Studies on Mass Spectra and Appearance Potentials of Acetic Acid and Deuteroacetic Acid CD_3COOH

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(Received June 8, 1960)

Recently the data of mass spectra have often been utilized in the discussion of radiation-induced reactions of organic compounds[1]. On such an occasion it is indispensable to determine the chemical species corresponding to each peak in the spectra by some methods, e. g. by comparing the spectra of the compounds marked by isotopes. For the same purpose, ionization potentials of these compounds are required, if possible. Although the data of this kind have been accumulated to some extent, those of the appearance potentials which are necessary to produce fragment ions do not exist so much yet in spite of their increasing importance. Such being the situation, as a part of our research on radiation chemistry of oxygen-containing compounds, mass spectra of acetic acid and deuteroacetic acid CD_3COOH were measured at several accelerating voltages and temperatures of the ion source on one hand, and also the appearance potentials of parent ions and main fragment ions of these acids on the other hand.

Experimental

Materials.— The purest commercial acetic acid was used without any treatment. Deuteroacetic-d_3 acid was synthetized as follows; carbon suboxide C_3O_2 obtained by dehydrating commercial malonic acid with phosphorus pentoxide was reacted with deuterium oxide. The deuteromalonic acid thus produced was decomposed thermally into deuteroacetic-d_3 acid-d CD_3COOD. The deuterium atom of the carboxylic group of this acid was replaced by protium atom, bubbling gaseous hydrogen chloride through the acid. The result of mass spectrometric analysis of the acid thus obtained showed that the amount of CD_3COOH in the deuterated acid was 95.6 atomic per cent, while CD_2HCOOH was the major parts of the impurities, CH_3COOH being negligibly small.

Apparatus. — The specifications of the mass spectrometer (Hitachi type RMU-5) are as follows: 90° focusing type, the temperature of the ion source is variable from 120 to 240°C, and electron accelerating voltage is also variable between 0 and 200 V. The standard conditions for gas analysis were as follows: electron accelerating voltage, 82 eV.: ion accelerating voltage, 1500 V., total emission current, 130 μA; target current, 35 μA; standard temperature of the ion source, 130°C.

Results

Mass Spectra.—Mass spectra of both acids are shown in Table I, where each peak height is per cent of total ion yield. From the table, the peak heights of the ions produced from CH_3COOH are in the order: $m/e=43>45>15>60>29$. The result is concordant with that of some other research[2], but not with that of Kambara[3] who found the ion of $m/e=28$ to be the most abundant followed by the ions of $m/e=43>45>15>14>12$ (cf. Table II). The discrepancy between the two data is too great to be explained by the discrimination peculiar to the respective apparatus. However, larger values of the peaks of $m/e=28$, 14 and 12 of Kambara may be explained by the contamination of carbon monoxide and nitrogen, and this explanation is supported by the fact that the peak at $m/e=28$ in the mass spectrum of

TABLE I. MASS SPECTRA OF CH_3COOH AND CD_3COOH

m/e	CH_3COOH %	CD_3COOH %	m/e	CH_3COOH %	CD_3COOH %
1	0.9	0.6	30	0.3	1.9
2	0.03	0.6	31	2.0	0.1
3	—	0.03	32	0	0.1
4	—	0.03	33	0	0.6
12	0.7	0.5	40	0.4	0.2
13	1.8	0.1	41	1.3	0.1
14	4.0	1.5	42	4.5	0.8
15	11.0	0.6	43	26.5	0.7
16	1.7	3.6	44	1.0	3.3
17	1.4	2.7	45	21.2	19.9
18	2.6	13.8	46	0.9	28.4
19	—	1.4	47	0	0.3
24	0.2	0.1	60	9.4	0.3
25	0.4	0	61	—	0
26	0.4	0.4	62	—	0.7
27	0.1	0.1	63	—	13.0
28	1.6	1.9	64	—	0.3
29	4.7	1.0			

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[1] For instance, see, J. G. Burr, *J. Phys. Chem.*, 61, 1483 (1957).

[2] Catalog of Mass Spectral Data of the American Petroleum Institute, Project, 44, Spectrum Serial No. 640.

[3] T. Kambara, *J. Phys. Soc., Japan*, 5, 84 (1950).

TABLE II. MASS SPECTRA OF CH_3COOH IN THE LITERATURE

m/e	Ions	Relative peak height*		
		Kambara[3]	API Table No. 640	The present research
12	C^+	34		4
13	CH^+	16		7
14	CH_2^+	43		15
15	CH_3^+	64		42
25	C_2H^+	4		2
26	$C_2H_2^+$	5	1.3	2
27	$C_2H_3^+$	5	0.40	0
28	$C_2H_4^+$, CO^+	130	5.6	6
29	CHO^+	33	15.6	18
30	CH_2O^+	1	0.7	1
31	CH_3O^+	8.5	4.5	8
32	—	—	0.1	0
41	C_2HO^+	19	4.5	5
42	$C_2H_2O^+$	28	14.5	17
43	$C_2H_3O^+$	100	100	100
44	$C_2H_4O^+$, CO_2^+	12	4.9	4
45	CHO_2^+	81	93.6	80
46	$CH_2O_2^+$	—	1.2	3
55		—	0.08	—
56		—	0.13	—
57		—	0.06	—
60	$C_2H_4O_2^+$	29	57.7	36

* The peak height of $m/e=43$ is normalized to 100.

CD_3COOH obtained under the same experimental condition is also small. Moreover, the heights of the main peaks of both spectra of CH_3COOH and CD_3COOH can be explained without contradiction, i. e., the peaks at $m/e=43$, 15 and 60 in CH_3COOH, corresponding to CH_3CO^+, CH_3^+ and CH_3COOH^+, shift to those at $m/e=46$, 18 and 63 in CD_3COOH, corresponding to CD_3CO^+, CD^+ and CD_3COOH^+, while the peak of $COOH^+$ ($m/e=45$) occupies the second height in both spectra. Therefore it may be concluded that our spectra are free from the peaks due to some impurities or thermally decomposed products.

In Fig. 1, the effect of temperature on the mass spectrum of acetic acid is shown over a temperature range 130~230°C, taking the temperature of the ion source as abscissa and the percentage of the peak height as ordinate. It is found that the observed effect is not so large, as to be explained by such a mechanism as that the fragment ions are produced monomolecularly from the parent ions with some activation energies for bond breaking processes. However, considering that the gaseous acetic acid molecules may not be in thermal equilibrium completely with the wall of the ion source this result may not be curious. But from this figure, it might be said that the temperature effect has the following tendencies: ions $m/e=15$, 43 and 45 are practically independent on temperature, while others

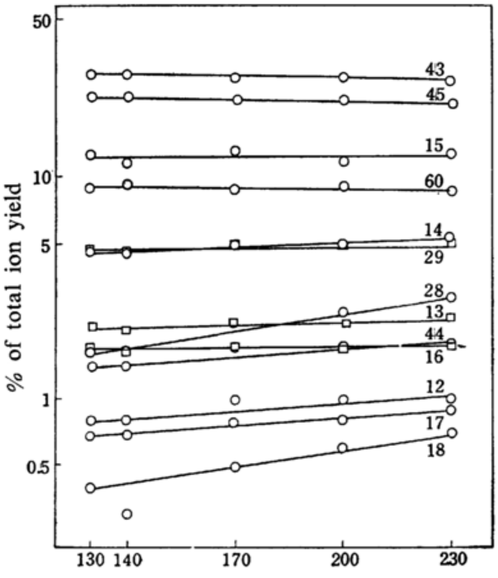

Fig. 1. The effect of ion source temperature on the mass spectrum of acetic acid.

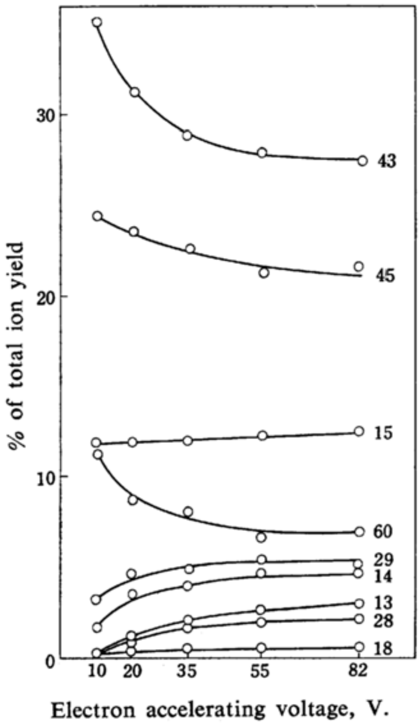

Fig. 2. The effect of electron accelerating voltage on the mass spectrum of acetic acid.

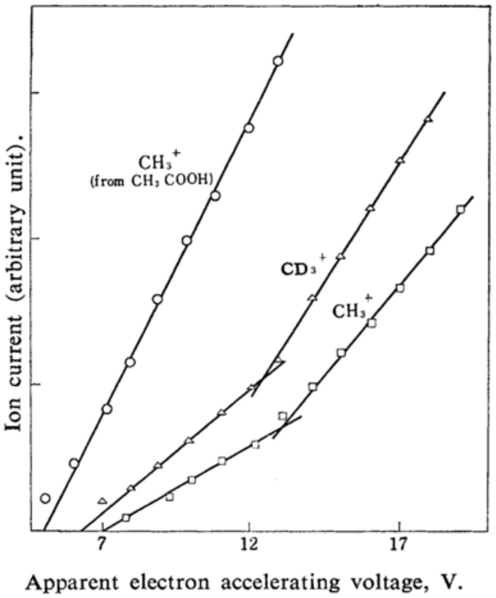

Fig. 3. Ionization efficiency curves of CH_3^+, CD_3^+ and $COOH^+$ ions.

increase, especially those of CO_2^+ ($m/e=44$), CO^+ ($m/e=28$) and H_2O^+ ($m/e=18$), HO^+ ($m/e=17$) and C^+ ($m/e=12$), which are the parent and fragment ions from molecules probably produced by the thermal decomposition of acetic acid.

The effect of electron accelerating voltage on the spectrum of acetic acid is shown in Fig. 2, where the voltage is varied from 9 to 82 V., and the sum of each peak height is normalized to 100 at each voltage. It is evident that the main peaks can be classified into three groups, i. e., the first group, CH_3^+ ion is practically constant, the second group, CH_3COOH^+ ($m/e=60$), CH_3CO^+ ($m/e=43$) and $COOH^+$ ($m/e=45$) ions, decreases and the residual third group, COH^+ ($m/e=29$) and CH_2^+ ($m/e=14$) increases with the increasing electron accelerating voltage. These tendencies may be reasonable if it is assumed, as is done by King and Long[4] on the mass-spectra of formic esters, that most of the ions which belong to the first and the third groups are produced from the ions of the second group. Detailed mechanism of production of CH_3^+ will be discussed again.

Appearance Potential.—As described above, the ions, CH_3^+, CH_3CO^+, $COOH^+$ and CH_3COOH^+ can be regarded as the main peaks in the spectrum of CH_3COOH, because the total contribution of the other ions to the spectrum is below 30%. The appearance potential of the above four ions were measured by the following procedure. The ionization efficiency curve for the ion under investigation was determined up to about 10 V. above the expected value of appearance potential and then the accurate one was determined by extrapolating the linear portion of the curve to the voltage axis. Thus, the obtained value of the ionization potential was calibrated by use of Moore's photo-ionization datum of argon ion, i. e., 15.76 V.[5]

In Fig. 3, the measurements on CH_3^+, CD_3^+ and $COOH^+$ are plotted against apparent voltage of electron acceleration. The results of these and other ions are summarized in Table III.

TABLE III. APPEARANCE POTENTIALS IN VOLT

Ions	CH_3COOH	CD_3COOH
CH_3COOH^+ or CD_3COOH^+	10.7_2	10.7_1
CH_3CO^+ or CD_3CO^+	12.6_8	12.9_7
$COOH^+$	14.1_5	14.0_8
CH_3^+ or CD_3^+	16.0_8	15.5_6
Break point of CH_3^+ or CD_3^+ curve	22.3	21.5

General discussion.—In order to confirm the reliability of our data, the appearance potential of the parent ion CH_3COOH^+ (10.7_2 V.) was compared with those in the literatures. Among the latter values, our appearance potential coincides fairly well with those obtained by the critical slope method of Honig (10.70[6] and 10.6_6[7] V.), but is higher than the value $10.3_3 \pm 0.03$ V. obtained by the method of photo-ionization[8]. Such a situation may be plausible considering the generally accepted fact that the former method as well as our linear extrapolation method gave higher values than the latter.

Thus it has been found that the degree of accuracy of our measurement is sufficient for discussing the appearance potentials of other fragment ions and of other ions produced from CD_3COOH. The first point to be discussed will be the fact that the appearance potentials of the parent ions of both acids are 10.7_2 and 10.7_1 V.; i. e., they coincide with each other within the experimental errors, while those of the corresponding fragment ions differ definitely from each other.

Secondly, it may be noteworthy that the appearance potential of CD_3CO^+ ion is higher by 0.3 V. than that of CH_3CO^+ ion. On the other hand, the appearance potentials of $COOH^+$ (from deuterated acid) and CD_3^+ ions are lower than those of $COOH^+$ and CH_3^+ ions by 0.1 and 0.5 V., respectively. According

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[4] A. King and F. Long, *J. Chem. Phys.*, **29**, 374 (1958).

[5] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[6] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[7] I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 504 (1956).

[8] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

to the results hitherto published, it seems to be a rule that the ionization potential of a molecule increases by deuteration; e. g. 13.04 V. for CH_4^+ against 13.21 V. for CD_4^+ 9). Our data, therefore, seem to be an exceptional case. At present, such an anomaly can not be explained easily. The next point to be mentioned may be the breaks of the curves observed in cases of CH_3^+ and CD_3^+ ions. The breaks occur at about 6 V. higher than the corresponding appearance potentials in both cases.

The occurrence of these breaks might be explained by assuming that above this break point the simultaneous fragmentation process (1b) of the parent ion at two bonds occurs in addition to the single fragmentation process (1a) to form CH_3^+ ion:

$$CH_3COOH \rightarrow CH_3^+ + COOH \qquad (1a)$$
$$\searrow CH_3^+ + CO_2 + H \qquad (1b)$$

However, according to the theoretical result10) which has been derived by the quasi-equilibrium theory, most of the CH_3^+ ions must be produced secondarily, i. e., by the decomposition of highly excited CH_3CO^+ ion. This explanation may not be extraordinary, because a similar shape of ionization efficiency curve of CH_3NO_2, in which a sharp break point occured about 4.3 V. above the first appearance potential of NO_2^+, was explained reasonably by the existence of a bent excited state of NO_2^+ 11). Therefore, the mechanism of producing the CH_3^+ ions whose appearance potentials are different is not such as that described by Scheme 1, but both ions are produced by Scheme 2,

$$CH_3COOH \rightarrow CH_3CO^+ + OH$$
$$\rightarrow CH_3^+ + CO + OH \qquad (2)$$

The states of the CH_3^+ produced below and above the break point in the curve are therefore different.

Summary

In order to obtain information on the decomposition process of acetic acid in radiation chemistry, not only mass spectra of both acetic acid and deuteroacetic acid but also appearance potentials of parent and main fragment ions of both acids have been measured.

By studying the effects of ion source temperature and of electron accelerating voltage on the spectra, and by comparing the mass spectra of both acids, it has been possible to identify the chemical species produced by electron impact without ambiguity and also to estimate the process of their production to some extent.

It has been found that, although the appearance potentials of the parent ion of both acids coincide fairly well, those of CH_3^+ and $COOH^+$ from CH_3COOH are higher than those of corresponding ions from deuterated acid. The breaks of ionization-efficiency curves have been observed in CH_3^+ and CD_3^+ ions at about 6 volts higher than the appearance potentials suggesting a possibility of the presence of an excited state of the product ions.

The authors express their sincere thanks to Dr. I. Kanomata of Tokyo Metropolitan University and also to Dr. K. Fueki of Osaka University for their discussions.

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9) R. E. Honig, ibid., **16**, 105 (1948).

10) Cf. K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 356 (1960).

11) J. Collin, *J. Chem. Phys.*, **30**, 1621 (1959).