Thermodynamics of Proton Ionization in Dilute Aqueous Solution. VII. ΔH° and ΔS° Values for Proton Ionization from Carboxylic Acids at 25°[1a]

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Abstract: A calorimetric study has been made of proton ionization from 14 mono- and 12 dicarboxylic acids in aqueous solution at 25°. The resulting ΔH° values are combined with literature ΔG° values to calculate corresponding ΔS° values. A compilation of ΔG°, ΔH°, and ΔS° values reported here and in the literature is given for proton ionization from 103 mono-, di-, and tricarboxylic acids. A linear relationship is found between ΔG° and ΔS° for these 103 carboxylic acids. The effects which give rise to this linear relationship are discussed. The changes in ΔH° and ΔS° from the first to the second step of ionization for 25 dicarboxylic acids have been examined in the light of published theories of electrostatic interaction in aqueous solutions. By introducing a term for the effective dielectric constant into the electrostatic calculations after the method of Kirkwood and Westheimer, the changes in ΔH° and ΔS° were found to be primarily electrostatic in nature. Deviations from the resulting correlations were taken as a measure of nonelectrostatic effects for dicarboxylic acids.

This study was undertaken as part[2] of a program to determine the thermodynamic quantities associated with proton ionization in aqueous solution from a variety of donor atom types. The present study deals with proton ionization from mono- and dicarboxylic acids. These acids are characterized generally by small ΔH° values with the dicarboxylic acids having simultaneous equilibria requiring the separation of the observed small energy change into two component changes of nearly equal magnitude. A thermometric titration calorimeter, recently designed and constructed in this laboratory,[3,4] makes possible the rapid and precise determination of these small enthalpy changes.

Precise pK values for many carboxylic acids are available,[5,6] but few reliable ΔH° or ΔS° values have been reported. Consequently, most discussions of the relative strengths of carboxylic acids have been based on pK data. However, the magnitude of a pK value is determined by the relative magnitudes of the corresponding ΔH° and ΔS° values. Therefore, it is possible for two series of acids to exhibit the same pK trends for entirely different reasons, and a knowledge of ΔH° and ΔS° values becomes important for an understanding of acid strength trends in any series.

Two major approaches, based on electrostatics and intramolecular effects, have been used to correlate and understand the relative acidities of related acids. These theories including their application and shortcomings have been discussed by King.[7] Both approaches have been used to explain trends and absolute magnitudes of pK values. Recently, however, several workers have attempted to interpret acid strength in terms of ΔH° and ΔS° rather than ΔG° alone. Hepler[8] has attempted to separate heats of ionization into two parts, *i.e.*, internal and external. By assuming a linear relationship between $\Delta H_{external}$ and the change in entropy for the ionization, values of $\Delta H_{internal}$ were calculated and found for several organic acids to be in accord with qualitative predictions based on electronegativities, even though the ΔH° values seem anomalous. The results of Laidler and associates summarized by Mortimer[9] show that, in the case of proton ionization from methyl substituted phenols and anilines, a linear relationship exists between ΔH° and $T\Delta S^\circ$. However, in more recent work Chen and Laidler[10] point out that serious errors were made in the previous calorimetric study on the phenols and anilines and that the results for the phenols should be disregarded and that suspicion should be attached to the results for the anilines. These same authors using new experimental data[10] found only a slight statistical correlation between ΔH° and $T\Delta S^\circ$. Also, a linear ΔS°–pK (ΔG°) relationship has been shown[11] for 43 mono-, di-, and tricarboxylic acids.

It seemed to us that the carboxylic acids would be an excellent model system for further study of enthalpy–entropy–free-energy relationships for proton ionization in aqueous solution. Also, by comparing the thermodynamic values for the first and second ionization steps of dicarboxylic acids, it may be possible, as shown by King,[12] to eliminate the nonelectrostatic

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(2) (a) Part I: R. M. Izatt and J. J. Christensen, *J. Phys. Chem.*, **66**, 359 (1962); (b) part II: J. J. Christensen and R. M. Izatt, *ibid.*, **66**, 1030 (1962); (c) part III: D. P. Wrathall, R. M. Izatt, and J. J. Christensen, *J. Am. Chem. Soc.*, **86**, 4779 (1964); (d) part IV: L. D. Hansen, J. A. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **5**, 569 (1966); (e) part V: R. M. Izatt, J. H. Rytting, L. D. Hansen, and J. J. Christensen *J. Am. Chem. Soc.*, 88, 2641 (1966); (f) part VI: J. J. Christensen, J. H. Rytting, and R. M. Izatt, *ibid.*, 88, 5105 (1966).

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(10) D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58**, 480 (1962).

(11) L. Eberson and I. Wadso, *Acta Chem. Scand.*, **17**, 1552 (1963).

(12) Reference 7, pp 138, 156.

part of the interaction, *i.e.*, bond dissociation energies, changes in rotational, vibrational, and translational motions, and specific solvation effects, and to quantitatively evaluate the electrostatic and nonelectrostatic parts of proton ionization from dicarboxylic acids.

In this paper are presented $\Delta H°$ and $\Delta S°$ values valid at 25° and zero ionic strength, μ, together with selected literature pK values for proton ionization from 14 mono- and 12 dicarboxylic acids. In addition, literature pK, $\Delta H°$, and $\Delta S°$ values for 77 mono-, di-, and tricarboxylic acids are compiled.

Experimental Section

Materials. The following chemicals were obtained in the best grade available and were used without further purification: sodium acetate (Baker, Analyzed), adipic acid (Matheson Co.), *dl*-alanine (Calbiochem., Grade A), β-alanine (Matheson Coleman and Bell, Reagent), aspartic acid (Eastman, White Label), benzoic acid (Eastman, White Label), α-bromopropionic acid (Eastman, White Label), β-bromopropionic acid (Eastman, White Label), butyric acid (Fisher, Highest Purity), α-chloropropionic acid (Eastman, White Label), β-chloropropionic acid (B. F. Goodrich, Reagent), cyclohexanecarboxylic acid (Eastman, White Label), diethylmalonic acid and ethylisoamylmalonic acid (prepared by Dr. William Epstein, University of Utah), formic acid (Baker, Analyzed), fumaric acid (Calbiochem, Grade A), glutaric acid (Eastman, White Label), glycine (Calbiochem, Grade A), glycolic acid (Matheson Coleman and Bell, Reagent), maleic acid (Eastman, White Label), malonic acid (Matheson Coleman and Bell, Reagent), oxalic acid (Baker, Analyzed), pimelic acid (Columbia Organic Chemicals, Inc., mp 103–105°), propionic acid (Eastman, White Label), suberic acid (Matheson Coleman and Bell, mp 140–142°), succinic acid (Matheson Coleman and Bell, Reagent), sodium hydroxide (Baker, Analyzed Reagent, carbonate free, 50% solution), and perchloric acid (Baker and Adamson).

Calorimetric Equipment. The thermometric titration calorimeter used in this study together with its calibration and operation has been described.[3,4] This type of calorimeter was found to be ideally suited for the determination of very small ΔH values since the solution in the calorimeter is always homogeneous making very high output amplification possible. Consequently, small temperature changes could be measured with high accuracy. In addition, for the dicarboxylic acids the two ΔH values for proton ionization could be measured in a single determination thus eliminating the necessity of calculating the $\Delta H°$ values by combination of data from two or more runs.

Procedure. Solutions of the sodium salts of each acid were titrated with $HClO_4$ solutions at 25°. Four thermometric titrations were made in each of two μ regions (μ approximately 0.01 to 0.02 and 0.05 to 0.06). The ΔH values obtained showed no significant variation with μ; therefore, all values were averaged in each case to obtain the final $\Delta H°$ value. The standard state used in this study is defined to be an ideal 1 M solution behaving as an infinitely dilute solution. Heat of dilution data for the $HClO_4$ titrant were taken from the literature.[13]

Calculations. The method used to calculate $\Delta H°$ from the thermometric titration data has been described.[4,14] The calculations were aided by an IBM 7040 computer. The computer programs (FORTRAN IV), input data, and the average output data for each run are available.[4]

Results

In Table I are presented for each acid investigated representative heats of reaction, Q, and moles of products formed as a function of moles of $HClO_4$ titrant added to the calorimeter. The reported Q values have been corrected for heat of stirring, heats of dilution of titrant, heat losses from the calorimeter, and heat due to water formation.

In Table II are presented the $\Delta H°$ values determined in this study together with previous pK and $\Delta H°$ data for carboxylic acid proton ionization. The pK values in Table II used in connection with the calorimetric data obtained in the present study are valid at 25° and μ = 0 unless otherwise noted. The accuracy of these pK values is difficult to estimate; however, the accuracy of most of the data appears to be between ±0.01 and ±0.02 pK unit. The accuracy of the pK values reported in conjunction with the other ΔH data in Table II can be obtained by referring to the reference source for the ΔH data.

The accuracy of the $\Delta H°$ values determined in this study is estimated to be about ±50 cal/mole although the precision in many cases is considerably better than this. This uncertainty was obtained from a consideration of the accuracy of the value previously obtained for the heat of ionization of H_2O using the same equipment[3,4] and the accuracy of the pK data used in the heat calculations. Both random and systematic uncertainties caused by the equipment, procedures, and calculations are included in the estimated ±50 cal/mole. When the listed uncertainties of the $\Delta H°$ values are greater than about ±50 cal/mole, the probable causes are either a large error in the equilibrium constant values or impurities in the materials used (including possible decomposition in the solution being titrated). The combined uncertainties in the pK and $\Delta H°$ values will cause an estimated uncertainty of about ±0.2 cal/deg mole in the $\Delta S°$ term.

Discussion

Good agreement is observed between the $\Delta H°$ values determined in this study and, where available, those reported by previous workers.

The $\Delta H°$ values in Table II are generally much smaller than the corresponding $T\Delta S°$ values for proton dissociation from carboxylic acids. In comparing any two acids, differences in either $\Delta H°$ or $T\Delta S°$ or both may be the cause of differences in acid strength. For instance, maleic and fumaric acids have nearly the same $\Delta H°$ values, but their pK values differ markedly because of a large difference between the $T\Delta S°$ values. On the other hand, the α- and β-halopropionic acids have nearly the same $T\Delta S°$ values with the difference in pK values being due to the differences in the $\Delta H°$ values.

A plot of $\Delta G°$ *vs.* $\Delta S°$ for all acids in Table II is shown in Figure 1. The significance of this plot is that the slope of the line drawn through the points as determined by a least-squares fit is −243, which approximates closely the value of −218 predicted by the Bjerrum theory of electrostatics.[15] Similar plots of $\Delta G°$ *vs.* $\Delta S°$ for the aliphatic carboxylic acids listed in Table II have least-squares slopes of −214 and −209 for the first and second dissociation, respectively. These results indicate that the interactions involved in proton ionization for the acids in Table II and especially for the aliphatic acids are primarily electrostatic. A similar correlation between pK and $\Delta S°$ has been previously noted for a somewhat smaller number of mono-, di-, and tricarboxylic acids.[11]

It is possible using the thermodynamic data for the dicarboxylic acids to investigate further the electro-

(13) J. A. Swanson, Ph.D. Dissertation, University of Nebraska, 1962; *cf. Dissertation Abstr.*, 23, 62-2618 (1962).

(14) J. J. Christensen, R. M. Izatt, L. G. Hansen, and J. Partridge, *J. Phys. Chem.*, 70, 2003 (1966).

(15) Reference 7, p 211.

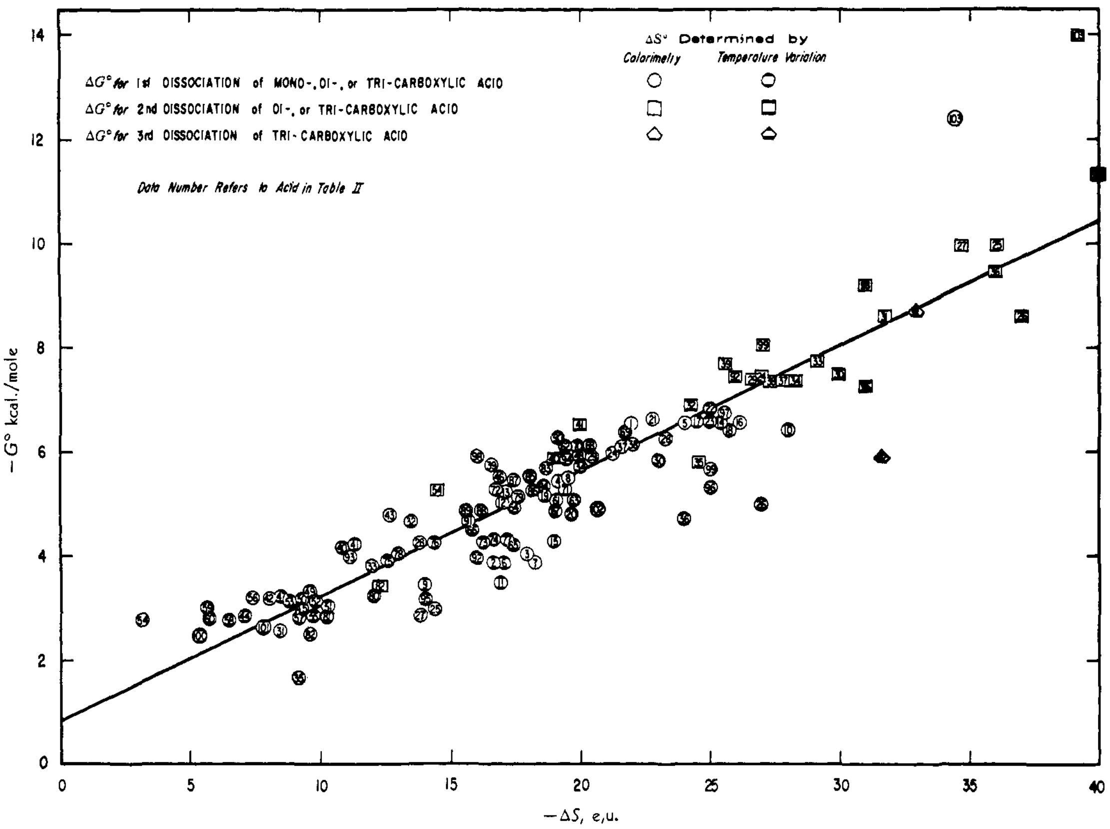


Figure 1. Plot of $\Delta G°$ *vs.* $\Delta S°$ for mono-, di-, and tricarboxylic acid proton ionization.

static and nonelectrostatic parts of the thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$. For a given dicarboxylic acid, one can largely cancel the nonelectrostatic parts of the changes in free energy, enthalpy, and entropy by taking the difference of these quantities between the second and the first ionization steps.[12]

Consider the following four steps to represent the first and second steps of the ionization of a dicarboxylic acid where the ionization has been separated into electrostatic (elect) and nonelectrostatic (non) parts.

$H_2A \longrightarrow HA^- — H^+$ ΔX_1^{non} (covalent bond is changed to an ionic bond) (1)

$HA^-—H^+ \longrightarrow HA^- + H^+$ ΔX_1^{elect} (proton is removed from electrostatic field of HA^-) (2)

$HA^- \longrightarrow A^{2-} — H^+$ ΔX_2^{non} (covalent bond is changed to an ionic bond) (3)

$A^{2-}—H^+ \longrightarrow A^{2-} + H^+$ ΔX_2^{elect} (proton is removed from electrostatic field of A^{2-}) (4)

Here $X = G$, H, or S. Subtracting (1) and (2) from the sum of (3) and (4) results in (5)

$$\Delta(\Delta X) = \Delta X_2^{non} + \Delta X_2^{elect} - \Delta X_1^{non} - \Delta X_1^{elect} + y \quad (5)$$

where y is a statistical correction as applied to dibasic acids and equal to $RT \ln \sigma$ for $X = G$, 0 for $X = H$, and $-R \ln \sigma$ for $X = S$. (σ is the symmetry correction factor for acid ionization constants[16] and equals 4 for dicarboxylic acids.)

The nonelectrostatic terms for dicarboxylic acids, which include the dissociation energy, changes in translational, rotational, and vibrational motions, and specific solvation effects should essentially cancel in (5) giving the following expressions for $\Delta(\Delta X)$

$$\Delta(\Delta G) = \Delta G_2^{elect} - \Delta G_1^{elect} + RT \ln \sigma \quad (6)$$

$$\Delta(\Delta H) = \Delta H_2^{elect} - \Delta H_1^{elect} \quad (7)$$

$$\Delta(\Delta S) = \Delta S_2^{elect} - \Delta S_1^{elect} - R \ln \sigma \quad (8)$$

ΔX_2^{elect} can further be considered to consist of two parts—one being the change, ΔX_a^{elect}, as the proton is removed from the electrostatic field of the carboxylate group from which it is dissociating, and the other being the change, ΔX_b^{elect}, due to the proton being removed from the electrostatic field of the other previously ionized carboxylate group. For dicarboxylic acids, since the process of proton ionization from either carboxylate group is very similar, it can be assumed that $\Delta X_a = \Delta X_1$ and eq 6, 7, and 8 further reduce to expressions for the removal of a proton from the electrostatic field of a previously ionized carboxylate group.

$$\Delta G_b^{elect} = \Delta(\Delta G) - RT \ln \sigma \quad (9)$$

$$\Delta H_b^{elect} = \Delta(\Delta H) \quad (10)$$

$$\Delta S_b^{elect} = \Delta(\Delta S) + RT \ln \sigma \quad (11)$$

Relationships among ΔG_b^{elect}, ΔH_b^{elect}, and ΔS_b^{elect} obtained from electrostatics, are given in

$$\Delta S_b^{elect} = \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P \Delta G_b^{elect} \quad (12)$$

$$\Delta H_b^{elect} = \left[\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P^{-1} + T\right] \Delta S_b^{elect} \quad (13)$$

where ϵ is the dielectric constant defined as being that of the medium, ϵ_{water}, according to the Bjerrum theory[17]

(16) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(17) Reference 7, p 209.

Table I. Corrected Heat Changes,[a] Q (cal), and Millimoles of H_2A and/or HA Formed as a Function of Millimoles of $HClO_4$ Added for the Protonation of Several Mono- and Dicarboxylate Anions[b–e]

	$HClO_4$ (0.3931 *F*), mmoles									
	0.4031	0.6046	0.8062	1.0071	1.2092	1.4108	1.6123	1.8139	2.0154	2.2170
Acetic Acid (0.02048)										
Q, cal	−0.0008	0.0065	0.0133	0.0216	0.0293	0.0397	0.0490	0.0587	0.0676	0.0711
HA, mmoles	0.4025	0.6037	0.8047	1.0055	1.2060	1.4058	1.6041	1.7976	1.9624	2.0223
Adipic Acid (0.02445)										
Q, cal	0.0432	0.0580	0.0783	0.2394	0.4037	0.5551	0.6670	0.6919	0.3873	−0.2227
HA, mmole	0.3310	0.4402	0.5004	0.5056	0.4552	0.3550	0.2162	0.0629	0.0214	0.0004
H_2A, mmole	0.0358	0.0818	0.1522	0.2499	0.3752	0.5246	0.6915	0.8565	0.9428	0.9603
α-Alanine (0.01974)										
Q, cal	−0.2120	−0.3134	−0.4058	−0.4945	−0.5634	−0.6427	−0.7109	−0.7679	−0.8227	−0.8679
HA, mmoles	0.2598	0.3791	0.4909	0.5950	0.6913	0.7798	0.8609	0.9348	1.0019	1.0627
β-Alanine (0.01979)										
Q, cal	−0.4368	−0.6549	−0.8628	−1.0667	−1.2733	−1.4686	−1.6525	−1.8068	−1.9273	−2.0063
HA, mmoles	0.3960	0.5924	0.7872	0.9795	1.1676	1.3485	1.5164	1.6604	1.7677	1.8356
Aspartic Acid (0.00930), Sodium Hydroxide (0.0090)										
Q, cal	−0.5411	−0.8015	−1.0436	−1.2621	−1.4308	−1.5688	−1.6609	−1.7324	−2.2028	−2.9909
HA, mmole	0.3787	0.5419	0.6588	0.7005	0.6803	0.6342	0.5823	0.5321	0.4861	0.4450
H_2A, mmole	0.0059	0.0177	0.0446	0.0947	0.1608	0.2293	0.2933	0.3506	0.4011	0.4452
Benzoic Acid (0.01955)										
Q, cal	−0.0629	−0.0923	−0.1201	−0.1465	−0.1756	−0.2006	−0.2242	−0.2472	−0.2585	−0.2682
HA, mmoles	0.4010	0.6010	0.8006	0.9993	1.1966	1.3910	1.5787	1.7465	1.8584	1.9040
α-Bromopropionic Acid (0.02013), Sodium Hydroxide (0.01967)										
Q, cal	0.3847	0.6022	0.8180	1.0236	1.2029	1.3627	1.4878	1.5874	1.6597	1.7161
HA, mmoles	0.3700	0.5493	0.7232	0.8898	1.0468	1.1912	1.3199	1.4304	1.5216	1.5946
β-Bromopropionic Acid (0.01954), Sodium Hydroxide (0.01899)										
Q, cal	0.0256	0.0470	0.0561	0.0598	0.0651	0.0702	0.0750	0.0772	0.0778	0.0785
HA, mmoles	0.3994	0.5984	0.7964	0.9928	1.1867	1.3752	1.5518	1.6986	1.7898	1.8322
***n*-Butyric Acid (0.01926), Sodium Hydroxide (0.01889)**										
Q, cal	0.2493	0.3807	0.5161	0.6448	0.7827	0.9174	1.0504	1.1741	1.2378	1.2503
HA, mmoles	0.4026	0.6037	0.8047	1.0055	1.2058	1.4052	1.6017	1.7832	1.8715	1.8858
α-Chloropropionic Acid (0.01978), Sodium Hydroxide (0.01967)										
Q, cal	0.4933	0.7606	1.0122	1.2601	1.4895	1.7000	1.8763	2.0302	2.1518	2.2495
HA, mmoles	0.3638	0.5392	0.7085	0.8701	1.0215	1.1603	1.2839	1.3905	1.4796	1.5520
β-Chloropropionic Acid (0.01959), Sodium Hydroxide (0.01897)										
Q, cal	0.0562	0.1006	0.1540	0.2061	0.2370	0.2502	0.2563	0.2582	0.2643	0.2580
HA, mmoles	0.3995	0.5984	0.7964	0.9929	1.1867	1.3753	1.5518	1.6983	1.7889	1.8309
Cyclohexanecarboxylic Acid (0.01780), Sodium Hydroxide (0.01762)										
Q, cal	0.3685	0.5447	0.7065	0.8932	1.0764	1.2597	1.4373	1.5686	1.5963	1.6072
HA, mmoles	0.4026	0.6038	0.8048	1.0056	1.2057	1.4044	1.5966	1.7278	1.7495	1.7540
Diethylmalonic Acid (0.01028)										
Q, cal	0.1187	0.1872	0.2527	0.5427	0.4732	0.3539	0.3516	0.3361	0.3088	0.2632
HA, mmole	0.4024	0.6039	0.8054	1.0000	0.9010	0.8070	0.7244	0.6526	0.5905	0.5369
H_2A, mmole	0.0000	0.0000	0.0000	0.0025	0.1059	0.2000	0.2826	0.3544	0.4165	0.4701
Ethylisoamylmalonic Acid (0.00865)										
Q, cal	0.1440	0.2509	0.3401	0.4721	0.5891	0.4678	0.2313	−0.0649	−0.1112	−0.1592
HA, mmole	0.4030	0.6044	0.6618	0.5658	0.4831	0.4128	0.3534	0.3035	0.2614	0.2258
H_2A, mmole	0.0000	0.0000	0.0498	0.1458	0.2285	0.2989	0.3582	0.4082	0.4503	0.4859
Formic Acid (0.01983)										
Q, cal	−0.0150	−0.0146	−0.0151	−0.0146	−0.0151	−0.0156	−0.0181	−0.0216	−0.0274	−0.0353
HA, mmoles	0.3971	0.5945	0.7905	0.9844	1.1749	1.3593	1.5320	1.6818	1.7917	1.8578
Fumaric Acid (0.01066)										
Q, cal	0.0487	0.0705	0.0725	0.0443	−0.0771	−0.1072	−0.2064	−0.3192	−0.4340	−0.5490
HA, mmole	0.3820	0.5481	0.6793	0.7510	0.7438	0.6692	0.5597	0.4434	0.3397	0.2586
H_2A, mmole	0.0092	0.0256	0.0586	0.1196	0.2167	0.3426	0.4790	0.6088	0.7192	0.8034
Glutaric Acid (0.01158)										
Q, cal	0.0095	0.0086	0.0023	−0.0140	−0.0466	−0.0900	−0.1435	−0.2100	−0.2842	−0.3691
HA, mmole	0.3538	0.4899	0.5886	0.6419	0.6445	0.5961	0.5020	0.3714	0.2169	0.0677
H_2A, mmole	0.0245	0.0570	0.1083	0.1821	0.2811	0.4054	0.5520	0.7159	0.8885	1.0449
Glycine (0.02257)										
Q, cal	−0.3271	−0.4703	−0.6167	−0.7497	−0.8455	−0.9988	−1.1078	−1.2118	−1.3068	−1.3909
HA, mmoles	0.3267	0.4815	0.6297	0.7702	0.9023	1.0253	1.1385	1.2417	1.3349	1.4182
Glycolic Acid (0.01957), Sodium Hydroxide (0.01899)										
Q, cal	−0.0744	−0.1100	−0.1406	−0.1746	−0.2103	−0.2424	−0.2708	−0.2964	−0.3073	−0.3228
HA, mmoles	0.3978	0.5956	0.7921	0.9864	1.1772	1.3611	1.5306	1.6700	1.7611	1.8094

Table I (*Continued*)

					HClO₄ (0.3931 *F*), mmoles					
	0.4031	0.6046	0.8062	1.0071	1.2092	1.4108	1.6123	1.8139	2.0154	2.2170
					Maleic Acid (0.00970)					
Q, cal	0.1244	0.1907	0.4512	0.6210	0.3600	0.0238	−0.0911	−0.2109	−0.3313	−0.4535
HA, mmole	0.4030	0.6043	0.8050	0.8979	0.8316	0.7713	0.7176	0.6697	0.6271	0.5890
H_2A, mmole	0.0000	0.0001	0.0003	0.0293	0.0968	0.1572	0.2110	0.2589	0.3016	0.3397
					Malonic Acid (0.00995)					
Q, cal	0.1346	0.2231	0.3598	0.6267	0.5523	0.3679	0.1118	−0.2254	−0.3692	−0.5064
HA, mmole	0.4017	0.6002	0.7909	0.8903	0.7706	0.6310	0.5060	0.4019	0.3199	0.2577
H_2A, mmole	0.0006	0.0019	0.0068	0.0529	0.1948	0.3378	0.4639	0.5686	0.6508	0.7132
					Oxalic Acid (0.00977)					
Q, cal	0.3814	0.5722	0.7469	0.9364	0.8335	0.7659	0.6923	0.5991	0.5023	0.3923
HA, mmole	0.3955	0.5874	0.7635	0.8808	0.9092	0.9041	0.8910	0.8758	0.8603	0.8449
H_2A, mmole	0.0004	0.0012	0.0037	0.0124	0.0300	0.0499	0.0695	0.0883	0.1061	0.1230
					Pimelic Acid (0.01012)					
Q, cal	0.1644	0.1937	0.2158	0.2354	0.3045	0.4719	0.6196	0.7242	0.6858	0.2182
HA, mmole	0.3364	0.4586	0.5376	0.5681	0.5478	0.4783	0.3652	0.2191	0.0747	0.0221
H_2A, mmole	0.0271	0.0667	0.1278	0.2130	0.3234	0.4581	0.6138	0.7834	0.9361	0.9895
					Propionic Acid (0.01998), Sodium Hydroxide (0.01899)					
Q, cal	0.0552	0.0958	0.1345	0.1743	0.2162	0.2572	0.2974	0.3359	0.3604	0.3662
HA, mmoles	0.4026	0.6038	0.8049	1.0058	1.2062	1.4059	1.6030	1.7862	1.8742	1.8871
					Suberic Acid (0.07890)					
Q, cal	0.1450	0.3504	0.4247	0.4857	0.5388	0.5945	0.6591	0.7455	0.4227	
HA, mmole	0.3137	0.3953	0.4170	0.3768	0.2792	0.1377	0.0190	0.0039	0.0000	
H_2A, mmole	0.0444	0.1042	0.1937	0.3139	0.4619	0.6283	0.7530	0.7761	0.7811	
					Succinic Acid (0.00992)					
Q, cal	−0.2329	−0.3547	−0.5295	−0.5344	−0.5704	−0.6556	−0.7831	−0.9631	−1.2934	−1.8655
HA, mmole	0.3771	0.5325	0.6411	0.6740	0.6190	0.4972	0.3396	0.1740	0.0051	0.0168
H_2A, mmole	0.0129	0.0358	0.0820	0.1658	0.2932	0.4531	0.6289	0.8019	0.9227	0.9612

[a] Corrected for heat of stirring, heat loss from the calorimeter, heat due to water formation, and heat of dilution of the titrant. [b] A representative run is given for each system; complete data and IBM computer programs are given in ref 4. [c] Initial volume, 100.0 ml. [d] Initial molar acid concentrations are given in parentheses. [e] Initial molar base concentrations are given in parentheses for those cases where (1) the base was not added in stoichiometric amounts or (2) the sodium salt was used.

or the effective dielectric constant, ϵ_{eff}, calculated from the dielectric constants of the medium and acid, and

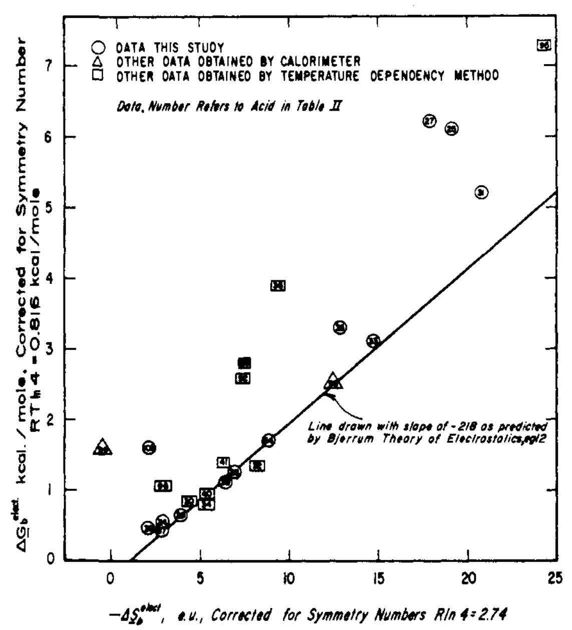


Figure 2. Plot of ΔG_b^{elect} *vs.* ΔS_b^{elect} for dicarboxylic acid proton ionization.

from structural data according to the Kirkwood–Westheimer theory.[18]

(18) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

Figures 2 and 3 show the dicarboxylic acid data from Table II plotted as ΔG_b^{elect} *vs.* ΔS_b^{elect} and ΔH_b^{elect}

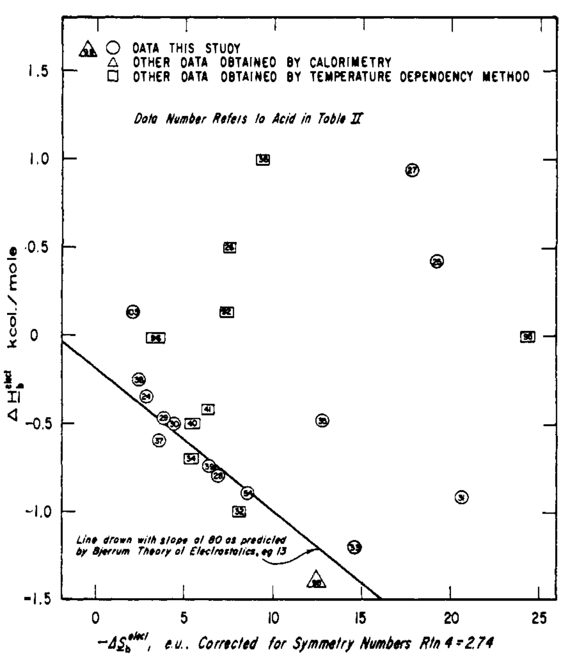


Figure 3. Plot of ΔH_b^{elect} *vs.* ΔS_b^{elect} for dicarboxylic acid proton ionization.

vs. ΔS_b^{elect}, respectively. On each figure is drawn a line having the slope predicted from the Bjerrum model

Table II. Thermodynamic Quantities for Proton Ionization from Carboxylic Acids in Aqueous Solutions at 25°[a]

	Name	Formula[b]	pK	$\Delta H°$, kcal/mole	$\Delta S°$, cal/deg mole	Method	Ref.
		Aliphatic Monocarboxylic Acids					
1	Acetic	CH_3-	(4.766)[c]	−0.02 ± 0.05 (−0.11,[c] −0.07,[y] −0.11[z])	−21.9	C	*hh*
2	Bromoacetic	$BrCH_2-$	2.90	−1.24	−17	T	*ii*
3	α-Bromopropionic	CH_3CHBr-	(2.971)[h]	−1.31 ± 0.20	−18.0	C	*hh*
4	β-Bromopropionic	$Br(CH_2)_2-$	(3.992)[h]	−0.32 ± 0.30	−19.3	C	*hh*
5	*n*-Butyric	$CH_3(CH_2)_2-$	(4.820)[i]	−0.64 ± 0.05 (−0.69[i], −0.73[y], −0.70,[bb] −0.72[z])	−24.2	C	*hh*
6	Chloroacetic	$ClCH_2-$	2.87	−1.12	−17	T	*ii*
7	α-Chloropropionic	CH_3CHCl-	(2.880)[h]	−1.50 ± 0.05	−18.2	C	*hh*
8	β-Chloropropionic	$Cl(CH_2)_2-$	(3.992)[j]	−0.32 ± 0.15 (−0.59[bb])	−19.3	C	*hh*
9	Cyanoacetic	$CNCH_2-$	2.47	−0.90	−14	T	*ii*
10	Diethylacetic	$(CH_3CH_2)_2CH-$	4.74	−2.03	−28	T	*ii*
11	Fluoracetic	FCH_2-	2.59	−1.39	−17	T	*ii*
12	Formic	$H-$	(3.751)[m]	+0.01 ± 0.05 (−0.01,[m] −0.13,[y] −0.04[z])	−17.1	C	*hh*
13	Glycolic	$OHCH_2-$	3.381[q]	+0.11 ± 0.07	−17.2	C	*hh*
			(3.832)[r]	(+0.218)			
14	Hexanoic	$CH_3(CH_2)_4-$	4.86	−0.70	−25	T	*ii*
15	Iodoacetic	ICH_2-	3.18	−1.42	−19	T	*ii*
16	Isobutyric	$(CH_3)_2CH-$	4.86	−1.01	−26	C	*ii*
17	Isohexoic	$(CH_3)_2CH(CH_2)_2-$	4.85	−0.72	−25	T	*ii*
18	Isovaleric	$(CH_3)_2CHCH_2-$	4.78	−1.22	−26	T	*ii*
19	Lactic	CH_3CHOH-	3.860	−0.17	−18.2	T	*jj*
20	Methoxyacetic	CH_3OCH_2-	3.570	−0.960	−19.6	T	*oo*
21	Propionic	CH_3CH_2-	(4.874)[v]	−0.14 ± 0.05 (−0.17,[v] −0.08[y], −0.23[z])	−22.8	C	*hh*
22	Trimethylacetic	$(CH_3)_3C-$	5.03	−0.72	−25	T	*ii*
23	Valeric	$CH_3(CH_2)_3-$	4.84	−0.72	−25	T	*ii*
24	Adipic	$-(CH_2)_4-$	(4.418)[d]	−0.30 ± 0.05	−21.5	C	*hh*
			(5.412)[d]	−0.64 ± 0.05	−26.9	C	*hh*
25	Diethylmalonic	$-C(CH_3CH_2)_2-$	(2.211)[d]	−1.25 ± 0.05	−14.3	C	*hh*
			(7.292)[d]	−0.82 ± 0.05	−36.1	C	*hh*
26	β,β-Dimethylglutaric	$-CH_2C(CH_3)_2CH_2-$	3.70	−3	−27	T	*ii*
			6.34	−2.5	−37	T	*ii*
27	Ethylisoamylmalonic	$CH_3CH_2\overset{\mid}{\underset{\mid}{C}}(CH_2)_2CH(CH_3)_2$	(2.50)[l]	−1.31 ± 0.15	−14.2	C	*hh*
			(7.31)[l]	−0.36 ± 0.10	−34.7	C	*hh*
28	Fumaric	$-CH{:}CH-$	(3.095)[n]	+0.11 ± 0.05	−13.8	C	*hh*
			(4.602)[n]	−0.68 ± 0.05	−23.3	C	*hh*
29	Glutaric	$-(CH_2)_3-$	(4.344)[d]	−0.12 ± 0.05	−20.3	C	*hh*
			(5.420)[d]	−0.58 ± 0.05	−26.7	C	*hh*
30	β-Isopropylglutaric	$(CH_3)_2(CH)_2(CH_2-)_2$	4.30	−1	−23	T	*ii*
			5.51	−1.5	−30	T	*ii*
31	Maleic	$-Cl{:}CH-$	(1.910)[n]	+0.08 + 0.10	−8.5	C	*hh*
			(6.332)[n]	−0.83 ± 0.05	−31.8	C	*hh*
32	Malic	$-CH_2CHOH-$	3.459	+0.707	−13.5	T	*ww*
			5.097	−0.283	−24.3	T	*ww*
33	Malonic	$-CH_2-$	(2.826)[d]	+0.29 ± 0.05	−12.0	C	*hh*
			(5.696)[s]	−0.92 ± 0.05 (−1.15[s])	−29.2	C	*hh*
34	β-Methylglutaric	$-CH_2CHCH_3CH_2-$	4.25	−0.3	−20	T	*ii*
			5.41	−1.0	−28	T	*ii*
35	Oxalic	. . .	(1.271)[t]	−1.02 ± 0.05	−9.2	C	*hh*
			(4.266)[u]	−1.50 ± 0.05 (−1.55[ff] −1.66[u])	−24.6	C	*hh*
36	β,β-Pentamethylene-glutaric	$-CH_2C(CH_2)_5CH_2-$	3.49	−2.5	−24	T	*ii*
			6.96	−1.5	−36	T	*ii*
37	Pimelic	$-(CH_2)_5-$	(4.484)[d]	−0.33 ± 0.10	−21.6	C	*hh*
			(5.424)[d]	−0.93 ± 0.10	−27.9	C	*hh*
38	Suberic	$-(CH_2)_6-$	(4.512)[d]	−0.39 ± 0.05	−21.9	C	*hh*
			(5.404)[d]	−0.64 ± 0.12	−26.9	C	*hh*
39	Succinic	$-(CH_2)_2-$	(4.207)[w]	+0.80 ± 0.05 (+0.76,[w] + 0.60[gg])	−16.6	C	*hh*
			(5.635)[x]	+0.06 ± 0.05 (+ 0.11[x])	−25.6	C	*hh*
40	Tartaric	$-CHOHCHOH-$	3.04	+0.74	−11	T	*ii*
			4.31	+0.24	−19	T	*ii*

Table II (*Continued*)

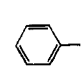
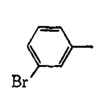
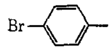
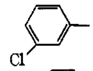
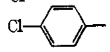
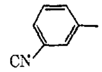
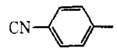
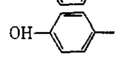
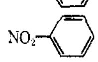
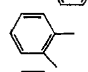
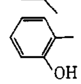
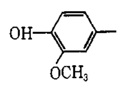
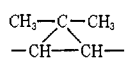
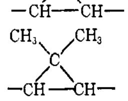
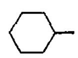
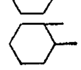
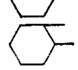
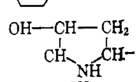
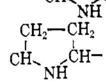
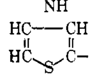
	Name	Formula[b]	p*K*	$\Delta H°$, kcal/mole	$\Delta S°$, cal/deg mole	Method	Ref
			Aliphatic Tricarboxylic Acids				
41	Citric	$-CH_2COHCH_3{}^+-$	3.13	+1.00	−11	T	*ii*
			4.76	+0.58	−20	T	*ii*
			6.40	−0.80	−33	T	*ii*
			Amino Acids and Derivatives, Amino Acids				
42	α-Alanine	$CH_3CHNH_3{}^+$	(2.348)[e] (2.340)[f]	+0.75 ± 0.10 (+0.72,[f] + 0.62,[dd] + 0.80[e])	−8.2	C	*hh*
43	β-Alanine	$NH_3{}^+(CH_2)_2-$	(3.551)[aaa]	+1.08 ± 0.05	−12.6	C	*hh*
44	Allothreonine	$CH_3CHOHCHNH_3{}^+-$	2.105	+0.77	−7.0	T	*ll*
45	α-Aminobutyric	$CH_3CH_2CHNH_3{}^+-$	2.284	+0.30	−9.5	T	*nn*
46	γ-Aminobutyric	$NH_3{}^+(CH_2)_3-$	4.03	+0.40	−17	T	*ii*
47	α-Amino-*n*-caproic	$CH_3(CH_2)_3CH(NH_3{}^+)-$	2.33	+0.56	−8.8	T	*rr*
48	ε-Aminocaproic	$NH_3{}^+(CH_2)_5-$	4.37	0	−20	T	*ii*
49	α-Aminoisobutyric	$(CH_3)_2CNH_3{}^+-$	2.357	+0.492	−9.1	T	*nn*
50	α-Aminoisocaproic	$CH_3CHCH_3CH_2CHNH_3{}^+-$	2.329	+0.42	−9.2	T	*rr*
51	α-Aminoisovaleric	$CH_3CHCH_3CHNH_3{}^+-$	2.287	+0.08	−10.2	T	*rr*
52	α-Amino-β-methyl-*n*-valeric	$CH_3CH_2CHCH_3CHNH_3{}^+-$	2.320	+0.30	−9.6	T	*rr*
53	α-Amino-*n*-valeric	$CH_3(CH_2)_2CH(NH_3{}^+)-$	2.316	+0.55	−8.8	T	*rr*
54	Aspartic	$-CH_2CHNH_3{}^+-$	(2.05)[bbb]	+1.85 ± 0.07 (+1.76)[ee]	−3.2	C	*hh*
			(3.87)[bbb]	+0.96 ± 0.05	−14.5	C	*hh*
55	N,N-Dimethylglycine	$(CH_3)_2NH^+CH_2-$	2.146	−0.155	−9.3	T	*tt*
56	Glycine	$NH_3{}^+CH_2-$	(2.351)[o,p]	+0.98 ± 0.05 (+ 0.95,[o] + 1.16,[p] +0.93,[cc] + 1.18[y])	−7.5	C	*hh*
57	Methionine	$CH_3S(CH_2)_2CHNH_3{}^+-$	2.125	+0.14	−9.3	T	*tt*
58	β-Methoxy-DL-alanine	$CH_3OCH_3CHNH_3{}^+-$	2.037	+0.82	−6.56	T	*oo*
59	Serine	$OHCH_2CHNH_3{}^+-$	2.187	+1.320	−5.57	T	*oo*
60	Threonine	$CH_3CHOHCHNH^+{}_3-$	2.096	+1.18	−5.6	T	*nn*
			Amino Acids and Derivatives, Peptides				
61	N-Acetyl-α-alanine	$CH_3CH(NHCOCH_3)-$	3.7152	−0.631	−19.12	T	*mm*
62	N-Acetyl-β-alanine	$CH_3CONH(CH_2)_2-$	4.4452	+0.255	−19.48	T	*mm*
63	N-Acetyl-α-amino-*n*-butyric	$CH_3CH_2CH(CH_3CONH)-$	3.7158	−0.773	−19.59	T	*mm*
64	N-Acetylglycine	$CH_3CONHCH_2-$	3.6698	−0.150	−17.3	T	*kk*
65	L-Alanyl-D-alanine	$CH_3CHNH_3{}^+CONHCHCH_3-$	3.12	−1.023	−17.3	T	*uu*
66	L-Alanyl-L-alanine	$CH_3CHNH_3{}^+CONHCHCH_3-$	3.30	−0.134	−15.7	T	*uu*
67	Carbamoyl-α-alanine	$NH_3{}^+CONHCHCH_3-$	3.8924	−0.232	−18.59	T	*pp*
68	Carbamoyl-β-alanine	$NH_3{}^+CONH(CH_2)_2-$	4.4873	+0.194	−19.88	T	*pp*
69	Carbamoyl-γ-amino-butyric	$NH_3{}^+CONH(CH_2)_3-$	4.6831	−0.115	−21.83	T	*pp*
70	Carbamoyl-α-amino-isobutyric	$NH_3{}^+CONHC(CH_3)_2-$	4.4627	+0.217	−19.69	T	*pp*
71	Carbamyl-α-amino-*n*-butyric	$NH_3{}^+CONHCHCH_3CH_2-$	3.8856	−0.493	−19.43	T	*pp*
72	Carbamoylglycine	$NH_3{}^+CONHCH_2-$	3.8758	+0.290	−16.76	T	*pp*
73	Glycylalanine	$NH_3{}^+CH_2CONHCHCH_3-$	3.1532	−0.563	−16.32	T	*kk*
74	Glycyl-α-amino-*n*-butyric	$NH_3{}^+CH_2CONHCHCH_3CH_2-$	3.1546	−0.672	−16.69	T	*kk*
75	Glycylasparagine	$NH_3{}^+CH_2CONHCH(CH_2CONH_2)-$	2.9420	+0.133	−13.01	T	*kk*
76	Glycylglycine	$NH_3{}^+CH_2CONHCH_2-$	3.1397	+0.032	−14.26	T	*kk*
77	Glycylleucine	$NH_3{}^+CH_2CONHCHCH_2CH(CH_3)_2$	3.1800	−0.752	−17.07	T	*kk*
78	Glycylserine	$NH_3{}^+CH_2CONHCHCH_2OH-$	2.9808	+0.189	−13.0	T	*kk*
79	N-Propionylglycine	$CH_3CH_2CONHCH_2-$	3.7176	−0.140	−17.5	T	*mm*
			Amino Acids and Derivatives, N-Substituted				
80	N-Hydroxyethylethylene-diaminetriacetic	$HO(CH_2)_2NH^+(CH_3-)_2(CH_2)_2NH^+-(CH_3-)_2$	2.39	−0.34	−12	T	*xx*
81	N-Methylaminediacetic	$CH_3NH_2{}^+(CH_2-)_2$	2.148	0	−9.5	T	*vv*
82	Nitrilotriacetic	$NH^+(CH_2-)_3$	1.88	−0.30	−9.6	C	*qq*
			2.48	−0.30	−12.3	C	*qq*
			4.28	+3.70	−31.9	C	*qq*
			Aromatic				
83	Benzoic		(4.201)[d,g]	+0.15 ± 0.05 (+0.10,[g,zz] +0.09,[y] +0.11[bb])	−18.7 (−18.9)[g]	C	*hh*
84	*m*-Bromobenzoic		3.809	−0.17	−17.6	T	*jj*

Table II (*Continued*)

	Name	Formula[b]		pK	$\Delta H°$, kcal/mole	$\Delta S°$, cal/deg mole	Method	Ref
85	*p*-Bromobenzoic			4.002	+0.11	−17.9	T	*jj*
86	*m*-Chlorobenzoic			3.827	−0.18	−18.1	T	*jj*
87	*p*-Chlorobenzoic			3.986	+0.23	−17.4	T	*jj*
88	*m*-Cyanobenzoic			3.598	−0.04	−16.6	T	*jj*
89	*p*-Cyanobenzoic			3.551	+0.03	−16.1	T	*jj*
90	*p*-Hydroxybenzoic			4.582	+0.54	−19.1	T	*jj*
91	*p*-Nitrobenzoic			3.442	+0.03	−15.6	T	*jj*
92	Phthalic			2.95 5.42	−0.64 −0.50	−16 −26	T T	*ii* *ii*
93	Salicylic			2.973	+0.73	−11.1	C	*ss*
94	*p*-Hydroxy-*m*-methoxy-benzoic			4.355	+0.145	−19.50	T	*yy*
			Alicyclic					
95	*cis*-Caronic			2.34 8.31	−1 −1	−14 −41	T T	*ii* *ii*
96	*trans*-Caronic			3.92 5.32	−2 −2	−25 −31	T T	*ii* *ii*
97	Cyclohexanecarboxylic			4.903[k]	−0.92 ± 0.06	−25.5	C	*hh*
98	*cis*-Cyclohexane-1,2-dicarboxylic			4.34 6.76	+1.1 −0.30	−16 −31	C C	*ii* *ii*
99	*trans*-Cyclohexane-1,2-dicarboxylic			4.18 5.93	−1.9 −0.24	−25 −27	C C	*ii* *ii*
10	Hydroxyproline			1.815	+0.918	−5.2	T	*nn*
101	Proline			1.970	+0.342	−7.8	T	*nn*
102	Thiophen-2-carboxylic			3.529	−1.3	−20.6	T	*tt*
103	1,12-$B_{12}H_{10}(COOH)_2^{2-}$	$-^1[B_{12}H_{10}]^{12}-$		9.07 10.236	2.15 2.30	−34.4 −39.1	C C	*hh* *hh*

[a] Values determined in the present study indicated by referenced letter *hh* are valid at 25° and μ = 0 except as indicated. The uncertainties are given as standard deviations. The pK values used in the $\Delta H°$ determinations reported in this study are given in parentheses. Values for ΔH determined by previous investigators for the acids studied here are given in parentheses. The letter in the method column indicates in each case whether ΔH was determined by calorimetry (C) or by temperature variation studies (T). The letter in the reference column indicates in each case the origin of the ΔH value. The pK value used can also be found in this reference. [b] The formula given is R corresponding to RCOOH for mono-, $R(COOH)_2$ for di-, and $R(COOH)_3$ for tricarboxylic acids. [c] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 655 (1933). [d] R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2158 (1931). [e] P. K. Smith, A. C. Taylor, and E. R. B. Smith, *J. Biol. Chem.*, **122**, 116 (1937). [f] L. F. Nims and P. K. Smith, *ibid.*, **101**, 411 (1933). [g] A. V. Jones and H. N. Parton, *Trans. Faraday Soc.*, **48**, 8 (1952). [h] E. Larson, *Z. Physik. Chem.*, **A165**, *53*, (1933). [i] H. S. Harned and R. O. Sutherland, *J. Am. Chem. Soc.*, **56**, 2040 (1934). [j] H. M. Dawson, G. V. Hall, and A. Key, *J. Chem. Soc.*, 2848 (1928). [k] M. Kilpatrick, R. D. Eanes, and J. G. Morse, *J. Am. Chem. Soc.*, **75**, 588 (1953). [l] Personal communication, Dr. Edward Eyring, University of Utah; μ = 0.1 (KCl). [m] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1044 (1934). [n] G. Dalgren, Jr., and F. A. Long, *ibid.*, **82**, 1306 (1960). [o] E. J. King, *ibid.*, **73**, 158 (1951). [p] B. B. Owen, *ibid.*, **56**, 27 (1934). [q] L. F. Nims, *ibid.*, **58**, 987 (1936). [r] P. B. Davies and C. B. Monk, *Trans. Faraday Soc.*, **50**, 128 (1954). [s] W. J. Hamer, J. O. Burton, and S. F. Acree, *J. Res. Natl. Bur. Std.*, **24**, 290 (1940). [t] L. S. Darken, *J. Am. Chem. Soc.*, **63**, 1010 (1941). [u] G. D. Pinching, and R. G. Bates, *J. Res. Natl. Bur. Std.*, **40**, 412 (1948). [v] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2383 (1933). [w] G. D. Pinching and R. G. Bates, *J. Res. Natl. Bur. Std.*, **45**, 448 (1950). [x] G. D. Pinching and R. G. Bates, *ibid.*, **45**, 327 (1950). [y] W. J. Canady, H. M. Pappée, and K. J. Laidler, *Trans. Faraday Soc.*, **54**, 505 (1958). [z] D. H. Everett D. A. Landsman, and B. R. W. Pinsent, *Proc. Roy. Soc.* (London), **A215**, 409 (1952). [aa] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2379 (1933). [bb] T. L. Cottrell, G. W. Drake, D. L. Levi, K. J. Tully, and J. H. Wolfenden, *J. Chem. Soc.*, 1016 (1948). [cc] J. M. Sturtevant, *J. Am. Chem. Soc.*, **63**, 93 (1941). [dd] J. M. Sturtevant, *ibid.*, **64**, 768 (1942). [ee] C. L. A. Schmidt, P. L. Kirk, and W. K. Appleman, *J. Biol. Chem.*, **88**, 285 (1930). [ff] H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 3112 (1939). [gg] T. L. Cottrell and J. H. Wolfenden, *J. Chem. Soc.*, 1019 (1948). [hh] This paper. [ii] L. Eberson and I. Wadso, *Acta Chem. Scand.*, **17**, 1552 (1963). [jj] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 64. [kk] E. J. King, *J. Am. Chem. Soc.*, **79**, 6151 (1957). [ll] P. K. Smith, A. T. Gorham, and E. R. B. Smith, *J. Biol. Chem.*, **144**, 737 (1942). [mm] E. J. King and G. W. King, *J. Am. Chem. Soc.*, **78**, 1089 (1956). [nn] J. T. Edsall and J. Wyman, "Biophysical Chemistry", Vol. 1, Academic Press Inc., New York, N. Y., 1958, pp 452, 464. [oo] E. J. King, *J. Am. Chem. Soc.*, **82**, 3575 (1960). [pp] E. J. King, *ibid.*, **78**, 6020 (1956). [qq] P. N. Milyukov and N. V. Polenova, *Izv. Vysshikh Uchebn. Zavadenii, Khim. i Khim. Technol.*, **8**,

Table II (*Continued*)

42 (1965). [rr] P. K. Smith, A. C. Taylor, and E. R. B. Smith, *J. Biol. Chem.*, **122,** 109 (1937). [ss] Z. L. Ernst, R. J. Irving, and J. Menashi, *Trans. Faraday Soc.*, **60,** 56 (1964). [tt] L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964. [uu] E. Ellenbogen, *J. Am. Chem. Soc.*, **78,** 369 (1956). [vv] N. E. Ockerbloom and A. E. Martell, *ibid.*, **78,** 267 (1956). [ww] M. Eden and R. G. Bates, *J. Res. Natl. Bur. Std.*, **62,** 161 (1959). [xx] T. Moeller and R. Ferrus, *J. Inorg. Nucl. Chem.*, **20,** 261 (1961). [yy] R. K. Chaturvedi, P. Dinkar, and B. Biswas, *Proc. Natl. Acad. Sci. India*, **34,** 22 (1964). [zz] L. P. Fernandez and L. G. Hepler, *J. Phys. Chem.*, **63,** 110 (1959). [aaa] M. May and W. A. Felsing, *J. Am. Chem. Soc.*, **73,** 409 (1951). [bbb] H. S. Simms, *J. Phys. Chem.*, **32,** 1128 (1928).

($\epsilon = \epsilon_{water} = 78.4$ at 25°), *i.e.*, -218.0 for ΔG_b^{elect} *vs.* ΔS_b^{elect} and 80 for ΔH_b^{elect} *vs.* ΔS_b^{elect}. Many of the experimental data fall on the line predicted by eq 12 and 13. Deviation from the straight-line relationship can be taken to mean that either (a) the simple electrostatic theory is not adequate in these cases,[17] or (b) the nonelectrostatic parts of the thermodynamic quantities were not eliminated. An approach to testing (a) is to use the Kirkwood–Westheimer theory involving substitution of ϵ_{eff} for ϵ in eq 12. In effect, proton ionization from substances which show deviations from the simple electrostatic theory may in fact be electrostatic in nature but have ϵ_{eff} values $< \epsilon_{solvent}$.

The effect of using ϵ_{eff} in place of ϵ_{water} on ΔH_b^{elect} can be shown by solving for $(\partial \ln \epsilon/\partial T)_P$ in (13) and substituting this value in (12) where $\Delta G_b^{elect} = Ne^2z/R\epsilon_{water}$ according to the Bjerrum theory and $\Delta G_b^{elect} = N\epsilon^2 z/R\epsilon_{eff}$ according to the Kirkwood–Westheimer (KW) theory.

$$[\Delta H_b^{elect}]_{Bjerrum} = \frac{Ne^2z}{R\epsilon_{water}} - T\Delta S_b^{elect} \qquad (14)$$

$$[\Delta H_b^{elect}]_{KW} = \frac{Ne^2z}{R\epsilon_{eff}} - T\Delta S_b^{elect} \qquad (15)$$

In eq 14 and 15, R is the proton-charge distance, e is the charge on a proton, and z is the charge number on the ion. For a given ΔS value, the difference in ΔH_b^{elect} calculated from (14) and (15) is given by

$$[\Delta H_b^{elect}]_{KW} - [\Delta H_b^{elect}]_{Bjerrum} = \Delta H_D = \frac{Ne^2z}{R}\left[\frac{1}{\epsilon_{eff}} - \frac{1}{\epsilon_{water}}\right] \qquad (16)$$

or

$$\Delta H_D = \frac{A}{R}\left[\frac{1}{\epsilon_{eff}} - \frac{1}{\epsilon_{water}}\right] \qquad (17)$$

where

$$A = Ne^2z$$

ΔH_D was calculated from Figure 3 and was taken as the difference between the experimental value of ΔH_b^{elect} and the value predicted by the Bjerrum theory. The values of ΔH_D are given in Table III together with the values of ϵ_{eff} and R which were obtained from the literature[18–20] or were calculated from ΔpK data in Table II using the Kirkwood–Westheimer equations.[18]

A plot of ΔH_D *vs.* $(1/R)[(1/\epsilon_{eff}) - (1/\epsilon_{water})]$ was constructed to learn if a straight line with slope A resulted as indicated by (17). Only a fair correlation was obtained with many of the data points falling off the least-squares line representing all the data. The slope of the line was 1.4×10^5 cal A/g mole compared with a predicted value of A from (17) of 3.3×10^5 cal A/g mole. In an effort to improve this correlation ΔH_D was plotted *vs.* various functions of ϵ_{eff} and R. The most successful is that of ΔH_D *vs.* $[(1/\epsilon_{eff}) - (1/\epsilon_{water})]$ or just $1/\epsilon_{eff}$ which is given in Figure 4 and shows a strong correlation between these two quantities. The form of the correlation between ΔH_D and ϵ_{eff} is not the same as that predicted from eq 17; however, the direct relationship between ΔH_D and $1/\epsilon_{eff}$ is felt to be significant since changing ϵ_{eff} should affect only electrostatic interaction terms. Figure 4 indicates that the heats of ionization of dicarboxylic acids can in most cases be explained from electrostatic theories without resorting to reasoning involving inductive and resonance terminology.

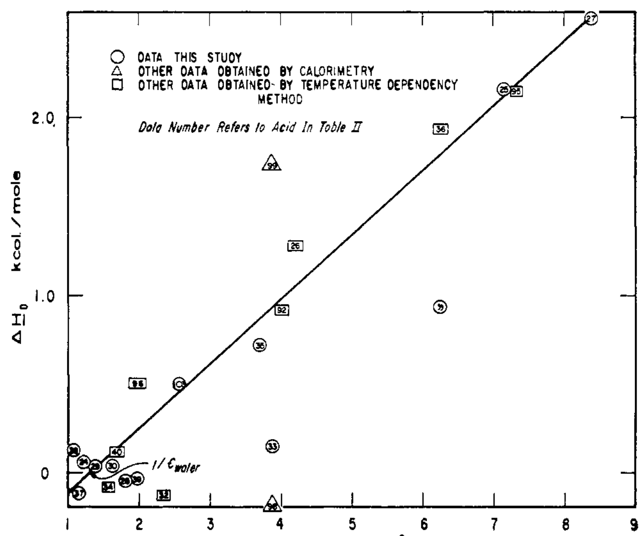


Figure 4. Plot of ΔH_D *vs.* $1/\epsilon$ for dicarboxylic acid proton ionization.

The relation shown in Figure 4 was further tested using a dicarboxylic acid, studied previously,[2d] $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ (no. 103, Table II), which had a fixed distance between carboxyl groups. Because of the rigid structure of this ion, the distance R can be determined precisely, thus allowing a value of ϵ_{eff} to be calculated without any arbitrary assumptions regarding the size and shape of the cavity and the location of charges inside of it as required by the Kirkwood–Westheimer theory. A value of ΔH_D was calculated for this acid and found to fall on the line in Figure 4 confirming the correlation between ΔH_D and ϵ_{eff}.

It is now of interest to examine the five acids which are not correlated in Figure 4. Of the acids, one falls above and four fall below the line. If we assume that the linear relationship seen in Figure 4 results from only electrostatic interactions for those acids falling on or near the line, then deviations from the line should be a

(19) F. H. Westheimer and M. W. Shookhoff, *J. Am. Chem. Soc.*, **61,** 555 (1939).
(20) C. Tanford, *ibid.*, **79,** 5348 (1957).

Table III. Dicarboxylic Acids, Thermodynamic Quantities Together with Structural and Solvent Parameters

Acid	Acid no.[e]	$\Delta(\Delta H)$, kcal/mole	$\Delta(\Delta S)$, eu	$\Delta(\Delta S^*)$,[f] eu	ΔH_D, kcal/mole	ϵ_{eff}	$1/\epsilon_{eff}$ $\times 10^2$	R, A	$\left(\frac{1}{\epsilon_{eff}} - \frac{1}{\epsilon_{water}}\right) \times 10^2$	$\frac{1}{R}\left(\frac{1}{\epsilon_{eff}} - \frac{1}{\epsilon_{water}}\right) \times 10^5$
Suberic	38	−0.25	−5.0	−2.3	+0.13	94[a]	1.06	9.3	−0.22	−0.24
Adipic	24	−0.34	−5.4	−2.7	+0.06	83[a]	1.20	7.75	−0.08	−0.10
Glutaric	29	−0.46	−6.4	−3.7	+0.04	74[a]	1.35	7.00	+0.07	+0.10
β-Isopropylglutaric	30	−0.50	−7.0	−4.3	+0.04	63[a]	1.60	5.84	+0.32	+0.55
Pimelic	37	−0.60	−6.3	−3.6	−0.11	87[a]	1.15	8.3	−0.13	−0.16
Tartaric	40	−0.50	−8.0	−5.3	+0.125	61[b]	1.64	6.00	+0.36	+0.60
β-Methylglutaric	34	−0.70	−8.0	−5.3	−0.08	64[a]	1.56	6.85	+0.28	+0.41
Succinic	39	−0.74	−9.0	−6.3	−0.04	51[b]	1.96	5.75	+0.68	+1.18
Fumaric	28	−0.79	−9.5	−6.8	−0.05	56[a]	1.80	4.56	+0.52	+1.14
Aspartic	54	−0.89	−11.3	−8.6	0.00					
Malic	32	−0.99	−10.8	−8.1	−0.14	44[d]	2.27	5.0	+0.99	+1.98
Malonic	33	−1.21	−17.2	−14.5	+0.15	26[a]	3.85	4.10	+2.57	+6.27
cis-Cyclohexane-1,2-dicarboxylic	98	−1.4	−15	−12.3	−0.20	26[d]	3.85	4.34	+2.57	+5.92
Citric	41	−4.2	−9	−6.3	+0.28					
Oxalic	35	−0.48	−15.4	−12.7	+0.73	27[a]	3.7	3.85	+2.4	+6.25
trans-Caronic	96	0	−6	−3.3	+0.48	50[b]	2.0	5.45	+0.7	+1.285
Phthalic	92	+0.14	−10	−7.3	+0.92	25[d]	4.0	4.12	+2.7	+6.57
Maleic	31	−0.91	−23.3	−20.6	+0.94	16[d]	6.25	4.52	+4.97	+11.0
β,β-Dimethylglutaric	26	+0.50	−10	−7.3	+1.28	24[a]	4.18	5.25	+2.90	+5.54
trans-Cyclohexane-1,2-dicarboxylic	99	+1.6	−2	+0.7	+1.74	26[d]	3.85	4.34	+2.57	+5.92
β,β-Pentamethyleneglutaric	36	+1.0	−12	−9.3	+1.94	16[d]	6.25	4.24	+4.97	+11.7
Diethylmalonic	25	+0.43	−21.8	−19.1	+2.16	14[a]	7.15	3.75	+5.87	+15.6
cis-Caronic	95	0	−27	−24.3	+2.15	13.8[b]	7.30	3.30	+6.02	+18.3
Ethylisoamylmalonic	27	+0.95	−20.5	−17.8	+2.57	12[d]	8.34	4.39	+7.06	+16.1
$1,12\text{-}B_{12}H_{10}(COOH)_2^{2-}$	103	+0.19	−4.7	−2.0	+0.55	44[c]	2.27	11.0	+0.99	+0.90

[a] C. Tanford, *J. Am. Chem. Soc.*, **79**, 5348 (1957). [b] Calculated from data given by F. H. Westheimer and M. W. Shookhoff, *ibid.*, **61**, 555 (1939). [c] L. D. Hansen, J. A. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **5**, 569 (1966). [d] Calculated from pK data given in Tables I and II using equations presented by F. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 506, 513 (1938). [e] Refers to Table II. [f] Entropy changes corrected for change in symmetry number[16] $\Delta(\Delta S^*) = \Delta(\Delta S) + R \ln 4$.

measure of nonelectrostatic interactions which do not cancel in eq 5. Acids falling above the line are 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 electrostatics alone, *i.e.*, $\Delta H_2 - \Delta H_1 > \Delta H_2^{elect} - \Delta H_1^{elect}$. For acids falling below the line the opposite argument would hold, *i.e.*, $\Delta H_2 - \Delta H_1 < \Delta H_2^{elect} - \Delta H_1^{elect}$.

Of the five acids which do not follow the correlation in Figure 4 the data of only three, maleic (31), malonic (33), and malic (32) appear to be of sufficient accuracy to warrant discussion of their deviations from the linear relationship. The data for *trans*-cyclohexane-1,2-dicarboxylic acid (99) and *cis*-cyclohexane-1,2-dicarboxylic acid (98) were obtained by calorimetry but are questionable because of the abnormally large difference between the ΔH values for the ionization of the first proton from each acid. This difference between *trans* ($\Delta H_1 = -1.9$) and *cis* ($\Delta H_1 = +1.1$) of 3.0 kcal is larger by almost 2 kcal than the corresponding differences between ΔH_1 values for any other dicarboxylic acid listed in Table II having a *cis* and *trans* form. For this reason a discussion of these two acids will be postponed until a confirmation can be obtained of the ΔH values.

The data point for malic acid (32) falls below the line in Figure 4 by 0.48 kcal. This deviation parallels its abnormal behavior in the sequence succinic (39), malic (32), and tartaric (40), in that ΔH_2 for malic stands out as being more negative than either of the other acids by approximately 0.5 kcal. The malic anion could be stabilized by intramolecular hydrogen bonding resulting in the formation of a six-membered ring, or perhaps an inductive effect involving the OH group has made it easier to break the second O–H bond. In either case the magnitude of the effect can be tentatively assigned a value of −0.48 kcal. Maleic acid (31) falls 0.86 kcal below the line which could be interpreted as resulting from hydrogen bonding to form a seven-membered conjugated ring. Shifts in the infrared spectrum of hydrogen maleate ion have been reported as indicative of hydrogen bonding.[21] Malonic acid (33) which falls 0.77 kcal below the line is also probably best explained by hydrogen bonding to form a six-membered conjugated ring. No spectral evidence has been found for hydrogen bonds in hydrogen malonate ion,[22] but symmetrical intramolecular hydrogen bonding has been suggested based on thermodynamic data.[23]

It is not possible with the data available at the present time to pinpoint the exact effect being measured by the deviation of an acid from the correlation in Figure 4. However, it appears possible to place a numerical value on the effect or effects and to separate them from purely electrostatic effects. Further work is now in progress to determine the extent to which it is possible to assign values to inductive effects, resonance, hydrogen bonding, etc., using thermodynamic data.

(21) Reference 7, p 176.
(22) D. R. Lloyd and R. H. Prince, *Proc. Chem. Soc.*, 464 (1961).
(23) S. N. Das and D. J. G. Ives, *ibid.*, 373 (1961).