

## Chapter 1

# The Structures of $\text{RCOO}^-$ and $\text{CH}_3\text{O}^-$ by Resonance Theory

## Abstract

The purpose of this chapter is to quantitatively find the cause for the elongation of the R-C bond in  $\text{R-COO}^-$  ( $\text{R} = \text{H}$ ,  $\text{CH}_3$ , and  $\text{C}_2\text{H}_5$ ) and the shortening of the C-O bond in  $\text{CH}_3\text{-O}^-$  upon deprotonation in the gas phase. These elongations and shortening result from the contributions of  $\text{R}^-\dots\text{CO}_2$  and  $\text{H}^-\dots\text{CH}_2=\text{O}$  as resonance structures to the systems. Because these resonance structures must make only a small contribution in the crystal, the R-C bond lengths of  $\text{R-COO}^-$  ( $\text{R} = \text{H}$  and  $\text{CH}_3$ ) in the crystal structure are shorter than those in the gas phase.

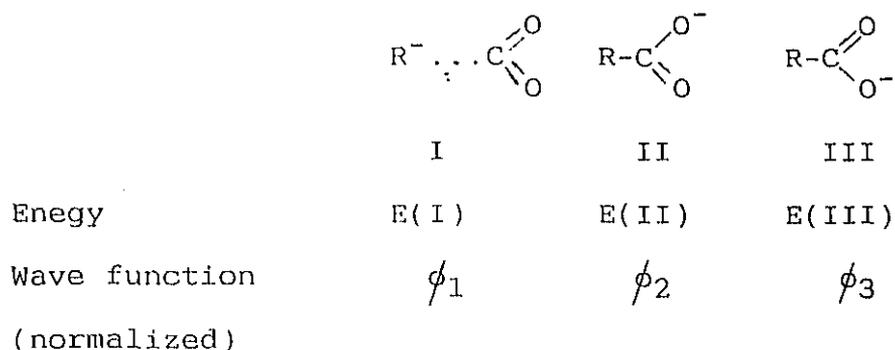
## 1. Introduction

Information on the structures of deprotonated species in the gas phase and in crystal structures is of interest from the point of view of understanding the geometries of deprotonated species in aqueous solution. However, Table 1 shows that the R-C bond lengths of R-COO<sup>-</sup> (R = H, CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) (Fig. 1) in the gas phase are longer than those of R-COOH (Fig.1) in the gas phase and those of R-COO<sup>-</sup> (R = H and CH<sub>3</sub>) in a crystal structure. By way of contrast, in the gas phase, the C-O bond length of CH<sub>3</sub>O<sup>-</sup> (Fig. 1) is shorter than that of CH<sub>3</sub>OH (Fig. 1, Table 1). Chandrasekhar et al. reported that the R-C bonds in R-C<sup>-</sup>=O are also longer than those in their neutral counterparts [1]. The cause of these elongations and shortening upon deprotonation in the gas phase has not been quantitatively examined. In addition, why the R-C bond lengths of R-COO<sup>-</sup> are longer in the gas phase than in the crystal structure has not been studied.

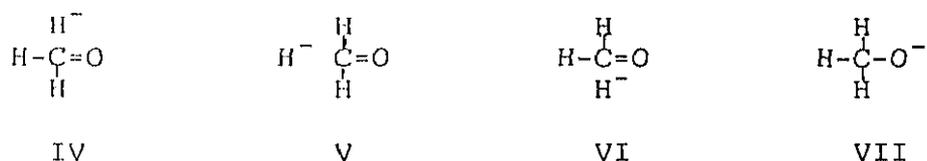
The purposes of this chapter are (1) to quantitatively find the cause for these elongations in R-COO<sup>-</sup> and shortening in CH<sub>3</sub>O<sup>-</sup> upon deprotonation in the gas phase, and (2) to discuss why the R-C bond lengths of R-COO<sup>-</sup> in the gas phase are longer than those in the crystal structure. I begin by quantitatively examining the characteristics of the structures of R-COO<sup>-</sup> and CH<sub>3</sub>O<sup>-</sup> in the gas phase.

## 2. Method

For  $R-COO^-$ , the only possible stable resonance structures are I, II and III:



The contributions of I, II and III to  $R-COO^-$  were analyzed by the method listed in Appendix I. Similarly, for  $CH_3O^-$ , the contributions of IV, V, VI and VII were analyzed:



All computations were carried out on HITAC M-680 and S-810/10 computers at the Computer Center of the Institute for Molecular Science (IMS). Programs Gaussian 80 [2], Gaussian 82 [3] and MOPAC (Version 3.0) [4] were used. The STO-3G [5], 3-21G [6], 6-31G(d) [7], 6-31+G [3], 6-31++G(d) [3], MP2/6-31G(d) [3] and MNDO [8] calculations were performed. For the MP2/6-31G(d) calculation, the full set of excitations was included. For the MNDO calculation including configuration interaction (CI), the two highest occupied molecular orbitals and the two lowest virtuals were included in the CI. The 6-31++G(d) basis set was likely to provide the most reliable results. Full geometry optimization with or without imposed symmetry constraints for all species including  $R-COO^-$ ,  $R-COOH$ ,  $CH_3O^-$ ,  $CH_3OH$ ,  $CH_2=O$ ,  $R^-$ ,  $CO_2$ ,

H<sub>2</sub>O and OH<sup>-</sup> was accomplished by the energy gradient methods at the programs. Several optimized structural parameters and energies were taken from [9-12]. The data relating to enthalpy in the gas phase were taken from [13-17].

### 3. Results

For R-COO<sup>-</sup> from Table 2 I can deduce the following: (1) from the relative enthalpies and energies of I, II and III in the gas phase, structure I is nearly as stable as II and III, (2) the three structures contribute nearly equally to the system, and (3) the total electron density on R and the Mulliken electron population between R-C expected for resonance among I, II and III agree with the optimized values by the molecular orbital methods (expect for the 6-31++G(d) calculations, and the Mulliken electron population in MNDO calculations; see Discussion).

For CH<sub>3</sub>O<sup>-</sup>, Table 3 shows that (1) the structures IV, V, VI and VII contribute to CH<sub>3</sub>O<sup>-</sup>, and (2) the total electron density on CH<sub>3</sub>, the Mulliken electron population between C-O and the C-O bond length expected for resonance among IV, V, VI and VII agree with the optimized values from the molecular orbital methods.

Table 2 and 3 show that (1) the relative energies of these resonance structures estimated by only the 6-31++G(d) basis set agree with the relative enthalpies, and (2) the amount of the contributions of each resonance structure to the systems estimated using the molecular orbital methods, especially the 6-31++G(d) basis set, nearly agrees with that estimated using

enthalpy.

#### 4. Discussion

The previous results suggested that (1) in the gas phase, the structure of  $R-COO^-$  is a resonance hybrid of I, II and III (although it is thought that the structure of  $CH_3COO^-$  in aqueous solution is a resonance hybrid of II and III [18]); (2) in the gas phase, the structure of  $CH_3O^-$  is a resonance hybrid of IV, V, VI and VII; (3) the structural changes with deprotonation in the gas phase result from distribution of the minus charge over all the deprotonated species; (4) the 6-31++G(d) basis set is reliable for the relative energies and the amount of the contribution of each resonance structure to the systems.

In the 6-31++G(d) calculations, the electron density on R (R = H) and the Mulliken electron population between R-C of  $R-COO^-$  expected from the resonance disagree with the optimized values. The breakdown of the Mulliken population analysis when diffuse functions are included in the basis set has been noted [19]. The disagreement must be due to this breakdown. (For example, the Mulliken electron population between C-C of  $CH_3COOH$  using the 6-31++G(d) basis set is -0.07.)

In MNDO calculations, the Mulliken electron population between R-C of  $R-COO^-$  expected from the resonance disagrees with the optimized values. The formula in MNDO method does not have overlap integrals. Thus, the Mulliken population analysis must be unsuitable for MNDO calculations. In fact, the Mulliken electron

populations in the MNDO calculations are far larger than those in ab initio.

Based on the previous suggestions, due to the contribution of resonance structure I to R-COO<sup>-</sup>, the R-C bond lengths of R-COO<sup>-</sup> are longer than those of R-COOH in the gas phase. (R<sup>-</sup>...COOH<sup>+</sup> may contribute to R-COOH just as the resonance structure I contributes to R-COO<sup>-</sup>. However, the contribution of R<sup>-</sup>...COOH<sup>+</sup> to R-COOH must be far smaller than that of resonance structure I because the electron density on R of R-COOH is far smaller than in R-COO<sup>-</sup>.) Due to the contributions of IV, V and VI to CH<sub>3</sub>O<sup>-</sup>, the C-O bond length of CH<sub>3</sub>O<sup>-</sup> is shorter than that of CH<sub>3</sub>OH in the gas phase.

Why is the C-C bond length (1.511, 1.52 Å) of CH<sub>3</sub>COO<sup>-</sup> in the crystal structure shorter than that in the gas phase (1.552 Å estimated using MP2/6-31++G(d,p)) ? The interaction between O<sup>-</sup> in II (and III) and cations (e.g. Na<sup>+</sup>) in the crystal structure stabilizes O<sup>-</sup>. As a result of the interaction, the resonance structures II and III must be much more stable than the resonance structure I in the crystal structure. Therefore, the C-C bond length of CH<sub>3</sub>COO<sup>-</sup> in the crystal structure is shorter than that in the gas phase. For a similar reason, the H-C bond length (0.997, 1.008, 1.100 Å) of HCOO<sup>-</sup> in the crystal structure is shorter than in the gas phase (1.125 Å estimated using MP2/6-31++G(d,p))

Briefly, because the minus charge of R-COO<sup>-</sup> in the crystal structure must be more localized than that in the gas phase, the structure of R-COO<sup>-</sup> in the crystal structure is different from

that in the gas phase.

## 5. Conclusions

(1) The structural changes with deprotonation in the gas phase result from distribution of the minus charge over all the deprotonated species.

(2) The bond elongations in  $R-COO^-$  and shortening in  $CH_3-O^-$  result from the contributions of  $R^-...CO_2$ , and  $H^-...CH_2=O$  respectively as resonance structures to the systems.

(3) Since the minus charge of the deprotonated species is more localized in a crystal structure than in the gas phase, the structures of the deprotonated species in the crystal structure are different from those in the gas phase.

(4) This idea may be applicable to other deprotonated species.

## Appendix I

### 1. $R-COO^-$

According to L. Pauling [20], the wave function for  $R-COO^- = C_1\phi_1 + C_2\phi_2 + C_3\phi_3$

$$\begin{pmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & H_{13} - S_{13}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E & H_{23} - S_{23}E \\ H_{31} - S_{31}E & H_{32} - S_{32}E & H_{33} - S_{33}E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

where  $E =$  the total energy of  $R-COO^-$

$$S_{ij} = \int \phi_i \phi_j \, d\tau,$$

$$H_{ij} = \int \phi_i H \phi_j d\tau,$$

and H is the Hamiltonian operator corresponding to the total energy of R-COO<sup>-</sup>.

To a reasonable degree of approximation

$$H_{11} \doteq E(I) \doteq E(R^-) + E(CO_2) \quad (1)$$

(E(X) denotes the energy of X.)

$$H_{22} \doteq H_{33} \doteq E(II) = E(R-COOH) - b \quad (2)$$

where  $b = E(R-COOH) - E(II) \doteq E(H_2O) - E(OH^-) \doteq E_D$

Evidently,

$$H_{23} = H_{32}; \quad S_{23} = S_{32}$$

$$H_{12} = H_{21} \doteq H_{13} = H_{31}; \quad S_{12} = S_{21} \doteq S_{13} = S_{31}$$

$$H_{22} \doteq H_{33}; \quad S_{11} = S_{22} = S_{33} = 1$$

Therefore,

$$\begin{pmatrix} E_1 & X & X \\ X & E_2 & Y \\ X & Y & E_2 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Thus,

$$E_1 C_1 + 2XC_2 = 0; \quad XC_1 + (E_2 + Y)C_2 = 0 \quad (3)$$

$$E_1 = H_{11} - S_{11}E \doteq E(I) - E > 0 \quad (\text{by (1)}) \quad (4)$$

$$E_2 = H_{22} - S_{22}E \doteq E(II) - E > 0 \quad (\text{by (2)}) \quad (5)$$

$$X = H_{12} - S_{12}E; \quad Y = H_{23} - S_{23}E \quad (6)$$

The following assumptions were adopted:

$$H_{12} = (H_{11} + H_{22})S_{12}/2; \quad H_{23} = (H_{22} + H_{33})S_{23}/2; \quad S_{12} = S_{23} < 0 \quad (7)$$

Because the total electron density on R and the Mulliken electron population between R-C expected for resonance agree with the optimized values from the molecular orbital methods, these

assumptions are acceptable.

From (1), (2), (3), (4), (5), (6) and (7), Eq. (8) is produced.

$$C_1:C_2 = 1:(kE_1 + ((kE_1)^2 + 8E_1E_2)^{1/2})/4E_2; \quad k = 2E_2/(E_1 + E_2) \quad (8)$$

Based on the following equations, the rate of contributions of I, II and III ( $con_i$ ;  $i = I, II, III, \dots, VII$ ) to  $R-COO^-$  can be estimated:

$$con_1 = C_1^2/(C_1^2 + 2C_2^2); \quad con_2 = con_3 = C_2^2/(C_1^2 + 2C_2^2) \quad (9)$$

The total electron density on R expected for resonance is  $con_1e_1 + 2con_2e_2$ , where  $e_i$  is the total electron density of structure  $i$  on R obtained using the Mulliken population analysis (for the MNDO calculation, the valence electron is considered, and the Mulliken population analysis is not used).

$e_1 \hat{=} \text{total electron density of } R^-$

$e_2 \hat{=} \text{total electron density of } R-COOH \text{ on } R$

The Mulliken electron population between R-C expected for resonance is  $con_1P_1 + 2con_2P_2$ , where  $P_i$  is the electron population between R-C of structure  $i$ .

$P_1 \hat{=} 0$

$P_2 \hat{=} \text{the electron population between R-C of } R-COOH$

## II. $CH_3O^-$

Similarly,

$E_4 \hat{=} E(H^-) + E(HCHO) - E(CH_3O^-)$

$E_7 \hat{=} E(CH_3OH) - b - E(CH_3O^-)$

where  $b = E(CH_3OH) - E(VII) \hat{=} E_b$

$$con_4 = C_4^2/(3C_4^2 + C_7^2); \quad con_7 = C_7^2/(3C_4^2 + C_7^2)$$

where

$$C_4:C_7 = 1:(-kE_7 + ((kE_7)^2 + 3E_4E_7)^{1/2}/E_7; \quad k = 2E_4/(E_4 + E_7)$$

The expected electron density on  $CH_3 = 3con_4e_4 + con_7e_7$  where

$e_4 \hat{=}$  total electron density of HCHO on  $CH_2 + 2(H^-)$

$e_7 \hat{=}$  total electron density of  $CH_3OH$  on  $CH_3$

The electron population between C-O =  $3con_4P_4 + con_7P_7$  where

$P_4 \hat{=}$  the electron population between C-O of HCHO

$P_7 \hat{=}$  the electron population between C-O of  $CH_3OH$

The expected C-O bond length =  $3con_4r_4 + con_7r_7$  where

$r_4 \hat{=}$  the C-O bond length of  $CH_2=O$

$r_7 \hat{=}$  the C-O bond length of  $CH_3OH$

For the experimental results, enthalpy was used instead of energy in the previous equations, and the C-O bond length of  $CH_2=O$  is taken from [21].

## Appendix II

Fully optimized structural parameters determined by ab initio calculations in this study are available from the author (free of charge).

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Table 1

Effect of deprotonation on C-X bond lengths (Å)

Species	X	Gas phase					Crystal	
		STO-3G	3-21G	6-31G(d) (+MP2)	6-31++G(d) (6-31+G)	MNDO (+CI)	Expt	Expt
H-COO <sup>-</sup>	H	1.152 <sup>b</sup>	1.125 <sup>b</sup>	1.127 <sup>b</sup>	1.117	1.142	-	1.008 <sup>f</sup>
				(1.142)		(1.145)		0.997 <sup>f</sup>
								1.100 <sup>g</sup>
H-COOH	H	1.104 <sup>a</sup>	1.074 <sup>a</sup>	1.083 <sup>a</sup>	1.083	1.105	1.097 <sup>e</sup>	1.02 <sup>h</sup>
				(1.096)		(1.104)		
CH <sub>3</sub> -COO <sup>-</sup>	C	1.631 <sup>b</sup>	1.576 <sup>b</sup>	1.554	1.547	1.553	-	1.511 <sup>i</sup>
						(1.560)		1.52 <sup>i</sup>
CH <sub>3</sub> -COOH	C	1.537 <sup>a</sup>	1.497 <sup>a</sup>	1.502	1.501	1.522	1.520 <sup>n</sup>	1.501 <sup>j</sup>
						(1.520)		1.482 <sup>k</sup>
								1.478 <sup>k</sup>
C <sub>2</sub> H <sub>5</sub> -COO <sup>-</sup>	C	1.640	1.572	-	(1.540)	1.568	-	-
						(1.566)		
C <sub>2</sub> H <sub>5</sub> -COOH	C	1.543	1.501	-	(1.496)	1.530	1.509 <sup>o</sup>	1.50 <sup>l</sup>
						(1.530)		
CH <sub>3</sub> -O <sup>-</sup>	O	1.368 <sup>a</sup>	1.348 <sup>c</sup>	1.311 <sup>d</sup>	1.329	1.288	-	-
				(1.323)		(1.281)		
CH <sub>3</sub> -OH	O	1.433 <sup>a</sup>	1.440 <sup>a</sup>	1.400 <sup>a</sup>	1.402	1.391	1.425 <sup>e</sup>	1.42 <sup>m</sup>
				(1.423)		(1.388)		

- <sup>a</sup>Ref. [8]
- <sup>b</sup>Ref. [10]
- <sup>c</sup>Ref. [11]
- <sup>d</sup>Ref. [12]
- <sup>e</sup>Ref. [21]
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Table 2

The contributions of  $R^{\ominus} \cdots CO_2$  (I) and  $R-C \begin{matrix} O^- \\ // \\ O \end{matrix}$  (II) as resonance structures to  $R-COO^{\ominus}$  in gas phase

R	Basis set	Relative energy (enthalpy) kcal/mol		Rate of contribution %		Electron density on R		Mulliken electron population between R-C	
		I	II or III	I	II or III	Opti- mized	Reso- nance	Opti- mized	Reso- nance
H	STO-3G	144	87	24	38	1.13	1.18	0.62	0.56
	3-21G	90	76	30	35	1.04	1.13	0.53	0.48
	6-31G(d)	79	65	29	35	1.07	1.17	0.76	0.58
	6-31++G(d)	52	50	33	34	1.01	1.21	0.89	0.53
	MP2/6-31G(d)	82	69	30	35	1.08	1.18	0.62	0.53
	MNDO	100	64	25	38	1.12	1.16	1.47	1.28
	Expt	(52)	(45)	30	35	-	-	-	-
CH <sub>3</sub>	STO-3G	91	87	32	34	9.22	9.29	0.56	0.47
	3-21G	83	73	31	35	9.22	9.25	0.23	0.24
	6-31G(d)	78	62	29	36	9.21	9.25	0.64	0.53
	6-31++G(d)	67	46	26	37	9.18	9.29	0.46	-0.05
	MNDO	92	64	26	37	7.11	7.16	1.41	1.23
	Expt	(59)	(42)	27	37	-	-	-	-
C <sub>2</sub> H <sub>5</sub>	STO-3G	84	88	34	33	17.23	17.31	0.55	0.46

3-21G	85	75	30	35	17.26	17.28	0.18	0.20
6-31+G	92	42	19	40	17.02	17.10	-2.21	-1.93
MNDO	68	65	32	34	13.13	13.24	1.42	1.10
Expt	(54)	(43)	29	36	-	-	-	-

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Table 3

The contributions of  $\text{H}_2\text{C}=\overset{\text{H}^-}{\text{O}}$  (IV) and  $\text{H}_3\text{C}-\text{O}^-$  (VII) as resonance structures to  $\text{CH}_3\text{O}^-$  in gas phase

Basis set	Relative energy (enthalpy) kcal/mol		Rate of contribution %		Electron density on R		Mulliken electron population between R-C		C-O bond length $\overset{\circ}{\text{Å}}$	
	IV, V or VI	VII	IV, V, VI	VII	Opt <sup>a</sup>	Res <sup>b</sup>	Opt	Res	Opt	Res
STO-3G	121	36	14	57	9.36	9.29	0.53	0.68	1.37	1.34
3-21G	64	28	18	46	9.13	9.15	0.85	0.74	1.35	1.31
6-31G(d)	60	21	16	52	9.11	9.13	0.80	0.75	1.31	1.30
6-31++G(d)	33	7	11	66	9.08	9.04	0.39	0.52	1.33	1.33
MP2/6-31G(d)	66	25	17	49	9.21	9.23	0.86	0.74	1.32	1.32
MNDO	81	37	19	43	7.25	7.34	1.22	1.24	1.29	1.29
Expt	(43)	(11)	13	60	-	-	-	-	-	1.34

<sup>a</sup>Optimized.

<sup>b</sup>Resonance.

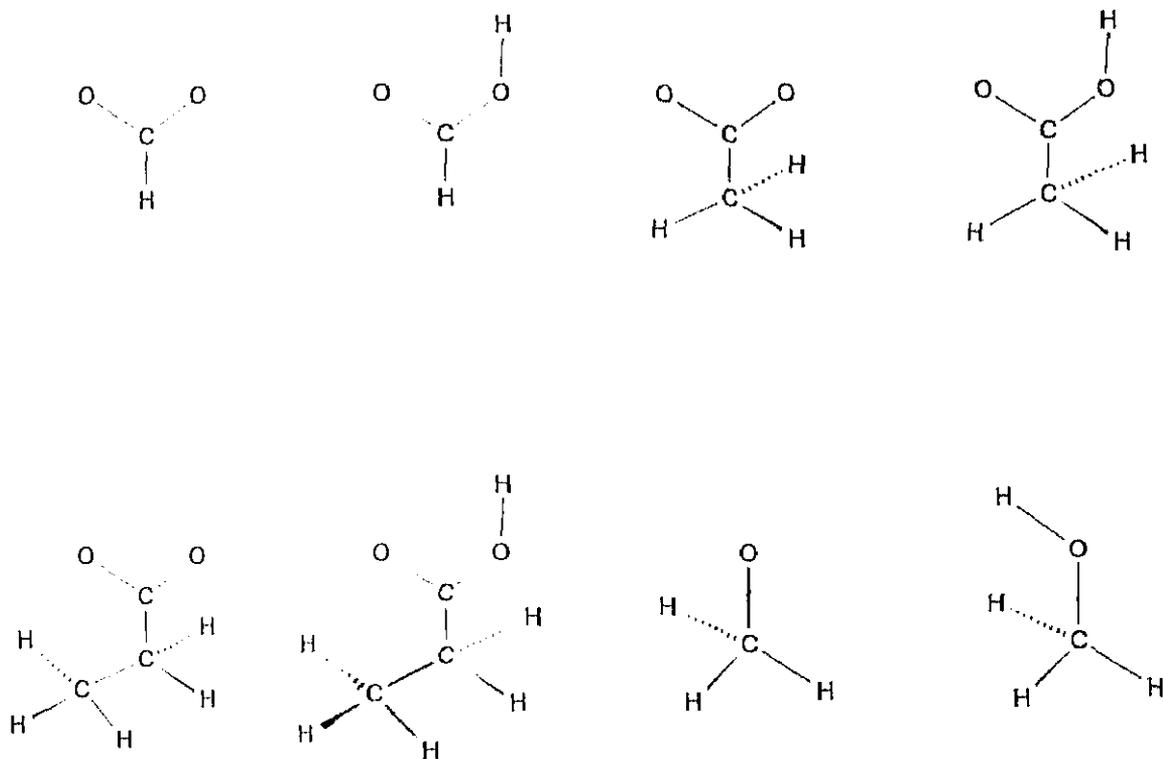


Fig.1. The structures of  $R\text{-COO}^-$ ,  $R\text{-COOH}$  ( $R=\text{H}$ ,  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$ ),  $\text{CH}_3\text{O}^-$  and  $\text{CH}_3\text{OH}$ .