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# Ionization and Dissociation of Formic Acid, Acetic Acid, Propanoic Acid, and Butanoic Acid under Electron Impact

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The mass spectra of DCOOD, DCOOH, $CD_3COOD$, $CD_3COOH$, $CH_3COOD$, $C_2H_5COOD$, and $C_3H_7COOD$ are compared with spectra of the H-containing compounds. Besides, the $^{18}O$-labeled acetic acid is measured. The labeling helps to determine the origin of a number of fragment ions. It is found that the two fragment ions $C_3H_5O_2^+$ and $C_4H_7O_2^+$ are produced by the removal of the hydrogen atom from the alkyl group and have the structures of $C_2H_4CO_2H^+$ and $C_3H_6CO_2H^+$ respectively. Neither $CH_2CO_2H^+$ nor $CH_3CO_2^+$ is produced. The rerrangement ion $CH_3O^+$ is found to have the structure of $CH_2OH^+$, one of whose hydrogen atoms comes from the carboxyl group. The origins of the hydrogen atom and the oxygen atom in the other rearrangement ions are also determined. The mechanisms for the fragmentation of the molecular ions are discussed.

Mass spectrometric studies of the ions from the carboxylic acids have been carried out by several investigators.[1-5] Melton[3] discussed the fragmentation of formic acid by a comparison of the mass spectra of an H-containing compound and a deutero-isomer. Other works have concerned themselves only with the appearance potentials. However, there have been no studies of either acetic acid or of the higher acids.

In this paper we will discuss the ionization and the ionic fragmentation of formic acid, acetic acid, propanoic acid, and butanoic acid molecules, each of which consists of an alkyl group and a carboxyl group. Emphasis has been placed in the atomic rearrangement during the fragmentation. For this purpose, it is useful to study the systems in some detail with the help of suitably-labeled compounds. In the present work the deuterium and the oxygen-18 labeling have been utilized particularly for the study of some rearrangement processes as well as for the identification of some fragment ions. Also, the presence of the metastable ions and the ion-molecule reactions have been utilized.

## Experimental

**Materials.** The purest commercial acids were used without purification. Three deuterated compounds, $CD_3COOD$, CDOOD, and $D_2O$, were obtained from Merck, Ltd., while the other deuterated compounds were synthesized as follows: $CD_3COOH$: the deuterium atom of the carboxyl group of $CD_3COOD$ was replaced by a hydrogen atom by bubbling gaseous hydrogen chloride through the acid.

DCOOH: The deuterium atom of the carboxyl group of DCOOD was replaced by a hydrogen atom by the addition of $H_2O$.

$CH_3COOD$ and $n$-$C_3H_7COOD$: The anhydride of each acid reacted with $D_2O$ at room temperature or higher.

**Apparatus.** The mass spectra were taken with a CEC 21-401 Mass Spectrometer, modified in order to determine the appearance potentials of the ions. The standard conditions for analysis were as follows: electron-accelerating voltage, 70 V; ion-accelerating voltage, 210 V; total emission current, 10.0 $\mu$A; temperature of the ion source, 250±0.2°C. When necessary, the temperature of the ion source, the repeller voltage, and the electron energy were changed.

As the compounds are adsorbed strongly on the walls, precaution was taken against the effects of adsorption. In advance the sample inlet-system was sufficiently flashed with argon and then with the sample. The contamination of the sampling systems was examined by the measurement of the background of the mass spectra with a flow of argon. In order to avoid as much as possible the influence of the isotope exchange during the measurement, the mass spectra were taken as soon as

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[1] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

[2] G. P. Happ and D. W. Stewart, *J. Am. Chem. Soc.*, **74**, 4404 (1952).

[3] G. A. Ropp and C. E. Melton, *ibid.*, **80**, 3509 (1958).

[4] K. Hirota, K. Nagoshi and M. Hatada, This Bulletin, **34**, 226 (1960).

[5] "Catalog of Mass Spectral Data," Am. Pet. Inst. Res. Proj. Nat. Bur. Stds., Washington D. C., Serial No. 300.

possible after the sample had been introduced.

## Results and Discussion

Certain ions in the mass spectra of the H-containing and deuterated acids are given in Tables 1—4. The intensities are expressed as the intensities relative to those of the parent ions except in the cases of *n*-$C_3H_7COOH$ and *i*-$C_3H_7COOH$. In these cases, the intensities are expressed as the percentages of total ionization. It was possible to give the structural formulas for the various ions by comparing the mass distribution of the normal compound with that of the deutero-isomer. These formulas are given in the third column of Table 1. When it is likely that more than one ion is associated with the intensity as the given mass, the measured intensity has been partitioned among the contributing ions. The assignments of the individual contributions were made somewhat arbitrarily, assuming that the loss of an H or D atom in the deutero-isomer occurred with the same probability as the loss of H in the H-containing compound. Similarly, the loss of a given group such as methyl was assumed to occur with the same probability in both isomers.

**Fragment ions: $C_nH_{2n}CO_2H^+$ or $C_nH_{2n+1}$-$CO_2^+$.** It is of interest to determine whether the hydrogen atom is eliminated from the

TABLE 1. SOME IONS IN THE MASS SPECTRA OF FORMIC ACID AND DEUTEROFORMIC ACIDS

| | HCOOH | | DCOOH | | DCOOD | |
|---|---|---|---|---|---|---|
| *m/e* | Intensity* | Ion | Intensity* | Ion | Intensity* | Ion |
| 28 | 16.2 | $CO^+$ | 15.5 | $CO^+$ | 10.0 | $CO^+$ |
| 29 | 76.6 | $COH^+$ | 14.6 | $COH^+$ | 0.54 | |
| 30 | — | — | 66.7 | $DCO^+$ | 68.6 | $DCO^+$ |
| 44 | 20.3 | $CO_2^+$ | 15.6 | $CO_2^+$ | 7.38 | $CO_2^+$ |
| 45 | 73.9 | $CHO_2^+$ | 35.7 | $CO_2H^+$ | — | — |
| 46 | **100** | $HCO_2H^+$ | 41.0 | $DCO_2^+$ | 54.5 | $CDO_2^+$ |
| 47 | | | **100** | $DCO_2H^+$ | 0.6 | |
| 48 | | | | | **100** | $DCO_2D^+$ |

* Relative intensity for ionizing voltage 70 V

TABLE 2. SOME IONS IN THE MASS SPECTRA OF ACETIC ACID-d AND DEUTEROACETIC ACIDS

| | $CH_3COOH$ | | $CH_3COOD$ | | $CD_3COOH$ | | $CD_3COOD$ | |
|---|---|---|---|---|---|---|---|---|
| *m/e* | Intensity* | Ion | Intensity* | Ion | Intensity* | Ion | Intensity* | Ion |
| 14 | 12.3 | $CH_2^+$ | 11.9 | $CH_2^+$ | 2.48 | | 2.12 | |
| 15 | 46.3 | $CH_3^+$ | 41.5 | $CH_3^+$ | 0.87 | | 0.21 | |
| 16 | | | | | 6.70 | $CD_2^+$ | 6.49 | $CD_2^+$ |
| 17 | | | | | 5.82 | | 1.44 | |
| 18 | | | | | 45.3 | $CD_3^+$<br>$CO^+$ | 46.0 | $CD_3^+$ |
| 28 | 8.81 | $CO^+$ | 5.31 | $CO^+$ | 6.82 | $C_2D_2^+$ | 6.46 | $CO^+$ |
| 29 | 11.8 | $CHO^+$ | 7.78 | $HCO^+$ | 3.17 | $COH^+$ | 0.07 | |
| 30 | 0.54 | | 5.53 | $COD^+$ | 6.44 | $DCO^+$ | 10.6 | $DCO^+$ |
| 31 | 2.53 | $CH_2OH^+$ | 0.89 | | 0.29 | | 0.11 | |
| 32 | — | — | 3.19 | $CH_2OD^+$ | 0.13 | | 0.44 | |
| 33 | — | — | — | — | 2.05 | $CD_2OH^+$ | | |
| 34 | — | — | — | — | — | — | 2.59 | $CD_2OD^+$ |
| 43 | 118 | $CH_3CO^+$ | 119 | $CH_3CO^+$ | 0.78 | | 0.39 | |
| 44 | 5.90 | | 11.4 | | 14.8 | | 14.2 | |
| 45 | 112 | $COOH^+$ | 6.90 | | 107 | $COOH^+$ | 1.35 | |
| 46 | 2.08 | | 115 | $COOD^+$ | 148 | $CD_3CO^+$ | 270 | $CD_3CO^+$<br>$COOD^+$ |
| 60 | **100** | $CH_3CO_2H^+$ | | | — | — | — | — |
| 61 | 2.18 | | **100** | $CH_3COOD^+$ | — | — | — | — |
| 62 | — | — | 3.18 | | — | — | — | — |
| 63 | — | — | — | — | **100** | $CD_3CO_2H^+$ | — | — |
| 64 | — | — | — | — | 2.27 | | **100** | $CD_3CO_2D^+$ |
| 65 | — | — | — | — | — | — | 2.72 | |

* Relative intensity for ionizing voltage 70 V

TABLE 3. SOME IONS IN THE MASS SPECTRUM OF PROPANOIC ACID AND DEUTERO-PROPANOIC ACID

| | $C_2H_5COOH$ | | $C_2H_5COOD$ | |
|---|---|---|---|---|
| *m/e* | Intensity* | Ion | Intensity* | Ion |
| 28 | 125 | $C_2H_4^+$, $CO^+$ | 66.4 | $C_2H_4^+$, $CO^+$ |
| 29 | 114 | $C_2H_5^+$, $HCO^+$ | 145 | $C_2H_5^+$, $COH^+$ |
| 30 | 17.5 | | 24.0 | $COD^+$ |
| 31 | 4.33 | $CH_2OH^+$ | 13.5 | |
| 32 | — | — | 4.46 | $CH_2OD^+$ |
| 45 | 68.9 | $COOH^+$ | 0.08 | |
| 46 | 9.95 | | 71.4 | $COOD^+$ |
| 55 | 13.9 | $C_2H_3CO^+$ | 13.6 | $C_2H_3CO^+$ |
| 56 | 11.9 | $C_2H_4CO^+$ | 9.05 | $C_2H_4CO^+$ |
| 57 | 27.4 | $C_2H_5CO^+$ | 29.2 | $C_2H_5CO^+$ |
| 73 | 59.4 | $C_2H_4CO_2H^+$ | — | — |
| 74 | **100** | $C_2H_5CO_2H^+$ | 60.6 | $C_2H_4COOD^+$ |
| 75 | | | **100** | $C_2H_5COOD^+$ |

TABLE 4. SOME IONS IN THE MASS SPECTRA OF $n$-$C_3H_7COOH$ and $i$-$C_3H_7COOH$

| *m/e* | Ion | $n$-$C_3H_7COOH$ Intensity %* | $i$-$C_3H_7COOH$ Intensity %* |
|---|---|---|---|
| 14 | $CH_2^+$ | 0.23 | 0.36 |
| 15 | $CH_3^+$ | 0.63 | 2.51 |
| 26 | | 0.86 | 0.96 |
| 27 | $C_2H_3^+$ | 6.70 | 8.46 |
| 28 | $C_2H_4^+$, $CO^+$ | 1.66 | 1.40 |
| 29 | $C_2H_5^+$, $HCO^+$ | 3.90 | 1.98 |
| 30 | | 0.08 | 0.07 |
| 31 | $CH_2OH^+$ | 0.38 | 0.28 |
| 39 | | 2.70 | 2.79 |
| 40 | | 0.47 | 0.51 |
| 41 | $C_3H_5^+$ | 5.91 | 11.9 |
| 42 | $C_3H_6^+$ | 5.91 | 3.70 |
| 43 | $C_3H_7^+$, $C_2H_3O^+$ | 6.06 | 39.5 |
| 44 | $CO_2^+$ | 0.41 | 1.75 |
| 45 | $CO_2H^+$ | 4.60 | 3.01 |
| 55 | | 1 72 | 1.11 |
| 56 | | 0.15 | 0.08 |
| 57 | | 0.14 | 0.17 |
| 58 | | 0.10 | 3.06 |
| 59 | | 0.04 | 0.24 |
| 60 | $C_2H_4O_2^+$ | 37.9 | 0.97 |
| 71 | $C_3H_7CO^+$ | 1.02 | 0.60 |
| 72 | | 0.08 | 0.04 |
| 73 | $C_2H_4CO_2H^+$ | 10.8 | 8.62 |
| 74 | | 0.54 | 0.43 |
| 87 | $C_3H_6CO_2H^+$ | 0.66 | 0.28 |
| 88 | $C_3H_7CO_2H^+$ | **1.82** | **2.76** |

* Ion abundance in % of total ionization

alkyl group or from the carboxyl group.

In the spectrum of HCOOH the relative intensity of the $CHO_2^+$ ion ($m/e=45$) is 73.9. In the spectrum of the deutero-isomer DCOOH, the intensities of $CO_2H^+$ ($m/e=45$) and $DCO_2^+$ ($m/e=46$) are 35.7 and 41.0 respectively. Therefore, the ions at the mass $(M-1)$ in the spectrum of HCOOH must be $HCO_2^+$ and $CO_2H^+$, occurring in the same abundance.

In the spectrum of $CH_3COOH$ the ion at the mass $(M-1)$ was not observed. In the spectra of the other acids, $C_2H_3O_2^+$ ($m/e=59$) was never observed. This ion may be unstable, or the $C_2H_3O_2$ fragment may have the negative charge more stably.[*1]

In the mass spectrum of $C_2H_5COOH$ the relative intensity of $C_3H_5O_2^+$ ($m/e=73$) is 59.4. The mass spectrum of the deutero-isomer $C_2H_5COOD$ shows that the corresponding intensity has moved to mass 74. Therefore, $C_3H_5O_2^+$ must be $C_2H_4CO_2H^+$.

The ion of this type was found in the mass spectrum of $C_3H_7COOH$. The occurrence of the metastable ions provides further information concerning the process leading to this ion. In the mass spectra of both $n$-$C_3H_7COOH$ and $i$-$C_3H_7COOH$ the metastable ion peak of mass 60.6 was found. In the mass spectrum of the deuterated-compound $n$-$C_3H_7COOD$, this metastable ion peak shifted to mass 61.5. The transitions consistent with these masses are:

$$C_3H_7CO_2H^+(88) \longrightarrow C_2H_4CO_2H^+(73) + CH_3(15)$$

$$m^* = \frac{(73)^2}{88} = 60.6,$$

$$C_3H_7CO_2D^+(89) \longrightarrow C_2H_4CO_2D(74) + CH_3(15)$$

$$m^* = \frac{(74)^2}{89} = 61.5.$$

In the mass spectrum of $C_3H_7COOH$, the relative intensity of $C_4H_7O_2^+$ ($m/e=87$) is 36.2. In the mass spectrum $C_3H_7COOD$, the corresponding ion intensity moved to mass 88. In the same way as in $C_2H_5COOH$, the $C_4H_7O_2^+$ ion must have the structure of $C_3H_6CO_2H^+$.

From the above discussion, we are led to the conclusion that, except for HCOOH and $CH_3CO_2H$, the $C_{n+1}H_{2n+1}O_2^+$ ions in the mass spectrum of $C_nH_{2n+1}CO_2H$ have the $C_nH_{2n}CO_2H^+$ structure.

**Fragment Ion R-C≡O⁺.** It is well known that the carbonyl compounds produce very stable ions, R-C≡O⁺, the oxygen atom of which has a triple bond.[6] In the spectra of the acids these ions occur in appreciable amounts. The H-C≡O⁺ ion in the mass spectra of HCOOH will be discussed later.

Although, in the mass spectrum of $CH_3$-

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[*1] The ion at mass 59 has been measured appreciably on the background of the negative ion mass spectra. This ion is thought to come from the oil of the diffusion pumps. *Cf.* our unpublished data.

6) I. Kanomata, This Bulletin, **34**, 1964 (1961).

COOH, the $CH_3$-C≡$O^+$ ion peak is the highest of all, neither the $C_2H_5$-C≡$O^+$ from $C_2H_5CO_2H^+$ nor the $C_3H_7$-C≡$O^+$ from $C_3H_7CO_2H^+$ is so high as expected. This may be partly because $C_2H_5$-C≡$O^+$ and $C_3H_7$-C≡$O^+$ are not stable, further decomposing to $C_3H_7^+$, $C_2H_5^+$, $CO^+$, *etc.*

**Rearrangement Ion $CH_2OH^+$.** It is well known that, in the mass spectra of many esters,[7] the rearrangement ion $CH_3O^+$ (mass 31), with the $CH_2OH^+$ structure, occurs as the most abundant ion. In the spectrum of $CH_3COOH$, the relative intensity of the $CH_3O^+$ ion (mass 31) is 2.53. In view of the $CH_3COOH$ structure, it seemed of interest to investigate closely the process responsible for the production of this ion.

The spectra of the three deutero-isomers $CH_3COOD$, $CD_3COOH$, and $CD_3COOD$ show that the corresponding ion intensity has moved to masses 32, 33, and 34 respectively. These ions must be $CH_2OD^+$, $CD_2OH^+$, and $CD_2OD^+$ respectively. The appearance potentials of all these ions are the same within the limits of experimental error. These ions proved to be primary ions judging from the effect of the repeller voltage and the sample pressure on the intensities of these ions.

In order to obtain further information on the process producing this type of ion, measurements were made with $^{18}O$. The oxygen-18-labeled acetic acid was synthesized by the reaction of $H_2{}^{18}O$ (oxygen-18 atomic % 7) with $CH_3COCl$.

In the spectrum of the oxygen-18-labeled isomer, half of the intensity of $CH_2OH^+$ ion has moved to mass 33. This shows that the oxygen atom in this ion may, with equal probability, be either of the two oxygen atoms in $CH_3COOH$. The reason for this may be either that the two oxygen atoms in the molecular ion are equivalent due to resonance, or that it is essentially impossible to replace the hydroxylic oxygen atom selectively with oxygen-18.

Also, in the spectra of $C_2H_5COOH$ and *n*-$C_3H_7COOH$, the $CH_3O^+$ (mass 31) occurs in an appreciable abundance. A comparison of the mass spectra of $C_2H_5COOH$ and *n*-$C_3H_7COOH$ with those of $C_2H_5COOD$ and *n*-$C_3H_7COOD$ respectively shows that the $CH_3O^+$ ion must have the $CH_2OH^+$ structure.

To summarize, the $CH_3O^+$ ion (mass 31) must be $CH_2OH^+$, two of whose hydrogens come from the alkyl group and the rest, from the carboxyl group. The origin of the carbon and the oxygen atoms can not be determined. An experiment with $^{13}C$ is desirable.

**Rearrangement Ion and Fragment Ion $CHO^+$.** The spectrum of HCOOH shows that the $CHO^+$ ion (mass 29) occurs with the highest abundance except for the parent ion. This ion also occurs in the spectra of $CH_3COOH$, $C_2H_5COOH$, and $C_3H_7COOH$. In order to determine the mechanism of producing this ion, the same method was used as for the $CH_2OH^+$ ion.

In the case of HCOOH, the spectra of HCOOD and DCOOH were compared with that of HCOOH. The relative intensity of the $HCO^+$ ion (mass 29) is 77 in the mass spectrum of HCOOH. In the spectrum of DCOOD, the corresponding ion, whose intensity is 68.6, has moved to mass 30. On the other hand, in DCOOH, two ions, $COH^+$ and $DCO^+$, occurred; their relative intensities were 14.6 and 66.7 respectively. The reason why the intensity of the $COH^+$ is weaker than that of $DCO^+$ may be that, while $DCO^+$ is formed by a one-bond fission, the formation of $COH^+$ requires the fission of two bonds. In addition, $DCO^+$ has a stable structure, D-C≡$O^+$, which is well known in carbonyl compounds. From these facts it may be supposed that two structures, H-C≡$O^+$ and C-$OH^+$, contribute to the mass 29.

Also, in the spectrum of $CH_3COOH$, the $CHO^+$ ion (mass 29) occurs with a relative intensity of 11.8. In the spectrum of $CD_3COOH$ the corresponding ion must be considered to be $CDO^+$ and $CHO^+$, whose intensities were 6.44 and 3.17 respectively. The deuterium of $CDO^+$ must have come from the methyl group of the acetic acid, so this ion is the rearrangement ion. In $CH_3COOD$, $CDO^+$ and $CHO^+$ were found also, indicating that rearrangement had occurred. Their intensities were 5.33 and 7.78 respectively. Of course, the appearance potentials of these ions were the same within the limits of experimental error, and the examination of the effect of the repeller voltage and the pressure shows that these ions are primary ions.

From the mass spectrum of acetic acid containing oxygen-18, the origin of the oxygen atom in this ion was not determined unequivocally, as in the case of $CH_2OH^+$.

We can conclude that, in the spectrum of $CH_3COOH$, $CHO^+$ (mass 29) consists of the simple fragment ion $COH^+$ and the rearrangement ion $HCO^+$. The hydrogen of the former comes from the carboxyl group, and that of the latter, from the methyl group. The abundance of the simple fragment ion is

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7) E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962).

TABLE 5. THE RELATIVE INTENSITY* OF REARRANGEMENT IONS TO THE LOWER ACID

| | $M-CH_2$ | | $M-C_2H_4$ | | $M-C_3H_6$ | |
|---|---|---|---|---|---|---|
| | Ion | Intensity | Ion | Intensity | Ion | Intensity |
| $CH_3COOH$ | $CH_2O_2^+$ | 0.4—0.5 | —— | —— | —— | —— |
| $C_2H_5COOH$ | $C_2H_4O_2^+$ | 0.32 | $CH_2O_2^+$ | 9.0 | —— | —— |
| $n$-$C_3H_7COOH$ | $C_3H_6O_2^+$ | 11 | $C_2H_4O_2^+$ | 2080 | $CH_2O_2^+$ | 11.5 |
| $i$-$C_3H_7COOH$ | $C_3H_6O_3^+$ | 6 | $C_2H_4O_2^+$ | 35 | $CH_2O_2^+$ | 5.3 |

* The relative abundance with each parent ion peak being taken as 100 %

equivalent to, or a little less than, that of the rearrangement ion. In the spectra of $C_2H_5COOH$ and $C_3H_7COOH$, the mass-29 ion also occurs, but we could not determine the origin of this ion because of the presence of the $C_2H_5^+$ ion, which gives a strong peak at the same mass.

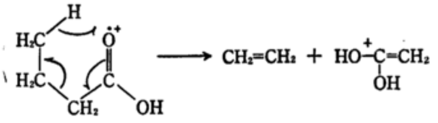
**Rearrangement Ion $C_nH_{2n}O_2^+$.** The spectrum of $n$-$C_3H_7COOH$ shows that $C_2H_4O_2^+$ occurs very abundantly. This ion has the same mass as the acetic acid molecular ion, so it is considered to be a rearrangement ion. Other ions of the same type as this are also observed. The relative intensities of these ions; $CH_2O_2^+$, $C_2H_4O_2^+$, and $C_3H_6O_2^+$, are given in Table 5. Except in the case of $CH_3COOH$, many ions of this type produced in the acids. It is of interest to discuss the mechanism for producing these rearrangement ions. As for $C_2H_4O_2^+$, in the spectra of $n$-$C_3H_7COOH$ a metastable ion peak of mass 40.9 was observed. The transition consistent with this mass is:

$$C_3H_7COOH^+(88) \longrightarrow C_2H_4O_2^+(60) + C_2H_4(28)$$

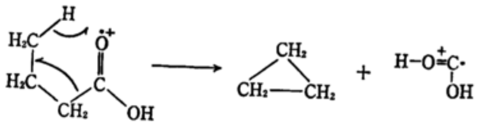
$$m^* = \frac{(60)^2}{(88)} = 40.9$$

The neutral fragment $C_2H_4$ has the stable structure[8] $CH_2{=}CH_2$. The high intensity of the $C_2H_4O_2^+$ ion may be due to this stability.

The mechanism for this rearrangement ion may be speculated to be as follows:



and for $CH_2O_2^+$



The ring-formation mechanisms shown above are well-known in the electron impact of organic compounds.

In the mass spectra of $C_2H_5COOH$ and $i$-$C_3H_7COOH$, no such rearrangement mechanism can be expected in view of the orientation and steric hindrance. In spite of this, the mass spectra of $C_2H_5COOH$ and $i$-$C_3H_7COOH$ show that $CH_2O_2^+$ and $C_2H_4O_2^+$ occur in an appreciable abundance. Therefore, for these ions we must consider other mechanisms.

**Ion-molecule Reaction "Protonated Molecular Ions"** The mass spectra of acids show ions of appreciable intensities whose masses are larger than that of the molecular ion by one mass.

Sharkey[9] and Kebarle[7] have pointed out

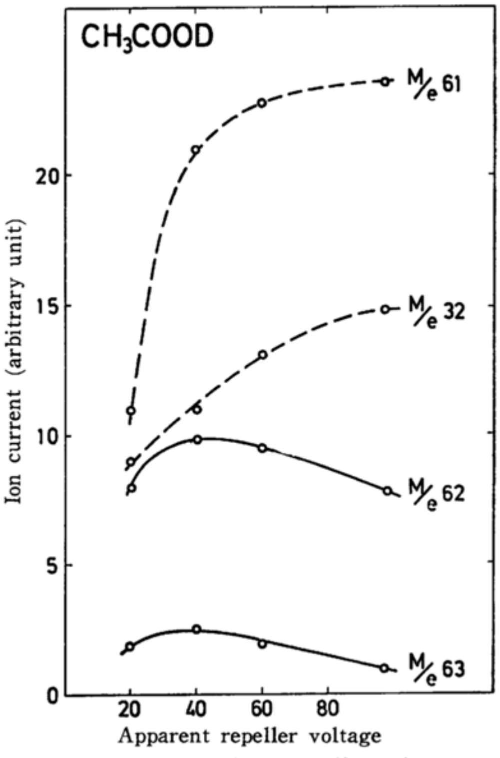


Fig. 1. The effect of the repeller voltage on the ion intensity

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[8] F. W. McLafferty "Mass Spectrometry of Organic Ions," Academic Press, New York and London (1963).

[9] A.G. Sharkey, Jr., J.L. Shultz and R.A. Friedel, *Anal. Chem.*, **31**, 87 (1959).

that analogous ions occur as rearrangement ions in appreciable intensities in the mass spectra of most aliphatic esters.

The mass spectra of the deuterated acids show that some of the corresponding ions have moved to a mass larger than that of molecular ions by one mass or two—such as the ion of mass 50 in DCOOD(48), that of mass 66 in $CD_3COOD$, and those of mass 64 and mass 65 in $CD_3COOH$. Those ions were observed in appreciable amounts when the sample pressure in the ionization chamber was higher than $10^{-6}$ mmHg. The intensities of these ions were in proportion to the square of the sample pressure.

Generally, the intensity of the primary ion increases as the repeller voltage increases (*cf.* Fig. 1). However, the intensities of these protonated molecular ions decreased as the repeller voltage increased. These properties are those of secondary or higher-order ions. Therefore, these ions may be considered to be produced by the ion-molecule reaction.

## Summary

The mass spectra of several carboxylic acids, *i.e.*, HCOOH, DCOOH, DCOOD, $CH_3COOH$, $CH_3COOD$, $CD_3COOH$, $CD_3COOD$, $C_2H_5COOH$, $C_2H_5COOD$, $n$-$C_3H_7COOH$, $i$-$C_3H_7COOH$, and $n$-$C_3H_7COOD$, were examined. The ions of the mass spectra were then classified into the simple fragment ions, the rearrangement ions, and the ion-molecule reaction ions.

The main fragment ions were $R^+$, $RCO^+$, and $CO_2H^+$. One of the most interesting fragment ions was $C_nH_{2n}CO_2H^+$ ($n \geqq 2$), which was found to occur upon the loss of one hydrogen atom from the alkyl group. $CH_2CO_2H^+$ was not observed in any case.

Among the rearrangement ions, $CH_3O^+$ ($m/e=31$) was of special interest; two of its hydrogen atoms were proved to come from the alkyl group, and the rest, from the carboxyl group. From this, we concluded the structure to be $CH_2OH^+$.

About half of $CHO^+$ ($m/e=29$) was also proved to be a fragment ion whose hydrogen atom came from the alkyl group, while the other half was the simple fragment ion $COH^+$.

In addition, we observed protonated molecular ions which had been produced by the ion-molecule reactions.