Thermochimica Acta, 5 (1972) 35–39
© Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMODYNAMICS OF PROTON DISSOCIATION IN DILUTE AQUEOUS SOLUTION

XVII*. pK, $\Delta H°$, AND $\Delta S°$ VALUES FOR PROTON IONIZATION FROM SEVERAL MONO-SUBSTITUTED PYRIDINES AT 10, 25, AND 40°C

J. J. CHRISTENSEN, D. E. SMITH, M. D. SLADE, and R. M. IZATT

Departments of Chemical Engineering and Chemistry, and Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601 (U. S. A.)

(Received March 8th, 1972)

SUMMARY

A calorimetric study has been made of proton ionization from several mono-substituted protonated pyridines in aqueous solution at 10, 25, and 40°. Values of ΔC_p° were calculated from the variation of the $\Delta H°$ values with temperature. A linear relationship was found between pK and $\Delta H°$ with the exception of the *ortho*-halogen substituted protonated pyridines. A discussion of the resulting thermodynamic quantities is given.

INTRODUCTION

This study was undertaken as part[1] of a program to determine the thermodynamic quantities associated with proton ionization from a variety of donor atom types in aqueous solution. The present study deals with proton ionization from *ortho*-, *meta*-, and *para*-substituted (NH_2–, OH–, Cl–, Br–, and CH_3–) pyridines.

Many pK values for proton ionization from substituted protonated pyridines are available[2,3] but few reliable $\Delta H°$, $\Delta S°$, and ΔC_p° values have been reported. Consequently, most discussions of the relative acid strengths of protonated pyridines have been based on pK data. The magnitude of a pK value is determined by the relative magnitudes of the corresponding $\Delta H°$ and $\Delta S°$ values; therefore, a knowledge of these latter two quantities becomes important for an understanding of acid strength trends in any series.

EXPERIMENTAL

Materials. — The following compounds were obtained from Baker Chemical Co. (Baker Grade): 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-bromopyridine, 3-bromopyridine, 2-chloropyridine, 3-chloropyridine, 2-picoline, 4-picoline, 3-pyridinol; (Baker Practical) 3-picoline, 2-pyridone, 4-pyridone. These compounds

---

*Contribution from the Departments of Chemical Engineering and Chemistry, and No. 23 from the Center for Thermochemical Studies.

were purified by fractional distillation under reduced pressure. Reagent grade perchloric acid was obtained from Baker and Adamson Chemical Co. The solutions were prepared under a nitrogen atmosphere by diluting the purified pyridine with double-distilled and boiled water. A nitrogen atmosphere was maintained over the solutions at all times.

Procedure. — The titration calorimeter used in this study together with its calibration and operation has been reported[4,5]. This calorimeter makes possible the measurement of heats of 1–10 cal with a precision of 0.1%. Solutions of the pyridines (0.005–0.015 *F*) were titrated with standard solutions of perchloric acid (0.1–0.2 *F*) at 10, 25, and 40°C. The ionic strengths, μ, of the final solutions were always <0.02. At least four calorimetric titrations were made for each pyridine studied.

The pK values were either taken from the literature (see Table I) or determined using a calorimetric titration procedure which has been described[5–9].

Calculations. — The general method used to calculate ΔH and pK values from the calorimetric titration data has been described[5–9]. Values for the heat of dilution of the perchloric acid titrant were determined calorimetrically[10] at 10, 25, and 40°. Values for the heat of ionization of water have been determined[11,12] to be 14.216 and 12.695 kcal/mole at 10 and 40°, respectively, and 13.334 kcal/mole at 25°. At the low ionic strength ($\mu<0.02$) used in the calorimetric determinations, ΔH values do not vary significantly with μ; therefore, they are assumed to be equal to ΔH° values[13]. The standard state to which ΔH° refers is defined to be an ideal 1 *M* solution behaving as an infinitely dilute solution. Values for ΔC_p° were calculated from the variation of the ΔH° values with temperature. The calculations were aided by an IBM 360-50 computer. The computer programs (Fortran IV) together with the input data, and the output data for each run are available[10].

TABLE I

THERMODYNAMIC QUANTITIES FOR THE REACTION $HB^+ = H^+ + B$ WHERE B IS A PYRIDINE WITH THE INDICATED SUBSTITUENT[a]

Substituent	*T* (°*C*)	p*K*	ΔG° *(kcal/mole)*	ΔH° *(kcal/mole)*	ΔS° *(cal/deg mole)*	ΔC_p° *(cal/deg mole)*
H	25	$(5.17)^b$	7.03	$(4.795)^b$	−7.6	
	25	$(5.30)^c$	7.21	$(4.721, \mu=0.05)^c$	−8.4	
o-CH_3	10	6.19±0.02	8.03	5.94±0.02 $(5.93, \mu=0.05)^c$	−7.3	
	25	$(5.96)^d$	8.13	6.22±0.02 $(5.99)^b$ $(6.10, \mu=0.05)^c$	−6.4	17
	40	5.74±0.01	8.22	6.48±0.02	−5.5	
m-CH_3	10	5.76±0.02	7.46	5.33±0.04	−7.5	
	25	$(5.63)^d$	7.68	5.71±0.02 $(5.64)^b$	−6.2	21
	40	5.33±0.02	7.65	5.96±0.02	−5.3	
p-CH_3	10	6.12±0.02	7.93	5.96±0.02	−7.9	
	25	$(5.98)^d$	8.16	6.10±0.03 $(6.02)^b$	−6.5	25

TABLE I (*Con'd.*)

Substituent	*(T °C)*	p*K*	*ΔG°* (*kcal/mole*)	*ΔH°* (*kcal/mole*)	*ΔS°* (*cal/deg mole*)	*ΔC°ₚ* (*(cal/deg mole)*
	40	5.67 ± 0.01	8.13	6.45 ± 0.03	−5.3	
o-NH_2	10	6.25 ± 0.01	8.99	8.43 ± 0.03	−1.9	
	25	(6.71)[e]	9.15	8.40 ± 0.03	−2.5	−2
	40	6.43 ± 0.01	9.21	8.38 ± 0.02	−2.6	
m-NH_2	10	6.25 ± 0.01	8.10	6.46 ± 0.02	−5.7	
	25	(6.03)[e]	8.23	6.43 ± 0.04	−6.0	1
	40	5.80 ± 0.01	8.31	6.50 ± 0.03	−5.7	
p-NH_2	10	(9.549)[f]	12.376	11.33 ± 0.04 (11.31)[f]	−3.6	
	25	(9.114)[f]	12.431	11.31 ± 0.04 (11.25)[f]	−3.7	−2 (−4)[f]
	40	(8.717)[f]	12.491	11.27 ± 0.04 (11.20)[f]	−3.9	
o-OH	10	1.26 ± 0.02	1.63	−0.01 ± 0.05	−5.8	
	25	(1.25)[g]	1.71	−0.07 ± 0.04	−5.9	−2
	40	1.22 ± 0.03	1.75	−0.05 ± 0.05	−5.7	
m-OH	10	4.95 ± 0.01	6.42	3.92 ± 0.03	−8.8	
	25	(4.80)[h]	6.55	4.01 ± 0.03	−8.5	−5
	40	4.68 ± 0.02	6.71	3.87 ± 0.05	−9.0	
p-OH	10	3.29 ± 0.01	4.26	1.57 ± 0.03	−9.5	
	25	(3.23)[i]	4.41	1.49 ± 0.02	−9.7	−9
	40	3.18 ± 0.02	4.56	1.28 ± 0.02	−10.4	
o-Cl	10	0.49 ± 0.02	0.63	0.00 ± 0.01	−2.2	
	25	(0.49)[j]	0.67	0.02 ± 0.01	−2.1	2
	40	0.48 ± 0.02	0.70	0.07 ± 0.03	−2.0	
m-Cl	10	2.92 ± 0.01	3.78	1.86 ± 0.02	−6.7	
	25	(2.84)[k]	3.87	2.11 ± 0.05	−5.9	14
	40	2.74 ± 0.02	3.93	2.30 ± 0.05	−5.1	
o-Br	10	0.72 ± 0.02	0.92	−0.01 ± 0.01	−3.2	
	25	(0.71)[j]	0.97	0.08 ± 0.02	−2.9	2
	40	0.66 ± 0.02	0.95	0.05 ± 0.03	−2.8	
m-Br	10	2.95 ± 0.01	3.82	1.32 ± 0.02	−8.8	
	25	(2.89)[l]	3.94	1.35 ± 0.05	−8.6	2
	40	2.80 ± 0.02	4.01	1.36 ± 0.04	−8.4	

---

[a] The uncertainties in p*K* and *ΔH°* are given as the standard deviations among runs for each substance. The combined uncertainties in the p*K* and *ΔH°* values result in an estimated uncertainty of ±0.2 cal/deg/mole in the *ΔS°* values. The uncertainties in the *ΔH°* values at each temperature give an estimated uncertainty of ±5 cal/deg/mole in the ΔC_p° values. Values are valid in aqueous solution and at $\mu = 0$ unless otherwise indicated. Values for p*K*, *ΔH°*, and ΔC_p° determined by previous investigators for the pyridines studied here are given in parentheses. [b] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 82 (1960) 3831. [c] D. L. Levi, W. S. McEwan, and J. H. Wolfenden, *J. Chem. Soc.*, (1949) 760. [d] R. J. L. Auden, J. D. Cox, and E. F. G. Herington, *Trans. Faraday Soc.*, 50 (1954) 918. [e] H. B. Jonassen and C. C. Rolland, *Report to the Office of Naval Research.*, Project No. Nnr 685. [f] R. G. Bates and H. B. Hetcer, *J. Res. Nat. Bur. Stand.*, 64A (1960) 427. [g] C. G. Swain and J. F. Brown, *J. Amer. Chem. Soc.*, 74 (1952) 2538. [h] H. H. Jaffe and G. O. Doak, *J. Amer. Chem. Soc.*, 77 (1955) 4441. [i] A. Albert and J. H. Phillips, *J. Chem. Soc.*, (1956) 1294. [j] R. H. Linnell, *J. Org. Chem.*, 25 (1960) 290. [k] H. C. Brown and D. H. McDaniel, *J. Amer. Chem. Soc.*, 77 (1955) 3752. [l] J. M. Essery and K. Schofield, *J. Chem. Soc.*, (1961) 3939.

RESULTS

The pK, ΔG°, ΔH°, ΔS°, and ΔC_p° values determined in this study together with those reported by others are given in Table I.

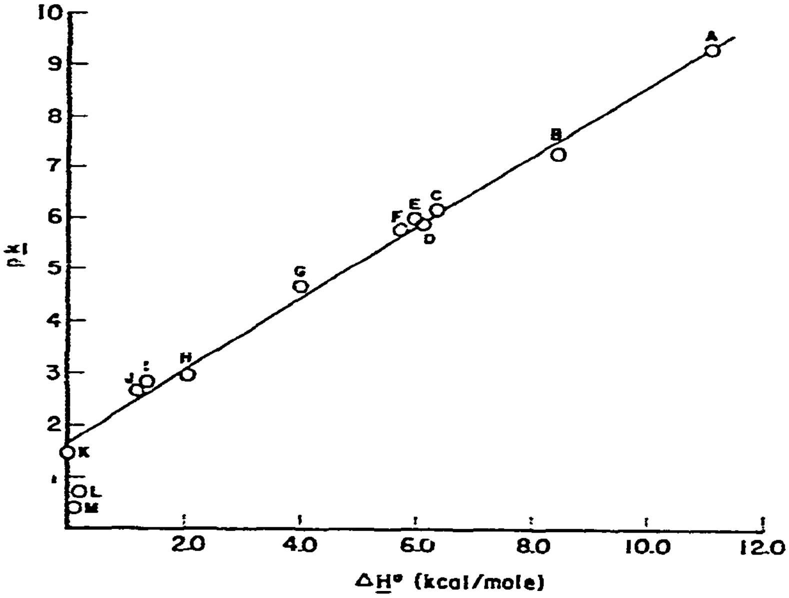

Fig. 1. Plot of pK *vs.* ΔH° for proton dissociation from several protonated pyridines at 25°C. A, *p*-NH_2; B, *o*-NH_2; C, *m*-NH_2; D, *o*-CH_3; E, *p*-CH_3; F, *m*-CH_3; G, *m*-OH; H, *m*-Cl; I, *p*-OH; J, *m*-Br; K, *o*-OH; L, *o*-Br; and M, *o*-Cl.

DISCUSSION

For those protonated pyridines where ΔH° values have been reported, good agreement is found between these values and those determined in this study.

A plot of pK *vs.* ΔH° was found to be linear in the case of proton ionization from substituted anilinium ions, with the exception of the *ortho*-halogen substituted pyridines[14–16]. A similar plot (Fig. 1) for the data in Table I was also linear with the same exception being found for the *ortho*-halogen substituted pyridines (points L and M). These deviations are probably of a steric nature[14].

The alkylpyridines are stronger bases than pyridine (Table I), with the *ortho*- and *para*-alkylpyridines being stronger bases than the *meta* derivative. This has been explained[17] as being due to inductive and hyperconjugative effects. The differences in pK values for the alkyl-substituted pyridines are a result of enthalpy effects, as the ΔS° values remain essentially constant. The aminopyridines are also stronger bases than pyridine (Table I) with the differences in the pK values being a result of enthalpy effects, as in the case of the alkylpyridines. However, in the *meta*-aminopyridine there is a significant ΔS° effect possibly deriving from the inability of the *meta*-aminopyridine to have a tautomeric form[18].

The hydroxyl-substituted pyridines are weaker bases than pyridine, with the *ortho*- and *para*-hydroxylpyridines being weaker bases than the *meta*-hydroxylpyridine. The *meta*-hydroxylpyridine exists in the pyridinal structure and the *ortho*- and *para*-hydroxylpyridines exist in the pyridone structures. The thermodynamic quantities reflect this structural difference[19].

ACKNOWLEDGMENT

Financial support for this work was received from the U. S. Public Health Service through Research Career Development Awards No. 1-K3-GM24361-05 (J. J. C.) and No. 1-K3-GM35250-05 (R. M. I.).

REFERENCES

1 For Part XVI, see J. J. Christensen, D. E. Smith, M. D. Slade, and R. M. Izatt, *Thermochim. Acta*, 4 (1972) 17.
2 E. Klingsberg (Ed.), *Heterocyclic Compounds, Vol. 14, Pyridine and Derivatives*, Interscience, New York, 1960.
3 R. M. Izatt and J. J. Christensen, in H. A. Sober (Ed.), *Handbook of Biochemistry and Selected Data for Molecular Biology*, The Chemical Rubber Co., Cleveland, Ohio, 1970.
4 J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instrum.*, 36 (1965) 779.
5 L. D. Hansen, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1965; *cf. Diss. Abstr.*, 26 (1965) 65-14556.
6 J. J. Christensen and R. M. Izatt, in H. A. O. Hill and P. Day (Eds.), *Physical Methods in Advanced Inorganic Chemistry*, Interscience, New York, 1968, p. 538.
7 J. J. Christensen, J. Ruckman, D. J. Eatough, and R. M. Izatt, *Thermochim. Acta*, 3 (1972) 203.
8 D. J. Eatough, J. J. Christensen, and R. M. Izatt, *Thermochim. Acta*, 3 (1972) 219.
9 D. J. Eatough, R. M. Izatt, and J. J. Christensen, *Thermochim. Acta*, 3 (1972) 233.
10 D. E. Smith, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1972.
11 J. J. Christensen, G. L. Kimball, H. D. Johnston, and R. M. Izatt, *Thermochim. Acta*, 4 (1972) 141.
12 J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 67 (1963) 2605.
13 J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, 89 (1967) 213.
14 P. D. Bolton and F. M. Hall, *Austr. J. Chem.*, 21 (1968) 939.
15 P. D. Bolton and F. M. Hall, *J. Chem. Soc. (B)*, (1969) 259.
16 P. D. Bolton and F. M. Hall, *J. Chem. Soc. (B)*, (1969) 1047.
17 Ref. 2, Part I, p. 30.
18 S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, (1952) 1461.
19 Ref. 2, Part III, p. 617.