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THERMODYNAMICS OF PROTONATION OF SOME DICARBOXYLIC ACIDS CONTAINING HETEROATOMS FROM GROUP 6B

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ABSTRACT

Using potentiometric and calorimetric techniques, we have determined the protonation constants and the relative protonation enthalpies of the diacetate and dipropionate derivatives $X(CH_2 \cdot COO^-)_2$ and $X(CH_2 \cdot CH_2 \cdot COO^-)_2$ (X = O, S, Se), and of the iminodiacetate and pyridine-2,6-dicarboxylate anions at 25°C and $I = 0.1$ mole dm^{-3} (Na[ClO$_4$]). From the data obtained in this work together with those in the literature we have been able to obtain a relationship between log K and the temperature and ionic strength for the above acids. The thermodynamic protonation parameters are discussed in relation to the structures of the acids studied, and compared to those of analogous compounds.

INTRODUCTION

Recent work in these laboratories has been concerned with the coordination of some tridentate dicarboxylic ligands with silver(I) and copper(II) ions in aqueous solution [1--3].

As a preliminary part of our comparative studies of the effect of the donor properties of the group 6B donor centre on the coordination of copper(II) ions in binary and ternary complexes, we report here a potentiometric and calorimetric investigation of hydrogen-ion complex formation with the ligands (L) $X(CH_2 \cdot COO^-)_2$ and $X(CH_2 \cdot CH_2 \cdot COO^-)_2$, where X = O, S and Se. In order to characterize fully the influence of different central groups on the thermodynamic properties of the protonation reactions, the log K and ΔH^0 values for the protonation of the iminodiacetate and pyridine-2,6-dicarboxylate anions were determined. Both potentiometric and calorimetric measurements were carried out at 25°C and $I = 0.1$ mole dm^{-3} (Na[ClO$_4$]). Values for log K and ΔH^0 for the protonation of some of the ligands studied have been reported in the literature. It therefore seemed useful to suggest recommended values for these quantities as a function of the ionic strength and of temperature.

EXPERIMENTAL

Chemicals

Oxydiacetic ($odaH_2$), thiodiacetic ($tdaH_2$) and pyridine-2,6-dicarboxylic ($dipicH_2$) acids were supplied by Fluka; thiodipropionic ($tdpH_2$) and iminodiacetic ($idaH_2$) acids were supplied by BDH. Their purity (always >99.2%) was checked by means of alkalimetric titrations using standard CO_2-free NaOH. Selenodiacetic and selenodipropionic ($sedaH_2$, $sedpH_2$) acids were synthesized as described previously [1]. Sodium perchlorate was prepared according to Holmes and Williams [4]. $HClO_4$ and NaOH stock solutions, made up from concentrated perchloric acid (70% C. Erba RP) and from Normex (C. Erba) ampoules, were standardized by THAM and by potassium hydrogen phthalate, respectively. All solutions were prepared by means of CO_2-free twice-distilled water. The ionic strength was kept at 0.1 mole dm^{-3} by the addition of $Na[ClO_4]$.

Apparatus

Potentiometric measurements were carried out using a Radiometer PHM 52-B pH-meter with a glass electrode Ingold 201 NS and a saturated calomel electrode Ingold 303 NS. The titrant was delivered from a motor burette Metrohom Dosimat E 415. The reproducibility of pH was ±0.01.

The calorimetric measurements were performed by an LKB precision calorimeter, model 8700. The titrant was delivered from a motor burette Radiometer ABU-12-b. The reproducibility of Q was ± 0.015 cal.

Potentiometric procedure

Twenty-five to 100 cm^3 of dicarboxylic acid solution (2—10 mmole dm^{-3} with a sufficient amount of $HClO_4$ to complete the formation of H_2L species) were titrated by standard CO_2-free NaOH (0.2 mole dm^{-3}) until neutralization. At least five titrations were carried out for each acid. The electrode system was checked, before and after each run, titrating $HClO_4$ (5—10 mmole dm^{-3}) with standard NaOH, in the same ionic strength conditions as those used for the titrations of the dicarboxylic acids. The titration vessels, equipped with a thermostatic jacket, were kept at 25 ± 0.1°C; magnetic stirring was employed. A value of $pK_w = -13.75 \pm 0.02$ was obtained from NaOH—$HClO_4$ titrations.

Calorimetric procedure

Eighty-five to 90 cm^3 of dicarboxylic acid solution (6—17.5 mmole dm^{-3}) neutralized at 98% by NaOH, were titrated by means of $HClO_4$ (0.1—0.2 mole dm^{-3}) until H_2L formation was complete. At least four titrations were performed for each acid. The ΔH_w^0 value used was —13.48 kcal $mole^{-1}$ [5].

TABLE 1

Experimental details for the calorimetric measurements

L	C_L (mmol dm^{-3})	No. of titrations	No. of points	σ_Q [a]	R [b]
oda	7.5—15	7	51	0.020	0.08
tda	7.5—15	7	43	0.027	0.09
seda	6.3—11	4	32	0.032	0.09
tdp	7.5—15	5	36	0.014	0.07
sedp	6.3—11	4	31	0.017	0.08
ida	8.7—17.5	5	48	0.021	0.03
dipic	8.4—17.5	4	32	0.014	0.04

[a] Q in cal; 1 cal = 4.184 J.

[b] $R = (\Sigma \delta Q_{corr}/\Sigma Q_{corr})^{1/2}$; see refs. 5 and 7.

Calculations

The calculations relative to (i) electrode checks; (ii) the purity of the acids, and (iii) protonation constants, were performed by means of the least-squares computer program ACBA [6]. The calculations involved in determining the protonation enthalpies were performed by means of the least-squares program DOEC [7]. Throughout the paper the uncertainties of parameter values are expressed as $\pm 3\sigma$. Experimental details of the calorimetric measurements are reported in Table 1.

RESULTS AND DISCUSSION

The values of log K and ΔH^0 for protonation of the ligands studied in this paper are reported in Table 2. The uncertainties (3σ) associated with the parameter values are comparatively small and are comparable to those from the literature [8—45]. The ionic strength was maintained constant within the limits of ±2.5% which involves an additional error considerably lower than the uncertainties reported. The parameter values also agree well with those reported in the literature (see Tables 3 and 4). Values of ΔH^0 for the protonation of thiodipropionic acid and the seleno derivatives have not been reported previously. Considering together the thermodynamic data obtained by us and those reported in the literature (excluding those with a clearly insufficient reliability) we have calculated (except for the seleno derivatives) the variations of log K as a function of temperature and ionic strength for each acid. The protonation constant can be expressed as a function of temperature by means of a polynomial of the type

$$\log {}^{T}K = \sum_{i=m}^{n} a_i T^i \text{ (T expressed in Kelvin)} \quad (1)$$

from which we obtain

$$\Delta H^0/R'T = \sum_{i=m}^{n} i a_i T^i (R' = R \ln 10) \quad (2)$$

TABLE 2

Log K^H and ΔH^0 values [a] for the protonation of dicarboxylic acids at 25°C and $I = 0.1$ mole dm^{-3} (Na[ClO$_4$])

L	j	$\log K_j^H$	$\log \beta_j^H$	$\Delta H^0_{K_j}$	$\Delta H^0_{\beta_j}$
oda	1	3.90(1) [b]		1.48(4)	
	2	2.83(2)	6.73(3)	0.01(4)	1.49(4)
tda	1	4.12(3)		0.66(5)	
	2	3.14(4)	7.26(4)	0.06(5)	0.72(5)
seda	1	4.33(1)		0.61(11)	
	2	3.35(2)	7.68(3)	—0.11(12)	0.50(15)
tdp	1	4.64(1)		0.18(4)	
	2	3.90(1)	8.54(2)	0.10(4)	0.28(4)
sedp	1	4.72(5)		0.14(9)	
	2	3.97(5)	8.69(7)	0.11(10)	0.25(10)
ida	1	9.30(3)		—7.73(8)	
	2	2.60(5)	11.90(6)	—0.75(9)	—8.48(9)
	3	1.65(15)	13.45(17) [c]	—0.86(15)	—9.34(15)
dipic	1	3.63(1)		0.98(3)	
	2	2.04(4)	6.67(5) [d]	—0.73(4)	0.25(5)

[a] ΔH^0 values in kcal mole^{-1} ; 1 cal = 4.184 J.

[b] 3 σ in parentheses.

[c] From calorimetric data: $\log \beta_3^H$ = 13.6(1).

[d] From calorimetric data: $\log \beta_2^H$ = 6.64(5).

It may also be expressed as a function of the ionic strength using a Davies-type equation

$$\log K = \log {}^TK - Z^*A(\sqrt{I}/(1+\sqrt{I}) - CI) = \log {}^TK - \mathrm{f}(I) \qquad (3)$$

where A is the Debye—Hückel constant, $Z^* = 4$ (first step) and 2 (second step) and $\log {}^TK$ is the protonation constant calculated at infinite dilution. In eqn. (1) the polynomial coefficient-limits m and n are chosen on the basis of their temperature range and the reliability of the data from the literature [46]. The most commonly used form of eqn. (1) is that proposed by Harned and Robinson [47] with $m = -1$ and $n = 1$. We have fitted our values, together with the literature values for $\log K$ and ΔH^0, with an equation which is a combination of eqns. (1) and (3)

$$\log K = a_{-1}T^{-1} + a_0 + a_1T - \mathrm{f}(I) \qquad (4)$$

for the tdaH$_2$, idaH$_2$, dipicH$_2$ and tdpH$_2$ acids. A value of $a_1 = 1.5 \times 10^{-2}$ in eqn. (4) corresponds to Harned and Robinson's equation with $\Delta C_p = 40$ ($T = 298$, $I = 0$) [48]. The values for a_{-1}, a_0, a_1 and C are given in Table 5.

In the case of oxydiacetic acid, since there is a greater number of thermodynamic data available over a wide range of temperatures, a more extended

TABLE 3

Literature values for the protonation constants of oda, tda, seda, sedp, tdp, ida and dipic (the deviations from the values calculated by means of eqns. (1—6) are reported in parentheses)

T	I	Medium	log K_1^H	log K_2^H	Ref.
Oxydiacetic acid					
30	0.1	KCl	4.03	2.90	8
25	0.1	$NaClO_4$	3.92(0)	2.77	9
20	0.1	—	4.11	3.06	10
25	1	$NaClO_4$	3.756(2)	2.69(7)	11
25	0.5	$NaClO_4$	3.76(3)	2.80(6)	14
20	1	$NaClO_4$	3.75(1)	2.82(5)	15
25	2	$NaClO_4$	3.97(1)	2.91(0)	13
25	0	—	4.37(1)	2.97(8)	43
25	0.1	KNO_3	3.95	2.78	17
25	0.1	$NaClO_4$	3.89(3)	2.83(1)	3
Thiodiacetic acid					
30	0.1	KCl	4.29	3.26	8
25	0.1	$NaClO_4$	4.13(0)	3.15(2)	9
20	0.1	—	4.35	3.30	10
25	0	—	4.54(4)	3.27(8)	43
20	1	$NaClO_4$	4.04(7)	3.14(4)	15
25	0.1	$NaClO_4$	4.14(1)	3.13(0)	20
25	1	$NaClO_4$	3.99(2)	3.13(3)	21
25	0.1	KCl	4.12	3.09	20
25	2	$NaClO_4$	4.14(7)	3.22(5)	13
25	0.5	$NaClO_4$	4.03(9)	3.10(4)	14
25	4	$NaClO_4$	4.56	3.66	21
25	0.1	$NaClO_4$	4.09(4)	3.14(1)	3
Selenodiacetic acid					
25	0.1	KNO_3	4.35	3.27	1
Iminodiacetic acid					
20	0	—	9.89(2)	2.98(14)	22
30	0.1	KCl	9.12	2.54	23
20	0.1	KNO_3	9.45	—	24
25	0.1	KNO_3	9.40	2.50	25
25	0.1	KNO_3	9.33	2.58	26
25	0.3	KCl	9.60	3.01	27
25	0.1	NaCl	—	2.39 [a]	29
25	0.5	$NaClO_4$	9.17(0)	2.56(1) [a]	31
25	1	$NaClO_4$	9.34(11)	2.58(2) [a]	32
20	1	$NaClO_4$	9.33(10)	2.52(9)	15
25	0.1	$NaClO_4$	9.34(1)	2.62(1)	30
25	0.5	$NaClO_4$	9.23(6)	2.57(2)	30
25	1	$NaClO_4$	9.30(7)	2.64(4)	30
25	0.1	$NaClO_4$	9.29(4)	2.60(1) [a]	2
25	2	$NaClO_4$	9.52(1)	2.79(0)	30
25	0	—	9.79(1)	2.84(1)	30

TABLE 3 (continued)

T	I	Medium	log K_1^H	log K_2^H	Ref.
Pyridine-2,6-dicarboxylic acid					
30	0.1	KCl	4.76	2.16	8
20	0.1	$NaNO_3$	4.68(5)	2.10(5)	36
25	0.1	—	4.67	2.24	37
25	0.5	$NaClO_4$	4.532(21)	2.092(42)	39
25	0.5	$NaClO_4$	4.500(11)	2.001(49)	11
20	0	—	5.07(2)	2.24(6)	43
25	0	—	4.81	2.36	38
20	0.5	KNO_3	4.55	2.27	41
25	0.5	$NaNO_3$	4.47	2.00	40
25	0.1	$NaClO_4$	4.632(2)	2.05(3)	2
Thiodipropionic acid					
25	2	$NaClO_4$	4.80(0)	4.15(0)	13
18	0	—	5.08(1)	4.09(0)	19
25	0.1	$NaClO_4$	4.66(1)	3.84(4)	42
25	0.1	KNO_3	4.672(22)	3.901(21)	1
20	0.1	—	4.91	4.09	10
Selenodipropionic acid					
25	0.1	KNO_3	4.70	3.90	1

[a] Log K_3^H = 1.82 (ref. 29); 1.76 (ref. 31); 1.87 (ref. 32); 1.6 (ref. 2).

TABLE 4

ΔH^0 values for the protonation of oda, tda, ida and dipic taken from the literature

T	I	Medium	ΔH_1^0 [a]	ΔH_2^0	Ref.
Oxydiacetic acid					
5	1	$NaClO_4$	0.14(3) [b]	−0.99(3)	12
20	1	$NaClO_4$	0.64(4)	−0.42(11)	12
25	1	$NaClO_4$	0.76(1)	−0.38(1)	11
35	1	$NaClO_4$	1.09(4)	−0.03(5)	12
50	1	$NaClO_4$	1.64(1)	0.57(2)	12
25	1	KCl	0.75(1)	−0.58	18
Thiodiacetic acid					
25	1	$NaClO_4$	0.44(12)	−0.10(4)	21
Iminodiacetic acid					
20	0.1	KNO_3	−8.15		24
25	0.02	—	−6.98		34
25	0.1	KNO_3	−7.9(1)		33
25	1	$NaClO_4$	−8.52(1)	−0.81(9) [c]	32
Pyridine-2,6-dicarboxylic acid					
25	0.5	$NaClO_4$	0.15(<1)	−1.10(<1)	11

[a] ΔH^0 values in kcal $mole^{-1}$.
[b] Deviation from calculated value.
[c] $\Delta H_3^0 = -1.0(1)$.

TABLE 5

Parameters for the dependence of the protonation constants of the oda, tda, tdp, ida and dipic anions on temperature and ionic strength

Reaction	a_{-1}	a_0	a_1	C'	$(\delta C'/\delta T)10^4$	$R(\%)$ [a]	I
ida + H $\rightleftharpoons$ idaH	1.649×10^3	4.244		0.23		0.8	0–2
	2.104×10^3	1.078	5.5×10^{-3}	0.23	−8.6	0.6	
idaH + H $\rightleftharpoons$ idaH$_2$	1.299×10^2	2.395		0.27		1.5	0–2
	1.433×10^3	6.348	1.5×10^{-2}	0.27		0.4	
idaH$_2$ + H $\rightleftharpoons$ idaH$_3$	1.846×10^2	1.070		0.18		0.5	0.1–1
	1.488×10^3	7.672	1.5×10^{-2}	0.18	−3.3	0.1	
tda + H $\rightleftharpoons$ tdaH	-2.162×10^2	5.305		0.20		1.0	0–2
	1.087×10^3	−3.438	1.5×10^{-2}	0.20		0.3	
tdaH + H $\rightleftharpoons$ tdaH$_2$	-4.923×10^1	3.517		0.25		0.5	0–2
	1.254×10^3	−5.525	1.5×10^{-2}	0.25		0.2	
tdp + H $\rightleftharpoons$ tdpH	-1.156×10^2	5.485		0.22		0.1	0–2
	1.219×10^3	−3.468	1.5×10^{-2}	0.22		0.1	
tdpH + H $\rightleftharpoons$ tdpH$_2$	-6.022×10^1	4.295		0.32		0.1	0–2
	1.274	−4.658	1.5×10^{-2}	0.32		0.1	
dipic + H $\rightleftharpoons$ dipicH	-2.743×10^2	5.987		0.29	−33.7	1.3	0–0.5
	1.051×10^3	−2.905	1.5×10^{-2}	0.29		0.7	
dipicH + H $\rightleftharpoons$ dipicH$_2$	1.087×10^2	1.931		0.36		0.6	0–0.5
	1.434×10^3	−6.962	1.5×10^{-2}	0.36	−13.9	0.1	

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[a] Ref. 7.

equation has been used with $m = -1$ and $n = 3$; therefore

$$\log {}^{T}K_1 = 6.86547 \times 10^{2} \times T^{-1} - 2.72372 \times 10^{-1} + 4.16327 \times 10^{-3} \times T + 9.96944 \times 10^{-6} \times T^{2} + 8.21046 \times 10^{-9} \times T^{3} \quad (5)$$

$$\log {}^{T}K_2 = 6.54166 \times 10^{2} \times T^{-2} - 2.09030 \times 10^{-1} + 6.35239 \times 10^{-4} \times T + 5.23254 \times 10^{-6} \times T^{2} + 1.53769 \times 10^{-8} \times T^{3} \quad (6)$$

The value of C in eqn. (3) is 0.20 and 0.23 for the first and second protonation steps of oxydiacetic acid, respectively. The temperature coefficient of C is very low. In fact, using an equation of the type

$$\log K = \log {}^{T}K = Az^{*}(\sqrt{I}/(1 + \sqrt{I}) + (C_0 + C_1T + C_2T^{2})I$$
$$= \log {}^{T}K - Az^{*}(\sqrt{I}/(1 + \sqrt{I}) + C'(T)I \quad (7)$$

we have, again for oxydiacetic acid

1st step: $C'_1(T) = 0.64108 - 8.1461 \times 10^{-4} \times T + 3.278 \times 10^{-8} \times T^{2}$
2nd step: $C'_2(T) = 0.82424 - 3.5315 \times 10^{-3} \times T + 5.183 \times 10^{-6} \times T^{2}$
and $(\delta C'_1/\delta T)_{298\ \mathrm{K}} = -7.95 \times 10^{-4}$, $(\delta C'_2/\delta T)_{298\ \mathrm{K}} = 4.42 \times 10^{-4}$

From eqns. (5) and (6) for $T = 298$ K and $I = 1$ we obtain $\Delta C_{p_1} = 31.9 \pm 1.7$ and $\Delta C_{p_2} = 33.0 \pm 3.5$ cal deg^{-1} mole^{-1}.

These values are in good agreement with the findings of Grenthe and Ots [12] (29.1 and 29.5, respectively). In Tables 3 and 4 we report (in parentheses) the deviations of the literature parameter values from the same quantities calculated from eqns. (1—6); from the comparatively small values of these deviations the fit can be considered satisfactory. For all acids, except dipicH_2, the C value is 0.25 ± 0.05, a value slightly below that to be expected on the basis of the literature data for acid protonation [34,49,50]. This could point to the formation of weak complexes with sodium ions used to maintain constant ionic strength [51].

For ligands which are the diacetic acid derivatives of elements of group 6B, the enthalpy changes accompanying protonation determine the order of formation constants as the central donor atom is varied. The enthalpy contribution to the first step in the protonation of the oda dianion is more endothermic than those for the same protonation step with the tda and seda dianions, for which ΔH^0 values are very close to each other. This behaviour is in accordance with the decreasing electronegativity of the group 6B atoms, going down the group. A similar trend has been found in the enthalpy changes accompanying protonation of the anion $C_6H_5XCH_2CO_2^-$, for which ΔH^0 values were 1.12, 0.80 and 0.22 kcal mole^{-1} for O, S and Se analogues, respectively [52]. The effect of differing electronegativity of the central atom on the second protonation step is less evident from the values for the enthalpy changes when one considers the rather high uncertainties. At first sight values for the entropy changes have the same trend as the ΔH^0 values mentioned above. However, considering the $\Delta(\Delta S^0)$ values (Table 6) there is an apparent difference between oda, on the one hand, and the analogous S and Se derivatives on the other. This may be the result of different conformational contributions. The effect of the high electronegativity value of the

TABLE 6

Thermodynamic parameters for the protonation of dicarboxylic acids studied in this work, at $I = 0$ [a] and $T = 25^{\circ}C$; thermodynamic parameters of other ligands are also reported for comparison

L	j	$\log K_j$	$-\Delta G_j^0$	ΔH_j^0 [b]	ΔS_j^0 [c]	$\Delta(\Delta S^0)$	Ref.
oda	1	4.37	5.96	1.86	26.2	11.6	This work
	2	3.05	4.16	0.20	14.6		
tda	1	4.58	6.24	0.99	24.3	8.2	
	2	3.35	4.57	0.23	16.1		
seda	1	4.76	6.49	0.9	24.8	8.1	
	2	3.57	4.87	0.1	16.7		
ida	1	9.77	13.32	−7.39	19.9	8.9	
	2	2.83	3.86	−0.59	11.0		
	3	1.69	2.30	−0.84	4.9		
dipic	1	5.07	6.91	1.47	28.1	19.3	
	2	2.29	3.12	−0.50	8.8		
tdp	1	5.10	6.95	0.53	25.1	5.5	
	2	4.10	5.59	0.24	19.6		
sedp	1	5.15	7.02	0.45	25.1	4.9	
	2	4.19	5.71	0.3	20.2		
glta [d]	1	5.42	7.39	0.58	26.7	6.4	50
	2	4.34	5.92	0.12	20.3		
pima [e]	1	5.42	7.39	0.93	27.9	6.3	50
	2	4.48	6.11	0.33	21.6		
aspa [f]	1	10.00	13.63	−9.03	15.5	1.3	49, 50
	2	3.90	5.32	−1.11	14.2		
py [g]	1	5.17	7.05	−4.92	7.2		34
2-pyca [h]	1	5.32	7.25	−2.35	16.5	13.6	34
	2	1.01	1.38	−0.52	2.9		
3-pyca [i]	1	4.81	6.56	−2.71	12.9	6.0	34
	2	2.07	2.82	−0.75	6.9		
4-pyca [j]	1	4.86	6.62	−3.02	12.1	5.3	34
	2	1.84	2.51	−0.48	6.8		

[a] Calculated by means of eqns. (1—6).
[b] ΔH^0 values in kcal mole^{-1}.
[c] ΔS^0 values in cal deg^{-1} mole^{-1}.
[d] glta = glutaric acid.
[e] pima = pimelic acid.
[f] aspa = aspartic acid.
[g] py = pyridine.
[h] 2-pyca = pyridine-2-carboxylic acid.
[i] 3-pyca = pyridine-3-carboxylic acid.
[j] 4-pyca = pyridine-4-carboxylic acid.

oxygen atom on the ΔH^0 and ΔS^0 values is confirmed by comparing the thermodynamic parameters of the diacetic derivatives with those of glutaric acid (Table 6), in which a CH_2 group replaces the heteroatom. The $\Delta(\Delta S^0)$ value of glutaric acid is significantly lower than that for oxydiacetic acid. Instead it is close to the values for tda and seda, just as the electronegativities of carbon (2.5), sulphur (2.5) and selenium (2.4) are close. A similar trend is found when the thermodynamic parameters of the propionic acid derivatives are compared to those of pimelic acid (Table 6). Unfortunately the absence of thermodynamic data for oxydipropionic acid does not allow us to evaluate the effect of the oxygen atom on the thermodynamic parameters for protonation of this acid.

Since the $=NH$ group protonates readily to give $=NH_2^+$, replacement of the central heteroatom by the NH group does not allow direct comparison of the thermodynamic values with those for group 6B heteroatoms. The first protonation constant ($\log K_1^H$) corresponds to protonation of the nitrogen atom while the second and third constants correspond to carboxyl protonation. Since these latter reactions involve protonation of an ion which already contains a cationic nitrogen atom, a considerably lower value for $\log K$ is to be expected.

The thermodynamic behaviour of dipicolinic acid in the protonation equilibria is very interesting because the thermodynamic parameters for protonation of the pyridine nitrogen are remarkably different from both the imino nitrogen of ida and from the nitrogen of pyridine itself (see Table 6). The large endothermic values for ΔH^0 must be attributed to the disappearance of resonance in the dianion resulting from protonation. The reaction is, therefore, enthalpically unfavoured. The high ΔS_1^0 and $\Delta(\Delta S^0)$ values suggest the formation of a hydrogen bond between the protonated nitrogen and one of the carboxylic anions, even if the ΔS_1^0 value is lower than that of simple dicarboxylic acids [53—55]. This hypothesis is in agreement with the literature values for pyridine-monocarboxylate derivatives. In fact, whereas the $\Delta(\Delta S^0)$ value of pyridine-2-carboxylic acid is 13.6 e.u., it is 6.0 and 5.3 e.u. in the cases of pyridine-3 and 4-derivatives, respectively, where the intramolecular hydrogen bond is not possible.

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