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A Simple Method for the Evaluation of Enthalpy of Proton Dissociation in Water

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A method is proposed for evaluating the ΔH° value for the proton dissociation of an acid HB from the temperature dependence of the dissociation constant K_a: Instead of differentiating the pK_a ($=-\log K_a$) value of acid HB with respect to temperature, we select an appropriate acid HA as a reference and plot the quantity $X=pK_a(HB)-pK_a(HA)$ as a function of reciprocal temperature. The plot was found to be linear with sufficient accuracy for most non-charged or negatively charged acids, for which pK_a itself is a complex function of temperature. ΔH° values are thus readily evaluated by linear least-squares fitting. The theoretical background is discussed.

The quantity ΔH° for the reaction is obtainable either from the temperature dependence of the thermodynamic equilibrium constant (van't Hoff equation) or directly by the calorimetric measurement. In recent years the instrumentation for the calorimetric method has advanced remarkably and the ΔH° values from calorimetry are generally preferred. However, the application of calorimetric method is difficult to some reactions, for example, those involving sparingly soluble species.

The purpose of this paper is to propose a simple and practical method which enables us to evaluate reliable ΔH° values by analyzing the temperature dependence of equilibrium constants. We will demonstrate how the proposed method works for determining ΔH° values of the proton dissociation of non-charged or negatively charged acids as well as for positively charged acids in aqueous solutions.

Theoretical Background

Protolysis Constant as a Function of Temperature. Variation of $\log K_a$ with temperature is not simple: $\log K_a$ values of a non-charged or negatively charged acid often pass through a maximum at a certain temperature.[1] If the functional form is well prescribed for $\log K_a=f(T)$, then the differentiation of $\log K_a$ with respect to temperature is straightforward. The problem on the form of $f(T)$ has long been discussed by many investigators, yet it seems to be unsettled.[2–10] If we adopt an expression such as

$$\log K_a=A+B/T+C\log T+DT+ET^2, \tag{1}$$

then we must determine the five coefficients with sufficient precision. Even if we rely upon an expression simpler than Eq. 1, $\log K_a$ values which are significant to the fourth decimal at several temperatures over as wide a range as possible should be available to obtain accurate ΔH° values. It is also to be noted that the description of K_a or $\log K_a$ as a function of temperature is to determine the expression for ΔH° and $\Delta C_P{}^\circ$.

Gurney[1] proposed the following as a function for the temperature variation of proton dissociation constants of non-charged and negatively charged acids:

$$\log K_a=-C\frac{(A+\exp(T/\theta))}{T}, \tag{2}$$

where C and A are constants characteristic of the system concerned, while the parameter θ is dependent only on the solvent. Eq. 2 indicates that $\log K_a=f(1/T)$ shows a maximum: The temperature at this maximum value of K_a will be indicated by T_{max}.

The problem of functional form of $\log K_a$ does not arise for most of the positively charged acids. The enthalpy change ΔH° of the protolysis of these acids is independent of the temperature, or $\Delta C_P{}^\circ$ is small over the temperature ranges where the variation of $\log K_a$ is considered. Thus these acids show a linear variation of $\log K_a$ with $1/T$. The proton dissociation of such acids is free from the work necessary to separate two charged species in solution. Therefore, the contribution of the $\exp(T/\theta)$ term, which reflects the effects of dielectric constant of the solvent, is negligible; in other words we have small $\Delta C_P{}^\circ$ values for these acids. In fact $\log K_a$ values of positively charged acids depend on the solvent systems to a lesser extent than in the case of non-charged or negatively charged acids. In addition to the linear variation of $\log K_a$ with $1/T$, the positive $\Delta C_P{}^\circ$ is one of the characteristic features for the proton dissociation of positively charged acids including aliphatic ammoniums. This is in contrast to the negative $\Delta C_P{}^\circ$ for practically all other types of acids. In this connection it may be noted that for positively charged acids $|\Delta C_P{}^\circ|$ is found to be much smaller than for neutral or negatively charged acids. Similarly for reactions $HB+A^-=HA+B^-$, the charge separation is not involved and $|\Delta C_P{}^\circ|$ is small.

Relation between ΔH° and T_{max}. In Fig. 1 the reported values[3] of ΔH° (298.15 K) are plotted against T_{max} for 23 non-charged acids. It is evident from Fig. 1

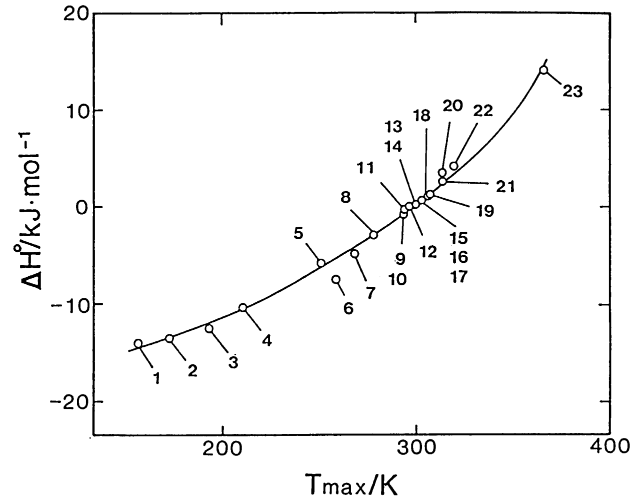

Fig. 1. Relation between ΔH° (298.15 K) of the proton dissociation of neutral acids and the temperature at which $\log K_a$ passes the maximum (T_{max}).

1. *o*-Nitrobenzoic acid
2. *o*-Iodobenzoic acid
3. α-Bromocinnamic acid
4. *o*-Chlorobenzonic acid
5. *o*-Toluic acid
6. Phosphoric acid (1st dissociation)
7. Chloroacetic acid
8. Butyric acid
9. Propionic acid
10. Lactic acid
11. Acetic acid
12. Formic acid
13. Benzoic acid
14. *m*-Toluic acid
15. Hydroxyacetic acid
16. *m*-Iodobenzoic acid
17. *m*-Hydroxybenzoic acid
18. *p*-Toluic acid
19. *m*-Nitrobenzoic acid
20. *p*-Methoxybenzoic acid
21. *trans*-β-Phenylacrylic acid
22. *o*-Hydroxybenzoic acid
23. Metaboric acid

that T_{max} increases with increasing ΔH°. Diagrams like Fig. 1 should be useful to estimate ΔH° of proton dissociation for an acid for which T_{max} is known.

Further Assumption on the Temperature Dependence of logK_a. For acids HA and HB, Eq. 2 leads to the following equation:

$$\Delta\log K_a = \log K_a(\mathrm{HA}) - \log K_a(\mathrm{HB})$$
$$= -\frac{(C_{\mathrm{HA}}A_{\mathrm{HA}} - C_{\mathrm{HB}}A_{\mathrm{HB}}) + (C_{\mathrm{HA}} - C_{\mathrm{HB}})\exp(T/\theta)}{T}, \quad (3)$$

where C_{HX} and A_{HX} denote constants C and A of Eq. 2, respectively, for HX. For non-charged acids such as acetic acid and several carboxylic acids we have determined the constants C of Eq. 2 by the least-squares fitting of $-T\log K_a$ against $\exp(T/\theta)$. We found they are similar, for example, 271 for acetic acid, 281 for propionic acid, and 298 K for butyric acid. Thus,

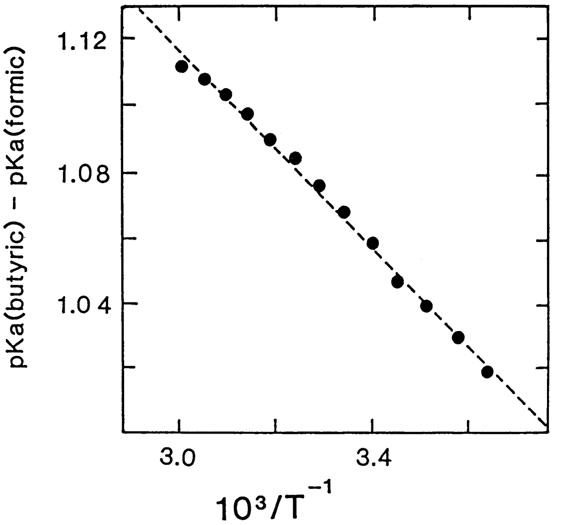

Fig. 2. pK_a(Butyric acid) $-K_a$ (Formic acid) plotted against reciprocal temperature.

$\Delta\log K_a$ is expected to vary linearly with the reciprocal temperature with sufficient accuracy.

We then consider the two-step mechanism for the dissociation of non-charged acid HA:

$$\mathrm{HA} \rightleftarrows \mathrm{H^+A^-}, \qquad \text{equilibrium constant } K_\mathrm{i}$$
$$\mathrm{H^+A^-} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{A^-}, \text{ equilibrium constant } K_\mathrm{d}$$

$K_a = K_\mathrm{i} \times K_\mathrm{d}$ and since the first step is free from charge separation, $\log K_\mathrm{i}$ can be expressed as a linear function of $1/T$. As for the second step, the electric charge and the radius of anion $\mathrm{A^-}$ is considered to remain constant within the same type of acids. For example, in the dissociation of non-charged monocarboxylic acids, conjugate bases A have unit electric charge and it is appropriate to consider the ionic radius of carboxylic group instead of the radius of the carboxylic acid molecule as a whole. Then $\Delta\log K_a = \log K_a(\mathrm{HA}) - \log K_a(\mathrm{HB})$ can also be described as a linear function of $1/T$.

In summing up all considerations described above we may expect that the enthalpy of the reaction for which no electrical work is required

$$\mathrm{HA} + \mathrm{B^-} = \mathrm{HB} + \mathrm{A^-} \qquad (4)$$

remains constant over the relevant temperature range. Figure 2 is an example of the plot of pK_a(HB)$-$pK_a(HA) against $1/T$ where HB is butyric acid and HA is formic acid taken as a reference. As seen in Fig. 2, the plot falls on a straight line. Consequently, by selecting as a reference an appropriate acid HA which belongs to the same type of acid (non-charged acids, amino acids, (−1) charged acids, phenols etc.) and for which accurate K_a and enthalpy values are known, we can evaluate a reliable enthalpy value for protolysis of the acid HB by adding the ΔH°(HA) to the slope determined by the simple linear least-squares fitting of the plot of pK_a(HB)$-$pK_a(HA) against $1/T$.

Results

Values of ΔH° evaluated are summarized in Tables 1 to 4 along with the values recommended by Larson and Hepler.[11] In Table 1 are also included the ΔH° values for fluorobenzoic acids for which Strong et al. have recently reported the very precise K_a values and the ΔH° values calculated therefrom.[9,10] Larson and Hepler only listed the ΔH° values without mentioning the procedure of evaluation. Agreement between the two

Table 1. Enthalpies for the Proton Dissociation of Non-Charged Acids Determined by the Present Method[a] and the Recommended Values[b] at 25 °C

Acid	T/°C	Runs	ΔH°/kJ mol^{-1} This work	ΔH°/kJ mol^{-1} Recommended	Ref.
		Aliphatic carboxylic acids			
Formic	0—60	13	—	0	c)
Acetic	0—25	6	−0.57±0.03	−0.42	d)
Propanoic	5—30	6	−0.81±0.05	−0.67	e)
Butyric	0—60	13	−2.80±0.05	−2.85	f)
Chloroacetic	0—40	4	−4.68±0.13	−4.77	g)
Succinic(I)	0—50	11	3.38±0.19	3.18	h)
Malic(I)	0—50	11	3.06±0.08	2.97	i)
Lactic	5—45	9	−0.35±0.06	−0.29	j)
Tartaric	0—50	11	3.23±0.05	3.10	k)
Citric(I)	0—50	11	4.28±0.12	4.18	l)
		Benzoic acid derivatives			
Benzoic	5—80	16	—	0.32	m)
2-Fluorobenzoic	5—85	17	−3.79±0.07	−4.31	n)
	5—45	9	−4.36±0.11		n)
3-Fluorobenzoic	5—85	17	0.74±0.03	0.61	n)
	5—45	9	0.73±0.08		n)
4-Fluorobenzoic	5—85	17	1.23±0.02	1.09	n)
	5—45	9	1.18±0.08		n)
2,4-Difluorobenzoic	5—85	17	−2.94±0.06	−3.52	n)
	5—45	9	−3.47±0.10		n)
2,6-Difluorobenzoic	5—85	17	−10.92±0.15	−11.97	n)
	5—45	9	−11.85±0.16		n)

a) Reference is formic acid for aliphatic carboxylic acids and is benzoic acid for benzoic acid derivatives. b) Ref. 11 for aliphatic acids and Ref. 10 for benzoic acid derivatives. c) H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934). d) H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 652 (1933). e) H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2379 (1933). f) H. S. Harned and R. O. Sutherland, *J. Am. Chem. Soc.*, **56**, 2039 (1934). g) D. D. Wright, *J. Am. Chem. Soc.*, **56**, 314 (1934). h) G. D. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, **45**, 322 and 444 (1950). i) M. Eden and R. G. Bates, *J. Res. Nat. Bur. Stand.*, **62**, 161 (1959). j) A. W. Martin and H. V. Tartar, *J. Am. Chem. Soc.*, **59**, 2672 (1937). k) R. G. Bates and A. G. Canham, *J. Res. Nat. Bur. Stand.*, **47**, 343 (1951). l) R. G. Bates and G. D. Pinching, *J. Am. Chem. Soc.*, **71**, 1274 (1949). m) Ref. 10 based on the data of Ref. 9. n) Ref. 10.

Table 2. Enthalpies for the Proton Dissociation of Amino Acids Determined by the Present Method[a] and the Recommended Values[b] at 25 °C

Acid	T/°C	Runs	ΔH°/kJ mol^{-1} This work	ΔH°/kJ mol^{-1} Recommended	Ref.
		First dissociation			
Glycine	10—50	9	—	3.93	c)
α-Alanine	20—45	6	3.05±0.10	2.59	d)
Glycylalanine	10—50	9	−2.22±0.10	−2.34	e)
Glycylleucine	10—50	9	−3.02±0.10	−3.14	e)
Glycylserine	10—50	9	0.78±0.05	0.80	e)
DL-α-Aminobutyric	1—50	5	1.39±0.11	1.30	f)
2-Amino-2-methylpropanoic	1—50	5	2.21±0.12	2.34	f)
DL-α-Amino-valeric	1—50	5	2.20±0.21	2.30	f)
DL-Leucine	1—50	5	2.15±0.53	1.76	f)
DL-Norleucine	1—50	5	2.30±0.16	2.34	f)
DL-Valine	1—50	5	0.40±0.07	0.33	f)
DL-Alanine	1—50	5	3.40±0.04	2.59	f)

Table 2. (Continued)

Acid	T/°C	Runs	ΔH°/kJ mol^{-1}		Ref.
			This work	Recommended	
		Second dissociation			
Isoleucine	1—50	5	—	44.64	f)
DL-Alanine	1—50	5	45.62±0.19	45.40	f)
DL-α-Aminobutyric	1—50	5	44.43±0.23	44.39	f)
2-Amino-2-methylpropanoic	1—50	5	47.92±0.22	48.15	f)
DL-α-Aminovaleric	1—50	5	44.89±0.20	44.85	f)
DL-Norleucine	1—50	5	45.41±0.18	45.56	f)
DL-Leucine	1—50	5	44.91±0.20	44.94	f)
DL-Valine	1—50	5	44.22±0.16	44.94	f)

a) Reference is glycine for first dissociation, while reference is isoleucine for second dissociation. b) Ref. 11. c) E. J. King, *J. Am. Chem. Soc.*, **73**, 155 (1951). d) I. F. Nims and P. K. Smith, *J. Biol. Chem.*, **101**, 401 (1933). e) E. J. King, *J. Am. Chem. Soc.*, **79**, 6151 (1957). f) P. K. Smith, A. C. Taylor, and E. R. B. Smith, *J. Biol. Chem.*, **122**, 109 (1937).

Table 3. Enthalpies for the Proton Dissociation of (−1) Charged Acids Determined by the Present Method[a] and the Recommended Values[b] at 25 °C

Acid	T/°C	Runs	ΔH°/kJ mol^{-1}		Ref.
			This work	Recommended	
Hydrogen oxalate	0—50	11	—	−6.57	c, d)
Hydrogen malonate	0—50	11	−4.83±0.07	−4.81	c, e)
Hydrogen succinate	0—50	11	−0.48±0.07	0.17	c, f)
Hydrogen tartarate			0.10±0.05	0.17	d, f)
	0—50	11	0.98±0.07	0.84	c, g)
			1.03±0.19	0.84	d, g)
Hydrogen citrate	0—50	11	2.44±0.16	2.43	c, h)
			2.81±0.12	2.43	d, h)
Dihydrogenphosphate	5—50	10	4.65±0.08	4.14	d, i)
Hydrogencarbonate	0—50	11	15.14±0.08	14.85	c, j)
			15.20±0.57	14.85	d, j)

a) Reference is the second dissociation of oxalic acid. b) Ref. 11. c) H. S. Harned and S. R. Scholes, *J. Am. Chem. Soc.*, **63**, 1706 (1939). d) G. D. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, **40**, 405 (1948). e) H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 3111 (1939). f) Ref. h of Table 1. g) Ref. k of Table 1. h) Ref. 1 of Table 1. i) A. K. Grzybowski, *J. Phys. Chem.*, **62**, 555 (1958). j) H. S. Harned and S. R. Scholes, Jr., **63**, 1706 (1948).

Table 4. Enthalpies for the Proton Dissociation of Phenols Determined by the Present Method[a] and the Recommended Values[b] at 25 °C

Acid	T/°C	Runs	ΔH°/kJ mol^{-1}		Ref.
			This work	Recommended	
Phenol	5—38	7	—	23.7	c)
o-Cresol	5—38	7	24.0±0.14	23.85	c)
m-Cresol	5—38	7	23.1±0.14	23.0	c)
p-Cresol	5—38	7	23.3±0.25	23.0	c)
2,3-Xylenol	5—38	7	23.9±0.12	23.7	c)
2,4-Xylenol	5—38	7	24.1±0.15	24.1	c)
2,5-Xylenol	5—38	7	23.5±0.14	23.5	c)
2,6-Xylenol	5—38	7	22.9±0.06	23.0	c)
3,4-Xylenol	5—38	7	22.5±0.13	22.4	c)
o-Chlorophenol	5—38	7	17.9±0.24	18.4	c)
o-Nitrophenol	5—60	12	—	19.2	d)
4-Nitro-*m*-cresol	5—60	12	19.3±0.14	19.2	d)
m-Nitrophenol	5—50	10	21.6±0.4	21.5	e)
m-Chlorophenol	10—60	11	22.9±0.19	22.3	f)
m-Bromophenol	10—60	11	22.9±0.1	22.3	f)
m-Iodophenol	10—60	11	23.4±0.1	23.1	f)

a) Reference is phenol except for the last five samples for which reference is nitrophenol. b) Ref. 11. c) D. T. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58**, 480 (1962). d) R. A. Robinson and A. Peiperl, *J. Phys. Chem.*, **67**, 1723 (1963). e) R. A. Robinson and A. Peiperl, *J. Phys. Chem.*, **67**, 2860 (1963). f) P. D. Bolton, F. M. Hall, and I. H. Reece, *Spectrochim. Acta*, **22**, 1825 (1966).

sets of ΔH° values given in Tables 1 to 4 is satisfactory for most acids including the case of chloroacetic acid for which K_a values are known only at four different temperatures (see Table 1). In some cases differences are observed beween the ΔH° values we have determined and the recomended values. Reasons for this are not clear at present.

The great practical advantage of the present method lies in that a reliable ΔH° value is obtainable, in principle, from accurate Ka values at two different temperatures, since we utilize the simple linear least-squares method.

As for the selection of the reference acid HA, it is noted that ΔH° for the proton dissociation of weak acids is successfully determined by using rather strong acid formic acid as a reference acid (see, Table 1). Therefore, acidity of the reference acid HA is not important. Requirements for reference acid are that it belongs to the same type of acid as the acid we are considering and that accurate K_a values are available over as wide a range of temperature as possible. It is preferable that K_a values of the reference acid are known as a proper function of temperature enabling one to calculate K_a values at any temperatures.

Though for reactions $HA + B^- = HB + A^-$ $|\Delta C_P^\circ|$ is obviously much smaller than for $HA + H_2O = H_3O^+ + A^-$, ΔC_P° is not strictly zero for the former proton exchange reactions. Thus the plot of $\Delta \log K_a$ against T^{-1}, which may mostly be approximated to a straight line, is more or less curved. It is therefore recommended to utilize data from $(298-t)$ K to $(298+t)$ K in the determination of ΔH° at 298 K: For instance, even if data from 273 to 373 K are available, it is preferable to pick up data in the temperature range from 273 to 323 K. Then it is possible to determine the ΔH° value closer to the tangent of the plot at 298 K by the proposed method (cf. the results for fluorobenzoic acids given in Table 1).

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