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The structures of $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$ and CH_3O^- in gas phase and in crystal structure by *ab initio* and resonance theory

M. Masamura

Department of Preventive Dentistry, Okayama University Dental School, Shikata-cho, Okayama 700, Japan

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The purpose of this report is to quantitatively find the cause for the elongation of the R—C bond in R—COO^- (R = H, CH_3 and C_2H_5) and the shortening of the C—O bond in CH_3—O^- upon deprotonation in the gas phase. These elongations and shortenings result from the contributions of R^----CO_2 and H^----CH_2=O as resonance structures to the systems. Because these structures must make only a small contribution in the crystal, the R—C bond lengths of R—COO^- (R = H and CH_3) in the crystal structure are shorter than those in the gas phase.

Key words: Deprotonated species — Bond length — Structure — Gas phase — *Ab initio*

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 biological systems such as enzyme-substrate complexes and receptor-drug complexes. However, Table 1 shows that the R—C bond lengths of R—COO^- (R = H, CH_3 and C_2H_5) (Fig. 1) are longer in a gas phase than those of R—COOH (Fig. 1). in the gas phase and those of R—COO^- (R = H and CH_3) in a crystal structure. By way of contrast, in the gas phase, the C—O bond length of CH_3—O^- (Fig. 1) is shorter than that of CH_3OH (Fig. 1, Table 1). Chandrasekhar et al. reported that the R—C bonds in R—C^-=O are also longer than those in their neutral

Table 1. Effect of deprotonation on C—X bond lengths (Å)

Species	X	Gas phase						Crystal
		STO-3G	3-21G	6-31G* (+MP2)	6-31++G* (6-31+G)	MNDO (+CI)	Expt	Expt
H—COO$^-$	H	1.152^b	1.125^b	1.127^b (1.142)	1.117	1.142 (1.145)	—	1.008^f 0.997^f 1.100^g
H—COOH	H	1.104^a	1.074^a	1.083^a (1.096)	1.083	1.105 (1.104)	1.097^e	1.02^h
CH_3—COO$^-$	C	1.631^b	1.576^b	1.554	1.547	1.553 (1.560)	—	1.511^i 1.52^i
CH_3—COOH	C	1.537^a	1.497^a	1.502	1.501	1.522 (1.520)	1.520^n	1.501^j 1.482^k 1.478^k
C_2H_5—COO$^-$	C	1.640	1.572	—	(1.540)	1.568 (1.566)	—	—
C_2H_5—COOH	C	1.543	1.501	—	(1.496)	1.530 (1.530)	1.509^o	1.50^l
CH_3—O$^-$	O	1.368^a	1.348^c	1.311^d (1.323)	1.329	1.288 (1.281)	—	—
CH_3—OH	O	1.433^a	1.440^a	1.400^a (1.423)	1.402	1.391 (1.388)	1.425^e	1.42^m

[a] [8]
[b] [10]
[c] [11]
[d] [12]
[e] [21]
[f] $Ca(HCOO)_2$. Neutron diffraction. Bargouth MO, Will G (1980) Cryst Struct Comm 9:605-613
[g] NaHCOO. Neutron diffraction. Fuess H, Bats JW (1982) Acta Cryst B38:736-743
[h] The C—D bond length. Neutron powder diffraction. Albinati A, Rouse KD, Thomas MW (1978) Acta Cryst B34:2188-2190
[i] $NaCH_3COO$. Hsu Leh-Yeh and Nordman CE (1983) Acta Cryst C39:690-694
[j] Jönsson Per-Gunnar (1971) Acta Cryst B27:893-898
[k] Nahringbauer I (1970) Acta Chem Scand 24:453-462
[l] Strieter FJ, Templeton DH, Scheuerman RF, Sass RL (1962) Acta Cryst 15:1233-1239
[m] Tauer KJ, Lipscomb WN (1952) Acta Cryst 5:606-612
[n] Derissen JL (1971) J Mol Struct 7:67-80
[o] Stiefvater OL (1975) J Chem Phys 62:244-256

counterparts [1]. The cause of these elongations and shortenings upon deprotonation in the gas phase has not been quantitatively examined. In addition, why the R—C bond lengths of R—COO$^-$ are longer in the gas phase than in the crystal structure has not been studied.

The purposes of this report are (1) to quantitatively find the cause for these elongations in R—COO$^-$ and shortening in CH_3O^- upon deprotonation in the gas phase, and (2) to discuss why the R—C bond lengths of R—COO$^-$ in the gas phase are longer than those in the crystal structure. We begin by quantitatively examining the characteristics of the structures of R—COO$^-$ and CH_3O^- in the gas phase.

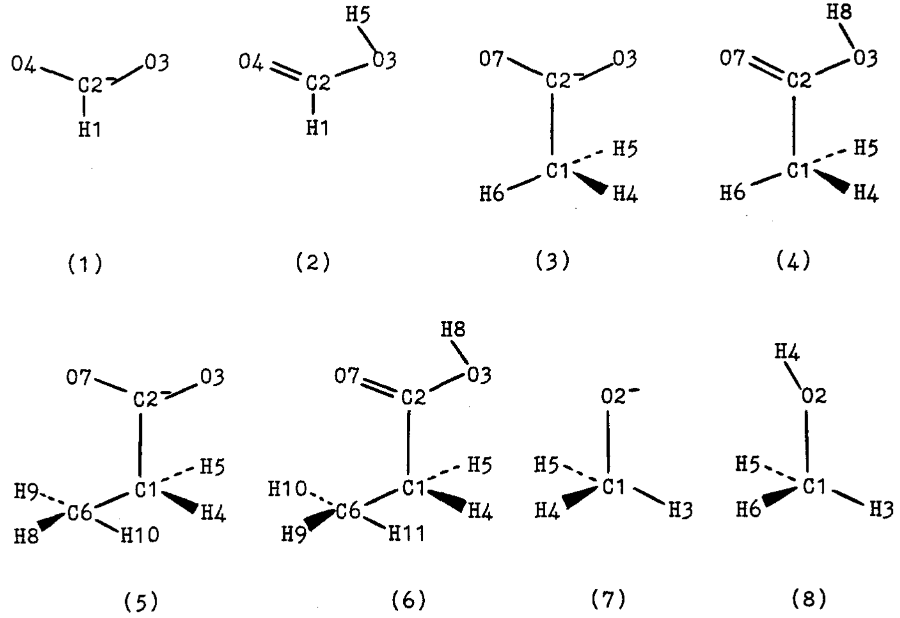
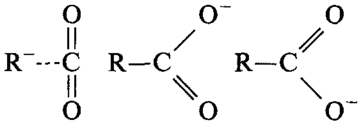


Fig. 1. Structures and atom numbering

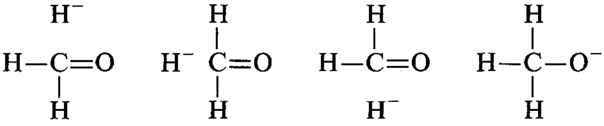
2. Method

For R—COO⁻, the only possible stable resonance structures are I, II and III:



	I	II	III
Energy	E(I)	E(II)	E(III)
Wave function (normalized)	ϕ_1	ϕ_2	ϕ_3

The contributions of I, II and III to R—COO⁻ were analysed by the method listed in Appendix 1. Similarly, for CH_3O^-, the contributions of IV, V, VI and VII were analysed:



$$\begin{array}{cccc} \mathrm{H}^- & \mathrm{H} & \mathrm{H} & \mathrm{H} \\ & \mid & \mid & \mid \\ \mathrm{H{-}C{=}O} & \mathrm{H}^-\ \mathrm{C{=}O} & \mathrm{H{-}C{=}O} & \mathrm{H{-}C{-}O}^- \\ \mid & \mid & & \mid \\ \mathrm{H} & \mathrm{H} & \mathrm{H}^- & \mathrm{H} \end{array}$$

IV V VI VII

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* [7], 6-31+G [3], 6-31++G* [3], MP2/6-31G* [3] and MNDO [8] calculations were performed. For the MP2/6-31G* 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* 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_2O and OH^- 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$^-$ from Table 2 we 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 (except for the 6-31++G* calculations, and the Mulliken electron population in MNDO calculations; see Discussion).

For CH_3O^-, Table 3 shows that (1) the structures IV, V, VI and VII contribute to CH_3O^-, and (2) the total electron density on CH_3, 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.

Tables 2 and 3 show that (1) the relative energies of these resonance structures estimated by only 6-31++G* 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 6-31++G*, nearly agrees with those estimated using enthalpy.

Tables 4 and 5 show optimized structural parameters and energies determined by *ab initio* calculations in this study.

4. Discussion

The previous results suggested that (1) in a 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* basis set is reliable for the relative energies and the amount of the contribution of each resonance structure to the systems.

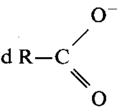


Table 2. The contributions of $R^{-}\cdots CO_2$ (I) and $R{-}C\overset{O^-}{\underset{O}{\lessgtr}}$ (II) as resonance structures to $R{-}COO^{-}$ in gas phase

R	Basis set	Relative energy (enthalpy) kJ mol^{-1}		Rate of contribution %		Electron density on R		Mulliken electron population between R—C	
		I	II or III	I	II or III	Optimized	Resonance	Optimized	Resonance
H	STO-3G	603	366	24	38	1.13	1.18	0.62	0.56
	3-21G	375	320	30	35	1.04	1.13	0.53	0.48
	6-31G*	331	274	29	35	1.07	1.17	0.76	0.58
	6-31++G*	216	210	33	34	1.01	1.21	0.89	0.53
	MP2/6-31G*	343	289	30	35	1.05	1.16	0.74	0.57
	MNDO	420	269	25	38	1.12	1.16	1.47	1.28
	Expt	(216)	(189)	30	35	—	—	—	—
CH_3	STO-3G	382	365	32	34	9.22	9.29	0.56	0.47
	3-21G	348	305	31	35	9.22	9.25	0.23	0.24
	6-31G*	326	259	29	36	9.21	9.25	0.64	0.53
	6-31++G*	280	191	26	37	9.18	9.29	0.46	−0.05
	MNDO	384	268	26	37	7.11	7.16	1.41	1.23
	Expt	(246)	(176)	27	37	—	—	—	—
C_2H_5	STO-3G	350	368	34	33	17.23	17.31	0.55	0.46
	3-21G	356	312	30	35	17.26	17.28	0.18	0.20
	6-31+G	384	175	19	40	17.02	17.10	−2.21	−1.93
	MNDO	284	272	32	34	13.13	13.24	1.42	1.10
	Expt	(226)	(181)	29	36	—	—	—	—

Table 3. The contributions of $H_2\overset{H^-}{C}{=}O$ (IV) and $H_3C{-}O^-$ (VII) as resonance structures to CH_3O^- in gas phase

Basis set	Relative energy (enthalpy) kJ mol^{-1}		Rate of contribution %		Electron density on CH_3		Mulliken electron population between C—O		C—O bond length Å	
	IV, V or VI	VII	IV, V, VI	VII	Optimized	Resonance	Optimized	Resonance	Optimized	Resonance
STO-3G	508	152	14	57	9.36	9.29	0.53	0.68	1.37	1.34
3-21G	269	116	18	46	9.13	9.15	0.85	0.74	1.35	1.31
6-31G*	251	87	16	52	9.11	9.13	0.80	0.75	1.31	1.30
6-31++G*	139	30	11	66	9.08	9.04	0.39	0.52	1.33	1.33
MP2/6-31G*	277	105	17	49	9.11	9.14	0.79	0.74	1.32	1.32
MNDO	338	157	19	43	7.25	7.34	1.22	1.24	1.29	1.29
Expt	(181)	(48)	13	60	—	—	—	—	—	1.34

Table 4. Optimized structural parameters[a]

(1)[b]	HCOO$^-$ (C_{2v})[c]		(2)	HCOOH (C_s)	
	6-31++G*	MP2/6-31G*		6-31++G*	MP2/6-31G*
C2H1	1.117	1.142	C2H1	1.083	1.096
O3C2	1.235	1.260	O3C2	1.322	1.351
			O4C2	1.183	1.213
			H5O3	0.954	0.980
C3C2H1	114.7	114.5	O3C2H1	110.6	109.5
			O4C2H1	124.6	125.4
			H5O3C2	109.4	106.0

(3)	CH$_3$COO$^-$		(4)	CH$_3$COOH	
	6-31G*	6-31++G*		6-31G*	6-31++G*
C2C1	1.554	1.547	C2C1	1.502	1.501
O3C2	1.235	1.239	O3C2	1.332	1.332
H4C1	1.089	1.088	H4C1	1.084	1.084
H5C1	1.089	1.088	H5C1	1.084	1.084
H6C1	1.086	1.085	H6C1	1.079	1.080
O7C2	1.233	1.237	O7C2	1.187	1.189
			H8O3	0.952	0.953
O3C2C1	114.5	114.9	O3C2C1	111.8	112.0
H4C1C2	109.7	109.6	H4C1C2	109.7	109.7
H5C1C2	109.7	109.6	H5C1C2	109.6	109.7
H6C1C2	112.1	111.8	H6C1C2	109.6	109.5
O7C2C1	116.0	116.3	O7C2C1	125.8	125.7
			H8O3C2	108.1	108.7
H4C1C2O3	58.5	58.6	H4C1C2O3	59.0	59.0
H5C1C2O3	−58.5	−58.6	H5C1C2O3	−59.0	−59.0
H6C1C2O3	180.0	180.0	H6C1C2O3	180.0	180.0
O7C2C1H6	0.0	0.0	O7C2C1H6	0.0	0.0
			H8O3C2C1	180.0	180.0

(5)	C$_2$H$_5$COO$^-$			(6)	C$_2$H$_5$COOH		
	STO-3G	3-21G	6-31+G		STO-3G	3-21G	6-31+G
C2C1	1.640	1.572	1.540	C2C1	1.543	1.501	1.496
O3C2	1.262	1.250	1.266	O3C2	1.392	1.359	1.355
H4C1	1.090	1.087	1.087	H4C1	1.089	1.084	1.085
H5C1	1.090	1.087	1.087	H5C1	1.089	1.084	1.085
C6C1	1.541	1.530	1.526	C6C1	1.539	1.531	1.525
O7C2	1.261	1.250	1.262	O7C2	1.216	1.202	1.212
H8C6	1.086	1.082	1.083	H8O3	0.990	0.969	0.954
H9C6	1.086	1.082	1.083	H9C6	1.086	1.082	1.082
H10C6	1.090	1.089	1.090	H10C6	1.086	1.082	1.082
				H11C6	1.086	1.083	1.083
O3C2C1	113.8	114.6	115.0	O3C2C1	111.3	110.9	111.9
H4C1C2	109.5	107.6	107.0	H4C1C2	108.1	107.6	107.4

Table 4 (continued)

(5)	$C_2H_5COO^-$			(6)	C_2H_5COOH		
	STO-3G	3-21G	6-31+G		STO-3G	3-21G	6-31+G
H5C1C2	109.5	107.6	107.0	H5C1C2	108.1	107.6	107.4
C6C1C2	113.6	112.1	115.3	C6C1C2	112.0	111.5	113.3
O7C2C1	115.3	115.6	117.5	O7C2C1	127.0	126.9	126.7
H8C6C1	110.6	109.6	110.8	H8O3C2	104.6	111.8	114.1
H9C6C1	110.6	109.6	110.8	H9C6C1	110.6	110.5	111.3
H10C6C1	112.5	112.4	111.1	H10C6C1	110.6	110.5	111.3
				H11C6C1	110.2	110.5	109.9
H4C1C2O3	58.1	57.3	56.6	H4C1C2O3	57.8	57.3	56.7
H5C1C2O3	−58.1	−57.3	−56.6	H5C1C2O3	−57.8	−57.3	−56.7
C6C1C2O3	180.0	180.8	180.0	C6C1C2O3	180.0	180.0	180.0
O7C2C1C6	0.0	0.0	0.0	O7C2C1C6	0.0	0.0	0.0
H8C6C1C2	−59.3	−58.4	−59.2	H8O3C2C1	180.0	180.0	180.0
H9C6C1C2	59.3	58.4	59.2	H9C6C1C2	−60.0	−59.6	−60.0
H10C6C1C2	180.0	180.0	180.0	H10C6C1C2	60.0	59.6	60.0
				H11C6C1C2	180.0	180.0	180.0

(7)	CH_3O^- (C_{3v})		(8)	CH_3OH	
	6-31++G*	MP2/6-31G*		6-31++G*	MP2/6-31G*
O2C1	1.329	1.323	O2C1	1.402	1.423
H3C1	1.122	1.149	H3C1	1.081	1.090
			H4O2	0.947	0.970
			H5C1	1.087	1.097
			H6C1	1.087	1.097
H3C1O2	115.1	117.2	H3C1O2	107.0	106.3
			H4O2C1	110.4	107.4
			H5C1O2	111.7	112.3
			H6C1O2	111.7	112.3
			H4O2C1H3	180.0	180.0
			H5C1O2H4	61.2	61.5
			H6C1O2H4	−61.2	−61.5

	H_2O (C_{2v})		OH^-		
	6-31+G	6-31++G*	6-31+G	6-31++G*	MP2/6-31G*
OH	0.949	0.948	0.950	0.954	0.980
HOH	112.7	106.6	—	—	—

(5)[d]	$C2H5^-$				$CH_2{=}O$ (C_{2v})
	STO-3G	3-21G	6-31+G		6-31++G*
H4C1	1.113	1.114	1.097	CO	1.186
H5C1	1.113	1.114	1.097	CH	1.091

Table 4 (continued)

(5)[d]	C2H5⁻		
	STO-3G	3-21G	6-31+G
C6C1	1.571	1.566	1.539
H8C6	1.094	1.096	1.092
H9C6	1.094	1.096	1.092
H10C6	1.103	1.113	1.109
H4C1X2	155.5	112.3	107.0
H5C1X2	115.5	112.3	107.0
C6C1X2	118.0	114.7	109.2
H8C6C1	111.7	110.4	110.7
H9C6C1	111.7	110.4	110.7
H10C6C1	118.3	119.0	117.2
H4C1X2X3	58.7	58.4	58.5
H5C1X2X3	−58.7	−58.4	−58.5
C6C1X2X3	180.0	180.0	180.0
H8C6C1X2	−58.7	−58.4	−58.7
H9C6C1X2	58.7	58.4	58.7
H10C6C1X2	180.0	180.0	180.0

	$CH_2{=}O$ (C_{2v})
	6-31++G*
HCO	121.8

	CH_3^- (C_{3v})
	6-31++G*
CH	1.097
HCH	109.2

	CO_2 ($C_{\infty v}$)		
	6-31+G	6-31++G*	MP2/6-31G*
CO	1.160	1.143	1.179

[a] Bond lengths in Å, and angles in degrees

[b] See Fig. 1

[c] If the imposed symmetry constraint on the optimization was used, the Schoenflies notation for the point group of the species is provided

[d] C2, O3 and O7 in (5) in Fig. 1 are dummy atoms

Table 5. Optimized energies (hartrees)

	STO-3G	3-21G	6-31G* (MP2/6-31G*)	6-31++G* (6-31+G)
$HCOO^-$	—	—	(−188.67806)	−188.20825
HCOOH	—	—	(−189.25187)	−188.76935
CH_3COO^-	—	—	−227.22507	−227.24966
CH_3COOH	—	—	−227.81065	−227.81809
$C_2H_5COO^-$	−262.62979	−264.75816	—	(−266.16503)
C_2H_5COOH	−263.39050	−265.35679	—	(−266.72868)
CH_3O^-	—	—	(−144.70950)	−114.41146
CH_3OH	—	—	(−115.35330)	−115.04113
H^-	—	—	—	−0.48707
CH_3^-	—	—	—	−39.50427
$C_2H_5^-$	−77.42841	−78.06125	—	(−78.49925)
CO_2	—	—	(−188.11836)	−187.63879 (−187.51943)
H_2O	—	—	—	−76.01789 (−75.99306)
OH^-	—	—	(−75.51544)	−75.37668 (−75.36257)

In the 6-31++G* 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 a 6-31++G* basis 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 I to R—COO$^-$, the R—C bond lengths of R—COO$^-$ are longer than those of R—COOH in the gas phase. (R$^-$---COOH$^+$ may contribute to R—COOH just as I contributes to R—COO$^-$. However, the contribution of R$^-$---COOH$^+$ to R—COOH must be far smaller than that of I because the electron density on R of R—COOH is far smaller than in R—COO$^-$.) Due to the contributions of IV, V and VI to CH_3O^-, the C—O bond length of CH_3O^- is shorter than that of CH_3OH in the gas phase.

Why is the C—C bond length (1.511, 1.52 Å) of CH_3COO^- in the crystal structure shorter than that in the gas phase (estimated in Appendix 2 to be 1.557 Å)? The interaction between O$^-$ in II (and III) and cations (e.g. Na^+) in the crystal structure stabilizes O$^-$. As a result of the interaction, structures II and III must be much more stable than I in the crystal structure. Thus, structure I must make a smaller contribution than II and III in the crystal structure. Therefore, the C—C bond length of CH_3COO^- 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 $HCOO^-$ in the crystal structure is shorter than in the gas phase (estimated in Appendix 2 to be 1.127 Å).

Briefly, because the minus charge of R—COO$^-$ in the crystal structure must be more localized than that in the gas phase, the structure of R—COO$^-$ 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_3O^- 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 1

I. R—COO$^-$

According to L. Pauling [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$^-$.

To a reasonable degree of approximation

$$H_{11} \fallingdotseq E(I) \fallingdotseq E(\mathrm{R}^-) + E(\mathrm{CO_2}) \tag{1}$$

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

$$H_{22} = H_{33} \fallingdotseq E(\mathrm{II}) = E(\mathrm{R{-}COOH}) - b \tag{2}$$

where $b = E(\mathrm{R{-}COOH}) - E(\mathrm{II}) \fallingdotseq E(\mathrm{H_2O}) - E(\mathrm{OH^-}) \equiv E_b$

Evidently,

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

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

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

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,

$$E_1C_1+2XC_2=0; \qquad XC_1+(E_2+Y)C_2=0 \tag{3}$$

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

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

$$X=H_{12}-S_{12}E; \qquad Y=H_{23}-S_{23}E \tag{6}$$

The following assumptions were adopted:

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

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.

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

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

$$\mathrm{con}_1=C_1^2/(C_1^2+2C_2^2); \qquad \mathrm{con}_2=\mathrm{con}_3=C_2^2/(C_1^2+2C_2^2) \tag{9}$$

The total electron density on R expected for resonance is $\mathrm{con}_1e_1+2\mathrm{con}_2e_2$, 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).

$e_1 \fallingdotseq$ total electron density of R$^-$

$e_2 \fallingdotseq$ total electron density of R—COOH on R

The Mulliken electron population between R—C expected for resonance is $\mathrm{con}_1P_1+2\mathrm{con}_2P_2$, where P_i is the electron population between R—C of structure *i*.

$P_1 \fallingdotseq 0$

$P_2 \fallingdotseq$ the electron population between R—C of R—COOH

II. CH_3O^-
Similarly,

$$E_4 \fallingdotseq E(\mathrm{H}^-)+E(\mathrm{HCHO})-E(\mathrm{CH_3O^-})$$

$$E_7 \fallingdotseq E(\mathrm{CH_3OH})-b-E(\mathrm{CH_3O^-}) \quad \text{where } b=E(\mathrm{CH_3OH})-E(\mathrm{XIII}) \fallingdotseq E_b$$

$$\mathrm{con}_4=C_4^2/(3C_4^2+C_7^2); \qquad \mathrm{con}_7=C_7^2/(3C_4^2+C_7^2)$$

where

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

The expected electron density on $CH_3 = 3\mathrm{con}_4 e_4 + \mathrm{con}_7 e_7$ where

$e_4 \fallingdotseq$ total electron density of HCHO on $CH_2 + 2(H^-)$

$e_7 \fallingdotseq$ total electron density of CH_3OH on CH_3

The electron population between C—O $= 3\mathrm{con}_4 P_4 + \mathrm{con}_7 P_7$ where

$P_4 \fallingdotseq$ the electron population between C—O of HCHO

$P_7 \fallingdotseq$ the electron population between C—O of CH_3OH

The expected C—O bond length $= 3\mathrm{con}_4 r_4 + \mathrm{con}_7 r_7$ where

$r_4 \fallingdotseq$ the C—O bond length of $CH_2{=}O$

$r_7 \fallingdotseq$ 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 2

We estimate the R—C bond lengths of R—COO^- and C—O bond length of CH_3O^- using the 6-31++G* results. Since the optimized R—C bond lengths of R—COOH and the C—O bond lengths of CH_3OH and $CH_2{=}O$ from the 6-31++G* calculation are shorter (by 0.01-0.02 Å) than experimental values, the R—C bond lengths of the structures II and III and the C—O bond lengths of IV, V, VI and VII estimated by 6-31++G* must also be short. Since diffuse functions improve description of the anion lone-pair orbitals [10], the distance between R and C in I estimated from the 6-31++G* calculation is expected to be adequate. The 6-31++G* calculation reproduces the amount each resonance structure contributes to the systems. Thus, the R—C bond lengths of R—COO^- and the C—O bond lengths of CH_3O^- estimated from the 6-31++G* calculation must be short. The following data support this conjecture; the C—O bond length (1.329 Å) of CH_3O^- estimated from the 6-31++G* calculation is shorter than that estimated using experimental data (1.338 Å) (Table 3). Using the correction for these bond lengths (+0.01 Å), the R—C bond lengths become 1.127 (R = H) and 1.557 Å (R = CH_3), and the C—O bond lengths become 1.339 Å. The 3-21G and 6-31G* results roughly agree with these values. The bond lengths estimated by the STO-3G calculations are longer than these values. The MNDO results roughly agree with these values except for the C—O bond length.

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