THERMODYNAMICS OF PROTON–LIGAND DISSOCIATION EQUILIBRIA IN MIXED SOLVENTS. ACID DISSOCIATION OF 2-ISOPROPYLTROPOLONE IN MIXTURES OF WATER AND DIOXANE

J.P. SHUKLA, P.M. RAVI * and M.S. SUBRAMANIAN

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 (India)

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ABSTRACT

Thermodynamic acid dissociation constants, TpK_a, of 2-isopropyltropolone (HIPT) have been determined by pH titration in aqueous and aqueous dioxane media at 25 and 35 ± 0.01°C applying an empirical pH correction for mixed aqueous media. HIPT is a very weak acid with TpK_a between 7 and 9. The TpK_a values do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of TpK_a vs. the mole fraction of dioxane is linear at a given temperature. The "true constant", K_a', and solvation number, n, in the expression $(H^+)(A^-)/(HA) = K_a'(S)^n = K_a^*$ for this reagent have been evaluated. Mean ionic radii, $r \pm$, for the tropolonate ion, being in the region of 2.0–2.4 Å, slightly increases with dioxane percentages. Values of ΔG^0, ΔH^0 and ΔS^0 have been evaluated. The effects of temperature as well as medium effects are briefly discussed.

INTRODUCTION

2-Isopropyltropolone (β-Thujaplicin, HIPT), a naturally occurring chelating product [1], is a powerful extracting agent for a host of metal ions [2–9] and offers certain advantages over its parent compound, tropolone [10]. Its remarkable versatility lies in its chemical stability and in the fact that it can extract many metal ions at considerably lower pH than several other extractants, such as oxine and TTA [11]. Numerous applications of HIPT have already been reviewed [12,13]. Relatively little data exist on the stabilities and structures of this reagent and its metal chelates [13,14]. Most of the effort has, however, been restricted to the evaluation of its stoichiometric acid dissociation constant valid for some specific set of conditions [11,15–17]. No value for the thermodynamic equilibrium constant for its enolization exists, except in one instance [18]. This prompted us to study in

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* Health Physics Division.

detail the proton ionization relations of this ligand and to arrive at theoretically comparable thermodynamic data.

The thermodynamic acid dissociation constants, TpK_a, of HIPT in aqueous as well as 10, 20, 30, 40 and 50 vol. % dioxane–water media at 25 and $35 \pm 0.01°C$ have been determined pH-metrically and the thermodynamic functions associated with its ionization calculated. Concentrations higher than 0.174 mole fraction of dioxane (n_2) were avoided because of the possible association of solutes, which may be expected in solvents of low dielectric constant; also, activity coefficient corrections would be considerably more in such solutions. In addition, experimental errors might be introduced in the TpK_a measurements owing to the higher pH-meter correction necessary in such cases. Based on the TpK_a values thus determined, mean ionic radii, $r \pm$, for the tropolonate ion have been evaluated adopting two different procedures. Values of solvation number and the true ionization constant for the dissociation of HIPT are also tabulated. Thermodynamic functions have been computed in the usual way.

EXPERIMENTAL

HIPT, procured from Koch Light, U.K., was used as supplied. 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 standardized against potassium hydrogen phthalate and diluted to 0.1 M, the proportions of dioxane and water being the same as used in preparing the titre solutions. p-Dioxane was purified as recommended [19].

The titration procedure for determining the ionization constants was essentially the same as outlined by Albert and Serjeant [20]. Generally, 0.01 M HIPT 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 standardized against phthalate and borax buffers before and after each titration.

In a thermostated (25 or $35 \pm 0.01°C$) titration vessel, accommodating a glass electrode, a limb of saturated KCl bridge and a microburette of 5.0 ml capacity, 0.5 mM of HIPT 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 [21]. For practical purposes, the error caused by volume correction is almost negligible (less than 0.01 pH unit for the inner five readings of a set of pH titrations) with a maximum error of 0.018 pH unit [22]. 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.

CALCULATIONS

$Tp K_a$ values have been determined by the pH titration method using a glass and saturated calomel electrode in cells with a liquid junction potential. The relationship of Van Uitert and Haas [23] was used to determine the hydrogen ion concentration from the values read on the pH-meter (B).

$$-\log[H^+] = B + \log U_H^0 + \log y \pm \qquad (1)$$

Values of the correction factor, $\log U_H^0$, were obtained experimentally [24] and those of the mean activity coefficient ($y \pm$) were computed by interpolation of the data given by Harned and Owen [25]. Here an assumption has been made that the mean activity coefficients are the same on both the molal and molar scales. The acid dissociation of HIPT (HA) in an aqueous medium gives hydrogen ion (H^+) and tropolonate ion (A^-) and in such a medium the equilibrium constant is given by eqn. (2)

$$TK_a(\text{aq.}) = ([H^+][A^-]/[HA])(y_{H^+} \cdot y_{A^-}/y_{HA}) \qquad (2)$$

or

$$Tp K_a(\text{aq.}) = -\log[H^+] + \log([HA]/[A^-]) + 2 \log(1/y \pm) \qquad (3)$$

Assuming y_{HA}, the mean activity coefficient of unionized acid, is unity, the final form of the equation for computing $Tp K_a$ in the dioxane–water mixture is obtained by eqns. (1) and (3)

$$Tp K_a = B + \log U_H^0 + \log([HA]/[A^-]) + \log 1/y \pm \qquad (4)$$

A correction for hydrolysis of the salt, which may be significant at the end of the titration (i.e. at pH > 10), was applied by substituting $\log[HA] + \{OH^-\}/[A^-] - \{OH^-\}$ for $\log[HA]/[A^-]$ in eqn. (3) or (4).

Hydroxyl ion activity, $\{OH^-\}$, was computed from the relationship [26]

$$\{OH^-\} = \text{antilog}(B - pK_w)$$

The ionic product of water, pK_w, has been obtained from the data of Agrawal [27] in different dioxane–water mixtures. The numerical equations expressed for the linear relationship are [28]

at 25°C: $pK_w = 11.92 \, n_2 + 14.00$
at 35°C: $pK_w = 12.01 \, n_2 + 13.68$

The experimental values indicate a maximum deviation from linearity of the order of 0.04 or about 0.3% in pK_w.

TABLE 1

Thermodynamic ionization constants of 2-isopropyltropolone

Vol.% dioxane	Mole fraction of dioxane (n_2)	TpK_a at 25°C				TpK_a at 35°C			
		Found [a]	Calcd. [b]	Graph	$\times 10^2$ (cols. 3 and 4)	Found [a]	Calcd. [b]	Graph	$\times 10^2$ (cols. 7 and 8)
0	0	7.29	7.23	7.26	+6	7.47	7.38	7.45	+9
10	0.023	7.49	7.46	7.49	+3	7.68	7.62	7.68	+6
20	0.050	7.75	7.73	7.76	+2	7.88	7.89	7.95	−1
30	0.083	7.99	8.06	8.09	−7	8.21	8.24	8.28	−3
40	0.123	8.50	8.47	8.49	+3	8.63	8.65	8.68	−2
50	0.174	8.97	8.99	9.00	−2	9.19	9.18	9.19	+1
Total					23				22
Ave.					3.83×10^{-2}				3.67×10^{-2}
Deviation					~ 0.04				~ 0.04

[a] TpK_a obtained using all nine values of a set.
[b] Calculated values of TpK_a obtained by subjecting experimental data to a least-squares analysis.

RESULTS

TpK_a values of HIPT in aqueous and different aqueous dioxane media at 25 and 35°C are summarized in Table 1. These constants invariably increase with increasing temperature in all the above cases. The average TpK_a usually falls within a spread of ± 0.02 but not beyond ± 0.03 in any instance. The effect of dilution studied with slightly varying concentrations of this ligand was found to be almost negligible as the TpK_a values do not differ markedly. The TpK_a values were plotted against $1/D$ (Fig. 1) or mole fraction of dioxane, n_2 (Fig. 2). Empirical relations derived therefrom are given in Table 2. Such relationships between TpK_a and n_2 were also obtained by subjecting the data to a least-squares analysis (Table 2). Values of mean ionic radii, $r\pm$, for the 2-isopropyltropolonate ion in different aqueous dioxane media are presented in Table 3 and those of "true constants" and solvation numbers in Table 4. Table 4 records the thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 associated with the proton–ligand dissociation reactions computed by the temperature variation method.
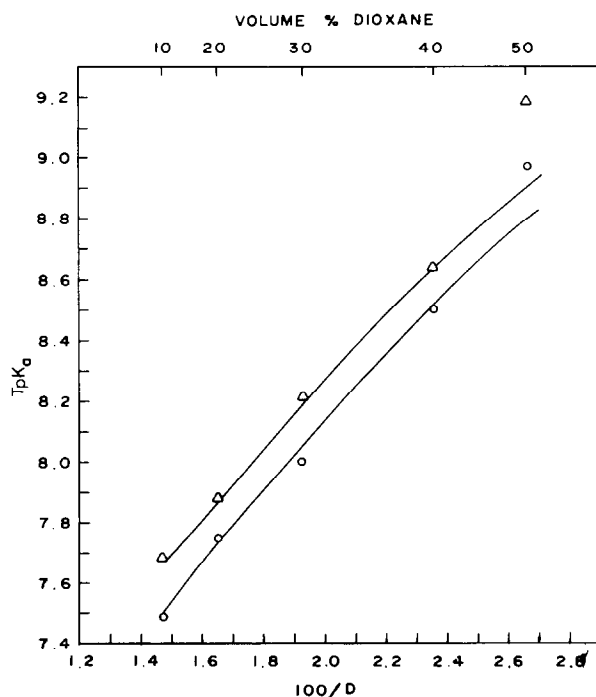
Fig. 1. Variation of TpK_a with the dielectric constant (D) of the medium at 25°C ($\bigcirc$) and 35°C ($\triangle$).

TABLE 2

Empirical relation between TpK_a and n_2 of dioxane for 2-isopropyltropolone

| $TpK_a = mn_2 + C$ at 25°C | | | | | | $TpK_a = mn_2 + C$ at 35°C | | | | | |
| Graph | | Least squares | | | | Graph | | Least squares | | | |
m	C	m	C	r	b	m	C	m	C	r	b
10.00	7.26	10.11	7.23	1.009	10.143	10.00	7.45	10.36	7.38	0.974	9.667

r and b refer to the correlation coefficient and regression coefficient (actual slope), respectively.

TABLE 3

Values of mean ionic radii ($r \pm$) for 2-isopropyltropolone ion (temperature 25°C)

Vol.% dioxane	Dielectric constant of aqueous dioxane media [a]	$\Delta TpK_a = TpK_{a(s)} - TpK_{a(w)}$	$r \pm$ [b] (Å)
10	69.69	0.20	1.97
20	60.79	0.46	1.96
40	42.98	1.21	2.12
50	34.26	1.68	2.38

[a] Ref. 62.
[b] Values of $r \pm$ determined graphically lie in the range 2.08–2.16 Å.

TABLE 4

Calculation of 'true constant', pK_a' for 2-isopropyltropolone [a]

Vol.% dioxane	pK_a^* (found)	$\log S$	pK_a' [b]	pK_a^* (calcd.)	pK_a^* (graph)
10	7.49	1.69	15.97	7.45	7.56
	7.68	1.69	16.64	7.59	7.80
20	7.75	1.64	15.94	7.74	7.83
	7.88	1.63	16.54	7.90	8.08
30	7.99	1.57	15.85	8.08	8.13
	8.21	1.57	16.52	8.25	8.42
40	8.50	1.49	15.97	8.47	8.57
	8.63	1.49	16.52	8.67	8.81
50	8.97	1.39	15.96	8.95	9.01
	9.19	1.39	16.57	9.18	9.29

Ave. $= 15.94 \pm 0.05$
$ 16.56 \pm 0.06$

[a] First and second row values at 25 and 35°C, respectively.
[b] At 25°C, $n = 5.01 \pm 0.10$ (calcd.); 4.92 (graph); $pK_a' = 15.90$ (graph). At 35°C, $n = 5.30 \pm 0.20$ (calcd.); 5.00 (graph); $pK_a' = 16.25$ (graph).
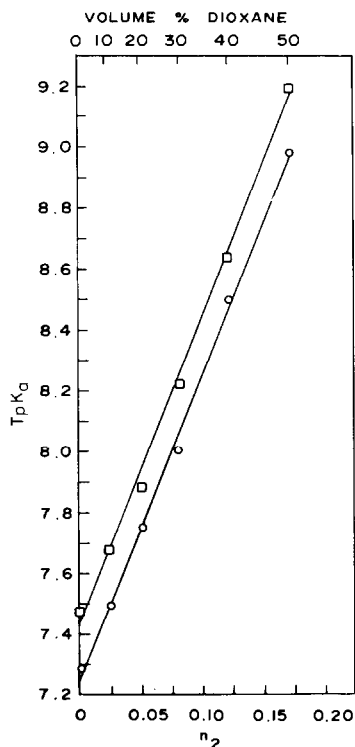
Fig. 2. Variation of TpK_a with n_2 (mole fraction of dioxane) at 25°C ($\bigcirc$) and 35°C ($\square$).

DISCUSSION

HIPT is derived from tropolone, a cyclic α-hydroxy ketone, and possesses a seven-membered ring containing three double bonds. It loses one of its electrons to the oxygen atom resulting in a closed shell of six π electrons [29]. The presence of $(4n + 2)$ π electrons and the planarity of the ring confer aromatic character on the molecule. This non-benzenoid molecule is stabilized by resonance and tautomerism so that the ketonic group is largely masked and its behaviour is that of the enol form. Actually, HIPT does not seem to undergo any such tautomeric or hydrogen equilibria as HTTA.
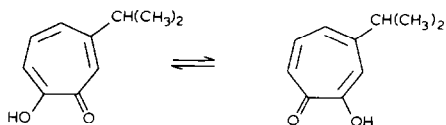
Infrared studies have also shown high planarity for the $-C{=}O$ [30]. On the basis of the present study, it is seen that HTTA is a stronger acid than HIPT by at least 1 TpK_a unit in different media.

Medium effects

Acid strength and thus pK_a values of proton acids are influenced by the intrinsic basicity of the solvent. The ionization equilibrium for HIPT is an ionogenic reaction and, therefore, the changes in TpK_a values with dioxane should be accounted for by the electrostatic and specific solvation effects. Considering its acid dissociation involving a net increase of ions

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
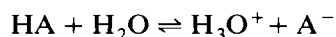
a decrease in the dielectric constant of the reaction medium enhances the electrostatic forces between the oppositely charged ions and thus facilitates the formation of molecular species [31] which should increase the TpK_a, as borne out in Table 1 for HIPT. This prediction has been amply confirmed for other diketones on the basis of previous similar studies [32–35].

Gurney [36] and others [37] have proposed that the free energy of ionization of acids in solutions at its infinite dilution might be expressed as the sum of an electrostatic term (el.) sensitive to the environment and a non-electrostatic term (non.) insensitive to the environment and independent of temperature.

$$\Delta G_{diss.}^0 = \Delta G_{el.}^0 + \Delta G_{non.}^0 \tag{5}$$

If the electrostatic part is expressed by Born's formula [38], eqn. (5) takes the form

$$\Delta G_{el.}^0 = \frac{Ne^2}{2D}\left(\frac{1}{r+} + \frac{1}{r-}\right)$$

where $r+$ and $r-$ denote the radii of the solvated ions, and D is the dielectric constant of the medium [39,40]. Hence

$$\Delta G_{diss.}^0 = \Delta G_{non.}^0 + \frac{Ne^2}{2D}\left(\frac{1}{r+} + \frac{1}{r-}\right)$$

Further, as $\Delta G_{diss.}^0 = 2.303\, RT\, pK_a$, the equation simplifies as

$$pK_a = \frac{\Delta G_{non.}^0}{2.303\, RT} + \frac{Ne^2}{4.606\, RTD}\left(\frac{1}{r+} + \frac{1}{r-}\right) \tag{6}$$

Conventionally, pK_a is plotted against $1/D$ assuming $\Delta G_{non.}^0$ to be independent of the solvent. Both linear, particularly for water-rich media ($D > 30$) [41–43], and non-linear relationships [44,45] have been reported. When TpK_a values of HIPT are plotted against $1/D$ it is seen that the plots possess distinct curvature (Fig. 1). This shows that non-electrostatic factors exert a considerable influence on the acid dissociation of such organic compounds. As Harned and Owen [46] observed, when the plots are extended over a wide range of dielectric constants such as represented by going from water to 82% dioxane–water, the linearity fails. Such a relationship is improved by taking into account the variation of the concentration of water

in the solution [47]. Here, (HOH) is introduced into the ionization expression for a weak acid in order to obtain a better pK_a-1/D plot. Curvature still occurs at high concentrations of organic solvent.

Likewise, the currently accepted Denison–Ramsay–Fouss Theory [48,49] of ion-pair formation also predicts that $-\log K$ (or pK_a) should be a linear function of $1/D$, with a slope 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 high, but the correlation failed over too wide ranges of solvent composition.

Aksnes [50] 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 the water only in the solvent mixture.

Similar views have been expressed by Ohtaki [51] while conducting a comprehensive study on the contribution of water molecules to ionic reactions in solution through observations of phenomena in mixed aqueous organic solvents. Here water is considered as a reactant in a chemical equation, provided that water molecules participate in the ionic reaction. Water concentration has also been taken into account in the discussions on dissociation of organic acids in aqueous organic mixtures [47,52].

Mean ionic radii (r ±)

To provide an electrostatic interpretation of the medium effect concerning an ionization process, e.g. the ionization of a molecular acid like HIPT studied here, Born's solvation energy eqn. (6) has been simplified by King [45] as

$$\Delta pK_a = pK_{a(s)} - pK_{a(w)} = \frac{Ne^2}{2.303\ RT\ r\pm}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \qquad (7)$$

where $r\pm$, mean ionic radii, is equal to

$$\frac{2}{r\pm} = \frac{1}{r+} + \frac{1}{r-}$$

Values of $r\pm$ have been computed via eqn. (7) at different dioxane percentages and are in the range 1.97–2.38 Å. From the data given in Table 3, it is obvious that the values of $r\pm$ increase slightly with aqueous dioxane concentrations. It is difficult to explain this variation with change in solvent composition. Similar increase in $r\pm$ values has been encountered while studying the acid dissociation of formic, acetic and propionic acids [53,54].

Values of $r\pm$ have also been evaluated graphically from eqn. (6). The

slope of the plot TpK_a vs. $1/D$ (Fig. 1) is equal to $Ne^2/2.303 \, RT \, r\pm$, where all the terms except $r\pm$ are known. The values thus calculated are in the range 2.1–2.2 Å, which seems to be reasonable if the effective size of the substituted tropolonate ion is regarded as being largely determined by the charged $-O^-$ group. Following a similar study, the radius of the propionate ion has been estimated to be around 2.3 Å [55]. Ohtaki [56] has, however, pointed out the limitations of the Born equation for the accurate estimation of the ionic radii. Graphical determination of $r\pm$ may therefore be in some error compared with the previous method, but the values are still within the range.

Mole fraction of dioxane

According to Glover [52], a consideration of the direct participation of the solvent in the acid ionization should lead to a better understanding of the compositions of solvent as well as of ion solvates. For instance, such a participation is quite evident from essentially straight line plots of pK_a vs. n_2 in several examples [57].

For HIPT, the change in TpK_a with n_2 is of considerable magnitude, as is seen from the difference in TpK_a in aqueous medium ($n_2 = 0$) and 50% aqueous dioxane ($n_2 = 0.174$) which is of the order of 2 TpK_a units. When TpK_a values of HIPT 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 10 which is as expected for diketones [33–35].

The goodness of fit was judged by calculating the correlation coefficient, r, defined by

$$r = \Sigma(x-\bar{x})(y-\bar{y})/\left[\Sigma(x-\bar{x})^2 \cdot \Sigma(y-\bar{y})^2\right]^{1/2}$$

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 value of r is $+1.0$ [58]. The value of b, "regression coefficient" or actual slope of the lines, is finally given by

$$b = \Sigma(x-\bar{x})(y-\bar{y})/\Sigma(x-\bar{x})^2$$

Since the value of r is nearly $+1.0$ at 25 and 35°C for HIPT (Table 2), it implies that there is quite a high probability of a linear relationship between TpK_a and n_2. Similar behaviour is found for several other acids such as benzoic, acetic, propionic and formic acids [57] and a number of β-diketones in aqueous dioxane [32,33]. Likewise, linear proportionality is also obtained for some other mixed water solvents, e.g. acetic, propionic, butyric and

benzoic acids in methanol–water mixtures [59] and dimedone in ethanol–water [60].

It is of interest to compare the accuracy of the experimentally determined values of TpK_a of HIPT in aqueous media with the extrapolated values at zero dioxane concentration ($n_2 = 0$). The data given in Table 1 show that there is excellent agreement in two sets of values, proving the validity of the extrapolation method for evaluating TpK_a of sparingly soluble organic ligands in aqueous media.

Evaluation of pK'_a and n

The acid dissociation constant (K'_a) of the acid HA in a mixed medium can be expressed as

$$n\ S + HA \overset{K'_a}{\rightleftharpoons} x\ SH^+ + y\ SA^- \tag{8}$$

where n is the total of x plus y moles of solvent S, aqueous dioxane being the medium in the present study.
Hence

$$\frac{(x\ SH^+)(y\ SA^-)}{(S)^n(HA)} = K'_a \tag{9}$$

where the parentheses denote activity. Equation (9) is usually written as

$$\frac{(H^+)(A^-)}{(HA)} = K'_a(S)^n = K_a{}^* \tag{10}$$

where it is understood that the ions are solvated and $K_a{}^*$ includes the solvent terms $(S)^n$. By taking logarithms of eqn. (10), we get

$$\log K_a{}^* = \log K'_a + n\ \log(S)$$

or

$$pK_a{}^* = pK'_a - n\ \log(S) \tag{11}$$

Since $pK_a{}^*$, defined in eqn. (11), is the thermodynamic constant, pK'_a 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 eqn. (11)

$$n = \left[pK_{a_2}^* - pK_{a_1}^*\right] / \left[\log(S_1) - \log(S_2)\right]$$

Values of n at 25 and 35°C are found to be 5.01 ± 0.10 and 5.30 ± 0.20, 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 mixtures [52]. The pK'_a values listed in Table 4 have been
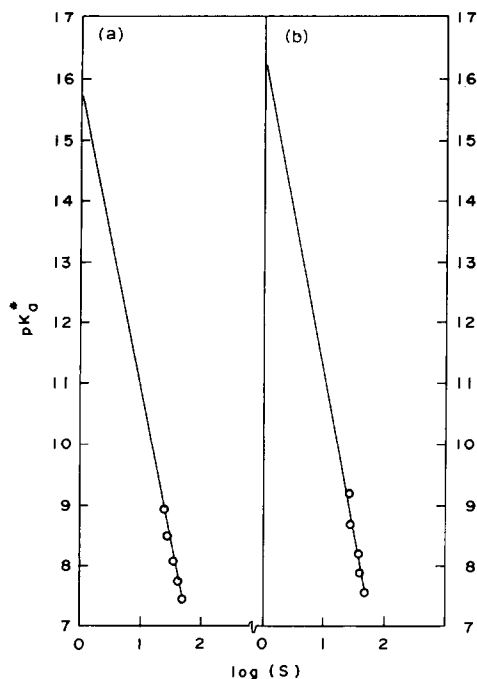
Fig. 3. Plot of pK_a^* vs. log (S). (a) 25°C, $m = 4.92$; (b) 35°C, $m = 5.00$.

computed by eqn. (11), yielding the equations

at 25°C: $pK_a^* = 15.94 \pm 0.05 - 5.01 \pm 0.10 \log(S)$
at 35°C: $pK_a^* = 16.56 \pm 0.06 - 5.30 \pm 0.20 \log(S)$

Values of n and pK_a' have also been obtained from a plot of pK_a^* (or TpK_a) against $\log(S)$ (Fig. 3) and are summarized in Table 4. Graphical values show some deviation from the experimental ones. It is of interest to note that there is excellent agreement between the two sets of values of TpK_a calculated independently via eqns. (4) and (11).

Thermodynamic functions for ionic equilibria

The TpK_a values have been determined with a precision of ± 0.02 to ± 0.03 and hence the error in ΔG^0 is estimated to be between ± 0.03 to ± 0.04 kcal mole^{-1}. The procedure followed here to evaluate ΔH^0 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 the use of a more precise method [61]. However, the negative value of ΔH^0 found in dioxane–water solutions for HIPT indicates that its ionization is accompa-

nied by liberation of heat and the process is exothermic. Further, the change in ΔH^0 with change in medium is relatively small and within experimental error. It is because of this that the slopes of straight lines in the plots of TpK_a vs. n_2 (Fig. 2) are the same at both temperatures (Table 2), and the two lines are parallel.

It is, therefore, justifiable to assume that ΔH^0 is independent of solvent media over the range investigated. On this basis, a fresh value of ΔH^0 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^0 at different percentages of dioxane are found to be practically the same, thereby showing that it is independent of solvent composition. This is in agreement with our earlier observation [34], wherein the large negative 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 the water molecules originally accompanying the undissociated reagent. The experimentally evaluated ΔH^0 and ΔS^0 values for the dissociation of HIPT 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.

When the acid dissociates in two media, the free energy change for the transfer reaction from one medium to the other is given by $2.303\,RT\,\Delta TpK_a$. For example, $\Delta G^0_{aq.}$ and $\Delta G^0_{(n_2 = 0.174)}$ are 9.87 and 12.26 kcal mole^{-1}, respectively, and ΔG^0 changes by 2.39 kcal mole^{-1} in the transfer reaction

$$HA_{(dioxane)} + H^+_{(aq.)} + A^-_{(aq.)} \rightleftharpoons HA_{(aq.)} + H^+_{(dioxane)} + A^-_{(dioxane)}$$

and this results in a change in entropy of 8.01 cal K^{-1} mole^{-1}.

ΔTpK_a (s–w), i.e TpK_a(s) $- TpK_a$(w) (where 's' and 'w' refer to mixed solvents and water, respectively) of HIPT at 25 and 35°C are presented in

TABLE 5

Free energy, enthalpy and entropy changes for ionization of 2-isopropyltropolone

Function [a]	Solvent medium, % (v/v) dioxane					
	0	10	20	30	40	50
ΔG^0 25°C	9.87	10.18	10.55	10.00	11.56	12.26
ΔG^0 35°C	10.41	10.74	11.13	11.62	12.21	12.95
$-\Delta H^0 = 7.99$						
$-\Delta S^0$ 25°C	59.90	60.92	62.18	63.70	65.55	67.91
$-\Delta S^0$ 35°C	59.70	60.79	62.03	61.63	65.53	67.95

[a] ΔG^0 and ΔH^0 in kcal mole^{-1}; ΔS^0 in cal mole^{-1} K^{-1}.

TABLE 6

$\Delta TpK_{a(s-w)} = TpK_{a(s)} - TpK_{a(w)}$

Dioxane (vol.%)	HIPT	
	25°C	35°C
10	0.20	0.21
20	0.46	0.41
30	0.70	0.74
40	1.21	1.16
50	1.68	1.72

Table 6. Temperature changes from 25 to 35°C has an almost negligible effect on $\Delta TpK_{a(s-w)}$ for this compound. Small variations in $TpK_{a(s-w)}$ in the range 0–0.174 mole fraction of dioxane are likely to be due to the hydrogen bonding capability of this tropolone.

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