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PROTON IONIZATION HEATS AND RELATED THERMODYNAMIC QUANTITIES OF CARBOXYLIC ACIDS IN FORMAMIDE AT 25°C

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ABSTRACT

The ΔG^0, ΔH^0 and ΔS^0 values for proton ionization from 36 mono-, 13 di- and 2 tricarboxylic acids have been evaluated in formamide at 25°C. A linear relationship is found between ΔG^0 and ΔS^0 for these acids and has been compared with that in water. The effects which give rise to this linear relationship in formamide are discussed with reference to water. The changes in ΔH^0 and ΔS^0 from the first to the second stage of ionization for 13 dicarboxylic acids in formamide have also been examined.

INTRODUCTION

Although the ΔG^0, ΔH^0 and ΔS^0 values for proton ionization from a number of weak and moderately strong acids in formamide are known[1-13], no information is available regarding the effects which give rise to a linear relationship between ΔG^0 and ΔS^0 for the acids in formamide, a solvent which resembles water in many respects and has a dielectric constant higher than that of water, whereas in an aqueous medium, attempts have been made by several workers[14-16] to interpret acid strength in terms of ΔH^0 and ΔS^0. Recently, King[17] and Christensen et al.[18] have reported the enthalpy–entropy–free energy relationships for proton ionization in aqueous solution. The present work aims at studying similar relationships for proton ionization from 36 mono-, 13 di- and 2 tri-carboxylic acids in formamide.

RESULTS AND DISCUSSION

A compilation of pK_a, ΔG^0, ΔH^0 and ΔS^0 values in formamide reported earlier[1-11] is given for proton ionization from 36 mono-*, 13 di- and 2 tricarboxylic acids. The standard thermodynamic quantities that accompany each of the ionization steps of the carboxylic acids at 25°C are listed in Table 1 along with their uncertainties.

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* Picric acid is treated as a monobasic acid and is included in Table 1 along with other monocarboxylic acids.

TABLE 1

THERMODYNAMIC QUANTITIES FOR PROTON IONIZATION FROM CARBOXYLIC ACIDS IN FORMAMIDE AT 25 °C

Acid	pK_a	$\Delta G^0 \times 10^{-3}$ $(J\ mole^{-1})$	$\Delta H^0 \times 10^{-3}$ $(J\ mole^{-1})$	ΔS^0 $(J\ deg^{-1}\ mole^{-1})$
1 Acetic	6.91	39.43 ± 0.04	20.65 ± 0.08	−62.72 ± 0.10
2 Chloro acetic	4.10	23.40 ± 0.08	50.76 ± 0.06	+91.81 ± 0.13
3 Phenyl acetic	6.57	37.49 ± 0.09	20.09 ± 0.05	−45.07 ± 0.08
4 Glycolic	4.98	28.41 ± 0.14	10.44 ± 0.25	−60.32 ± 0.13
5 Glyoxylic	5.96	34.01 ± 0.06	31.78 ± 0.10	− 7.46 ± 0.05
6 Propionic	7.26	41.42 ± 0.03	15.79 ± 0.004	−86.02 ± 0.02
7 Lactic	5.81	33.15 ± 0.10	11.96 ± 0.18	−71.11 ± 0.09
8 *n*-Butyric	7.34	41.88 ± 0.04	15.69 ± 0.003	−87.88 ± 0.02
9 *iso*-Butyric	7.47	42.62 ± 0.05	19.03 ± 0.007	−79.15 ± 0.03
10 Valeric	7.78	44.39 ± 0.05	15.83 ± 0.004	−95.84 ± 0.01
11 *iso*-Valeric	7.53	42.96 ± 0.04	13.24 ± 0.01	−99.75 ± 0.02
12 Caproic	7.23	41.25 ± 0.02	19.55 ± 0.002	−72.84 ± 0.01
13 *iso*-Caproic	7.16	40.85 ± 0.03	17.09 ± 0.001	−79.75 ± 0.02
14 Benzoic	6.36	36.29 ± 0.05	28.92 ± 0.08	−24.74 ± 0.12
15 *o*-Chlorobenzoic	5.82	33.23 ± 0.06	32.14 ± 0.05	−3.66 ± 0.03
16 *m*-Chlorobenzoic	6.22	35.46 ± 0.07	20.65 ± 0.08	−49.71 ± 0.12
17 *p*-Chlorobenzoic	6.58	37.57 ± 0.08	27.54 ± 0.07	−33.66 ± 0.13
18 *o*-Nitrobenzoic	4.41	25.16 ± 0.08	38.55 ± 0.08	+44.93 ± 0.10
19 *m*-Nitrobenzoic	5.40	30.81 ± 0.07	27.56 ± 0.05	−10.91 ± 0.12
20 *p*-Nitrobenzoic	5.88	33.55 ± 0.06	60.26 ± 0.06	+89.84 ± 0.09
21 Salicyclic	4.73	27.00 ± 0.08	19.28 ± 0.07	−25.90 ± 0.08
22 *m*-Hydroxy benzoic	6.38	36.38 ± 0.09	25.69 ± 0.06	−35.87 ± 0.06
23 *p*-Hydroxybenzoic	6.86	39.12 ± 0.04	21.81 ± 0.07	−58.09 ± 0.10
24 Acetyl salicyclic	5.65	32.24 ± 0.16	25.50 ± 0.28	−22.60 ± 0.15
25 2,4-Dihydroxy benzoic	5.95	33.95 ± 0.18	15.30 ± 0.29	−62.58 ± 0.26
26 3,4-Dihydroxy benzoic	8.64	49.30 ± 0.18	76.32 ± 0.32	+90.67 ± 0.16
27 Gallic	5.10	29.10 ± 0.12	36.30 ± 0.21	+24.18 ± 0.11
28 Anthranilic	3.08	17.57 ± 0.03	20.24 ± 0.08	+8.96 ± 0.01
	6.65	37.93 ± 0.05	35.04 ± 0.07	−9.70 ± 0.02
29 *m*-Amino benzoic	3.64	20.77 ± 0.06	24.13 ± 0.04	+11.28 ± 0.08
	6.42	36.63 ± 0.07	27.53 ± 0.08	−30.54 ± 0.10
30 *p*-Amino benzoic	2.41	13.81 ± 0.06	−8.77 ± 0.01	−75.77 ± 0.18
	6.94	39.62 ± 0.07	29.62 ± 0.06	−33.56 ± 0.10
31 Sulphamic	2.44	13.92 ± 0.32	0.16 ± 0.02	−47.26 ± 0.78
32 Orthanilic	1.99	11.35 ± 0.20	23.15 ± 0.08	+39.55 ± 0.38
	3.36	19.18 ± 0.05	9.57 ± 0.02	−32.24 ± 0.12
33 Metanilic	1.71	9.76 ± 0.12	33.85 ± 0.05	+80.82 ± 0.26
	4.35	24.82 ± 0.12	10.88 ± 0.05	−46.79 ± 0.26
34 Sulphanilic	1.81	10.33 ± 0.20	19.48 ± 0.08	+30.70 ± 0.38
	3.88	22.14 ± 0.32	−3.56 ± 0.03	−86.25 ± 0.78
35 Cinnamic	6.86	39.14 ± 0.04	8.76 ± 0.03	−101.93 ± 0.04
36 Picric	1.33	7.59 ± 0.02	53.52 ± 0.10	+154.10 ± 0.18
37 Oxalic	2.85	16.26 ± 0.08	16.06 ± 0.08	−0.67 ± 0.002
	6.39	36.45 ± 0.08	11.34 ± 0.06	−84.28 ± 0.10
38 Oxaloacetic	5.73	32.69 ± 0.18	17.03 ± 0.27	−52.53 ± 0.16
	9.10	51.82 ± 0.16	65.82 ± 0.28	+46.63 ± 0.14
39 Malonic	4.38	25.00 ± 0.09	19.28 ± 0.18	−19.20 ± 0.10
	8.34	47.62 ± 0.10	17.53 ± 0.13	−100.90 ± 0.19

TABLE 1 *(continued)*

Acid	pK_a	$\Delta G^0 \times 10^{-3}$ ($J\ mole^{-1}$)	$\Delta H^0 \times 10^{-3}$ ($J\ mole^{-1}$)	ΔS^0 ($J\ deg^{-1}\ mole^{-1}$)
40 Mesoxalic	5.29	30.18 ± 0.12	−11.80 ± 0.21	−140.9 ± 0.11
	9.93	56.66 ± 0.06	57.33 ± 0.02	+2.25 ± 0.05
41 Succinic	6.00	34.26 ± 0.13	27.57 ± 0.22	−22.55 ± 0.13
	8.03	45.81 ± 0.15	29.65 ± 0.18	−54.23 ± 0.12
42 Malic	5.80	33.09 ± 0.18	23.24 ± 0.29	−33.07 ± 0.16
	7.76	44.28 ± 0.16	43.08 ± 0.28	−4.00 ± 0.02
43 Tartaric	4.39	25.05 ± 0.18	6.71 ± 0.12	−61.34 ± 0.16
	7.49	42.73 ± 0.02	21.68 ± 0.04	−70.66 ± 0.02
44 Maleic	3.07	17.52 ± 0.04	5.38 ± 0.07	−40.73 ± 0.04
	8.61	49.12 ± 0.12	22.08 ± 0.21	−90.76 ± 0.11
45 Fumaric	5.52	31.49 ± 0.16	12.61 ± 0.28	−63.37 ± 0.14
	7.06	40.28 ± 0.06	14.95 ± 0.11	−85.00 ± 0.05
46 Glutaric	6.22	35.46 ± 0.18	30.84 ± 0.11	−15.50 ± 0.10
	8.21	46.81 ± 0.16	30.80 ± 0.13	−53.73 ± 0.63
47 Glutamic	3.89	22.19 ± 0.32	31.17 ± 0.16	+30.13 ± 0.12
	5.96	34.00 ± 0.32	23.27 ± 0.16	−36.01 ± 0.78
	9.91	56.54 ± 0.12	48.18 ± 0.05	−28.07 ± 0.26
48 Adipic	6.74	38.50 ± 0.19	24.08 ± 0.14	−48.40 ± 0.16
	8.01	45.68 ± 0.20	28.35 ± 0.13	−23.93 ± 0.36
49 Phthalic	4.21	24.04 ± 0.09	19.28 ± 0.08	−15.97 ± 0.10
	7.72	46.01 ± 0.08	42.81 ± 0.09	−10.74 ± 0.13
50 Citric	5.27	30.07 ± 0.02	4.92 ± 0.04	−84.39 ± 0.02
	7.33	41.82 ± 0.16	23.76 ± 0.28	−60.61 ± 0.14
	8.18	46.67 ± 0.16	14.14 ± 0.28	−109.21 ± 0.14
51 Aconitic	5.50	31.38 ± 0.02	31.99 ± 0.04	+2.05 ± 0.02
	7.32	41.76 ± 0.04	12.75 ± 0.07	−97.38 ± 0.04
	9.52	54.32 ± 0.08	43.16 ± 0.14	−37.44 ± 0.07

The accuracies of ΔG^0, ΔH^0 and ΔS^0 values for different ionization steps of the carboxylic acids obtained by the method of least-squares were estimated to be about ± 182, ± 200 and ± 0.62 J $mole^{-1}$, respectively, although the precision in many cases is considerably better than this.

In comparing the ΔH^0 and $T\Delta S^0$ values for proton dissociation from carboxylic acids in both formamide and water, the ΔH^0 values, unlike those in water[18], are generally found to be much greater than the corresponding $T\Delta S^0$ values in formamide, pointing to the fact that the solvation pattern is significantly altered by changing the solvent from water to formamide. For the structurally related acids, differences in acid strength were found to be due to the differences in either ΔH^0 or $T\Delta S^0$ or both. For instance, acetic and glycolic acids have nearly the same $T\Delta S^0$ values, but their pK_a values differ markedly because of large differences between the ΔH^0 values. On the other hand, propionic and lactic acids, succinic and malic acids and glutaric and glutamic acids have nearly the same ΔH^0 values with the difference in the pK_a values being due to the difference in the $T\Delta S^0$ values. A similar effect to that found in an aqueous medium[19] is also observed in formamide, (that of enhancing the strength

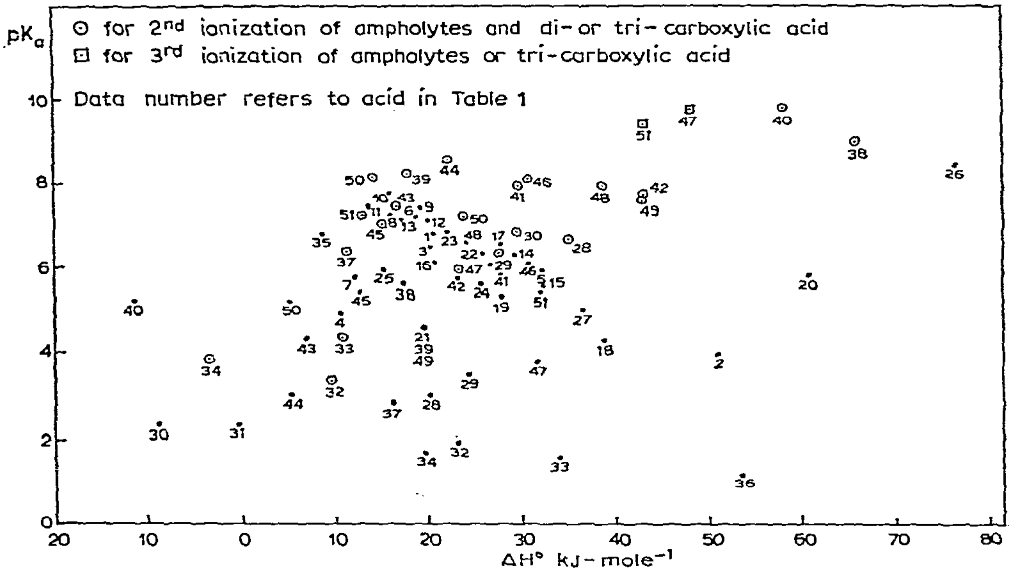

Fig. 1. Plot of pK_a vs. ΔH^0 for mono-, di- and tricarboxylic acid proton ionization.

of acidic groups) by the substitution of hydroxy groups in the carbon chain of related acids such as acetic and glycolic, propionic and lactic, and succinic, malic and tartaric acids.

A plot of $-\log K_a$ vs. ΔH^0 for all the acids mentioned in Table 1 is shown in Fig. 1, so that any relation between the ionization constant, K_a and the heat of ionization, ΔH^0 of the acids can be seen. This shows that in formamide the two constants seem to be in no way dependent upon each other as is found in water[20]. For example, the plotted points of benzoic acid, *o*-hydroxybenzoic acid and *p*-hydroxybenzoic acid form an isosceles triangle, while those of the three monochlorobenzoic acids form an equilateral triangle and those of *n*-butyric, *iso*-butyric, *n*-valeric and *iso*-valeric acids form a parallelogram.

It is of interest to interpret acid strengths in terms of a qualitative discussion of ΔH^0 and ΔS^0 for ionizations of organic acids in formamide. Recently, however, the effect of substituents on the strengths of acetic[4] and benzoic acids[6, 21] in this solvent has been discussed on the basis of inductive effects and resonance stabilization of the anions of the substituted acids. It is nevertheless worthwhile to compare the observed values of the thermodynamic quantities for acids of like structure so as to interpret the acid strengths. It is likely that the orientation of solvent molecules in the proximity of the ions formed by the dissociation of an acid plays an important role in determining the sign and to some extent the magnitude of the changes in entropy and heat capacity. Further, it is to be expected that when the dissociation produces an increase of charge, the orientation of solvent molecules should increase and hence lead to decreased entropy and heat capacity. Unfortunately, at present, it is not possible to determine the values of heat capacity for the dissociation of the carboxylic acids in formamide. However, the ΔS^0 values as determined in the present study for mono-, di- and tricarboxylic acids were found to be almost invariably negative. A

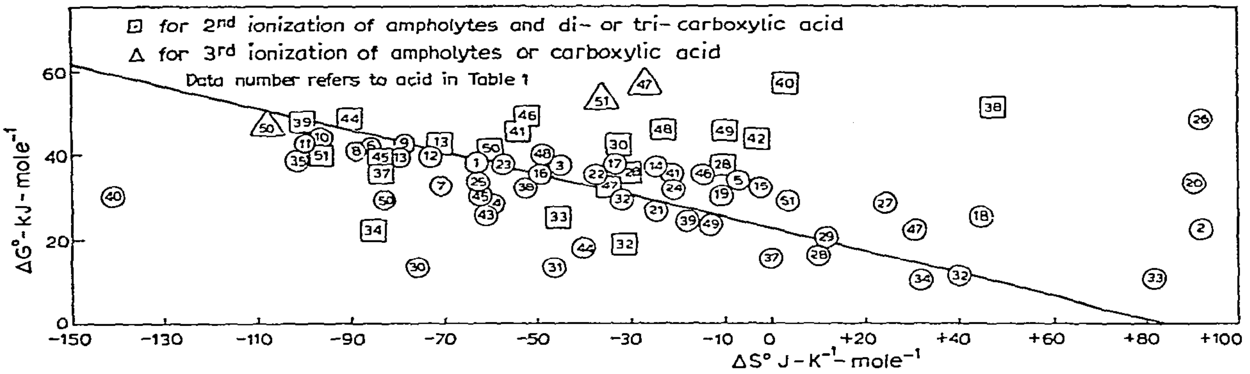

Fig. 2. Plot of ΔG^0 vs. ΔS^0 for mono-, di- and tricarboxylic acid proton ionization.

more negative value of ΔS^0 for one acid, compared with that of another may be evidence for a greater degree of reorientation and partial immobilization of formamide molecules by the ions formed by the dissociation of the former acid.

The linear relationship between the ΔG^0 and ΔS^0 values for all acids in Table 1 is shown in Fig. 2. The slope of the line drawn through the points as determined by a least-squares fit was found to be −262 which approximates closely the value of −274 predicted by the Bjerrum theory of electrostatics[22]. Similar plots of ΔG^0 vs. ΔS^0 for the dicarboxylic acids listed in Table 1 have least-squares slopes of −270 and −288 for the first and second dissociation, respectively. These results indicate the existence of electrostatic interactions involved in proton ionization for acids studied in formamide.

It is possible using the thermodynamic data for the substituted acetic and benzoic acids to investigate further the electrostatic and non-electrostatic parts of the thermodynamic quantities in formamide. Considering the electrostatic parts only, as the non-electrostatic part involves inductive effects on bond dissociation energies, it is possible to interpret the acid strength in terms of ΔH^0_{ext}, ΔH^0_{int}, ΔS^0_{ext} and ΔS^0_{int}, where ΔH^0_{ext} and ΔS^0_{ext} are associated with solute–solvent interactions, and ΔH^0_{int} and ΔS^0_{int} arise from differences in enthalpy and entropy within the acid molecule and its anion. Considering the following reactions[14] in formamide for effects of substituents on acetic and benzoic acids as

$$\mathrm{HA_u(solvent)} \rightleftharpoons \mathrm{H^+(solvated)} + \mathrm{A_u^-(solvated)} \tag{1}$$

$$\mathrm{HA_s(solvent)} \rightleftharpoons \mathrm{H^+(solvated)} + \mathrm{A_s^-(solvated)} \tag{2}$$

$$\mathrm{HA_s(solvent)} + \mathrm{A_u^-(solvated)} \rightleftharpoons \mathrm{A_s^-(solvated)} + \mathrm{HA_u(solvated)} \tag{3}$$

where HA represents acetic or benzoic acid, and subscripts u and s refer to the unsubstituted parent acid, and the substituted acid, respectively. The values of ΔH^0_3 and

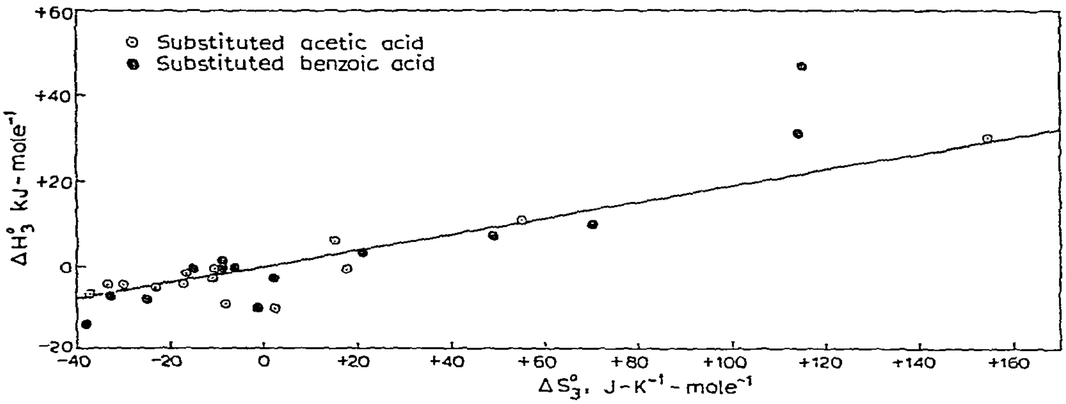

Fig. 3. Plot of ΔH_3^0 vs. ΔS_3^0 for the reactions of type 3.

ΔS_3^0 for reactions of type 3 can be obtained by combining ΔH^0 and ΔS^0 values for reactions of types 1 and 2, as

$$\Delta H_3^0 = \Delta H_s^0 - \Delta H_u^0$$

and

$$\Delta S_3^0 = \Delta S_s^0 - \Delta S_u^0$$

Following the procedure adopted by Hepler[14], the ΔH_3^0 and ΔS_3^0 values are obtained as the sums of external and internal contributions, and may be written as

$$\Delta H_3^0 = \Delta H_{\text{int}}^0 + \Delta H_{\text{ext}}^0 \tag{4}$$

and

$$\Delta S_3^0 = \Delta S_{\text{int}}^0 + \Delta S_{\text{ext}}^0 \tag{5}$$

Further, by following Pitzer's method[23] for the relation, $\Delta S_3^0 = \Delta S_{\text{ext}}^0$, and that of Born[24] and Powell–Latimer[25] for $\Delta H_{\text{ext}}^0 = \beta \Delta S_{\text{ext}}^0 = \beta \Delta S_0$, and applying them to symmetrical reactions of type 3, eqn. (4) may be written as

$$\Delta H_3^0 = \Delta H_{\text{int}}^0 + \beta \Delta S_3^0 \tag{6}$$

where β is a parameter having the same value for all acids of the same charge type. It is evident from eqn. (6) that β is the slope of the plot of ΔH_3^0 vs. ΔS_3^0, and was found to be 225° (Fig. 3) which is in reasonable agreement with a value of 280° obtained by Brown[26] for the ionization of organic acids in water. Values of ΔH_{int}^0 for various substituted acetic and benzoic acids calculated by means of eqn. (6) with $\beta = 225°$ for reactions of type 3 are listed in Table 2.

As expected the ΔH_{int}^0 values for substituted acetic or benzoic acids show the effect of substituents on the strength of acids. For example, the ΔH_{int}^0 values for chloroacetic and phenylacetic acids are in accord with qualitative predictions based on electronegativities. The ΔH_{int}^0 values of glycolic, glyoxylic and lactic acids show a similar effect. Further it is interesting to note that the values of ΔH_{int}^0 for alkyl

TABLE 2

$\Delta H^0_{\mathrm{int}}$ VALUES (REACTION 3) FOR SUBSTITUTED ACETIC AND BENZOIC ACIDS ($\beta = 225°$) IN FORMAMIDE

Substituted acetic acid	ΔH^0_{int} *(J mole^{-1})*	*Substituted benzoic acid*	ΔH^0_{int} *(J mole^{-1})*
Chloroacetic	− 4,659	*o*-Chloro-	− 1,523
Phenylacetic	− 4,531	*m*-Chloro-	− 2,652
Glycolic	− 10,750	*p*-Chloro-	+ 627
		o-Nitro-	− 6,046
Glyoxylic	− 1,303	*m*-Nitro-	+ 1,752
Lactic	− 6,802	*p*-Nitro-	− 5,560
Propionic	+ 382	*o*-Hydroxy-	− 9,379
Butyric	+ 701	*m*-Hydroxy-	− 726
iso-Butyric	+ 2,077	*p*-Hydroxy-	+ 394
Valeric	+ 2,632	*o*-Amino-	+ 2,736
iso-Valeric	+ 922	*m*-Amino-	− 85
Caproic	+ 1,177	*p*-Amino-	+ 2,685
iso-Caproic	+ 272	Acetylsalicylic	− 3,902
		2,4-Dihydroxy-	− 5,106
		2,5-Dihydroxy-	+ 21,432
		Gallic acid-	− 3,627

substituted acetic acids are positive in formamide as they are in aqueous medium[14]. Similarly, the $\Delta H^0_{\mathrm{int}}$ values of *o*-hydroxy benzoic, *m*-hydroxy benzoic, acetyl salicylic, 2,4-dihydroxy benzoic and gallic acids are in accordance with qualitative predictions based on hydroxyl substituent effects at different positions in the benzene ring.

Considering a similar approach to that of Christensen et al.[18] based on only the electrostatic part of the ΔG^0, ΔH^0 and ΔS^0 of proton ionization of dicarboxylic acids in formamide medium, the following expressions relate $\Delta(\Delta X)$ to ΔX of the electrostatic (elect.) part of the first and second ionization stages of a dicarboxylic acid, where X is G, H or S.

$$\Delta(\Delta G) = \Delta G_2^{\mathrm{elect}} - \Delta G_1^{\mathrm{elect}} + RT \ln \sigma \tag{7}$$

$$\Delta(\Delta H) = \Delta H_2^{\mathrm{elect}} - \Delta H_1^{\mathrm{elect}} \tag{8}$$

$$\Delta(\Delta S) = \Delta S_2^{\mathrm{elect}} - \Delta S_1^{\mathrm{elect}} - R \ln \sigma \tag{9}$$

In eqns. (7) and (9), σ is the symmetry correction factor for acid ionization constants[27] and equals 4 for dicarboxylic acids.

By following a similar procedure to that adopted by Christensen et al. for separating $\Delta X_2^{\mathrm{elect}}$ into $\Delta X_a^{\mathrm{elect}}$ and $\Delta X_b^{\mathrm{elect}}$, where the former is the change due to removal of proton from the electrostatic field of the carboxylate group undergoing proton dissociation and the latter being the change as the proton is removed from the electrostatic field of the other previously ionized carboxylate group, and assuming $\Delta X_a = \Delta X_1$ as the process of proton ionization from either carboxylate group is very

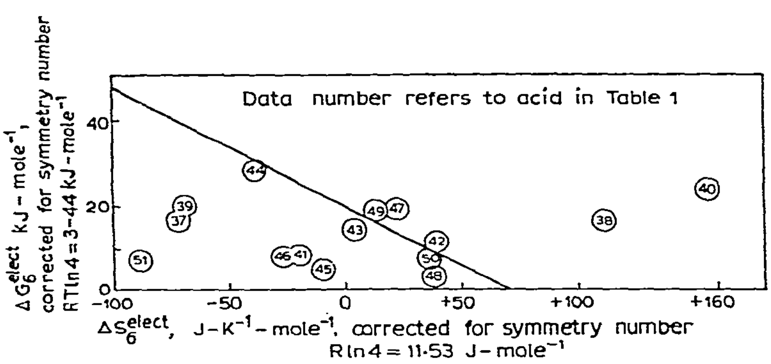

Fig. 4. Plot of $\Delta G_b^{\text{elect}}$ vs. $\Delta S_b^{\text{elect}}$ for dicarboxylic acid proton ionization.

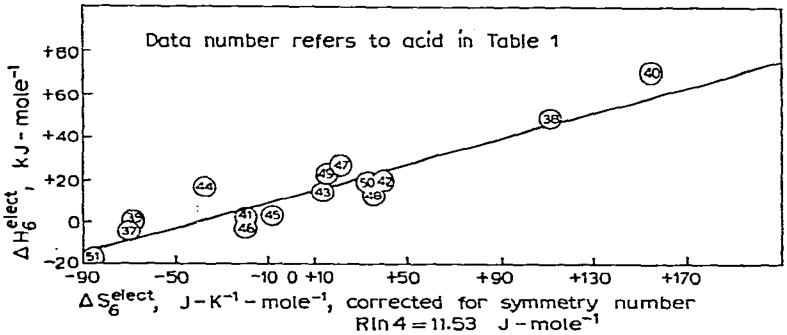

Fig. 5. Plot of $\Delta H_b^{\text{elect}}$ vs. $\Delta S_b^{\text{elect}}$ for dicarboxylic acid proton ionization.

similar in a dicarboxylic acid, eqns. (7), (8) and (9) reduce to the following expressions

$$\Delta G_b^{\text{elect}} = \Delta(\Delta G) - RT \ln \sigma \tag{10}$$

$$\Delta H_b^{\text{elect}} = \Delta(\Delta H) \tag{11}$$

$$\Delta S_b^{\text{elect}} = \Delta(\Delta S) + R \ln \sigma \tag{12}$$

The $\Delta G_b^{\text{elect}}$, $\Delta H_b^{\text{elect}}$ and $\Delta S_b^{\text{elect}}$ can be related[18] as

$$\Delta G_b^{\text{elect}} = \left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P^{-1} \Delta S_b^{\text{elect}} \tag{13}$$

$$\Delta H_b^{\text{elect}} = \left[\left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P^{-1} + T\right] \Delta S_b^{\text{elect}} \tag{14}$$

where ε is the dielectric constant[28] or the effective dielectric constant[29] of the medium.

In order to test the validity of eqns. (13) and (14) for the dicarboxylic acid data in Table 1 in formamide, plots of $\Delta G_b^{\text{elect}}$ vs. $\Delta S_b^{\text{elect}}$ and $\Delta H_b^{\text{elect}}$ vs. $\Delta S_b^{\text{elect}}$ are shown in Figs. 4 and 5, respectively. The lines are drawn in Figs. 4 and 5 have the slope predicted from the Bjerrum model −274 and 24, respectively. As is apparent in Figs. 4 and 5, few acids deviate from the line predicted by eqns. (13) and (14).

This shows that either (i) the simple electrostatic theory is not adequate for these acids, or (ii) the nonelectrostatic parts of the thermodynamic quantities were not eliminated in the same way as those observed in aqueous medium[18]. However, applying the Kirkwood–Westheimer theory involving the substitution of the effective dielectric constant for ε in eqn. (13) it is shown that the interactions in the acids are electrostatic in nature having $\varepsilon_{\mathrm{eff}} < \varepsilon_{\mathrm{formamide}}$.

It is of further interest to see whether the heats of ionization of dicarboxylic acids in formamide, ΔH_{D}, are explained from electrostatic theory. The values of ΔH_{D} are determined from the expression

$$[\Delta H_b^{\mathrm{elect}}]_{\mathrm{KW}} - [\Delta H_b^{\mathrm{elect}}]_{\mathrm{Bejerrum}} = \Delta H_{\mathrm{D}} = \frac{A}{r}\left[\frac{1}{\varepsilon_{\mathrm{eff}}} - \frac{1}{\varepsilon_{\mathrm{formamide}}}\right] \tag{15}$$

The values of $\Delta H_b^{\mathrm{elect}}$ were calculated according to the Kirkwood–Westheimer and Bjerrum theories by using the following equations[18]

$$[\Delta H_b^{\mathrm{elect}}]_{\mathrm{Bjerrum}} = \frac{A}{r\,\varepsilon_{\mathrm{formamide}}} - T\Delta S_b^{\mathrm{elect}} \tag{16}$$

$$[\Delta H_b^{\mathrm{elect}}]_{\mathrm{KW}} = \frac{A}{r\,\varepsilon_{\mathrm{eff}}} - T\Delta S_b^{\mathrm{elect}} \tag{17}$$

where $A = Ne^2z$, e is the charge on a proton, z is the charge number on the ion, and r is the proton-charge distance estimated from ΔpK_a data in Table 1 using the Kirkwood–Westheimer equations[29]. The values of ΔH_{D} so obtained are presented in Table 3 along with the values of $\varepsilon_{\mathrm{eff}}$.

TABLE 3

VALUES OF ΔH_{D} AND $\varepsilon_{\mathrm{eff}}$ IN FORMAMIDE

Acid	ΔH_D *(J mole^{-1})*	ε_{eff}	$\frac{1}{\varepsilon_{eff}} \times 10^2$	$\left(\frac{1}{\varepsilon_{eff}} - \frac{1}{\varepsilon_{formamide}}\right) \times 10^2$	$\frac{1}{r}\left(\frac{1}{\varepsilon_{eff}} - \frac{1}{\varepsilon_{formamide}}\right) \times 10^3$
Oxalic	5491	21.8	4.59	3.68	9.56
Oxaloacetic	5192	21.3	4.69	3.78	9.04
Malonic	6553	17.9	5.59	4.68	11.41
Mesoxalic	7995	16.3	6.13	5.22	13.92
Succinic	2418	30.0	3.33	2.42	4.21
Malic	2125	36.2	2.76	1.85	3.70
Tartaric	4968	16.4	6.10	5.19	8.65
Glutaric	2493	25.3	3.95	3.04	4.34
Glutamic	7013	11.0	9.09	8.18	12.21
Adipic	885	47.5	2.10	1.19	1.54
Maleic	10,396	11.0	9.09	8.18	18.10
Fumaric	1045	57.5	1.74	0.83	1.82
Phthalic	5537	20.5	4.88	3.97	9.64

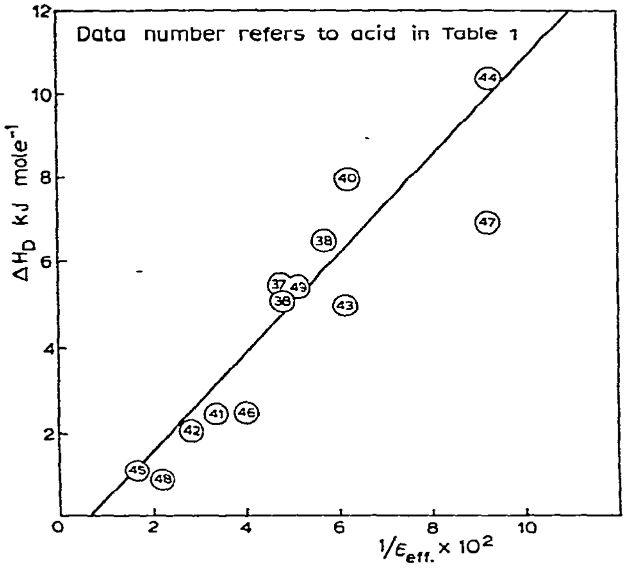

Fig. 6. Plot of ΔH_D vs. $1/\varepsilon_{eff}$ for dicarboxylic acid proton ionization.

In Fig. 6 the values of ΔH_D were plotted against $1/\varepsilon_{eff}$ showing a strong correlation between these quantities. The slope of the line was 1.16×10^5 J A/mole^{-1} which is in very good agreement with the value, 5.74×10^5 JA/mole^{-1} predicted from eqn. (15). As is apparent in Fig. 6, a linear relationship between ΔH_D and $1/\varepsilon_{eff}$ is obtained for all acids except mesoxalic, tartaric, glutaric and glutamic acids which do not fall on or near the line. Assuming that the linear relationship in Fig. 6 results from purely electrostatic interactions in the acids which fall on or near the line, the acid falling above the line (mesoxalic acid) may be characterized by either the second proton being held more strongly or the first proton being held more weakly (or a combination of both effects) than would be predicted from electrostatic effects alone, i.e. $\Delta H_2 - \Delta H_1 > \Delta H_2^{\mathrm{elect}} - \Delta H_1^{\mathrm{elect}}$ while for tartaric, glutaric and glutamic acids falling below the line the reverse is the case, i.e. $\Delta H_2 - \Delta H_1 < \Delta H_2^{\mathrm{elect}} - \Delta H_1^{\mathrm{elect}}$. It is evident from Table 1 that the deviations from the linear relationship of these acids parallel their abnormal behaviour with respect to their ΔH_1 and ΔH_2 values when compared with those of their related acids.

REFERENCES

1 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 25 (1972) 941.
2 U. N. Dash, *Aust. J. Chem.*, 26 (1975) 1653.
3 U. N. Dash, *Thermochim. Acta.*, 27 (1978) 379.
4 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 28 (1975) 793, 797, 1377, 1649.
5 B. Nayak and U. N. Dash, *Aust. J. Chem.*, 26 (1973) 111, 115.
6 U. N. Dash, *Thermochim. Acta.*, 17 (1976) 147.
7 U. N. Dash, *Thermochim. Acta.*, (1978) (in press).
8 U. N. Dash, *J. Chem. Thermodyn.*, (1978) (in press).
9 U. N. Dash, *J. Electroanal. Chem.*, (1978) (in press).
10 U. N. Dash, *Aust. J. Chem.*, 29 (1976) 1609.

11 R. K. Agarwal, U. N. Dash and B. Nayak, *Indian J. Chem.*, 13 (1975) 923.
12 U. N. Dash, *Aust. J. Chem.*, 30 (1977) 2621.
13 U. N. Dash, *Electrochim. Acta.*, (1978) (in press).
14 L. G. Hepler, *J. Am. Chem. Soc.*, 85 (1963) 3089.
15 D. T. Y. Chem and K. J. Laidler, *Trans. Faraday Soc.*, 58 (1962) 480.
16 L. Eberson and I. Wadso, *Acta. Chem. Scand.*, 17 (1963) 1552.
17 E. J. King, *Acid–Base Equilibria*, MacMillan, New York, 1965, Chaps. 7 and 8.
18 J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Am. Chem. Soc.*, 89 (1967) 213.
19 M. Eden and R. G. Bates, *J. Research Nat. Bur. Stand.*, 62 (1959) 2947.
20 A. W. Walde, *J. Chem. Soc.*, (1938) 431.
21 U. N. Dash, *Ph.D. Thesis*, Indian Institute of Technology, Kharagpur, India, 1973.
22 E. J. King, *Acid–Base Equilibria*, MacMillan, New York, 1965, p. 211.
23 K. S. Pitzer, *J. Am. Chem. Soc.*, 59 (1937) 2365.
24 M. Born, *Z. Phys.*, 1 (1920) 45.
25 R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, 19 (1951) 1139.
26 R. F. Brown, *J. Org. Chem.*, 27 (1962) 3010, 3015.
27 S. W. Benson, *J. Am. Chem. Soc.*, 80 (1958) 5151.
28 E. J. King, *Acid–Base Equilibria*, MacMillan, New York, 1965, p. 209.
29 J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6 (1938) 506.