH})$.

In the case of $\mathrm{HCO^+}$, then, it appears that the hydroxyl group is rejected in the dissociation of HCOOH and that the carbonyl bond in the ion is a triple bond, made possible only by ionization of the carbonyl oxygen. The two appearance potentials are consistent with the assumption that a *trans*-form of HCOOH exists.

M/e=28

Some of the appearance-potential curves for these ions showed a second appearance potential at about 16 volts; but this was shown to be due to $I(\mathrm{N_2})$ arising from a temporary leak.

The $\mathrm{CO^+}$ ions evidently arise from the reaction (cf. state *j*),

$$\mathrm{HCOOH} + A(\mathrm{CO^+}) \rightarrow \mathrm{CO^+} + \mathrm{H_2O} + W(X) + e.$$

The energy required is $I(\mathrm{CO}) + 0.2$ v. Using Vaughan's value[21] $I(\mathrm{CO}) = 13.9 \pm 0.2$ v, the calculated appearance potential is 14.1 ± 0.2 v, in fair agreement with the observed value of 14.6 ± 0.3 v. The excess energy in the reaction is 0.5 ± 0.5 v. Other reactions in which $\mathrm{CO^+}$ might be produced (cf. states *k*, *n*) would require an energy about 5 volts greater than the observed appearance potential.

M/e=18

$\mathrm{H_2O^+}$ ions appeared at 13.1 ± 0.1 volts electron energy, with no second appearance potential up to 25 volts. The reaction responsible for these ions must be:

$$\mathrm{HCOOH} + A(\mathrm{H_2O^+}) \rightarrow \mathrm{H_2O^+} + \mathrm{CO} + W(X) + e.$$

The minimum required energy is $I(\mathrm{H_2O}) + 0.18$ v, which, on the basis of $I(\mathrm{H_2O}) = 12.59 \pm 0.05$ v,[22] gives 12.77 ± 0.05 v in good agreement with the observed value. The excess energy of the reaction is 0.3 ± 0.15v.

It is interesting to note that the assigned reaction for the production of $\mathrm{H_2O^+}$ involves the same dissociation process as that for $\mathrm{CO^+}$ and that the dissociation energy is so small that the ions have appearance potentials not much different from their ionization potentials. This suggests that $\mathrm{H_2O^+}$ and $\mathrm{CO^+}$ may have occurred simply by ionization of the product molecules in the possible thermal decomposition,

$$\mathrm{HCOOH} \rightarrow \mathrm{H_2O} + \mathrm{CO},$$

at the filament or in the ionization chamber. However, the ions were much too abundant to be accounted for in this way. Since differential pumping was employed, there is little possibility that products of dissociation at the filament could have entered the ionization chamber. Moreover, as remarked under the discussion of the sample, Bonner and Hofstadter found no perceptible decomposition of formic acid vapor held for 36 hours at 150°C, which is probably only slightly lower than the temperature of the ionization chamber. Unless there was some strong catalytic effect favoring thermal decomposition in the present case, it seems most likely that the ions arose as the result of electron impact according to the assigned reactions.

M/e=17

There are two energetically indistinguishable reactions which are consistent with the observed appearance potential. Corresponding to states of aggregation designated as w_2 and *k*, these are, respectively,

$$\mathrm{HCOOH} + A(\mathrm{OH^+}) \rightarrow \mathrm{OH^+} + \mathrm{HCO} + W(X) + e$$

and

$$\mathrm{HCOOH} + A(\mathrm{OH^+}) \rightarrow \mathrm{OH^+} + \mathrm{H} + \mathrm{CO} + W(X) + e.$$

Using $I(\mathrm{OH}) \leqq 13.6 \pm 0.2$ as given by Mann *et al*,[23] and 5.3 and 5.4 volts as the dissociation energies, we calculate the expected appearance potentials 18.9 ± 0.2 v and 19.0 ± 0.2 v for the two reactions, leading to $W(X) \geqq 0.3 \pm 0.4$ v and $\geqq 0.2 \pm 0.4$ v. Other reactions in which $\mathrm{OH^+}$ might be produced require appearance potentials at least 4.6 volts greater than that observed.

M/e=16

For $\mathrm{O^+}$ ions there was only one acceptable measurement of the appearance potential not

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

[22] L. G. Smith and W. Bleakney, Phys. Rev. **49**, 883A (1936).

[23] M. M. Mann, A. Hustrulid, and J. J. Tate, Phys. Rev. **58**, 340 (1940).

interfered with by background. This gave 21.0 ±0.6 volt for the appearance potential. Bacher and Goudsmidt[7] give 13.55 v for $I(\mathrm{O})$, so the process giving rise to O^+ must be one in which the dissociation energy is equal to or less than 7.4±0.6 v. Of the thirteen modes of dissociation which might give rise to an oxygen atom, there are three with low enough dissociation energies not to be excluded as possibilities. These correspond to final states of aggregation and dissociation energies as follows:

v_1	H_2CO+O	5.14 volts,
v_2	$HCOH+O$	8.0 volts,
r	H_2+CO+O	5.19 volts.

$M/e=14$

There are two processes in which CH_2^+ ions might arise:

$$HCOOH+A(CH_2^+)\rightarrow CH_2^++O_2+W(X)+e$$

and

$$HCOOH+A(CH_2^+)\rightarrow CH_2^++2O+W(X)+e.$$

On the basis of the dissociation energies for states t and d and Smith's[1] value $I(CH_2)\leqq 12.0\pm 0.2$ v the calculated appearance potentials are, respectively, $\leqq 18.7\pm 0.2$ v and $\leqq 23.8\pm 0.2$ v. If the first reaction is the one occurring, $W(X)\geqq 6.0\pm 0.7$ v; if the second one occurs, $W(X)\geqq 0.9\pm 0.7$ v. It seems more likely, then, that the second reaction is the one which produces the observed ions.

$M/e=13$

There are four reactions in which CH^+ ions might be produced:

$HCOOH+A(CH^+)\rightarrow$
$CH^++HO_2+W(X)+e$ (cf. state x_1),
$HCOOH+A(CH^+)\rightarrow$
$CH^++O_2+H+W(X)+e$ (cf. state r),
$HCOOH+A(CH^+)\rightarrow$
$CH^++OH+O+W(X)+e$ (cf. state p),
$HCOOH+A(CH^+)\rightarrow$
$CH^++2O+H+W(X)+e$ (cf. state c).

The corresponding minimum required energies are:

$I(\mathrm{CH})+$ 9.5 volts, $I(\mathrm{CH})+10.2$ volts,
$I(\mathrm{CH})+11.0$ volts, $I(\mathrm{CH})+15.4$ volts.

It is unlikely that the last reaction is responsible for the second appearance potential. If it were, then we should deduce $I(\mathrm{CH})\leqq 12.0$ v; and, following the reasoning of Kusch, Hustrulid, and Tate,[24] we should calculate the rather improbable value $W(X)\geqq 3.4\pm 1.1$ v in their reaction $HCN\rightarrow CH^++N$. Therefore, either the second or third reaction is probably responsible for the second appearance potential. These choices give, respectively, $I(\mathrm{CH})\leqq 17.2\pm 0.6$ v and $I(\mathrm{CH})\leqq 16.4\pm 0.6$ v; and since the authors just mentioned give $I(\mathrm{CH})\leqq 15.4\pm 0.5$ v, we calculate $W(X)\geqq 1.8\pm 1.1$ v and $W(X)\geqq 1.0\pm 1.1$ v, respectively, for the two reactions. Neither of these values is unreasonable, and neither reaction can be excluded.

Since either the second or third reaction may be responsible for the second appearance potential, either the first or second reaction may be responsible for the first appearance potential. Considering these, we deduce $I(\mathrm{CH})\leqq 15.9\pm 0.5$ v and $I(\mathrm{CH})\leqq 15.2\pm 0.5$ v, or using $I(\mathrm{CH})\leqq 15.4\pm 0.5$ v, as above, we deduce $W(X)\geqq 0.5\pm 1.0$ v and $W(X)\geqq -0.2\pm 1.0$ v.

$M/e=12$

Any one of four reactions may account for the first appearance potential at 23.9±0.2 v. These correspond to the following states of aggregation of products, calculated minimum appearance potentials, and calculated excess energies:

	State	$A(\mathrm{C})_{\min}$ (volts)	$W(X)$ (volts)
e	$H_2+O_2+C^+$	$9.26+I(\mathrm{C})$	3.4 ± 0.2
o	H_2O+C^++O	$9.3\ +I(\mathrm{C})$	3.4 ± 0.2
q	$2OH+C^+$	$10.2\ +I(\mathrm{C})$	2.5 ± 0.2
x_1	HO_2+C^++H	$13.0+I(\mathrm{C})$	-0.3 ± 0.2

Likewise, there are at least four possibilities for the second appearance potential at 29.5±1.0 v:

	State	$A(\mathrm{C})_{\min}$ (volts)	$W(X)$ (volts)
g	H_2+2O+C^+	$14.2+I(\mathrm{C})$	4.0 ± 1.0
f	$2H+O_2+C^+$	$13.7+I(\mathrm{C})$	4.6 ± 1.0
m	$H+OH+C^++O$	$14.5+I(\mathrm{C})$	3.8 ± 1.0
b	$2H+2O+C^+$	$18.8+I(\mathrm{C})$	-0.5 ± 1.0

There are no strong arguments on the basis of which a more restricted assignment can be made.

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[24] P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. **52**, 843 (1937).

$M/e=2$

H_2^+ ions occurred in very low abundance, about 0.03 percent of mass 46 for 65-volt electrons. Their appearance potential, 16.0 ± 0.3 v, lay in the range of that of the background ions, 16.6 ± 0.5 v; but it is quite certain that the observed appearance potential is properly assigned to ions from HCOOH. The estimated error may be too small, however, both because of the low slope of the appearance-potential curves for these ions and because of the uncertainty introduced by applying, at low magnetic fields, the electron energy calibration obtained at high magnetic fields. If there had been time to do so, it would have been desirable to use molecular hydrogen for calibrating at low magnetic fields.

Unless the combined errors from all sources amount to several volts (which is unlikely), the only reaction by which the H_2^+ ions could have been produced from HCOOH is

$$\mathrm{HCOOH}+A(\mathrm{H_2^+})\rightarrow \mathrm{H_2^+}+\mathrm{CO_2}+W(X)+e.$$

On the basis of the energy of the state h (-0.25 v) and the value $I(\mathrm{H_2})=15.37$ v,[22] the calculated minimum appearance potential is 15.1 v, indicating an excess energy 0.9 ± 0.3 v.

$M/e=1$

The H^+ ions were definitely produced from HCOOH. The appearance potential and the value $I(\mathrm{H})=13.5$ v[7] require that the reaction involve not more than 5.5 ± 0.4 volts dissociation energy. Four possible states of aggregation and their corresponding dissociation energies are:

	State	$P(X)$ (volts)
i	CO_2+H+H	4.23
h	$OH+CO+H$	5.4
g	$HCOO+H$	4.6
z	$COOH+H$	4.5

Any one is plausible.

Negative Ions

The only negative ions found were very scarce, about 0.03 percent of $HCOOH^+$. They were definitely produced from HCOOH, since they disappeared on pumping out the sample, and they were tentatively identified as OH^- ions; but, since their appearance potential could be determined only to within ±5.0 v, it did not seem worth while to investigate them further.

IV. CONCLUSION

The electron-impact experiments on formic acid monomer required consideration of ions at one negative and seventeen positive values of M/e. The negative ions were tentatively identified as OH^- ions, but they were too rare to encourage a thorough investigation of them. Ions at $M/e=32$ were shown to be due to background, and ions at $M/e=33$, 34 were attributed to an impurity in the sample. The ions at $M/e=30$ were shown to be due almost entirely to isotope effect.

Of the positive ions arising from HCOOH as primary products of electron impact, those at $M/e=16$, 13, 12 and 1 could not be accounted for by any very restricted choice of possible reactions. Those at $M/e=17$ might have arisen from either of two possible reactions requiring nearly the same low dissociation energy and leading to calculated excess energy less than 0.5 v. Those at $M/e=14$ might have arisen from either of two reactions, but the reaction requiring the least dissociation energy involves so much excess energy as to make it unlikely, so that the ions probably arose from the reaction requiring the larger dissociation energy.

The first appearance potentials of the remaining fragment ions, namely those at $M/e=45$, 44, 29, 28, 18, and 2, were uniquely ascribable to origin of the ions in the reactions involving the least dissociation energy for the production of the corresponding radicals from HCOOH. The low appearance potentials of two of these ($M/e=45$, 29) led to the conclusion that the structure of these particular ions involved utilization of the trivalency of O^+, thus substantiating the conclusions of Cummings and Bleakney[2] regarding the production of some of the oxygen-bearing ions in methyl and ethyl alcohol. The first appearance potentials of the other four ions and the second appearance potential of CO_2^+, besides permitting determination of the five reactions involved, also permitted calculation of the excess energies required for the reactions. All of these excess energies were found to be less than 1.0 volt, thus substantiating the view that excess energies are usually low compared to bond energies.

Two not widely separated ionization potentials were observed for HCOOH; and, in addition, a second appearance potential close to the first was observed for both $COOH^+$ and HCO^+. The postulate of a *trans*-form of HCOOH was introduced to explain the fact that the electron-impact experiments yielded a value for the first ionization potential lower than that given by Price and Evans by 0.2 volt beyond the estimated experimental error, whereas their value is more consistent with a second electron-impact ionization potential. It was shown that the difference between the two ionization potentials, determined in the electron-impact experiments, is of the right order of magnitude to be explicable in terms of *trans*- and *cis*-forms of HCOOH, and it was shown that the concept of a *trans*-form of HCOOH is useful in explaining the two appearance potentials observed for both $COOH^+$ and HCO^+.

The appearance-potential curves for $HCOOH^+$, $COOH^+$, and HCO^+ might have been explicable in other ways if there had not been available the accurate spectroscopic value for the ionization potential of the molecule, and the postulate of a *trans*-form is therefore presented with caution. Perhaps the chief reason for hesitancy is that the appearance-potential curve for argon, Fig. 1, shows some of the "tailing-off" characteristic that is found in the appearance-potential curve for $HCOOH^+$, Fig. 2. In comparing these curves, however, it will be noted that the "tailing-off" is less pronounced for argon than for $HCOOH^+$.[†††] Also, some of the "tailing-off" in argon is probably due to transitions to the $^2P_{\frac{1}{2}}{}^0$ state of A^+ which lies 0.178 v above the lowest state of A^+. Purely circumstantial evidence that the proper interpretation of the formic acid data has been made is the fact that first and second appearance potentials were assigned in the case of $HCOOH^+$, $COOH^+$, and HCO^+ before knowledge of the work of Price and Evans was obtained, and when it was known that the explanation of second appearance potentials so close to the first would present some problems; whereas there was no tendency to consider that the appearance-potential curve of argon had a "break" in it. Thus, although further work would be desirable to permit a more certain demonstration that a *trans*-form of HCOOH exists, and although we cannot suggest that the existence of a *trans*-form has been proved, certainly the electron impact data are best interpreted in terms of such a postulate.

If the assumption of the existence of a *trans*-form of HCOOH is correct, the appearance-potential curves taken on low sensitivity for $HCOOH^+$, $COOH^+$, and HCO^+ can be used to get a rough estimate of its concentration relative to the *cis*-form. This has been done by comparing the ion current at the second appearance potential with that obtained at an electron energy greater than the second appearance potential by an amount equal to the difference between the two appearance potentials. Considering the curves for the three types of ions which can be treated, we obtain for C_t/C_c, the ratio of the concentration of molecules in the *trans*-form to the concentration of molecules in the *cis*-form, the rough average 0.12 and the rough probable limits 0.05 and 0.20. It would be interesting to learn whether Price and Evans' spectrograms could have shown the ionization series for molecules in this abundance.

If it is assumed that equilibrium was attained at the temperature of the ionization chamber, the relationship

$$\ln_e(C_t/C_c) = -\Delta E/kT$$

can be used to calculate the energy difference, ΔE (ergs/molecule), between the two forms. Using for the temperature the probable value 423°K and the limits 373°K and 500°K, the concentration ratios cited above give for ΔE the rough value 1.8 kcal/mole with probable limits 1.2 and 3.0 kcal/mole.

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[†††] The same remarks apply to a comparison of the appearance-potential curves taken on low sensitivity; but the low sensitivity curve for argon has not been reproduced here since the scale of reproduction would not show the differences which are apparent when the full-sized original curves are superposed.