Mass Spectrometric Studies of Some Carboxylic Acid Dimers Produced by a Nozzle Beam: HCO_2H, CH_3CO_2H, $C_2H_5CO_2H$, and n-$C_3H_7CO_2H$

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Characteristic ions $(M+1)^+$ and $(M+45)^+$, assigned to be the protonated monomer ion MH^+ and $(M\cdot CO_2H)^+$ respectively, have been detected in the mass spectrometric measurements of the dimer molecules M_2 and the higher clusters M_n of some carboxylic acids produced in their nozzle beams. It has been shown from the dependences of their relative intensities on the stagnation conditions that these ions are mainly formed through the fragmentation of the dimer ions. The MH^+ ion plays the most important role in these fragmentation processes of the dimers, while no dimer ion M_2^+ was observed. These results are discussed in terms of the enthalpy changes for the unimolecular decomposition reactions of M_2^+.

Protonated cluster ions $M_{n-1}H^+$ as well as $M_n^+(n\geq 2)$ have been observed in some hydrogeneous molecules, such as H_2O,[1] NH_3,[2] hydrogen halides,[3] and alcohols,[4] through electron or photon impact ionization of their cluster molecules produced using supersonic nozzle beams. The reactions to form these protonated ions have been explained by the unimolecular decomposition reaction of M_n^+.[5] However the detailed mechanisms vary with different molecules[3b] and the degree of their association,[5] and also depend on the impact energy of the electron or photon.[2]

A variety of new fragment ions other than the protonated ones have been observed in the ionization of van der Waals clusters of butane[6] and ethylene.[7] Some of them have been regarded as the key species in the ion-molecule reactions. These findings on the electron or photon impact induced fragmentations of the weakly bound clusters have enabled us to discuss the mechanisms of ion-molecule reactions[5,7] and the solvation of ions in the gas phase[1,2,5] from some different viewpoints. So it is of great interest to make clear such fragmentation processes of these cluster molecules and ions.

In this paper we report several common features observed in the electron impact induced fragmentations of the dimers of some aliphatic carboxylic acids produced in their nozzle beams. These acids have been well known to form a stable cyclic dimer through intermolecular hydrogen bonds even in the usual vapor phase.[8]

Experimental

The nozzle beam system in this experiment is shown in Fig. 1. A 60° conical nozzle source which has a 0.015 cm diameter orifice at the apex of this cone was used. The nozzle was fastened to the reservoir with a thin teflon gasket. No skimmer was used. Some copper plates with a circular opening of 1 cm diameter for the beam, cooled by liquid nitrogen, were used as a cryopump. This nozzle source has previously been employed in the optical measurements of naphthalene beams and has been compared with other nozzles having different shapes and orifice diameters.[9] Using this source, we could observe reasonable cooling effects and mach numbers, accompanied by the adiabatic expansion of pure naphthalene vapor.

The temperature T_0 at the nozzle throat was measured with a Fe-Constantan thermocouple mounted on the external face of the nozzle plate. The stagnation pressure P_0 behind the nozzle was determined by adjusting the temperature of the liquid carboxylic acid in the reservoir F according to the published data of vapor pressure.[10] Within the range of T_0 and P_0 in this work, the dimer fraction evaluated from the observed equilibrium constant[11] could be covered over the wide range from 0.1 to 0.6 in the stagnation conditions.

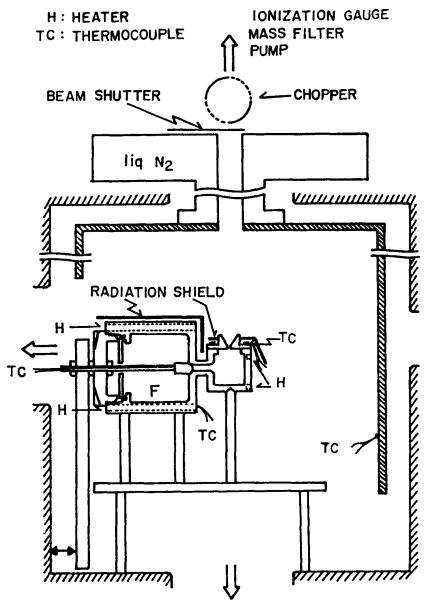

Fig. 1. Experimental apparatus for the measurements of mass spectra in the nozzle beam.

The beams were mechanically modulated at a frequency of 20—100 Hz and then directed into the ionizer of a quadrupole mass filter (Nichiden Varian model 531) equipped with a Bayard-Alpert gauge-type ionizer. Most measurements were carried out at the electron energy of 30 eV and the emission current of 1.0 mA. No marked dependences of mass spectra on the electron energy were observed in the range of 20 eV to 100 eV. To get the corrected intensities for the relative sensitivity of the secondary electron multiplier, the observed intensities of the ions with $m/e\geq 28$ were multiplied by the dimensionless factor $(m/28)^{1/2}$.[12]

Commercially available extra pure CH_3CO_2H, $C_2H_5CO_2H$, n-$C_3H_7CO_2H$, and HCO_2H were used after a distillation *in vacuo*. Deuterated CH_3CO_2D and CD_3CO_2D enriched more than 97—98% were commercially supplied.

Results and Discussion

Mass spectra of the four carboxylic acids RCO_2H (R=H, CH_3, C_2H_5, and n-C_3H_7) were measured in the nozzle beams as a function of T_0 and P_0 in stagnation conditions in the mass range from 1 up to 310. Two peaks, corresponding to the mass numbers of $(M+1)^+$ and $(M+45)^+$, were observed for all the acids, in addition to the previously reported mass spectrum of each monomer acid (M).[13]

Table 1. Mass shifts of MH^+ and $(M\cdot CO_2H)^+$ fragment ions in the deuterated acetic acid beams

Beam		CH_3CO_2H	CH_3CO_2D	CD_3CO_2D
T_0/K		374	369	381
P_0/Torr		100	120	160
Ion	*m/e*	Relative intensity		
M^+ and MH^+	60	1.0	0.028	
	61	0.35	1.0	
	62	0.008	0.044	
	63		0.39	0.025
	64		0.009	1.0
	65			0.025
	66			0.40
	67			0.010
$(M\cdot CH_3CO)^+$	103	0.0007		
and	104		0.0005	
$(M\cdot CO_2H)^+$	105	0.0048	0.0001	
	106	0.0002		
	107		0.0058	
	108		0.0002	
	109		0.0001	0.0002
	110			0.0054
	111			0.0002

In order to assign these ions, mass spectra were measured in the nozzle beams of deuterated acetic acid, CD_3CO_2D and CH_3CO_2D. According to the results of the corresponding mass shift, these ions were assigned to the protonated monomer ion MH^+ and the adduct ion $(M\cdot CO_2H)^+$ ions, respectively. Table 1 summarizes the results of the mass shift and their relative intensities around the mass ranges of MH^+ and $(M\cdot CO_2H)^+$ ions in CH_3CO_2H, CH_3CO_2D, and CD_3CO_2D beams.

Figure 2 shows the temperature dependences of the relative intensities of MH^+ and $(M\cdot CO_2H)^+$ ions. It is clearly shown in the figure that MH^+ ion as well as $(M\cdot CO_2H)^+$ ion increases with decreasing T_0. From Fig. 2 the intensity ratios between MH^+ and $(M\cdot CO_2H)^+$ ions were obtained to be about 100, 2000, and 5000 for CH_3CO_2H, $C_2H_5CO_2H$, and n-$C_3H_7CO_2H$, respectively. In the case of the formic acid beam, it is difficult to obtain quantitative results for a long period of experimental runs because of a gradual corrosive reaction inside the nozzle source. But the results were qualtatively in accord with those obtained in the other acids and the intensity ratio $I_{MH^+}/I_{(M\cdot CO_2H)^+}$ was about 500.

Similar behaviors were observed in their pressure P_0 dependences. For acetic acid, this intensity ratio I_{61}/I_{105} was found to be nearly constant or slightly increasing with increasing P_0 as shown in Fig. 3.

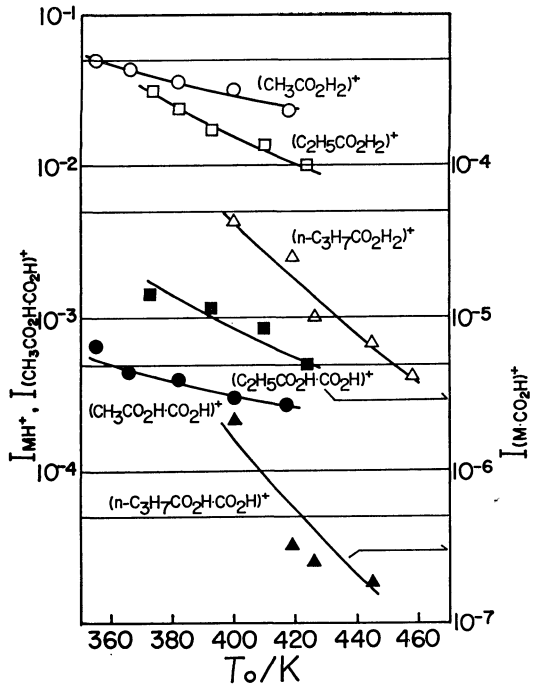

Fig. 2. Temperature dependences of the relative intensities of MH^+ and $(M\cdot CO_2H)^+$, I_{MH^+} and $I_{(M\cdot CO_2H)^+}$, normalized to the sum of each ion intensity, in CH_3CO_2H, $C_2H_5CO_2H$, and n-$C_3H_7CO_2H$ nozzle beams. The stagnation pressures were kept at about 140, 100, and 110 Torr, respectively. Open and full symbols represent MH^+ and $(M\cdot CO_2H)^+$, respectively. (1 Torr=133.322 Pa)

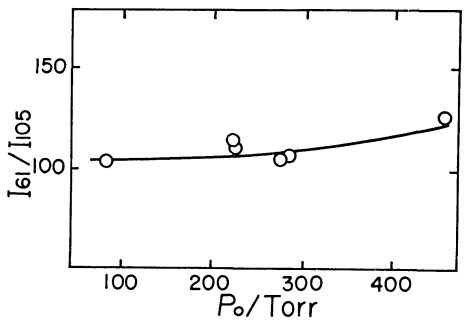

Fig. 3. Pressure dependence of intensity ratio between MH^+ and $(M\cdot CO_2H)^+$, I_{61}/I_{105}, at T_0=410 K for acetic acid. (1 Torr=133.322 Pa)

Other fragment ions than MH^+ and $(M\cdot CO_2H)^+$ did not show such marked T_0 dependences within the range of T_0 in this study. Only RCO^+ ions (R=CH_3, C_2H_5, and n-C_3H_7) were found to slightly increase with decreasing T_0. Some portion of these acyl ion intensities might be ascribed to the dehydration reaction of MH^+ ion with excess energy.[14]

From such similar dependences of MH^+ and $(M\cdot CO_2H)^+$ ions on the stagnation conditions, both ions are considered to be formed by the electron impact fragmentation of the same molecular species, namely

the cluster molecules $M_n(n\geq 2)$, produced in their nozzle beams. However no traces of the dimer ion M_2^+ or of $M_n^+(n=3,4,5)$ were observed within the limit of the detection sensitivity, 10^{-6} of M^+. For these carboxylic acids, M_2H^+ ions with very weak intensities (10^{-4}—10^{-6} of M^+) were observed. But we could not definitely ascribe them to the fragmentation from $M_n^+(n\geq 3)$ because of the nearly equal contribution of ion-molecule addition reaction which presumably occurred in the ionizer. Only a small contribution of the higher clusters is suggested by the slight increase of MH^+ ion relative to $(M\cdot CO_2H)^+$ when P_o increases, as can be seen in Fig. 3. This could be explained by the result that MH^+ fragment, not $M_{n-1}H^+$, is predominantly formed in the fragmentation processes of the parent cluster ion M_n^+.[15] Another reason for such an apparent small contribution of the higher clusters to these mass spectra is that some portion of the higher clusters and the dimer could be decomposed down to the dimer or the monomer on the electrode surface of the ionizer.

Thus we can conclude in this study that the observed MH^+ and also $(M\cdot CO_2H)^+$ ions are mainly formed through spontaneous decomposition of the dimer ions M_2^+, which can initially be generated in their vibrationally or electronically excited states by the electron impacts at 20—100 eV. The fragmentation to the protonated monomer ion is characteristic for these carboxylic acid dimer ions. These fragmentation behaviors resemble the case in $(HF)_2$,[3a] but are quite different from those in $(CH_3OH)_2$ and $(CH_3NH_2)_2$, where the intensity ratios $I_{M_2^+}/I_{MH^+}$ have been observed to be about 0.5.[4] Such differences can qualitatively be interpreted from some thermodynamical considerations about reaction (1):

$$M_2^+ \longrightarrow NH^+ + (M\text{-}H). \quad (1)$$

The enthalpy change ΔH_2 for this unimolecular decomposition reaction can be estimated using the binding energy of M_2^+ ion, $-\Delta H_s(M_2^+)$, or the solvation energy of MH^+ by M, $-\Delta H_s(M_2H^+)$, and several thermodynamical parameters for a monomer molecule. The values of $\Delta H_s(M_2^+)$ have recently been obtained from the ionization potential measurements of the dimers by means of photoionization ($(H_2O)_2$[1c] and $(NH_3)_2$[2b]) and photoelectron spectroscopy ($(CH_3CO_2H)_2$[16]). The calculated values of ΔH_2 are shown in Table 2. It is shown that $(HF)_2^+$ ion spontaneously decomposes into H_2F^+ and F, while the decompositions of $(H_2O)_2^+$, $(NH_3)_2^+$, and $(CH_3OH)_2^+$ are rather endothermic. These trends are consistent with the observations of their M_2^+ ions in the eletron or photon impact ionization.[1-5] The decomposition of acetic acid dimer ion seems to be more endothermic, although this endothermicity may be reduced by the contribution of the entropy terms $T\Delta S_2$ for this reaction (1).[17] Nevertheless, no dimer ions of acetic acid nor of the other carboxylic acids were observed in this study. This fact suggests that there exist very effective channels to promote proton transfer along the hydrogen bond in the excited states of the dimer ions which strongly couple with MH^+ ion formation. At the present stage we can't explore these channels further, because we lack the experimental evidence about the state selected ionization or fragmentation. But these channels must greatly depend upon the cyclic structure of the dimer ion, which includes two hydrogen bonds.

Furthermore, we note that the dominant fragmentation is to $(M\cdot CO_2H)^+$ rather than to the $(M\cdot RCO)^+$ in the dimer ions. Indeed the observed intensity of $(M\cdot CH_3CO)^+$ ion for acetic acid was so weak (0.1 of $(M\cdot CO_2H)^+$) that the origins of this adduct ion were undecided for the same reasons as in M_2H^+. For propionic and butyric acids, no $(M\cdot RCO)^+$ ions could be detected. This trend contrasts with the observations in ion-molecule reactions, in which the $(M\cdot RCO)^+$ adduct ions have often been observed.[14,18]

Concerning $(M\cdot CO_2H)^+$ ions, the hydrogen bonded cyclic ion $(HCO_2H\cdot CO_2H)^+$ has been theoretically predicted from the β^- decay processes of monotritiated formic acid dimer ($HCO_2H\cdot {}^3HCO_2H$).[19] It has been shown that in this ion the proton transfer occurs along the hydrogen bond with no activation energy to produce $HCO_2H_2^+$ and CO_2. This process could not be confirmed

Table 2. Estimated enthalpy changes ΔH_2 at 298 K for the reaction $M_2^+ \longrightarrow MH^+ + (M\text{-}H)$ (in kcal/mol) (1 kcal=4.184 kJ)

	$(H_2O)_2$	$(NH_3)_2$	$(CH_3OH)_2$	$(CH_3CO_2H)_2$	$(HF)_2$
ΔH_2[a]	10 (6)[b]	2 (2—11)[b]	(15)[b]	26—29	(−7)[b]
D(H-XY)[c]	120[h]	107[j]	101[k]	110—112[n]	136[q]
ΔH_I(M)[d]	291[h]	235[j]	251[l]	246—247[o,p]	369[q]
ΔH_{PA}(M)[e]	169[i]	202[i]	182[i]	187[p]	112[r]
$-\Delta H_s(M_2^+)$[f]	36[h]	18[j]		36[p]	
$-\Delta H_s(M_2H^+)$[g]	(32)[i]	(18—27)[j]	(33)[m]		(25)[q]

a) $\Delta H_2=D(H-XY)+I(H-H^+)-\Delta H_I(M)-\Delta H_{PA}(M)-\Delta H_s(M_2^+)$(or $\Delta H_s(M_2H^+)$), where $I(H-H^+)=314$ kcal/mol. b) The ΔH_2 values in parentheses are estimated by assuming that $\Delta H_s(M_2^+)$ can be approximated to $\Delta H_s(M_2H^+)$.[5] c) Bond dissociation energy of the H–X bond (X=O, N, or F). d) Ionization potential of M. e) Proton affinity of M. f) Binding energy of M_2^+, where the values of $\Delta H_s(M_2^+)$ at 298 K are nearly equal to those at 0 K within the experimental errors in the determinations of $\Delta H_s(M_2^+)$ (a few kcal/mol). g) Solvation energy of MH^+ by M. h) Ref. 1c. i) P. Kebarle, *Ann. Rev. Phys. Chem.*, **28**, 445 (1977). j) Ref. 2b. k) K. J. Reed and J. I. Brauman, *J. Am. Chem. Soc.*, **97**, 1625 (1975). l) F. M. Benoit and A. G. Harrison, *J. Am. Chem. Soc.*, **99**, 3980 (1977). m) E.P. Grimsrud and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 7939 (1973). n) K. W. Egger and A.T. Cocks, *Helv. Chim. Acta*, **56**, 1516 (1973); J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). o) D. J. Knowles and A. C. Nicholson, *J. Chem. Phys.*, **60**, 1180 (1974). p) Ref. 16. q) Ref. 3b. r) M.S. Foster and J. K. Beauchamp, *Inorg. Chem.*, **14**, 1229 (1975).

as the main channel of MH^+ ion formation in the present study, but our results suggest that the $(M\cdot CO_2H)^+$ ions are stable species.

Another point shown in this work is that the transferable proton in an M_2^+ ion to yield MH^+ fragment ion is the hydroxyl proton, not the alkyl ones. The proofs are given by comparing the amounts of $CH_3CO_2DH^+$ ion in the CH_3CO_2D beam. The relative intensity of $CH_3CO_2DH^+$ ion ($m/e=62$) to M^+ ($m/e=61$) was obtained to be 0.044 in Table 1. This value never exceeds the value estimated from the natural abundances of the isotopes (0.024) and the contribution of $CH_3CO_2DH^+$ ion produced from an impurity of CH_3CO_2H (0.025). Thus, no proton transfer can occur from those of acetyl group to the other M in a dimer ion in the fragmentation processes from the M_2^+. This result does not contradict the fact that $(M\cdot CH_3CO)^+$ ion has rarely been observed *via* fragmentation of M_2^+ ion, as mentioned above.

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References

1) a) J. Fricke, W. M. Jackson, and W. L. Fite, *J. Chem. Phys.*, **57**, 580 (1972); b) T. R. Dyke and J. S. Muenter, *ibid.*, **57**, 5011 (1972); c) C. Y. Ng, D. J. Trevor, P. W. Tiedemann, S. T. Ceyer, P. L. Kronebusch, B. H. Mahan, and Y. T. Lee, *ibid.*, **67**, 4235 (1977).

2) a) J. A. Odutola, T. R. Dyke, B. J. Howard, and J. S. Muenter, *J. Chem. Phys.*, **70**, 4884 (1979); b) S. T. Ceyer, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *ibid.*, **70**, 14 (1979).

3) a) T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, **56**, 2442 (1972); b) P. W. Tiedemann, S. L. Anderson, S. T. Ceyer, T. Hirooka, C. Y. Ng, B. H. Mahan, and Y. T. Lee, *ibid.*, **71**, 605 (1979).

4) J. A. Odutola, R. Viswanathan, and T. R. Dyke, *J. Am. Chem. Soc.*, **101**, 4787 (1979).

5) C. E. Klots and R. N. Compton, *J. Chem. Phys.*, **69**, 1644 (1978).

6) T. A. Milne, J. E. Beachey, and F. T. Greene, *J. Chem. Phys.*, **56**, 3007 (1972).

7) S. T. Ceyer, P. W. Tiedemann, C. Y. Ng, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 2138 (1979).

8) G. Allen and E. F. Caldin, *Quart. Rev.*, **7**, 255 (1953); P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).

9) K. Mawatari, H. Minami, Y. Mori, T. Kitagawa, and S. Nagahara, *Progress Report Studies of Atomic Collisions and Related Topics in Japan*, **3**, 96 (1977).

10) T. Boublik, V. Fried, and E. Hara, "The Vapour Pressure of Pure Substances," Elsevier, Amsterdam (1973).

11) CH_3CO_2H: J. R. Barton and C. C. Hsu, *J. Chem. Eng. Data*, **14**, 1841 (1969), $C_2H_5CO_2H$ and HCO_2H: M. D. Taylor and J. Bruton, *J. Am. Chem. Soc.*, **74**, 4151 (1952), n-$C_3H_7CO_2H$: R. E. Lundin, F. E. Harris, and L. K. Nash, *J. Am. Chem. Soc.*, **74**, 743 (1952).

12) J. Q. Searcy and J. B. Fenn, *J. Chem. Phys.*, **61**, 5282 (1974); sensitivity at $m/e\leq 28$ was regarded as constant.

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

14) G. I. Mackay, A. C. Hopkinson, and D. K. Bohme, *J. Am. Chem. Soc.*, **100**, 7460 (1978).

15) Y. Mori, T. Kitagawa, T. Yamamoto, and S. Nagahara, XIth International Conference on Physics of Electronic and Atomic Collisions, Kyoto, 1979, Abstr. 394.

16) K. Nomoto, Doctor thesis, Hokkaido University, Sapporo, 1978.

17) The largest term in $T\Delta S_2$ is given by $T\Delta S_s$ (M_2^+) for the reaction $M^+ + M \rightarrow M_2^+$. This contribution is estimated to be about -10 kcal/mol at 298 K, assuming that the entropy change ΔS_s (M_2^+) can be approximated by the entropy change for the neutral dimer formation of acetic acid. W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955).

18) J. Long and B. Munson, *J. Chem. Phys.*, **95**, 2427 (1973).

19) S. Hashimoto, S. Ikuta, and M. Imamura, *Chem. Phys. Lett.*, **62**, 567 (1979); S. Ikuta, S. Hashimoto, and M. Imamura, *Chem. Phys.*, **42**, 269 (1979).