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The Determination of the Dissociation Constants of Picric Acid and 2,2′,4,4′,6,6′-Hexanitrodiphenylamine in Ketone-Water Mixtures

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Synopsis. The acid dissociation constants, K_a, of picric acid and 2,2′,4,4′,6,6′-hexanitrodiphenylamine in acetone, ethyl methyl ketone, and isobutyl methyl ketone were determined in the presence of water. The pK_a values increased remarkably with a decrease in the water content. The pK_a values in water-free ketones were estimated.

Picric acid (HPic) and 2,2′,4,4′,6,6′-hexanitrodiphenylamine (HND) have widely been used as soft acids in the field of analytical chemistry. However, the reported acid dissociation constant values for these substances in ketones lack consistency.[1–5] The aim of the present paper is to determine the dissociation constant values, K_a, of HPic and HND in acetone, ethyl methyl ketone (EMK), and isobutyl methyl ketone (IBMK) as a function of the concentration of water in these solvents, and to show that small quantities of water play a decisive role in acid dissociation. The dissociation constants were determined by means of the spectrophotometric and vapor-pressure osmometric methods.

Experimental

Commercial HND and HPic were recrystallized from acetone and water respectively. The acetone was dried over anhydrous calcium sulfate. The EMK and IBMK were treated with potassium permanganate, washed with a concentrated aqueous potassium carbonate solution and then with water, and dried over anhydrous sodium sulfate for a week or more. These solvents were distilled just before use. The water concentration of the solutions was determined from the absorbances at 1.9 μm. The absorbances of the HND (3×10^{-5} mol dm^{-3}) and HPic (5×10^{-5} mol dm^{-3}) solutions were measured at 430 and 400 nm respectively. The absorbances of the undissociated acid species were evaluated by extrapolating the absorbance-water concentration curves to zero water concentration. The absorbances of the completely dissociated species were approximated by those of the corresponding potassium salts.

Vapor-pressure osmometric measurements of the solutions ($(3—24)\times10^{-2}$ mol dm^{-3}) were done on a Hitachi-Perkin-Elmer Model 115 vapor-pressure osmometer calibrated with 1,2-diphenylethanedione solutions. All the measurements were carried out at 25 °C.

Results and Discussion

The dissociation constant of a weak acid, HA, can be written as:

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-, \qquad (1)$$

$$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] = C\alpha^2/(1-\alpha), \qquad (2)$$

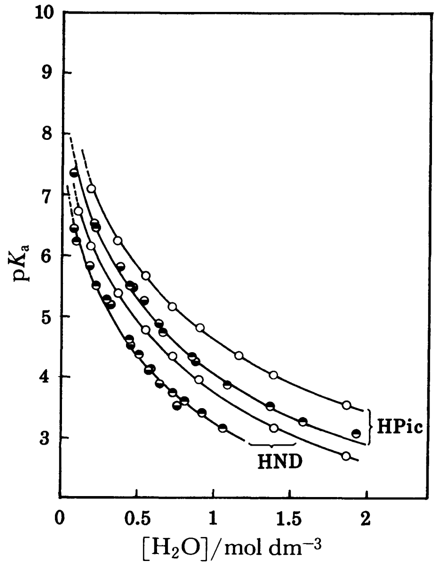

Fig. 1. pK_a *vs.* $[\mathrm{H_2O}]$ plots. ○: Acetone, ◓: EMK, ◒: IBMK.

where the brackets denote the molar concentration; C, the total molar concentration of the acid; and α, the degree of dissociation. The absorbance, E, of HA can be expressed as:

$$E = E_{\mathrm{HA}}(1-\alpha) + E_{\mathrm{A}}\alpha, \qquad (3)$$

where E_{HA} and E_{A} designate the absorbances of HA and A$^-$ respectively. Taking into account the fact that $[\mathrm{H}^+]=[\mathrm{A}^-]$, we obtain Eq. 4:

$$K_a = C(E-E_{\mathrm{HA}})^2/((E_{\mathrm{A}}-E)(E_{\mathrm{A}}-E_{\mathrm{HA}})). \qquad (4)$$

In Fig. 1, the pK_a values calculated from E by means of Eq. 4 are plotted against the water concentration. The pK_a values increased markedly with a decrease in the water concentration.

The dissociation constant values in the water-free ketones were determined from pK_a *vs.* $[\mathrm{H_2O}]^{1/2}$ plots (Fig. 2) to be pK_a (HPic)=9.3 (acetone), 8.8 (EMK), and 8.8 (IBMK) and pK_a (HND)=8.4 (acetone), 8.0 (EMK), and 8.0 (IBMK). The pK_a value of 9.3 for HPic in acetone is in good agreement with Foltin's value (pK_a=9.2).[1] However, it must be noted that the pK_a values reported by others are much smaller than the present values; Moor reported pK_a values of 3.86 (acetone) and 3.70 (EMK) for HPic;[2] Glover, a pK_a value of 3.3 for HND in acetone;[3] Majersky, pK_a values of 6.04 for HPic in acetone (0.09% water) and 6.54 in EMK (0.16% water);[4] and Majer, a pK_a value of 7.2 for HPic in acetone with a known content of water.[5]

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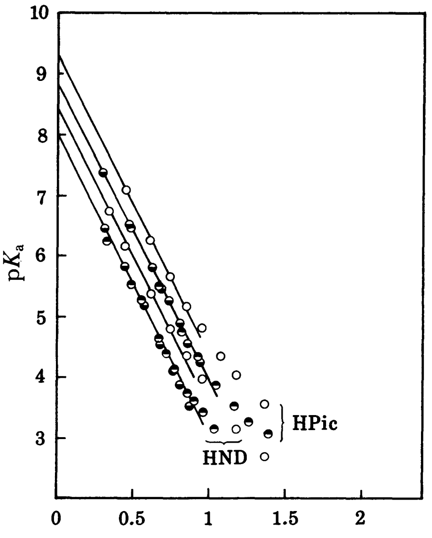

Fig. 2. pK_a *vs.* $[H_2O]^{1/2}$ plots. Symbols: see Fig. 1.

Taking into account the hydration of the solutes, the dissociation of HA can be expressed as:

$$HA_{x(H_2O)} + nH_2O \rightleftharpoons H^+_{y(H_2O)} + A^-_{z(H_2O)}, \tag{5}$$

where $n=x+y+z$. The equilibrium expression is given by:

$$K = [H^+][A^-]/([HA][H_2O]^n), \tag{6}$$

where K refers to the equilibrium constant; the symbols which denote hydration are omitted. Equation 6 can be rearranged as:

$$K_a = [H^+][A^-]/[HA] = K[H_2O]^n. \tag{7}$$

pK_a *vs.* log[H_2O] plots gave straight lines, as is shown in Fig. 3. From the slopes of the lines, the n values were determined to be 4.0±0.1 for all the acid-solvent systems. Since HA and A^- are bulky and hydrophobic in nature, the extent of their hydration is presumably very small or negligible as compared with that of the protons; this leads to the conclusion that the protons exist as $(H_9O_4)^+$ in ketonerich media, as observed in aqueous media.[6]

The dissociation constants can also be determined by means of vapor-pressure osmometry. When a solution and a solvent are placed together in a closed small room, the solvent vapor condenses on the solution, causing a rise in the temperature of the solution. The temperature difference, ΔT, is related to C as follows:

$$\Delta T = K_s(C + b_2C^2 + b_3C^3 + \cdots\cdots), \tag{8}$$

where K_s and b are constants, the values being calibrated with 1,2-diphenylethanedione as a reference substance.

For a dilute solution of electrolytes, Eq. 8 is approximated as:

$$\Delta T = K_s((1+\alpha)C + b_2(1+\alpha)^2C^2). \tag{9}$$

The pK_a values can thus be calculated from ΔT based on Eqs. 2 and 9. The dissociation constants of the potassium salts can also be determined in the same way.

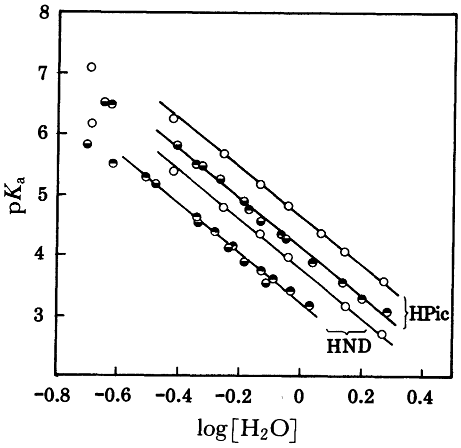

Fig. 3. pK_a *vs.* log[H_2O] plots. Symbols: see Fig. 1.

TABLE 1. pK_a VALUES[a] OBTAINED BY MEANS OF THE VAPOR-PRESSURE OSMOMETRIC METHOD

	$[H_2O]$/mol dm^{-3}								
	Acetone–H_2O					EMK–H_2O			
Compounds	0.03	1.24	1.29	1.95	4.05	0.03	1.18	2.09	2.52
HND	>6	3.7		2.8		>6	3.3		
K(HND)	2.1					2.2	(2.16)[b]		
HPic	>6		4.4		2.6	>6		3.0	2.6
KPic	2.6	(2.465)[c]							

a) For the K salts, $K_a=[K^+][A^-]/[KA]$. b) Ref. 9 (conductometric). c) Ref. 10 (conductometric).

Table 1 summarizes the dissociation constants. In the vapor-pressure osmometric method, the pK_a measurements of weak acids (pK_a>6) were unsuccessful because of the limited accuracy of the ΔT of the apparatus. The pK_a values in Table 1 agreed very closely with those obtained by means of the spectrophotometric method (*cf.* Fig. 3). Figures 1—3 and Table 1 show that HND is a stronger acid than HPic in ketone-water media, unlike as in aqueous media (pK_a(HND)= 2.75,[7] pK_a(HPic)=0.29[8]). The dissociation constants of the potassium salts also agreed well with those obtained conductometrically.[9,10]

References

1) M. Foltin and P. Majer, *Collect. Czech. Chem. Commun.*, **43**, 95 (1978).

2) F. J. Moor and I. B. Johns, *J. Am. Chem. Soc.*, **63**, 3336 (1941).

3) D. J. Glover, *J. Am. Chem. Soc.*, **87**, 5275 (1965).

4) P. Majersky and M. Dybalova, *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.*, **24**, 47 (1976).

5) P. Majer, D. Rurikova, and M. Foltin, *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.*, **22**, 1 (1975).

6) For example, R. P. Bell, "The Proton in Chemistry," Chapman and Hall, London (1973), p. 22.

7) D. -W. Fong and E. Grunwald, *J. Phys. Chem.*, **73**, 3909 (1969).

8) R. G. Bates and G. Schwarzenbach, *Experientia* **10**, 482 (1954).

9) T. Iwachido, unpublished work.

10) M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).