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Proton Dissociation Constants of Benzoylacetone and Isonitrosobenzoylacetone in Aqueous Dioxane Media

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Thermodynamic proton dissociation constants, *TpKa* of benzoylacetone(*HBA*) as well as isonitrosobenzoylacetone (*HINBA*) have been determined *pH*-metrically in 10–50% (*v*/*v*) dioxane-water mixtures at 25 and 35 ± 0.01 °C applying an empirical *pH* correction for mixed aqueous media. The *pKa*'s in aqueous medium (at 0% dioxane) are obtained following the method of extrapolation and least-squares. Both *HBA* and *HINBA* are very weak monoprotic acids with *TpKa* between 7.0 and 10.0. *TpKa*'s do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of *TpKa* vs. the mole fraction of dioxane is linear at a given temperature. The "true constant" *Ka'* and solvation number, *n*, in the expression $(\mathrm{H}^+)(A^-)/(\mathrm{H}A) = Ka'(S)^n = Ka^*$ for these reagents have been evaluated by analysing the experimental data mathematically. Values of ΔG^0, ΔH^0, and ΔS^0 are also computed. Temperature and medium effects are briefly discussed.

(Keywords: Dielectric constants; Ionization constants; Mixed solvents)

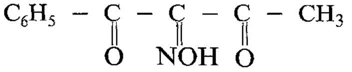
Protonen-Dissoziationskonstanten von Benzoylaceton und Isonitrosobenzoylaceton in wäßrigem Dioxan

Es wurden die thermodynamischen Protonen-Dissoziationskonstanten (*TpKa*) von Benzoylaceton (*HBA*) und Isonitrosobenzoylaceton (*HINBA*) *pH*-metrisch in 10—50% (*v*/*v*) Dioxan-Wasser-Mischungen bei 25 und 35 ± 0.01 °C bestimmt, wobei eine empirische *pH*-Korrektur für das gemischt-wäßrige Medium angewendet wurde. Die *pKa*-Werte in wäßrigem Medium (0% Dioxan) folgen aus der Extrapolation und der Methode kleinster Fehlerquadrate. Sowohl *HBA* als auch *HINBA* sind sehr schwache monoprotische Säuren mit *TpKa* zwischen 7.0 und 10.0. Die *TpKa*'s variieren nicht linear mit der reziproken Dielektrizitätskonstante des Mediums, ein Diagramm *TpKa* gegen Molenbruch Dioxan ergibt jedoch für eine konstante Temperatur eine Gerade. Die „wahre

Konstante“ *Ka'* und die Solvatationszahl *n* des Ausdrucks $(H^+)(A^-)/(HA) = Ka'(S)^n = Ka^*$ wurde aus den experimentellen Daten für beide Reagentien errechnet. Die thermodynamischen Parameter ΔG°, ΔH° und ΔS° wurden ebenfalls bestimmt, Temperatur- und Lösungsmitteleffekte werden diskutiert.

Introduction

Benzoylacetone(*HBA*) possesses remarkable versatility as a reagent for the solvent extraction of a host of metal ions [1–4] and is believed to be superior to the most popular extractant, acetylacetone, among the family of β-diketones [5]. Extensive systematic studies carried out by *Stary* et al. indicated that *HBA* can even successfully replace the widely used 2-thenoyltrifluoroacetone for many analytical and radiochemical separations [6]. Its isonitroso derivative, viz. isonitrosobenzoylacetone(*HINBA*) (**1**) has also received wide attention recently as potential analytical reagent [7–10]. Data on their proton dissociation constant would be of great interest in various analytical procedures and also in the elucidation of the structure of the resulting metal complexes. Besides, a precise knowledge of acid dissociation of an extractant is of utmost importance because this property determines the availability of chelating anion for complexation. As a prelude to our studies on the relationships of structure to the sensitivity and selectivity of β-diketones, thermodynamic acid dissociation constants, TpK_a, of these ligands have now been determined.



$$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

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Method

TpK_a's of *HBA* in 20–50% (*v*/*v*) dioxane-water media at 25 and 35 ± 0.01 °C have been determined *pH*-metrically and the thermodynamic functions ($\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$) associated with its ionization calculated. Similar studies were carried out with *HINBA* to assess the relative effect of (= NOH) group substitution. Concentrations higher than 0.174 mole fraction of dioxane (n_2) were avoided because of possible association of solutes, which may be expected in solvents of low dielectric constants; also, activity coefficient corrections would be larger in such solutions. In addition, experimental errors might be introduced in the TpK_a measurement owing to the higher *pH* meter correction necessary in such cases. Values of solvation number and the true ionization constant for their dissociation are also tabulated. TpK_a values have been determined by the *pH* titration method using a glass and saturated calomal electrode in cells with liquid junction potential. The relationship of *Van Uitert* and *Haas* [11] was utilised to evaluate the hydrogen ion concentration from the values read on the *pH* meter (B).

$$-\log[\mathrm{H}^+] = B + \log U_{\mathrm{H}}{}^{\circ} + \log \gamma \pm \qquad (1)$$

Values of correction factor, $\log U_{\mathrm{H}}{}^{\circ}$, were obtained experimentally [12] and those of mean activity coefficients ($\gamma \pm$) were computed by interpolation of the data given by *Harned* and *Owen* [13] assuming that the mean activity coefficients are the same on both the molal and molar scales. The acid dissociation of these ligands in an *aq.* medium gives hydrogen ion (H^+) and diketonate anion (A^-) and the equilibrium constant is given by Eq. (2) in such a medium.

$$TK_a(aq.) = ([\mathrm{H}^+][A^-]/[\mathrm{H}A])(\gamma_{\mathrm{H}^+}\gamma_{A^-}/\gamma_{\mathrm{H}A}) \qquad (2)$$

or

$$TpK_a(aq.) = -\log[\mathrm{H}^+] + \log([\mathrm{H}A]/[A^-]) + 2\log(1/\gamma \pm) \qquad (3)$$

Assuming that $\gamma_{\mathrm{H}A}$, the mean activity coefficient of non ionised acid, is unity, the final form of the equation for computing TpK_a in the dioxane-water mixtures is obtained by Eqs. (1) and (3).

$$TpK_a = B + \log U_{\mathrm{H}}{}^{\circ} + \log([\mathrm{H}A]/[A^-]) + \log 1/\gamma \pm \qquad (4)$$

Experimental

HBA, procured from B.D.H. England was used as supplied. *HINBA* was synthesized from *HBA* by the method reported earlier [14]; m.p. = 124–125 °C. All chemicals were of A.R. or G.R. grade from B.D.H. or E. Merck unless stated otherwise. An aqueous solution (10%) of tetramethylammonium hydroxide (*TMAH*) titrant was standardised against potassium hydrogen phthalate and diluted to 0.1 *M*, the proportion of dioxane and water being the same as used in preparing the titre solutions. *p*-Dioxane was purified as recommended [15].

The titration procedure for determining the ionization constants was essentially the same as described by *Albert* and *Serjeant* [16]. Generally, a 0.01 *M* solution of β-diketone was titrated without the addition of inert salt. Measurements of *pH* were made on an Orion research *pH* meter which can be read to 0.001 unit of *pH*. The instrument was standardised against phthalate and borax buffers before and after each titration.

In a thermostated (25 or 35 ± 0.01 °C) titration vessel, accommodating a glass electrode, a limb of saturated KCl bridge and a microburette of 5.0 ml capacity, 0.5 m*M* of β-diketone in the appropriate dioxane-water composition was taken and the contents stirred magnetically. The initial volume of the titre solution was 47.5 ml in all cases to allow for the change in the total volume of solution on the addition of titrant [17]. For practical purposes, the error caused by a volume correction is almost negligible (less than 0.01 *pH* unit for the inner five reading of a set of *pH* titrations) with a maximum error of 0.018 *pH* unit [18]. About 10 min after the settings, the titration was started by adding 0.5 ml aliquots of 0.1 *M* *TMAH* at a time and noting the highest stable *pH*. Titrations, carried out in duplicate, were reproducible within ± 0.01 *pH* unit.

Results and Discussion

TpK$_a$ values of *HBA* and *HINBA* in different water-dioxane media at 25 and 35 °C are summarised in Tables 1 and 2, respectively. Values of *TpK$_a$* for *HBA* at 25 °C, reported earlier by us [19], have been redetermined under the present set of conditions for comparision purposes. These constants considerably decrease with increasing temperature in the case of *HBA*. Contrary is the behaviour of its isonitroso derivative (*HINBA*) where *TpK$_a$* values slightly increase with increasing temperature indicating thereby that higher temperatures are not favourable for its ionization. The average *TpK$_a$* usually falls within a spread of ± 0.02 but not beyond ± 0.03 in any instance. Titration of perchloric acid in the presence and absence of these ligands proved that their protonation is negligible. The effect of dilution studied with slightly varying concentrations of both the ligands was found to be almost negligible as the *TpK$_a$* values do not differ markedly. The *TpK$_a$*'s were plotted against $1/D$ (Fig. 1) or mole fraction of dioxane (n_2) in Fig. 2. For brevity, *TpK$_a$* $- 1/D$ plots for these compounds only at 35 °C are given. Empirical relations derived therefrom are given in Table 3. Such relationships between *TpK$_a$* and n_2 were also obtained by subjecting the data to a least-squares analysis (Table 3). Values of "true constants" and the solvation numbers are presented in Table 4. Table 5 records the thermodynamic functions $\Delta G°$, $\Delta S°$ and $\Delta H°$ associated with the proton-ligand dissociation reactions computed by the temperature variation method.

Medium Effects

Considering the acid dissociation of these *β*-diketons involving a net increase of ions

$$\mathrm{H}A + \mathrm{H_2O} = \mathrm{H_3O^+} + A^-$$

a decrease in the dielectric constant of the reaction medium should increase the *TpK$_a$*, as borne out from the Tables 1 and 2. This prediction has been amply proved for other diketones on the basis of previous similar studies [19–22].

Medium effects and transfer energies for ions have sometimes been considered to consist of an electrostatic part, $\Delta G°_{el}$ arising mainly from differences in the dielectric constants of the solvent and a nonelectrostatic part, $\Delta G°_{nonel}$ reflecting the contributions of the solvation and the other specific ion-solvent interactions which depend on the solvent basicity [23–25]. Thus

$$\Delta G°_t = \Delta G°_{el} + \Delta G°_{nonel}$$

Table 1. *Thermodynamic proton dissociation constants of benzoylacetone*

Vol. % dioxane	Mole fraction of dioxane (n_2)	*TpKa* at 25 °C				*TpKa* at 35 °C			
		Found[a]	Calc.[b]	Graph	$\cdot 10^2$ (Col. 3–Col. 4)	Found[a]	Calc.[b]	Graph	$\cdot 10^2$ (Col. 7–Col. 8)
1	2	3	4	5	6	7	8	9	10
20	0.050	9.25	9.22	9.23	+3	9.10	9.09	9.10	+1
30	0.083	9.53	9.52	9.53	+1	9.39	9.39	9.39	0
40	0.123	9.83	9.89	9.87	−6	9.72	9.76	9.75	−4
50	0.174	10.39	10.36	10.37	+3	10.24	10.22	10.25	+2
Total					13				7
Average					$3.2 \cdot 10^{-2}$				$1.75 \cdot 10^{-2}$
Deviation					~0.03				~0.02

[a] *TpKa* obtained using all nine values of a set

[b] Calculated values of *TpKa* obtained by subjecting experimental data to a least-squares analysis

Table 2. *Thermodynamic proton dissociation constants of isonitrosobenzoylacetone*

Vol. % dioxane	Mole fraction of dioxane (n_2)	*TpKa* at 25 °C				*TpKa* at 35 °C			
		Found[a]	Calc.[b]	Graph	$\cdot 10^2$ (Col. 3– Col. 4)	Found[a]	Calc.[b]	Graph	$\cdot 10^2$ (Col. 7– Col. 8)
1	2	3	4	5	6	7	8	9	10
10	0.023	7.37	7.37	7.35	0	7.39	7.43	7.40	−4
20	0.050	7.74	7.73	7.75	+1	7.83	7.80	7.83	+3
30	0.083	8.13	8.17	8.13	−4	8.26	8.25	8.25	+1
40	0.123	8.75	8.71	8.83	+4	8.82	8.80	8.83	+2
50	0.174	9.39	9.40	9.37	−1	9.48	9.50	9.50	−2
Total					10				12
Average					$2.0 \cdot 10^{-2}$				$2.40 \cdot 10^{-2}$
Deviation					~ 0.02				~ 0.02

[a] *TpKa* obtained using all nine values of a set

[b] Calculated values of *TpKa* obtained by subjecting experimental data to a least-squares analysis

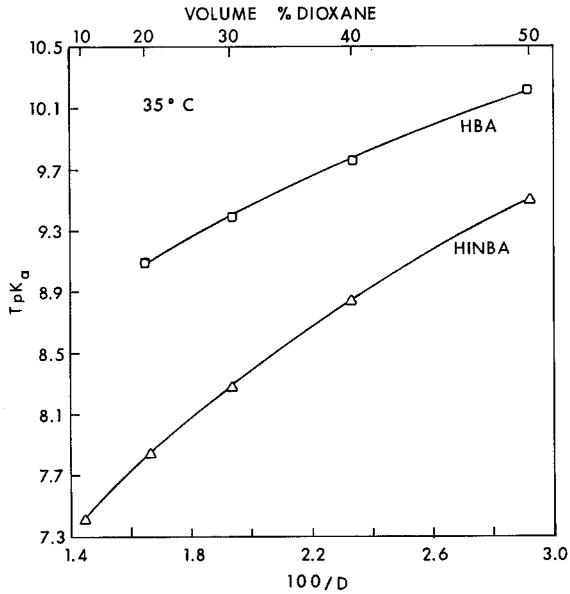

Fig. 1. Variation of TpK_a with the dielectric constant (D) of the medium

If the electrostatic part is expressed by *Born*'s formula [26], it follows:

$$\Delta G^\circ_{el} = -(Ne^2/2)(1 - 1/D)(1/r^+ + 1/r^-)$$

where r^+ and r^- denote the radii of the solvated ions and D the dielectric constant of the medium [27, 28]. Hence, on simultaneous transfer of ions from water (dielectric constant D_w) to dioxane-water medium:

$$\Delta G^\circ_t = \Delta G^\circ_{nonel} - (Ne^2/2)(1/D - 1/D_w)(1/r^+ + 1/r^-)$$

Further, as $\Delta G^\circ_t = 2.303\, RTpK_a$, the eq. simplifies as

$$pK_a = (\Delta G^\circ_{nonel}/2.303\, RT) - (Ne^2/4.606\, RT)(1/D - 1/D_w)(1/r^+ + 1/r^-)$$

Conventionally, pK_a is plotted against $1/D$ assuming ΔG°_{nonel} to be independent of the solvent and terms $(1/r^+ + 1/r^-)$ and $1/D_w$ are constant. Both types of relationship, viz. linear for water rich media ($D > 30$) [29, 30] as well as nonlinear [31] have been reported. When TpK_a values of *HBA* as well as *HINBA* are plotted against $1/D$ it is seen that the plots possesses distinct curvature (Fig. 1). Evidentally non-electrostatic factors exert a considerable influence on the acid dissociation of such diketones. As *Harned* and *Owen* [32] observed, when the plots are extended over a wide range of dielectric constants such as represented by going from water to 82% dioxane-water, linearity fails. Such a relationship is improved by taking into account the variation of the concentration of water in the solution [33]. Here, (HOH), is introduced into the ionization expression for a weak acid in order to get a better $pK_a - 1/D$ plot. Curvature still occurs at high concentrations of organic solvent.

Likewise, the currently accepted *Denison-Ramsay* and *Fouss* theory [34, 35] of ion-pair formation also predicts that $-\log K$ (or pK_a) should be a linear function of $1/D$, with a slope that is proportional to the ion size. The latter relationship was observed to be followed moderately well for most ionization constants when the concentration of added organic solvent was not great but the correlation failed too over wide ranges of solvent composition.

Aksnes [36] has also considered electrostatic effects in the ionization of weak acids in water-dioxane mixtures and concluded that the main reason for the decrease in the ionization was due to a statistical effect, that is, water must be regarded as a reactant because it hydrates the proton. Furthermore, he suggested that the dielectric constant to be used in the *Born* equation (for calculating the attraction between oppositely charged ions in solution) should be the dielectric constant of water in the solvent mixtures. Water concentration has also been taken into account in the discussions on dissociation of organic acids in aqueous organic mixture [33, 37, 38].

Lahiri and associates [39] have reported linearity in the plot of pKa vs. $1/D$ only up to 60 wt% ethanol, beyond which deviation occurred. Deviation at higher percentage of organic solvents was attributed to the fact that at these high percentages of organic solvents the H^+ values from *pH* meter reading may be inaccurate due to: (i) high liquid junction potential, and (ii) low sensitivity of the glass electrodes. Contrary to this, deviations were more recently encountered by these workers [40] at relatively low concentrations of *t*-butanol as compared to methanol water, and ethanol water mixtures.

Mole Fraction of Dioxane

A consideration of the direct participation of the solvent in the acid ionization should lead to a better understanding of the compositions of the solvent as well as of ion solvates [38]. For example, such a participation is quite evident from essentially straight line plots of pKa vs. n_2 in several instances [41].

For both *HBA* and *HINBA*, the change in TpK_a with n_2 is appreciably high. When TpK_a's are plotted against n_2, linear relationships are obtained (Fig. 2). The experimental values of TpK_a here indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% in TpK_a. These plots gave slopes equivalent to about 9 and 13 for *HBA* and *HINBA*,

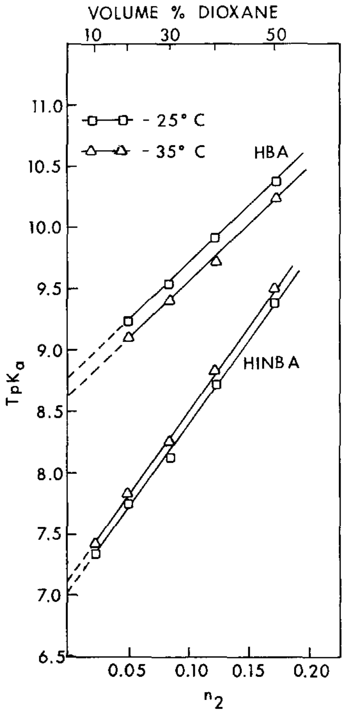

Fig. 2. Variation of TpK_a with n_2 (mole fraction of dioxane)

respectively which are as expected for diketones [21–22]. The goodness of fit was judged by calculating the correlation coefficient, r, defined by

$$r = \sum (X - \bar{X})(Y - \bar{Y}) / [\sum (X - \bar{X})^2 \cdot \sum (Y - \bar{Y})^2]^{1/2}$$

Where $\bar{X}$ and $\bar{Y}$ are the mean values of $X(TpK_a)$ and $Y(n_2)$ respectively. The summations are extended to all pairs (X, Y) available. Linear proportionality is readily indicated between the two variables when the values of r is $+1.0$ [42]. The values of b, „regression coefficient" or actual slopes of the lines, is finally given by

$$b = \sum (X - \bar{X})(Y - \bar{Y}) / \sum (X - \bar{X})^2$$

Since the value of r is nearly $+1.0$ at 25 and 35 °C for both *HBA* and *HINBA* (Table 3), it implies that there is quite a high probability of a linear relationship between TpK_a and n_2. A similar behaviour is found for several other acids such as benzoic, acetic, propionic and formic acids [41] and a number of β-diketones in aqueous dioxane [19–21]. Likewise, linear

Table 3. *Empirical relation between TpKa and n_2 of dioxane for HBA and HINBA*

β-diketone	$TpKa = mn_2 + c$, at 25 °C						$TpKa = mn_2 + c$, at 35 °C					
	Graph		Least-squares				Graph		Least-squares			
	m	c	m	c	r^1	b^2	m	c	m	c	r^1	b^2
HBA	9.15	8.78	9.16	8.76	0.996	9.16	9.60	8.63	9.14	8.63	0.999	9.14
HINBA	13.20	7.05	13.47	7.06	0.999	13.47	13.50	7.13	13.74	7.11	0.999	13.74

[1] and [2] refer to the correlation and regression coefficients (actual slope), respectively

proportionality is also obtained for some other mixed water solvents, e.g. acetic, propionic, butyric acids and benzoic acid in methanol-water mixtures [43] and dimedone in ethanol-water [44].

Evaluation of pKa′ and n

The acid dissociation constant (Ka') of the acid HA in a mixed medium, can be expressed as:

$$nS + \mathrm{H}A \overset{Ka'}{\rightleftharpoons} xS\mathrm{H}^+ + ySA^- \tag{5}$$

Where n is the total of x plus y moles of solvent S; aqueous dioxane being the medium in the present study.

Hence,

$$(xS\mathrm{H}^+)(ySA^-)/(S)^n(\mathrm{H}A) = Ka' \tag{6}$$

where the parentheses denotes activity. Eq. 6 is usually written as

$$(\mathrm{H}^+)(A^-)/(\mathrm{H}A) = Ka'(S)^n = Ka^* \tag{7}$$

where it is understood that the ions are solvated and Ka^* includes the solvent terms $(S)^n$. By taking logarithms of Eq. (7), we get

$$\log Ka^* = \log Ka' + n\log(S)$$

or

$$pKa^* = pKa' - n\log(S) \tag{8}$$

Since pKa^*, defined in Eq. (8) is the thermodynamic constant, pKa' thus evaluated should be a true constant, independent of the media provided the assumptions for S and n are correct.

Finally, the solvation number n, can be computed from the following equation derived from Eq. (8),

$$n = [pKa_2{}^* - pKa_1{}^*]/[\log(S_1) - \log(S_2)]$$

Values of n at 25° are found to be 4.71 ± 0.09 and 6.82 ± 0.08 for *HBA* and *HINBA* respectively. This is in fine accord with the values of solvation number reported for acid dissociation of acetic, formic and propionic acids in dioxane-water mixture [38]. The pKa' values listed in Table 4 have been computed by Eq. (8), yielding the equations:

for *HBA* $pKa^* = (16.92 \pm 0.06) - (4.71 \pm 0.09)\log(S)$

and for *HINBA* $pKa^* = (18.88 \pm 0.08) - (6.82 \pm 0.08)\log(S)$

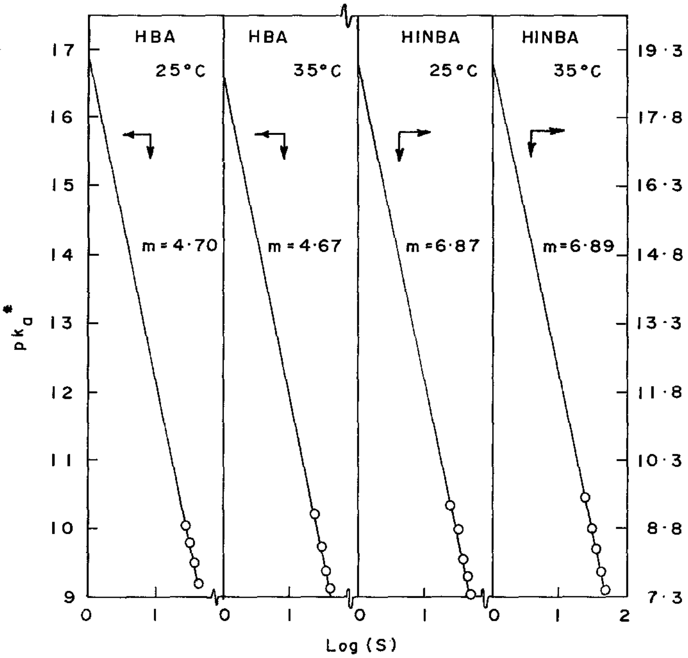

Fig. 3. Plot of pK_a* vs. log (S)

Thermodynamic Functions of Dissociation

The TpK_a values have been determined with a precision of ± 0.02 to ± 0.03 and hence the error in $\Delta G°$ is estimated to be between ± 0.03 to ± 0.04 kcal mol^{-1}. The procedure followed here to evaluate $\Delta H°$ is subject to some error because the enthalpy change is small and TpK_a values were not obtained at several temperatures which would have allowed use of more precise method [45]. However, the negative value of $\Delta H°$ found in dioxane-water solutions for *HINBA* indicates that its ionization is accompanied by liberation of heat and the process is exothermic. Contrary to this, the ionization of its parent compound i.e. *HBA* is found to be an endothermic process at least up to 35 °C in dioxane-water mixtures. Further, the change in $\Delta H°$ with change in medium is relatively small and negligible within experimental error. It is because of this that the slops of straight lines in the plots of TpK_a vs. n_2 (Fig. 2) are the same at both the temperatures (Table 3), and the two lines are parallel.

Table 4. *Calculation of "true constant", pKa' for HBA and HINBA*[a]

vol.% dioxane	*pKa** (Found)	log *S*	*pKa'*[b]	*pKa** (Calc.)	*pKa** (Graph)
10	Ins.	1.69	–	–	–
	7.37		18.91	7.34	9.35
20	9.25	1.64	16.95	9.22	9.20
	7.74		18.88	7.74	7.75
30	9.53	1.57	16.92	9.53	9.50
	8.13		18.82	8.20	8.12
40	9.83	1.49	16.85	9.90	9.85
	8.75		18.91	8.73	8.72
50	10.39	1.39	16.96	10.35	10.40
	9.39		18.89	9.38	9.34

[a] Upper values for *HBA* and lower values for *HINBA*

[b] For *HBA* at 25°, $n = 4.71 \pm 0.09$ (Calc.); 4.70 (Graph); $pKa' = 16.92 \pm 0.06$ (Calc.); 16.85 (Graph). For *HINBA* at 25°, $n = 6.82 \pm 0.08$ (Calc.); 6.87 (Graph); $pKa' = 18.82 \pm 0.05$ (Calc.); 18.92 (Graph)

It is, therefore, justifiable to assume that ΔH° is independent of solvent media over the range investigated. On this basis, a fresh value of ΔH° was calculated. Numerically, this is equal to 42.06 times the difference in the intercepts of the parallel lines on the TpK_a axis (Fig. 2) and it is this value that is given in Table 5.

Values of ΔS° at different percentages of dioxane were found to be practically the same, thereby showing that it is independent of solvent composition. This in agreement with our earlier observation [21], wherein the large native value of entropy has been explained as arising due to ionization of the ligand since the sum total of the number of water molecules "bound" is more than water molecules originally accompanying the undissociated reagent. The experimentally evaluated values of ΔS° and ΔH° for the dissociation of *HBA* and *HINBA* in aqueous dioxane media show that the large decrease of the ionization constant is chiefly due to a much larger negative value of the entropy of ionization. These facts are thus in accordance with the assumption that the decrease of the ionization constant in dioxane-water mixtures is chiefly due to a statistical effect. For any definite explanation, extensive data in mixed solvent would be needed.

It is seen that ΔG°_t values are positive and increase with increasing amounts of dioxane, indicating that the transfer of these ligands from

Table 5. *Free energy, enthalpy and entropy changes for proton dissociation of HBA and HINBA*

β-diketone	Parameter[a]	Solvent medium, % (v/v) dioxane				
		10	20	30	40	50
HBA	ΔG°_t 25 °C	[b]	12.62	13.00	13.41	14.18
	ΔG°_t 35 °C	[b]	12.83	13.25	13.71	14.44
	$\Delta H^\circ = 5.58$					
	$-\Delta S^\circ$ 25 °C	[b]	23.62	24.90	26.27	28.85
	$-\Delta S^\circ$ 35 °C	[b]	23.54	24.90	26.39	28.76
HINBA	ΔG°_t 25 °C	10.06	10.56	11.09	11.94	12.81
	ΔG°_t 35 °C	10.42	11.04	11.65	12.43	13.37
	$\Delta H^\circ = -2.52$					
	$-\Delta S^\circ$ 25 °C	42.20	43.87	45.65	48.50	51.42
	$-\Delta S^\circ$ 35 °C	41.99	44.00	46.00	48.52	51.57

[a] ΔG° and ΔH° in kcal mol^{-1}, ΔS° in cal mol^{-1} K^{-1}
[b] Insoluble

water to the mixed solvent is not spontaneous. Qualitatively it may be expected that ΔG°_{el} will be increasingly positive with the addition of dioxane due to the resulting decrease in the dielectric constant, while ΔG°_{nonel} possibly decreases continuously under the same conditions. The predominantly positive values of ΔG°_t presumably indicate a dominant contribution of the electrostatic over the nonelectrostatic interactions in the present case.

Substitution Effects

The introduction of substituents into the molecule of an organic chelating agent often results in a change of the chelating ability of proton or metal in addition to changes of other chemical and physical properties. β-Diketones in solution generally exist as equilibrium mixtures of the keto-enol forms. Values of TpK_a given in Table 1 and 2 should, therefore, in principle refer to their twin processes of enolization and ionization [46] viz.

$$Ka = [H^+][A^-]/[\text{keto}] + [\text{enol}]$$

The acid strength is affected by the nature and structure of the substituent. The acid strengthening effect of the electron-withdrawing =NOH substituent is evident in the substantial decrease in TpK_a of *HINBA* from those of *HBA* itself. Values of TpK_a for *HINBA* are consistently lower than those of *HBA* in all solvent media and follow the sequence.

	HINBA		*HBA*
TpK_a, 25 °C (aq. medium)	7.06	<	8.76
TpK_a, 35 °C (aq. medium)	7.11	<	8.63

This is what one would expect, as the introduction of the electronegative isonitroso (= NOH) group enhances the acidic character of the hydroxyl group.

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