work. We also wish to gratefully acknowledge the University of Southern California Computer Science Laboratory for unfunded time on the 360-65 to carry out this work. We also acknowledge numerous useful conversations with Dr. R. E. Williams and Professor T. Onak.

Thermodynamics of Proton Ionization in Dilute Aqueous Solution. XIII. $\Delta G°$ (pK), $\Delta H°$, and $\Delta S°$ Values for Proton Ionization from Several Methyl- and Ethyl-Substituted Aliphatic Carboxylic Acids at 10, 25, and 40°[1a]

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Abstract: A calorimetric study has been made of proton ionization in dilute aqueous solution from aliphatic carboxylic acids at 10, 25, and 40° (13 acids) and at 25° (3 acids). Values of $\Delta S°$ are calculated by combining the resulting $\Delta H°$ values with $\Delta G°$ values obtained from the literature or determined from potentiometric or calorimetric measurements. The trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ are described by an electrostatic model, and deviations from this model are taken as a measure of nonelectrostatic substituent effects for carboxylic acids.

This study was undertaken as part[2] of a program to determine the thermodynamic quantities associated with proton ionization from a variety of donor atom types in aqueous solution. Previously, the effects of polar substituents (Cl, Br, etc.)[3] and of a protonated amino group[4] on the magnitudes of the thermodynamic quantities for proton ionization from the –COOH group were reported. The present study provides an extension of these investigations to include methyl and ethyl substituents.

Experimental Section

Materials. The following compounds were obtained in the best grade available from the indicated sources: Baker, Baker grade 2,2-dimethylpropanoic acid, 2-methylpropanoic acid, 2-methylpentanoic acid, 3-methylpentanoic acid, 2-methylpentanoic acid, hexanoic acid; Eastman, White Label octanoic acid; Eastman, practical 2-ethylbutanoic acid, 3-methylbutanoic acid; Aldrich Chemical Corp., heptanoic acid, pentanoic acid, 2-propylpentanoic acid; Chemical Procurement, Inc., 2,2-dimethylbutanoic acid.

All acids were fractionally distilled under reduced pressure. They were then treated with slightly less than a stoichiometric amount of sodium hydroxide (Baker, Analyzed Reagent, carbonate free, 50% solution). The resultant solutions of the salts were washed with benzene and ether, the water was slowly evaporated, and ethanol was added until the solutions became slightly turbid. Following precipitation and separation from the cooled solutions, the salts were recrystallized twice from an alcohol–water solution and dried under vacuum. Standardized solutions of perchloric acid (Baker and Adamson) or imidazole (Eastman) were used as titrants in both the potentiometric and calorimetric determinations.

Procedure. The titration calorimeter used in this study has been described.[5,6] This calorimeter makes possible the measurement of heats of 1–10 cal with a precision of 0.1% or 0.02 cal, whichever is greater. Solutions of the sodium salts of the methyl- and ethyl-substituted carboxylic acids were titrated with perchloric acid solutions at 10, 25, and 40°. At least five calorimetric titrations were made for each acid with ionic strength, $\mu < 0.02$.

The pK values were either taken from the literature or determined using (1) a potentiometric titration method[7] or (2) in the case of 2,2-dimethylbutanoic acid, a calorimetric titration procedure[6,8] using an imidazole solution as titrant.[9,10]

Calculations. The general method used to calculate ΔH values from the thermometric titration data has been described.[6,8,11] Values for the heats of dilution of $HClO_4$ were determined calorimetrically at 10, 25, and 40°. Values for the heat of ionization of water at 10 and 40° were determined by us[12] to be 14.216 and 12.62 kcal/mol, respectively, and that at 25°, 13.335 kcal/mol, was taken from the literature.[13] At the low ionic strength ($\mu < 0.02$) used in the calorimetric determinations, ΔH values do not vary significantly with μ;[3] therefore, they were assumed to be equal to $\Delta H°$ values. The standard state to which $\Delta H°$ refers is defined to be an ideal 1 M solution behaving as an infinitely dilute solution. The calculations were aided by a P. E. Liberscope L-3055 computer.

Results

In Table I are presented the pK, $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ values determined in this study together with

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Table I. Thermodynamic Quantities for the Reaction HA = $H^+ + A^-$. Values Are Valid for Aqueous Solution at $\mu = 0$[a]

HA	Formula[b]	T, °C	pK	$\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(deg mol)	$\Delta C_p°$, cal/(deg mol)
Formic acid	H–	10	3.763[c]	4.875	0.37 ± 0.01 0.573[c]	−15.9	
		25	3.752[c]	5.118	−0.08 ± 0.01 −0.013[c] −0.02[d]	−17.4	−31
		40	3.766[c]	5.395	−0.57 ± 0.01 −0.657[c]	−19.0	
Acetic acid	CH_3–	10	4.762[e]	6.170	0.47[f]	−20.2	
		25	4.756[e]	6.487	−0.02[g]	−21.9	−32
		40	4.769[e]	6.834	−0.50[f]	−23.4	
Propanoic acid	CH_3CH_2–	10	4.877[h]	6.096	0.384[h]	−21.0	
		25	4.874[h]	6.648	−0.14[g]	−22.8	−38
		40	4.891[h]	7.009	−0.746[h]	−24.8	
2-Methylpropanoic acid	$(CH_3)_2CH$–	10	4.827[i]	6.254	−0.14 ± 0.08	−22.6	
		25	4.853[j]	6.621	−0.75 ± 0.02 −0.755[k]	−24.7	−36
		40	4.918[i]	7.047	−1.22 ± 0.04	−26.4	
2,2-Dimethylpropanoic acid	$(CH_3)_3C$–	10	5.014[i]	6.496	−0.21 ± 0.07	−23.7	
		25	5.03[l]	6.86	−0.69 ± 0.01	−25.3	−33
		40	5.067[i]	7.260	−1.19 ± 0.03	−27.0	
Butanoic acid	$CH_3(CH_2)_2$–	10	4.803[m]	6.004	−0.073[m]	−22.2	
		25	4.817[m]	6.576	−0.64[f]	−24.2	−35
		40	4.854[m]	6.958	−1.12[f]	−25.8	
2-Methylbutanoic acid	$CH_3CH_2CH(CH_3)$–	25	4.761 ± 0.002	6.67	−1.24 ± 0.03	−26.1	
2,2-Dimethylbutanoic acid	$CH_3CH_2C(CH_3)_2$–	25	4.93	6.73	−0.62 ± 0.05	−24	
3-Methylbutanoic acid	$(CH_3)_2CHCH_2$–	10	4.742[i]	6.144	−0.80 ± 0.01 −0.77[k]	−24.5	
		25	4.777[j]	6.517	−1.15 ± 0.01 −1.168[k]	−25.7	−23
		40	4.831[i]	6.922	−1.48 ± 0.01	−26.8	
2-Ethylbutanoic acid	$(CH_3CH_2)_2CH$–	25	4.751[i]	6.481	−1.97 ± 0.03 −2.03[i]	−28.4	
		40	4.813[i]	6.896	−2.34 ± 0.02	−29.5	
Pentanoic acid	$CH_3(CH_2)_3$–	10	4.763 ± 0.017	6.169	−0.11 ± 0.01	−23.0	
		25	4.842[i]	6.606	−0.66 ± 0.01 −0.72[i]	−24.4	−32
		40	4.861 ± 0.004	6.962	−1.07 ± 0.03	−25.7	
2-Methylpentanoic acid	$CH_3(CH_2)_2CH(CH_3)$–	10	4.742 ± 0.005	6.144	−0.96 ± 0.03	−28.4	
		25	4.782 ± 0.002	6.536	−1.28 ± 0.06	−26.2	−27
		40	4.877 ± 0.001	6.988	−1.77 ± 0.02	−27.9	
2,2-Dimethylpentanoic acid	$CH_3(CH_2)_2C(CH_3)_2$–	10	5.021 ± 0.036	6.505	−0.54 ± 0.07	−24.0	
		25	4.969 ± 0.013	6.774	−0.99 ± 0.01	−26.1	−31
		40	5.088 ± 0.013	7.291	−1.46 ± 0.02	−28.0	
3-Methylpentanoic acid	$CH_3CH_2CH(CH_3)CH_2$–	10	4.752 ± 0.043	6.159	−0.77 ± 0.02	−24.5	
		25	4.766 ± 0.001	6.597	−1.12 ± 0.01	−25.9	−26
		40	4.821 ± 0.002	6.908	−1.56 ± 0.02	−27.0	
4-Methylpentanoic acid	$(CH_3)_2CH(CH_2)_2$–	10	4.887[i]	6.331	−0.19 ± 0.03	−23.0	
		25	4.845[i]	6.610	−0.61 ± 0.01	−24.2	−28
		40	4.879[i]	6.991	−1.04 ± 0.02	−25.7	
Hexanoic acid	$CH_3(CH_2)_4$–	10	4.839[i]	6.270	−0.03 ± 0.02	−22.2	
		25	4.879[i]	6.657	−0.64 ± 0.01 −0.644[k] −0.70[n]	−24.5	−33
		40	4.890[i]	7.007	−1.03 ± 0.02	−25.7	
Heptanoic acid	$CH_3(CH_2)_5$–	10	4.794 ± 0.007	6.211	−0.02 ± 0.01	−22.0	
		25	4.893[j]	6.675	−0.61 ± 0.01	−24.4	−33
		40	4.88 ± 0.005	6.993	−1.01 ± 0.02	−25.5	
Octanoic acid	$CH_3(CH_2)_6$–	25	4.895[j]	6.677	−0.62 ± 0.01	−24.5	

[a] Uncertainties are given as the standard deviation among runs. [b] The formula given is R corresponding to R–COOH. [c] H. S. Harned and N. D. Embree, *J. Amer. Chem. Soc.*, **56**, 1042 (1934). [d] G. Aksnes, *Acta Chem. Scand.*, **16**, 1967 (1962). [e] H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 652 (1933). [f] See ref 4. [g] See ref 3. [h] H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 2383 (1933). [i] D. H. Everett, D. A. Landsman, and B. R. W. Pinsent, *Proc. Roy. Soc., Ser. A*, **215**, 403 (1952). [j] J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938). [k] T. L. Cottrell, G. W. Drake, D. L. Levi, K. J. Tully, and J. H. Wofenden, *ibid.*, 1016 (1948). [l] R. P. Bell and A. T. Kuny, *Trans. Faraday Soc.*, **59**, 1789 (1963). [m] H. S. Harned and R. O. Sutherland, *J. Amer. Chem. Soc.*, **56**, 2039 (1934). [n] E. J. King, *ibid.*, **79**, 6151 (1957).

those reported by others. All the data in Table I refer to $\mu = 0$. The precision of the pK values determined in this study is ±0.01 pK unit. The accuracy of the $\Delta H°$ values is estimated to be ±50 cal. This estimate was obtained from a consideration of the accuracy of the values previously obtained for the heat of ionization of water using the same equipment. The reported precision limits for the $\Delta H°$ values in Table I are given as the standard deviation of these values for each set of runs for a given acid. Stated precision values larger than ±50 cal are probably due to errors in the pK values used to calulate the amount of product formed in each case. The combined uncertainties in the pK and $\Delta H°$ values will result in an estimated precision of ±0.2 cal/(deg mol) in the $\Delta S°$ values. The combined uncertainties in the $\Delta H°$ values at each temperature result in an estimated precision of ±5 cal/(deg mol) in the $\Delta C_p°$ values.

Discussion

For those acids where pK and $\Delta H°$ values have been reported previously, generally good agreement is observed between the reported values and those determined in this study. Compilations containing some of the earlier thermodynamic quantities given in Table I have been published.[14,15]

In attempting to understand proton ionization from molecules having noncharged substituents, it is convenient to think of the thermodynamic properties as consisting of a nonelectrostatic part (including bond dissociation energies, changes in translational, rotational, and vibrational degrees of freedom, and specific solvent effects), an electrostatic part, and a statistical part.[3,16] The thermodynamic properties for reaction 1 can therefore be considered to represent the total

$$HA_1 + H_2O = A_1^- + H_3O^+ \qquad (1)$$

$$HA_1 + A_2^- = A_1^- + HA_2 \qquad (2)$$

properties, including all three of the above-mentioned quantities. However, thermodynamic properties for reaction 2 represent only electrostatic and statistical changes for the ionization of HA_1 if the nonelectrostatic changes are essentially eliminated by choosing a reference acid, HA_2, with the same nonelectrostatic changes in its thermodynamic properties as those of the substituted acid, HA_1. In this study, the reference acid will be the nonsubstituted acid corresponding to $CH_3(CH_2)_nCOOH$, where n = 0, 1, 2, 3, or 4.

The methyl-substituted acids were extensively studied and provide a basis for investigating the effect of the position of a methyl group on proton ionization from the carboxyl group. For reaction 2, the electrostatic theories of Born, Bjerrum, and Kirkwood–Westheimer[16] all lead to the same expression, eq 3, where ΔH^{elect} is the enthalpy change for the removal of a proton from

$$\Delta H^{\text{elect}} = -\frac{ed\cos\mathcal{F}}{\mathcal{E}R^2}\left[1 + T\left(\frac{\partial\ln\mathcal{E}}{\partial T}\right)_{\text{P}}\right] \qquad (3)$$

the electrostatic field created by the polar methyl group. All other electrostatic effects were eliminated by the process represented in reaction 2. In eq 3 e = proton charge, d = dipole moment, $\cos\mathcal{F}$ = contribution of dipole in direction of proton, R = proton–dipole distance, $\mathcal{E}$ = dielectric constant, and T = absolute temperature. In the Born and Bjerrum models $\mathcal{E}$ is defined to be the dielectric constant of the solvent, whereas in the Kirkwood-Westheimer model, it is defined as the effective dielectric constant and is calculated from the estimated dielectric constants of the acid and the solvent. Since

$$\left[T\left(\frac{\partial\ln\mathcal{E}_{\text{water}}}{\partial T}\right)_{\text{P}}\right] < -1$$

for water at 10, 25, and 40°,[17] the quantity in brackets in eq 3 will be negative and ΔH^{elect} will be positive. From eq 3, one would predict that the ΔH^{elect} values calculated for eq 2 should be positive for low R values and approach zero as R increases and as $\cos\mathcal{F}$ approaches 90°. The values of ΔH^{elect} calculated for reaction 2 using the data in Table I are negative for the α- and β-substituted acids, indicating the predominance in these cases of nonelectrostatic effects. The calculated ΔH^{elect} values for the remaining acids are approximately zero in agreement with the predictions of eq 3 as seen in Table II.

Table II. Calculated ΔH^{elect} Values for Reaction 2 at 25°

Acid	Reference acid	Number of carbon atoms between ionizing proton and methyl substituent	ΔH^{elect}, kcal/mol
2-Methylpropanoic	Propanoic	2	−0.61
2-Methylbutanoic	Butanoic	2	−0.60
2-Methylpentanoic	Pentanoic	2	−0.62
Butanoic	Propanoic	3	−0.50
3-Methylbutanoic	Butanoic	3	−0.51
3-Methylpentanoic	Pentanoic	3	−0.46
4-Methylpentanoic	Pentanoic	4	+0.02
Pentanoic	Butanoic	4	−0.02
Hexanoic	Pentanoic	5	+0.02
Heptanoic	Hexanoic	6	0.00
Octanoic	Heptanoic	7	−0.01

The proton–dipole distance, R, in eq 3, can be approximated by nr, where n = number of carbon atoms between the proton on the carboxyl group and the methyl group (*i.e.*, n = 2 for 2-methyl-substituted acids, n = 3 for 3-methyl-substituted acids, etc.) and r = the average distance between carbon atoms in the chain. Equations 4, 5, and 6 then[16] predict linear

$$\Delta G^{\text{elect}} = -\frac{eu\cos\mathcal{F}}{\mathcal{E}r^2}\left(\frac{1}{n^2}\right) \qquad (4)$$

$$\Delta H^{\text{elect}} = -\frac{eu\cos\mathcal{F}}{\mathcal{E}r^2}\left[1 + T\left(\frac{\partial\ln\mathcal{E}}{\partial T}\right)_{\text{P}}\right]\left(\frac{1}{n^2}\right) \qquad (5)$$

$$\Delta S^{\text{elect}} = -\frac{eu\cos\mathcal{F}}{\mathcal{E}r^2}\frac{(\partial\ln\mathcal{F})}{\partial T}P\left(\frac{1}{n^2}\right) \qquad (6)$$

relationships between $1/n^2$ and ΔG^{elect}, ΔH^{elect}, or ΔS^{elect}, and positive slopes for plots of $1/n^2$ *vs.* ΔH^{elect} or ΔS^{elect}. These plots for the data at 25° are shown in Figure 1. The linearity and positive slopes of the plots at high n values in the cases of ΔH^{elect} and ΔS^{elect} are consistent with the predictions of the electrostatic model. The deviation of the ΔH^{elect} and ΔS^{elect} values from those predicted at low n values (α and β substitution) is taken to be a measure of nonelectrostatic contributions

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to these quantities. It is noteworthy that the plot of ΔG^{elect} *vs.* $1/n^2$ is linear over the entire n range. Thus, ΔG^{elect} values alone provide excellent agreement with the electrostatic model since the ΔH^{elect} and ΔS^{elect} values just compensate each other. This compensation of each other by the $\Delta H°$ and $\Delta S°$ values has been observed earlier[18,19] and illustrates the danger of basing explanations of acid–base behavior on p*K* data alone. Plots at 10 and 40° are similar.

Table III. Calculated Average ΔH^{elect} and ΔS^{elect} Values

Substitution position	ΔH^{elect}, kcal/mol	ΔS^{elect}, cal/(deg mol)
$C_{\alpha 1}$	−0.16	−0.9
$C_{\alpha 2}$	−0.62	−1.9
$C_{\alpha 3}$	+0.06	−0.6
$C_{\beta 1}$	−0.50	−2.3
$C_{\beta 2}$	−0.51	−1.5
$C_{\beta 2}$	−0.73	−2.3
$C_{\gamma 1}$	−0.02	−0.2
$C_{\gamma 2}$	0.0	+0.2
$C_{\delta 1}$	0.0	0.0
$C_{\epsilon 1}$	0.0	+0.1

From the above discussion, it is seen that the electrostatic model predicts the effect of methyl substitution on the $\Delta H°$ and $\Delta S°$ values for proton ionization from carboxylic acids except when the substituent is in the 2 or 3 position. It has been suggested by McLafferty[20] and Happ and Stewart[21] that an acid with a methyl substituent in the 3 position can form a six-membered ring which would stabilize the anion after proton ionization. Thus, the ionized carboxyl group would be more stable, the energy of the ionized molecule would be lowered, and ΔH^{elect} would become more negative.[22] Our results with β-substituted acids are consistent with this explanation.

Table IV. Comparison of Experimental and Calculated $\Delta H°$ (kcal/mol) and $\Delta S°$ (cal/(deg mol)) Values

3-Methylpentanoic acid			2-Methylbutanoic acid		
Substituent	ΔH^{elect}	ΔS^{elect}	Substituent	ΔH^{elect}	ΔS^{elect}
$C_{\alpha 1}$	−0.12	−0.9	$C\alpha_1$	−0.12	−0.9
$C_{\beta 1}$	−0.50	−1.4	$C\alpha_2$	−0.62	−1.9
$C_{\gamma 1}$	−0.02	−0.2	$C\beta_1$	−0.50	−1.4
$C_{\beta 2}$	−0.51	−1.5			
Total	−1.15	−4.0	Total	−1.24	−4.2
ΔX,[a] calcd	−1.17	−25.9		−1.26	−26.1
ΔX,[a] exptl	−1.12	−25.9		−1.24	−26.1

[a] ΔX, calcd = $\Delta X_{\text{acetic acid}} + \Delta X_{\text{total}}^{\text{elect}}$. ΔX, exptl values taken from Table I. $X = H, S$.

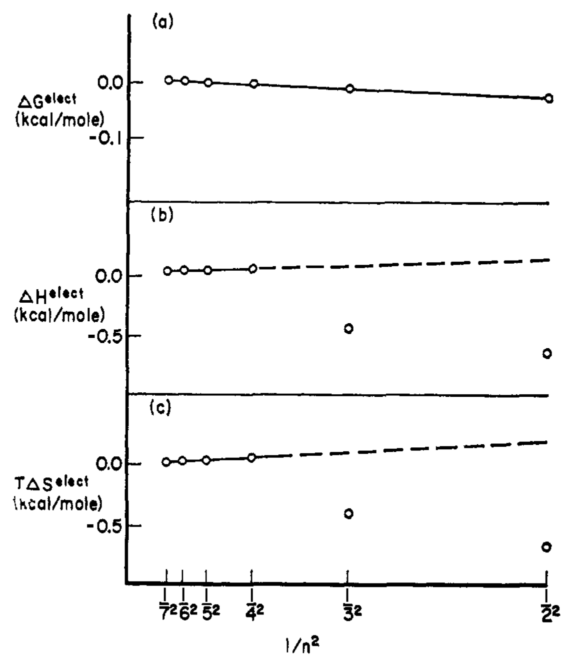
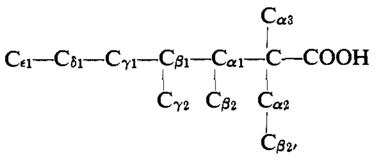


Figure 1. Plot of $1/n^2$ *vs.* (a) ΔG^{elect}, (b) ΔH^{elect}, and (c) $T\Delta S^{\text{elect}}$, where n = number of carbon atoms between substituent and ionizing proton.



$$C_{\epsilon 1}\text{—}C_{\delta 1}\text{—}C_{\gamma 1}\text{—}\underset{C_{\gamma 2}}{C_{\beta 1}}\text{—}\underset{C_{\beta 2}}{C_{\alpha 1}}\text{—}\overset{C_{\alpha 3}}{\underset{C_{\alpha 2}\text{—}C_{\beta 2'}}{C}}\text{—COOH}$$

1

Analysis of the data in Table I by the method of Ives and Marsden[19] reveals that as methyl groups are substituted systematically on the acids studied, $\Delta H°$ and $T\Delta S°$ values vary in a predictable manner. The acids in Table I can be formulated generally by **1**, where positions of substitution are indicated by the appropriate Greek subscript. Values of ΔH^{elect} and ΔS^{elect} for a given substitution can usually be calculated using more than one pair of acids (*e.g.*, values for 2-methyl substitution ($C_{\alpha 2}$) can be obtained from the 2-methylpropanoic acid–propanoic acid pair, the 2-methylpentanoic acid–pentanoic acid pair, etc.).

In Table III are listed average values of ΔH^{elect} and ΔS^{elect} calculated in each case from the possible pairs. The 3-methylpentanoic and 2-methylbutyric acids were not used in the calculation in order that the method might be tested by comparing experimental and calculated values in these cases. The results of this comparison are given in Table IV.

The good agreement between the calculated and experimental values indicates this method to be a useful tool in predicting $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for methyl-substituted aliphatic acids.

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