Thermochimica Acta, 179 (1991) 301–312
Elsevier Science Publishers B.V., Amsterdam

PROTON–LIGAND IONIZATION EQUILIBRIA OF 2,3-DIMETHYL-1-PHENYLPYRAZOL-5-ONE IN MIXTURES OF WATER AND DIOXANE: A THERMODYNAMIC STUDY

J.P. SHUKLA

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

S.K. ARORA

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

(Received 8 June 1990; in final form 6 August 1990)

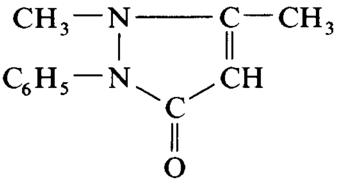
ABSTRACT

Thermodynamic proton–ligand ionization constants, ${}^{T}pK_a$, of 2,3-dimethyl-1-phenylpyrazol-5-one (HDPP) have been determined pH-metrically in 0–40 vol.% dioxane–water mixtures at 25 and 35 ± 0.1°C applying an empirical pH correction for mixed aquo-organic media. Both extrapolation and a least-squares method were used to obtain ${}^{T}pK_a$ values in pure water (0%). HDPP is a very weak monoprotic acid having a ${}^{T}pK_a$ value of between 11.4 and 13.0. ${}^{T}pK_a$'s do not vary linearly with the reciprocal of the dielectric constant of the medium; however, a plot of ${}^{T}pK_a$ versus the mole fraction of dioxane, n_2, is linear at a given temperature. The "true constant", K_a', and solvation number, n, in the expression $(H^+)(A^-)/(HA) = K_a'(S)^n = K_a^\star$ have been evaluated by analysing the experimental data mathematically. Changes in the standard free energy, enthalpy and entropy associated with the proton–ligand ionization of HDPP have also been calculated. Temperature and medium effects are briefly discussed.

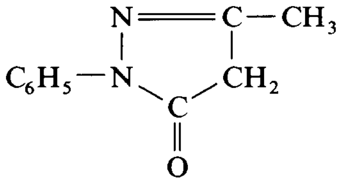
INTRODUCTION

Pyrazolones constitute an interesting class of reagents because of their varied medicinal, analytical and commercial applications; moreover, it has been demonstrated that they are excellent analytical reagents and also powerful drugs [1]. Their varied chemical and physical properties such as high extractive efficiency, quantitative extraction at low pH values, high selectivity and ease of stripping have led to their application in numerous industrial processes. Amongst the pyrazolones, 2,3-dimethyl-1-phenylpyrazol-5-one (HDPP), also commonly known as antipyrine, is an important derivative of pyrazol-5-one being extensively used for many trace organic as well as inorganic analyses [2–6].

0040-6031/91/$03.50



(HDPP)



(HMPP)

HDPP is tautomeric in nature and its most stable state is the ketoform in which most of the reactions occur. A few reactions also occur in the enolic form [7]. Most interestingly, it possesses remarkable versatility as a potential reagent and excels its parent compound, 3-methyl-1-phenylpyrazol-5-one (HMPP), in several respects [8]. For example, HDPP is easy to prepare in a pure state and is commercially available at lower cost. A value for the thermodynamic equilibrium constant of its enolization has not, as yet, been reported [9]. Therefore, the authors have conducted a detailed study of the proton-ionization reactions of this ligand and have derived theoretically comparable thermodynamic data. The thermodynamic functions ($\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$) associated with the ionization of HDPP have been computed following the standard equations. Solvation number values and the true dissociation constants have also been evaluated.

EXPERIMENTAL

HDPP, obtained from Merck, was used as received. 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 [10].

All other chemicals used were of Analar or G.R. grade.

Apparatus

A Beckman Research pH-meter with a glass combination electrode was used for pH measurements to 0.002 pH units. It was standardized with phthalate and borax buffers before and after each titration. A constant temperature was maintained (to an accuracy of ±0.1° C) by circulating water from the thermostat, Colora model K-4661 (F.R.G.), through the annular space of a double-walled titration vessel.

Titration procedure

The titration procedure used for determining ${}^{T}pK_a$ was essentially the same as that outlined by Albert and Serjeant [11]. In general, a 0.01 M reagent solution was titrated without the addition of inert salt. 47.5 ml of the appropriate dioxane–water mixture containing 0.01 M HDPP were introduced into a thermostatted (25.0 or 35.0 ± 0.1° C) titration vessel equipped with a magnetic stirring bar, a glass combination electrode and a microburette of 5.0 ml capacity. This initial volume of titre solution was taken to allow for the change in total volume of solution on titrant addition [12]. For practical purposes, the error caused by volume correction is almost negligible (less than 0.01 pH unit for the central five readings of the titration set, with a maximum error of 0.018 pH unit [13]). The titration was started after 5 minutes by adding 0.2 ml aliquots of 0.1 M TMAH and recording the highest stable pH value. Further titrant additions were made in the same manner. Titrations, conducted in duplicate, were reproducible to within ±0.01 pH unit.

CALCULATIONS

Two methods, namely non-logarithmic (N) and the logarithmic (L), were followed to calculate the ${}^{T}pK_a$ of this ligand.

Non-logarithmic method

The thermodynamic ionization constant, ${}^{T}K_a^{\blacktriangledown}$ of an acid in an aqueous medium can be written

$$ {}^{T}K_a^{\blacktriangledown} = [H^+][A^-]\Gamma^2 \pm /[HA] \qquad (1)$$

where $\Gamma \pm$ is the mean activity coefficient. The activity coefficient of the neutral molecule, HA, is assumed to be unity. Also

$$[HA] = [C_a] - [A^-] \qquad (2)$$

where C_a denotes the total concentration of the acid. Substituting the value of [HA] from eqn. (2) into (1) and rearranging

$$[A^-] = -1/{}^{T}K_a^{\blacktriangledown}([A^-][H^+]\Gamma^2 \pm) + C_a \qquad (3)$$

which is a straight line equation ($y = mx + C$) having slope m and intercept C equal to $-1/{}^{T}K_a^{\blacktriangledown}$ and C_a respectively, $x = ([A^-][H^+]\Gamma^2 \pm)$ and $y = [A^-]$. The least-squares method was used to evaluate the slope and intercept given by the above equation. Values of $[A^-]$ and $[H^+]$ were obtained analytically. The relationship of Van Uitert and Haas [13] was used to evaluate the hydrogen ion concentration from the values read on the pH-meter (B) in an aqueous dioxane medium

$$-\log[H^+] = B + \log U_H^{\ominus} - \log(1/\Gamma \pm) \qquad (4)$$

Values of the correction factor, $\log U_H^{\ominus}$, were obtained experimentally [14] and those of the mean activity coefficients, $\Gamma \pm$, were computed by interpolation of the data given by Harned and Owen [15] assuming that the mean activity coefficients are the same on both molal and molar scales.

Logarithmic method

Values of ${}^{T}pK_a$ in aqueous dioxane were calculated using the equation

$$ {}^{T}pK_a = B + \log U_H^{\ominus} + \log([HA]/[A^-]) + \log(1/\Gamma \pm) \qquad (5)$$

Details relating to the logarithmic method (L) of computation are essentially the same as given elsewhere [16].

The thermodynamic functions ($\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$) associated with the acid ionization were calculated using the following standard equations

$$\Delta G^{\ominus}(25\,^{\circ}C) = 5.71 pK_a(25\,^{\circ}C)(kJ) \qquad (6)$$

$$\Delta G^{\ominus}(35\,^{\circ}C) = 5.90 pK_a(35\,^{\circ}C)(kJ) \qquad (7)$$

$$\Delta H^{\ominus} = 176.06[pK_a(25\,^{\circ}C) - pK_a(35\,^{\circ}C)](kJ) \qquad (8)$$

$$-\Delta S^{\ominus}(25\,^{\circ}C) = 14.04[\Delta G^{\ominus}(25\,^{\circ}C) - \Delta H^{\ominus}](kJ) \qquad (9)$$

$$-\Delta S^{\ominus}(35\,^{\circ}C) = 13.58[\Delta G^{\ominus}(35\,^{\circ}C) - \Delta H^{\ominus}](kJ) \qquad (10)$$

RESULTS AND DISCUSSION

The ${}^{T}pK_a$ values for antipyrine obtained in different dioxane–water mixtures at 25 and 35 °C are summarised in Table 1. These constants decreased slightly with increasing temperature which is expected because the enol content increases with the rise in temperature [17]. Method N is superior to method L as the former does not involve the total concentration term. Furthermore, the accuracy of this method depends on the ability of the

TABLE 1

Thermodynamic proton–ligand ionization constants of HDPP

Vol. % dioxane	Mole fraction of dioxane (n_2)	${}^{T}pK_a$ at 25 °C			${}^{T}pK_a$ at 35 °C		
		Method L [a]	Method N [a]	Graph	Method L [a]	Method N [a]	Graph
0	0	11.44	11.50	11.50	11.36	11.41	11.35
10	0.023	11.71	11.75	11.79	11.48	11.51	11.61
20	0.050	12.13	12.18	12.10	12.03	12.06	11.98
30	0.083	12.45	12.48	12.49	12.38	12.41	12.38
40	0.123	12.99	12.99	12.99	12.87	12.86	12.88

[a] ${}^{T}pK_a$ obtained using at least ten values of a titration set.

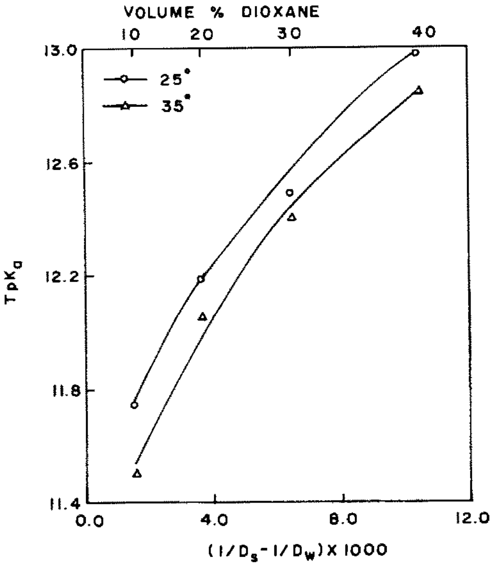


Fig. 1. Variation of ${}^{\mathrm{T}}\mathrm{p}K_a$ with $(1/D_s - 1/D_w)$ of the medium.

pH-meter to read correctly. Hence, the values obtained by the non-logarithmic method have been used for all other detailed calculations and the plots. The ${}^{\mathrm{T}}\mathrm{p}K_a$ values are plotted against $(1/D_s - 1/D_w)$ (D_s = dielectric constant of the solvent, D_w = dielectric constant of water) (Fig. 1) and the mole fraction of dioxane, n_2 (Fig. 2). The empirical relations derived therefrom are given in Table 2. Such relationships between ${}^{\mathrm{T}}\mathrm{p}K_a$ and n_2 were also

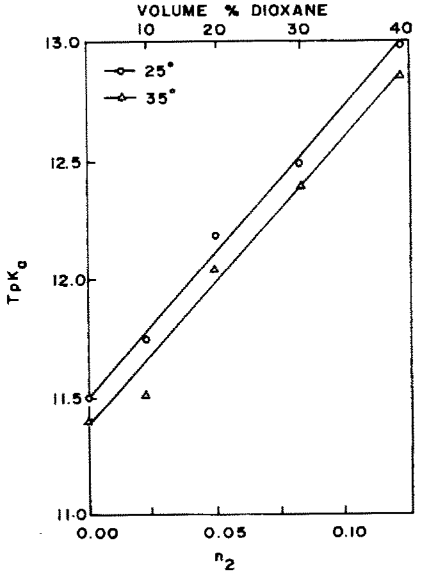


Fig. 2. Variation of ${}^{\mathrm{T}}\mathrm{p}K_a$ with n_2 (mole fraction of dioxane).

TABLE 2

Empirical relation between ${}^{T}pK_a$ and n_2 of dioxane for HDPP

${}^{T}pK_a = mn_2 + C$, at 25 °C				${}^{T}pK_a = mn_2 + C$, at 35 °C			
Graph		Least-squares		Graph		Least-squares	
m	C	m	C	m	C	m	C
12.12	11.50	12.16	11.50	12.39	11.36	11.66	11.41
Correlation coefficient		r	0.997			0.990	
Regression coefficient (Actual slope)		b	12.16			11.66	

calculated by subjecting the ${}^{T}pK_a$ data to least-square analysis (Table 2). Table 3 records the thermodynamic functions $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ computed by the temperature variation method.

Effect of solvent on ionization equilibria

In a mixed hydro-organic solvent, the proton–ligand ionization equilibria may be influenced by different solvent characteristics. These effects can be primarily the result of the dielectric constant of the mixed solvent, the change in the hydrogen bonding of water caused by the presence of an organic solvent and the proton solvation of the organic solvent.

Both Bates et al. [18] and Rorabacher et al. [19] have related the change in ${}^{T}pK_a$ to solvent composition by taking into account both electrostatic and non-electrostatic effects, and concluded that the non-electrostatic phenomenon becomes increasingly important in solvents containing relatively higher concentrations of organic solvent. 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 of

TABLE 3

Free energy, enthalpy and entropy changes for ionization of HDPP

Function [a]	Solvent medium (vol.% dioxane)				
	0	10	20	30	40
$\Delta G^{\ominus}$ (25 °C)	65.68	67.06	69.57	71.29	74.39
$\Delta G^{\ominus}$ (35 °C)	67.35	67.94	71.16	73.21	75.89
$\Delta H^{\ominus} = 23.57$					
$-\Delta S^{\ominus}$ (25 °C)	0.22	0.23	0.24	0.24	0.25
$-\Delta S^{\ominus}$ (35 °C)	0.22	0.22	0.23	0.24	0.25

[a] $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ in kJ mol^{-1}, $\Delta S^{\ominus}$ in kJ K^{-1} mol^{-1}.

the undissociated acid [20] which should increase the ${}^{T}pK_a$, as occurs for HDPP in Table 1.

Gurney [21] and Sagar et al. [22] have proposed that the free energy of ionization of acids in solutions at infinite dilution might be expressed as the sum of the electrostatic term (el.) sensitive to environment and a non-electrostatic term (non.) insensitive to environment and independent of temperature. Thus

$$\Delta G^{\ominus}_{\text{diss.}} = \Delta G^{\ominus}_{\text{el.}} + \Delta G^{\ominus}_{\text{non.}} \tag{11}$$

If the electrostatic part is expressed by Born's formula [23], it follows that

$$\Delta G^{\ominus}_{\text{el.}} = -(Ne^2/2)(1 - 1/D)(1/r^+ + 1/r^-) \tag{12}$$

where r^+ and r^- denote the radii of the solvated ions and D the dielectric constant of the medium. Hence for the simultaneous transfer of the ions from water to an aquo-organic mixed medium, eqn. (11) takes the form

$$\Delta G^{\ominus}_{\text{diss.}} = \Delta G^{\ominus}_{\text{non.}} - (Ne^2/2)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \tag{13}$$

where D_s and D_w are the dielectric constants of the mixed medium and pure water, respectively. Further, as

$$\Delta G^{\ominus}_{\text{diss.}} = 2.303RT\ pK_a \tag{14}$$

the equation simplifies as

$$pK_a = (\Delta G^{\ominus}_{\text{non}}/2.303RT) - (Ne^2/4.606RT)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \tag{15}$$

Conventionally, pK_a is plotted against $1/D$, assuming $\Delta G^{\ominus}_{\text{non.}}$ to be independent of the solvent and terms $(1/r^+ + 1/r^-)$ and $1/D_w$ are constant. Both types of relationships, namely, linear for water-rich media ($D_s > 30$) [24,25] and non-linear [26], have been reported. The plots of ${}^{T}pK_a$ as a function of $(1/D_s - 1/D_w)$ for HDPP do not obey a strict linear relationship; the plots possess distinct curvature (Fig. 1).

Mole fraction of dioxane

Direct participation of the solvent in the proton–ligand ionization should provide a good picture of the composition of the mixed solvent and of the ionic solvates [27]. For example, such a participation is quite evident in several instances from the straight line plot of pK_a vs. n_2 [28].

On altering the mole fraction of dioxane, an appreciable change is seen in the ${}^{T}pK_a$ values for HDPP. Thus on plotting ${}^{T}pK_a$ against n_2, linear relationships are obtained (Fig. 2). The experimental values of ${}^{T}pK_a$ show a maximum deviation from linearity of the order of approximately ± 0.03 in ${}^{T}pK_a$. The fit was judged by calculating the correlation coefficient r [16]. Linear proportionality between the two variables is quite evident from the values of r which are approximately unity (Table 2). A similar behaviour has been found for other mixed solvents, e.g. acetic, propionic, butyric and benzoic acids in methanol–water mixtures [29] and dimedone in ethanol–water [30].

It is of interest to compare the accuracy of the experimentally determined ${}^{T}pK_a$ values of HDPP 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 the two sets of values, proving the validity of the extrapolation method for deriving the ${}^{T}pK_a$ values of sparingly soluble organic compounds in aqueous media.

Evaluation of pK_a *and* n

The acid dissociation constant K_a' of an acid HA in a mixed medium can be expressed as

$$nS + HA \overset{K_a'}{=} xSH^+ + ySA^- \tag{16}$$

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

$$(xSH^+)(ySA^-)/(S)^n(HA) = K_a' \tag{17}$$

where the parentheses denote activity. Equation (17) is usually written as

$$(H^+)(A^-)/(HA) = K_a'(S)^n = K_a^\star \tag{18}$$

where it is understood that the ions are solvated and $K_a^\star$ includes the solvent terms $(S)^n$. By taking logarithms of eqn. (18), we obtain

$$\log K_a^\star = \log K_a' + n \log(S) \tag{19}$$

or

$$pK_a^\star = pK_a' - n \log(S) \tag{20}$$

As $pK_a^\star$, defined in eqn. (20), is the thermodynamic constant, pK_a' thus evaluated should be a true constant independent of the medium, provided that the assumptions for S and n are correct.

Finally, the solvation number, n, can be computed from the following equation derived from eqn. (20)

$$n = [pK_{a2}^\star - pK_{a1}^\star]/[\log(S_1) - \log(S_2)] \tag{21}$$

The pK_a' and n values listed in Table 4 were computed from the least-squares fitting of eqn. (20) and the plot of $pK_a^\star$ (or ${}^{T}pK_a$) against log(S) (Fig. 3). Graphical values show some deviation from the experimental ones. It is of interest to note that there is an excellent agreement between the two sets of values of ${}^{T}pK_a$ calculated independently via eqns. (3) and (20).

TABLE 4

Calculation of the true constant, pK'_a, for HDPP [a]

Vol.% dioxane	$pK_a^\star$ (found)	Log S	pK'_a	$pK_a^\star$ (calc.)	$pK_a^\star$ (graph)
10	11.71	1.694	22.26	11.72	11.72
	11.48	1.693	23.11	11.51	11.52
20	12.13	1.635	22.32	12.08	12.08
	12.03	1.634	23.26	11.92	11.90
30	12.45	1.568	22.22	12.50	12.51
	12.38	1.567	23.15	12.38	12.38
40	12.98	1.490	22.26	12.99	13.00
	12.86	1.488	23.09	12.93	12.93

[a] First and second row values at 25 and 35 °C, respectively. At 25 °C, $n = 6.23$ (calc.); 6.24 (graph); and $pK'_a = 22.27$ (graph). At 35 °C, $n = 6.87$ (calc.); 6.88 (graph); and $pK'_a = 23.17$ (graph).

Thermodynamic functions of ionization

The ${}^{T}pK_a$ values have been determined with a precision of $\pm 0.02 - \pm 0.03$ and hence the error in $\Delta G^{\ominus}$ is estimated to be between ± 2.35 and ± 2.60 kJ mol^{-1}. The procedure followed here to evaluate $\Delta H^{\ominus}$ is subject to some error because the enthalpy change is small and ${}^{T}pK_a$ values were not obtained at several temperatures which would have allowed use of a more

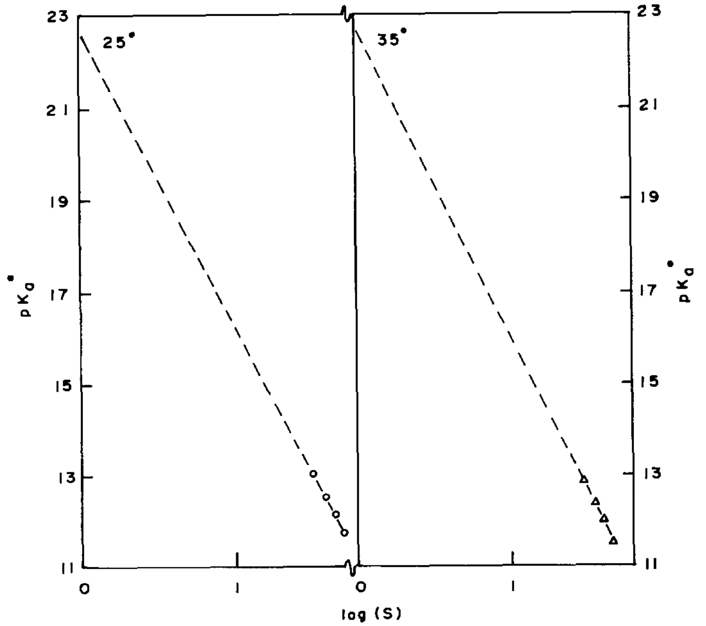


Fig. 3. Plots of ${}^{T}pK_a$ vs. log(S) at 25 and 35 °C.

precise method [31]. However, the positive value of $\Delta H^{\ominus}$ found in dioxane–water solutions for HDPP indicates that its ionization is accompanied by absorption of heat and the process is endothermic. In addition, the change in $\Delta H^{\ominus}$ with change in medium is relatively small and within experimental error. It is because of this that the slopes of the straight lines in the plot of ${}^{T}pK_a$ vs. n_2 (Fig. 2) are approximately the same at both temperatures (Table 2) and the two lines are parallel. It is therefore justifiable to assume that $\Delta H^{\ominus}$ is independent of solvent media over the range investigated. On this basis, a new value of $\Delta H^{\ominus}$ was calculated. Numerically, this is equal to 176.06 times the difference in the intercepts of the parallel lines on the ${}^{T}pK_a$-axis (Fig. 2) and it is this value that is given in Table 3. $\Delta S^{\ominus}$ values at different percentages of dioxane are found to be practically the same, thereby showing that it is independent of solvent composition.

When the acid dissociates in two media, the free energy change for the transfer reaction from one medium to the other is given by $2.303RT\,\Delta^{T}pK_a$. For example, $\Delta G^{\ominus}_{aq.}$ and $\Delta G^{\ominus}_{(n_2=0.123)}$ are 65.68 and 74.39 kJ mol^{-1}, respectively, and $G^{\ominus}$ changes by 8.71 kJ mol^{-1} in the transfer reaction

$$HA_{(dioxane)} + H^{+}_{(aq.)} \rightleftharpoons HA_{(aq.)} + H^{+}_{(dioxane)} + A^{-}_{(dioxane)} \tag{22}$$

and this results in a change in entropy of 23.57 kJ mol^{-1}.

$\Delta^{T}pK_{a(s-w)}$, i.e. ${}^{T}pK_a(s) - {}^{T}pK_a(w)$ (where (s) and (w) refer to mixed solvents and water, respectively) of HDPP at 25 and 35 °C are presented in Table 5. Temperature changes from 25 to 35 °C have an almost negligible effect on $\Delta^{T}pK_{a(s-w)}$ for HDPP. Small variations in ${}^{T}pK_{a(s-w)}$ in the range 0–0.123 mole fraction of dioxane are likely to be due to the hydrogen bonding capacity of this compound.

Effect of substitution on proton–ligand ionization

The acid ionization of substituted pyrazolones depends upon the nature of the substituent group attached to the functional –C=O group. ${}^{T}pK_a$ values of HDPP and its parent compound HMPP determined in several

TABLE 5

$\Delta^{T}pK_{a(s-w)} = {}^{T}pK_{a(s)} - {}^{T}pK_{a(w)}$

Dioxane (vol. %)	HDPP	
	25 °C	35 °C
10	0.27	0.13
20	0.69	0.68
30	1.01	1.02
40	1.55	1.51

dioxane–water mixtures show that $^{T}pK_a$ of the former is several orders of magnitude higher than the latter. For example, values of $^{T}pK_a$ for HDPP and HMPP in pure aqueous medium ($n_2 = 0$) at 25 °C are 11.50 and 7.14, respectively. This is what one would expect, as the introduction of the electropositive methyl group ($-CH_3$) reduces the acidic character of the hydroxyl group. The presence of the electron-repelling $-CH_3$ group in the near vicinity of the ionizable –OH group in HDPP produces the positive inductive effect ($+I$) which is responsible for the increased density of electrons at the ionizable site; this results in a lowering of the dissociation (or increase in $^{T}pK_a$) of this compound as compared with HMPP.

Pyrazolones in solution usually exist as equilibrium mixtures of the keto–enol forms. Therefore, the $^{T}pK_a$ values presented in Table 1 should in principle refer to both the enolization and ionization of the pyrazolones [32].

ACKNOWLEDGEMENTS

The authors wish to express their sincere thanks to Dr. P.R. Natarajan, Head, Radiochemistry Division and to Shri S. Sen, Director, Chemical Engineering Group for their keen interest in this work.

REFERENCES

1 R.H. Wiley and P. Wiley, Pyrazolones, Pyrazolidones and Derivatives, New York, 1964.
2 M. Qureshi, S.Z. Qureshi and N. Zehra, Mikrochim. Acta, (1970) 831.
3 K.G. Weiss and D.F. Boltz, Anal. Chim. Acta, 55 (1971) 77.
4 V.V. Akimov and A.I. Busev, Zh. Anal. Khim., 26 (1971) 134.
5 Z. Holzbecher, L. Divis, M. Kral, L. Sucha and F. Vlacil, Handbook of Organic Reagents in Inorganic Analysis, Ellis Horwood, Chichester, 1976, pp. 484, 608.
6 A. Ahmad, F.I. Nwabue and G.E. Ezeife, Talanta, 31 (1984) 265.
7 F.D. Snell, Colorimetric Methods of Analysis, Van Nostrand, Princeton, 1967, p. 50.
8 F.J. Welcher, Organic Analytical Reagents, Vol. 3, D. Van Nostrand, New York, 1955.
9 D.D. Perrin, Stability Constants of Metal–Ion Complexes, Part B, Organic Ligands, Pergamon, Oxford, 1979, p. 848.
10 A. Weissberger and E.S. Proskauer, Organic Solvents, Vol. 7, Interscience, New York, 1955, p. 139.
11 A. Albert and E.P. Serjeant, The Determination of Ionization Constants: A Laboratory Manual, Chapman and Hall, London, 3rd edn., 1984, p. 14, 26.
12 A. Albert and E.P. Serjeant, Ionization Constant of Acids and Bases, Methuen, London, 1962, pp. 98–99.
13 L.G. van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
14 J.P. Shukla and S.G. Tandan, J. Electroanal. Chem., 35 (1972) 423.
15 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 3rd edn., 1967, p. 716.
16 J.P. Shukla and R.S. Sharma, Electrochim. Acta, 31 (1986) 1449.
17 D.W. Thomson and A.L. Alfred, J. Phys. Chem., 75 (1971) 433.

18 R.G. Bates, M. Pabbo and R.A. Robinson, J. Phys. Chem., 70 (1966) 247.
19 D.B. Rorabacher, W.J. Meckeller, F.R. Shu and M. Bonavita, Anal. Chem., 43 (1971) 561.
20 M. Guilio, Electrochemistry, Principles, Practice and Applications, Elsevier, Amsterdam, 1963, p. 80.
21 R.W. Gurney, J. Chem. Phys., 6 (1938) 499.
22 E.E. Sagar, R.A. Robinson and R.G. Bates, J. Res. Natl. Bur. Stand., Sect. A, 68 (1964) 305.
23 M.Z. Born, Z. Phys., 1 (1920) 45.
24 R.G. Bates, in B. Pesce (Ed.), Electrolytes, Pergamon Press, London, 1962, p. 196.
25 T. Shedlovsky, in B. Pesce (Ed.), Electrolytes, Pergamon Press, London, 1962, p. 146.
26 E.J. King, Acid–Base Equilibria, Pergamon, Oxford, 1965, p. 256.
27 P.J. Glover, J. Am. Chem. Soc., 87 (1965) 5275.
28 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 3rd edn., 1967, p. 756.
29 R.A. Robinson and R.H. Stokes, Electrolytic Solutions, Butterworths, London, 1955, Table 7, p. 541.
30 R.G. Bates and G. Schwarzenbach, Helv. Chim. Acta, 38 (1955) 699.
31 J. Lewis and R.G. Wilkins, Modern Coordination Chemistry, Interscience, New York, 1960, p. 18.
32 G. Schwarzenbach and K. Lutz, Helv. Chim. Acta, 23 (1940) 1147.