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THERMODYNAMIC PROTON–LIGAND STABILITY CONSTANTS OF TROPOLONE IN MIXTURES OF WATER AND DIOXANE

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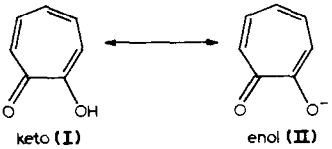
Thermodynamic proton–ligand stability constants, TpK_a, of tropolone have been determined pH-metrically in 0–50 vol.% dioxane–water mixtures at 25 and 35±0.01°C applying an empirical pH correction for mixed aqueous media. Tropolone is a very weak acid with a TpK_a value between 6.9 and 8.8. TpK_a values 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. Values of ΔG^0 and ΔH^0 and ΔS^0 are also computed. Temperature as well as medium effects are briefly discussed.

INTRODUCTION

Numerous analytical applications of tropolone (I) (2-hydroxy-2,4,6-cyclohepta-trienone) and its ring-substituted derivatives have already been reviewed by Singh and co-workers [1]. The versatility of tropolone is well established in the colorimetric determination of Fe(III), Nb(V) and germanium. Furthermore, its application has also been predicted in the separations of thorium and uranium from the rare earths by solvent extraction of the tropolone complexes during the reprocessing of nuclear fuels.



Some outstanding applications of this reagent include the photometric determinations of Ru(III) [2], Rh(III) [3], V(V) [4] and Cr(III) [5]. Besides, tropolone also has numerous medicinal applications [6,7].

Tropolone is a weak monoprotic acid. The proximity of carbonyl and hydroxyl group in this compound permits the formation of stable metal chelates with a host of metal ions [8–15]. Relatively, little data has been reported on the acid dissociation constant of tropolone. Most of the work to date, however, relates to the evaluation of the stoichiometric constant valid for some specific set of conditions [10,12–14]. No value of the thermody-

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namic equilibrium constant for its ionization exists, except in one instance [16]. This led us to study in detail the proton dissociation reactions of this ligand and to arrive at theoretically comparable thermodynamic data.

The thermodynamic acid dissociation constant, TpK_a, of tropolone in aqueous solution and 20, 30, 40 and 50 vol.% dioxane–water mixtures at 25 and 35 ± 0.01°C have been determined pH-metrically and the thermodynamic functions (ΔG^0, ΔH^0, ΔS^0) computed following the standard equations. 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 greater 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 instances.

TpK_a values have been determined by the pH titration method using a glass and saturated calomel electrode in cells with liquid junction potential. The relationship of Van Uitert and Haas [17] was followed to evaluate the hydrogen ion concentration from the values read on the pH meter (B)

$$-\log[\mathrm{H}^+] = B + \log U_{\mathrm{H}}^0 + \log y_\pm \qquad (1)$$

Values of the correction factor, $\log U_{\mathrm{H}}^0$, were obtained experimentally [18] and those of mean activity coefficients ($y_\pm$) were computed by interpolation of the data given by Harned and Owen [19] assuming that the mean activity coefficients are the same on both the molal and molar scales. The acid dissociation of tropolone (HA) in an aqueous medium gives the hydrogen ion (H^+) and tropolonate (A^-). The equilibrium constant is given by eqn. (2) in such a medium.

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

or

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

Assuming that y_{HA}, the mean activity coefficient of the non-ionized acid, is unity, the final form of the equation for computing TpK_a in the dioxane–water mixture is obtained by eqns. (1) and (3).

$$TpK_a = B + \log U_{\mathrm{H}}^0 + \log([\mathrm{HA}]/[\mathrm{A}^-]) + \log 1/y_\pm \qquad (4)$$

Tropolone (Alfa Chemicals, U.S.A.) was used as supplied. All chemicals were of A.R. or G.R. grade (BDH or Merck) unless otherwise stated. An aqueous solution (10%) of tetramethyl-ammonium hydroxide (TMAH) titrant was standardised against potassium hydrogen phthalate and diluted to 0.1 M, the proportions of dioxane and water being the same as those used in preparing the titre solutions. *p*-Dioxane was purified as recommended [20].

The titration procedure for determining the ionization constants was essentially the same as outlined by Albert and Serjeant [21]. Generally, 0.01

TABLE 1

Thermodynamic ionization constants of tropolone

Vol.% dioxane	Mole fraction of dioxane (n_2)	TpK_a at 25°C				TpK_a at 35°C			
		Found [a]	Calc. [b]	Graph	$\times 10^2$ (found − calc.)	Found [a]	Calc. [b]	Graph	$\times 10^2$ (found − calc.)
0	0	6.95	6.90	6.90	+5	7.09	7.05	7.10	+4
20	0.050	7.33	7.37	7.38	−4	7.52	7.54	7.59	−2
30	0.083	7.64	7.68	7.69	−4	7.81	7.86	7.91	−5
40	0.123	8.01	8.05	8.07	−4	8.24	8.26	8.30	−2
50	0.174	8.58	8.53	8.55	+5	8.79	8.76	8.79	+3
Total					22				16
Average					4.4×10^{-2}				3.2×10^{-2}
Deviation					~ 0.04				~ 0.03

[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.

M tropolone 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 pH units. 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 mM of tropolone 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 [22]. 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 units [23]. About 10 min after the settings, the titration was started by adding 0.5-ml aliquots of 0.1 M TMAH and noting the highest stable pH value. Titrations, carried out in duplicate, were reproducible to within ±0.01 pH units.

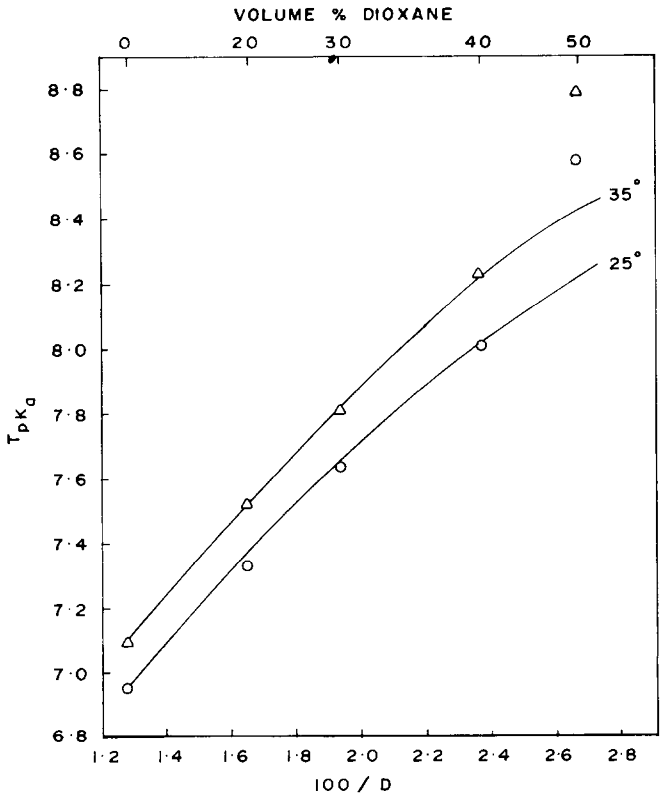

Fig. 1. Variation of TpK_a with the dielectric constant (D) of the medium.

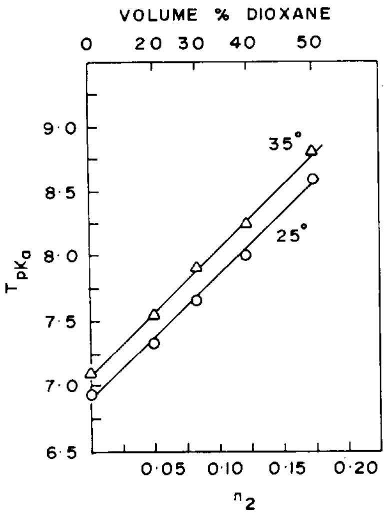

Fig. 2. Variation of TpK_a with n_2 (mole fraction of dioxane).

RESULTS

The TpK_a value of tropolone in aqueous solution and different aqueous–dioxane media at 25 and 35°C are summarised in Table 1. Our TpK_a value in pure aqueous medium (6.95 ± 0.03 at 25°C) is in good agreement with that of James and Speakman [16] who reported a value of 7.00 ± 0.04 at 20°C. These constants invariably increase with increasing temperature in all the above cases. The average TpK_a value usually falls within a range of ± 0.02, but not beyond ± 0.03 in any instance. The titration of perchloric acid in the presence or absence of this ligand proved that its protonation is negligible. 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. TpK_a was plotted against $1/D$ (Fig. 1) and 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

Empirical relationship between TpK_a and n_2 of dioxane for tropolone ($TpK_a = mn_2 + C$) [a]

Graph at 25°C		Least-squares at 25°C				Graph at 35°C		Least-squares at 35°C			
m	*C*	*m*	*C*	*r*	*b*	*m*	*C*	*m*	*C*	*r*	*b*
9.50	6.90	9.37	6.90	1.02	9.28	9.73	7.10	9.80	7.05	1.00	9.72

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

TABLE 3

Free energy, enthalpy and entropy changes for the ionization of tropolone

Function [a]	Solvent medium, vol.% dioxane				
	0	20	30	40	50
ΔG^0, 25°C	9.49	10.01	10.43	10.93	11.71
ΔG^0, 35°C	10.00	10.60	11.01	11.62	12.39
$-\Delta H^0 = 10.52$					
$-\Delta S^0$, 25°C	67.10	68.85	70.25	71.93	74.55
$-\Delta S^0$, 35°C	66.58	68.53	69.86	71.84	74.33

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

(Table 2). Table 3 records the thermodynamic functions (ΔG^0, ΔH^0 and ΔS^0) associated with the proton–ligand dissociation reactions computed by the temperature variation method.

DISCUSSION

The non-benzenoid aromatic molecule, tropolone, is stabilized by resonance and tautomerism, so that the ketonic group (**I**) is masked, and the behaviour is that of the enol form (**II**). IR studies of the OH groups in the enol form of this compound show that the strength of the hydrogen bond is considerably weaker, which has been explained to be due to five atoms in the tropolone chelate ring [10,24]. Electronic interaction between the carbonyl and enol groups in tropolone is facilitated by the planarity of the ring. It is therefore expected that this reagent might show reactions similar to diketones. On the basis of the present study, it is seen that HTTA is a stronger acid than tropolone by about one $Tp K_a$ unit in different media.

Medium effects

Considering the acid dissociation of tropolone involving a net increase of ions

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

a decrease in the dielectric constant of the reaction medium should increase TpK_a, as borne out by Table 1. This prediction has been amply confirmed for other diketones on the basis of previous studies [25–28].

Medium effects and transfer energies for ions have sometimes been considered to consist of a neutral part and an electrostatic term [29–31].

$$\Delta G^0 = \Delta G^0_{neut} + \Delta G^0_{el}$$

If the electrostatic part is expressed by Born's formula [32]

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

where r^+ and r^- denote the radii of the solvated ions and D the dielectric constant of the medium [33,34], it follows that

$$\Delta G^0 = \Delta G^0_{\mathrm{neut}} + \frac{Ne^2}{2D}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)$$

Further, as $\Delta G^0 = 2.303RT\mathrm{p}K_{\mathrm{a}}$, the equation simplifies as

$$\mathrm{p}K_{\mathrm{a}} = \frac{\Delta G^0_{\mathrm{neut}}}{2.303RT} + \frac{Ne^2}{4.606RTD}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)$$

Conventionally, $\mathrm{p}K_{\mathrm{a}}$ is plotted against $1/D$, assuming $\Delta G^0_{\mathrm{neut}}$ to be independent of the solvent. Both types of relationship, viz. linear for water-rich media ($D > 30$) [35,36] and non-linear [37], have been reported. When $T\mathrm{p}K_{\mathrm{a}}$ values of tropolone are plotted against $1/D$, it is seen that the plots possess a 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 [38] 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 [39]. Here, (HOH) is introduced into the ionization expression for a weak acid in order to get a better $\mathrm{p}K_{\mathrm{a}}$–$1/D$ plot. Curvature still occurs at high concentrations of organic solvent.

Lahiri et al. [40] reported a linearity in the plot $\mathrm{p}K_{\mathrm{a}}$ vs. $1/D$ only up to 60 wt% ethanol, beyond which deviation occurred. Deviation at a higher percentage of organic solvents was attributed to the fact that at such percentages, the H^+ values from pH meter reading may be inaccurate due to (i) high liquid junction potential and (ii) low sensitivity of the glass electrode. Contrary to this, deviations were more recently encountered [39] at relatively low concentrations of *t*-butanol as compared to methanal–water, and ethanol–water mixtures.

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 [41]. For example, such a participation is quite evident from essentially straight-line plots of $\mathrm{p}K_{\mathrm{a}}$ vs. n_2 in several cases [42].

For tropolone, the change in $T\mathrm{p}K_{\mathrm{a}}$ with n_2 is particularly high. When its $T\mathrm{p}K_{\mathrm{a}}$ values are plotted against n_2, linear relationships are obtained (Fig. 2). The experimental values of $T\mathrm{p}K_{\mathrm{a}}$ given here indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% in $T\mathrm{p}K_{\mathrm{a}}$. These plots gave slopes equivalent to about 10 which is as expected for diketones [26–28].

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

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

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 available pairs (x, y). Linear proportionality is readily indicated between the two variables when the value of r is 1.0 [43]. The "regression coefficient" or actual slope (b) of the lines, is 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 tropolone (Table 2), quite a high probability of a linear relationship between TpK_a and n_2 is implied. A similar behaviour is found for several other acids, such as benzoic, acetic, propionic and formic acids [42] and a number of β-diketones in aqueous dioxane [25,26]. Likewise, linear proportionality is also obtained for some other mixed aqueous solvents, e.g., acetic, propionic, butyric and benzoic acids in methanol–water mixtures [44] and dimedone in ethanol–water [45].

It is of interest to compare the accuracy of the experimentally determined values of TpK_a of tropolone 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 between the two sets of values, proving the validity of the extrapolation method for evaluating TpK_a values of sparingly soluble organic ligands in aqueous media.

Thermodynamic functions for acid dissociation

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 and ± 0.04 kcal mol^{-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 [46]. However, the negative value of ΔH^0 found in dioxane–water solutions for tropolone indicates that its ionization is accompanied by the liberation of heat and the process is exothermic. Further, the change in ΔH^0 with a change in medium is relatively small and within experimental error. Thus, the slopes of the straight lines in the plots of TpK_a vs. n_2 (Fig. 2) are the same at both the 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 this value is given in Table 3.

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 [27], wherein the large negative entropy value has been explained as arising due to the ionization of the ligand since the sum total of the number of "bound" water molecules is more than that originally accompanying the undissociated reagent. The experimentally evaluated ΔH^0 and ΔS^0 values for the dissociation of tropolone in aqueous dioxane media show that a large decrease in 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 in the ionization constant in dioxane–water mixtures is mainly due to a statistical effect. For any definite explanation, extensive data for mixed solvents would be needed.

It is interesting to note in this connection that ΔG^0 becomes increasingly positive with increasing dioxane content for the ionization process, which could not be necessarily correlated with the change in water structure, i.e., the structure of water is enhanced due to the addition of dioxane or due to the increase in the basicity of the solvents, but the results could be explained in terms of ionic solvations and a consequent change in entropy and enthalpy values. This indicates that the dielectric constant is not the major factor affecting ionization, the main factor being solute–solvent interactions [47,48].

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