

# PROTOLYTIC EQUILIBRIA OF SEVERAL 4-ACYL-SUBSTITUTED 1-PHENYL-3-METHYLPYRAZOL-5-ONES IN DIOXANE-WATER MIXTURES

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Thermodynamic proton ionization constants,  ${}^T pK_a$ , of several 4-acyl-substituted pyrazol-5-ones [acyl = trifluoroacetyl (HPMTFP), acetyl (HPMAP), hexanoyl (HPMHP)] were determined in various dioxane-water mixtures at 25 and  $35 \pm 0.1^\circ\text{C}$ . The  ${}^T pK_a$  values were determined by glass-electrode potentiometry and refined by using the extensive weighted least-squares FORTRAN program TPKA. Both extrapolation and least-squares methods were used to obtain  ${}^T pK_a$  values in pure water (0%). All three acyl derivatives are weak monoprotic acids with  ${}^T pK_a$  values between 2.5 and 3.9, following the order  $\text{HPMTFP} < \text{HPMAP} \leq \text{HPMHP}$ . The  ${}^T pK_a$  values 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. Values of standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes associated with their protolytic equilibria were also calculated. Temperature, medium and substituent effects are briefly discussed.

## INTRODUCTION

4-Substituted pyrazol-5-ones usually exhibit weak acidic properties and readily form stable cyclic metal chelates with a host of metal cations, which have conveniently formed the basis of the development of efficient methods for their extraction and determination. Of them, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) has drawn the maximum attention owing to its cheapness, easy storage and ability to extract many 'hard' metal ions at relatively low pH.<sup>1-4</sup> Most interestingly, a series of 4-acyl-substituted 1-phenyl-3-methylpyrazol-5-ones have also been synthesized by acylation of 1-phenyl-3-methylpyrazol-5-one (HMPP) and are generally characterized by good chemical stability, high proton displacement constant and reasonable solubility in common organic solvents.

Such novel pyrazolones are now established as powerful potential extractants, particularly for class 'a' metal ions such as lanthanides, actinides and alkaline earth metals.<sup>5-8</sup> Sasaki and Freiser<sup>9</sup> studied extensively the extraction of rare earths by pyrazolones having decanoyl or substituted benzoyl (in the 4-position) groups. Recently, Chun Hui and Freiser<sup>10</sup> extended the use of halogen-substituted 4-acylpyrazolones for the

uptake of lanthanides and suggested that future work with this family of reagents should focus on other acyl substitutions. Among them, 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one (HPMTFP) is of particular interest since it has a low  $pK_a$  value and extracts trivalent metal ions from acidic solutions more efficiently than HPMBP. In contrast to numerous analytical studies, there are relatively few data on their acid ionization constants and related thermodynamic parameters. Most of the effort has been confined to the evaluation of their stoichiometric acidity constants valid for some specific set of conditions.<sup>11-12</sup> No value for the thermodynamic equilibrium constant for their ionization exists, except in one instance.<sup>13</sup> This prompted us to study in detail the proton enolization reactions of 4-acylpyrazol-5-ones and to obtain theoretically comparable thermodynamic data. Differently substituted acyl derivatives were chosen because they can be compared with the widely used pyrazol-5-one HPMBP, so that the influence of acyl substituents could be established.

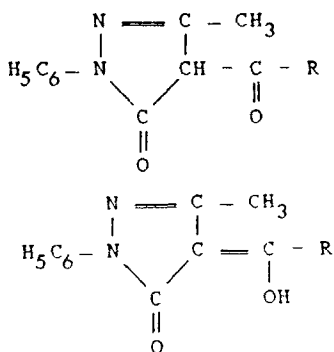
Data on thermodynamic proton ionization constants,  ${}^T pK_a$ , of acyl pyrazolones would be of great interest in various analytical procedures and also in the elucidation of the structure of the resulting metal complexes. In addition, a precise knowledge of the  $pK_a$  value of an extractant is of intrinsic importance in devising separative and analytical techniques because this prop-

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erty reveals the proportions of the different ionic species into which a substance is divided at any chosen pH. Moreover, these values are also needed for evaluating the complexing ability of pyrazolones with metals.

Values of  $^1pK_a$  for 4-acyl-substituted pyrazol-5-ones, namely 1-phenyl-3-methyl-4-acetylpyrazol-5-one (R = acetyl; HPMAP), 1-phenyl-3-methyl-4-hexanoyl pyrazol-5-one (R = hexanoyl; HPMHP) and HPMTFP (R = trifluoroacetyl) represented by the general formula have been determined pH-metrically in 10–70% (v/v) dioxane–water mixtures at  $25$  and  $35 \pm 0.1^\circ\text{C}$  and the changes in the standard thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) associated with their protolytic equilibria were calculated following the usual temperature coefficient method.



The 4-acylpyrazol-5-ones studied here are sparingly soluble in water, hence the use of dioxane–water media for their determinations. Further, the determination of  $^1pK_a$  values in binary mixed solvents provides useful data for the theoretical understanding of the ionization process in systems where two dipoles, i.e. water and dioxane in addition to the anion, can compete for the

proton. Water–dioxane is an excellent solvent system because it provides a wide range of dielectric constants, from 78 for pure water to 2.2 for pure dioxane, and consists of a polar hydrogen-bonding component.

## EXPERIMENTAL

**Apparatus.** A Beckman Research pH meter, equipped with a glass combination pH electrode (Orion 91-02), was used for all pH measurements. It was standardized with phthalate and borax buffers and is accurate to  $\pm 0.002$  pH unit. A Colara (Germany) model K-4661 water circulation thermostat was used and a constant temperature was maintained (to an accuracy of  $\pm 0.1^\circ\text{C}$ ) by circulating water through the annular space of a double-walled titration vessel.

**Reagents.** All the 4-acyl derivatives of 1-phenyl-3-methylpyrazol-5-one (HMPP), namely, HPMTFP, HPMAP, HPMHP and HPMBP, were synthesized according to a modified Jensen's method as described by Okafor<sup>14a</sup> from HMPP and the corresponding acid chloride. The compounds were recrystallized from *n*-hexane. Analytical data, colour and melting points of the reagents prepared are given in Table 1. *p*-Dioxane was purified as recommended.<sup>15</sup> An aqueous solution (10%) of tetramethylammonium hydroxide (TMAH) titrant (general-reagent grade) obtained from Merck (Germany) 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. All other chemicals were of analytical- or general-reagent grade.

**Ionization constants.** The titration procedure for determining the  $^1pK_a$  values was essentially the same as outlined by Albert and Serjeant.<sup>16</sup> Generally, a 0.01 M

Table 1. Physical and analytical data for 4-acylpyrazol-5-ones

Compound	Colour	Melting or decomposition temperature ( $^\circ\text{C}$ )	Elemental analysis (%)					
			Calculated			Found		
			C	H	N	C	H	N
C <sub>12</sub> H <sub>9</sub> O <sub>2</sub> N <sub>2</sub> F <sub>3</sub> (HPMTFP) (F.W. = 270.3)	Cream	144 145–146 <sup>a</sup>	53.3	3.4	10.3	52.9	3.7	10.3
C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> (HPMAP) (F.W. = 216.2)	Yellow	65–66 67 <sup>b</sup>	66.8	5.6	13.0	66.6	5.6	12.9
C <sub>16</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub> (HPMHP) (F.W. = 272.3)	Pinkish Cream	75 76 <sup>c</sup>	70.6	7.4	10.3	70.5	7.5	10.3

<sup>a</sup> Ref. 10.

<sup>b</sup> Ref. 14a.

<sup>c</sup> Ref. 14b.

solution of pyrazolones was titrated without the addition of inert salt. Into a thermostated ( $25$  or  $35 \pm 0.1^\circ\text{C}$ ) titration vessel equipped with a magnetic stirring bar, a glass combination electrode and a microburette of  $5.0\text{-ml}$  capacity,  $0.5\text{ mM}$  of a pyrazol-5-one in the appropriate dioxane–water mixture was taken and the contents were stirred magnetically. The initial volume of the titre solution was  $47.5\text{ ml}$  in all cases to allow for the change in the total volume of the solution on the addition of titrant.<sup>17</sup> After  $10\text{ min.}$ , titration was initiated by adding  $0.2\text{-ml}$  aliquots of  $0.1\text{ M}$  TMAH and noting the highest stable pH. Titrations were performed at least in duplicate and the values were reproducible to within  $\pm 0.01\text{ pH}$  unit.

### CALCULATIONS

Two methods, non-logarithmic (N) and logarithmic (L), were followed to calculate the  ${}^T\text{p}K_a$  values of the reagents. The extensive weighted least-squares FORTRAN program TPKA was coded on a Norsk Data computer for calculations.

#### Method N

The ionization constant of an acid in an aqueous medium can be written as

$${}^T K_{a(\text{aq})} = [\text{H}^+] [\text{A}^-] \Gamma_{\pm}^2 / [\text{HA}] \quad (1)$$

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

$$[\text{HA}] = [C_a] - [\text{A}^-] \quad (2)$$

where  $C_a$  denotes the total concentration of the acid. Substituting the value of  $[\text{HA}]$  from equation (2) into equation (1) and rearranging,

$$[\text{A}^-] = -1/{}^T K_{a(\text{aq})} ([\text{A}^-] [\text{H}^+] \Gamma_{\pm}^2) + C_a \quad (3)$$

which is a straight-line equation ( $y = mx + c$ ) having slope  $m$  and intercept  $c$  equal to  $-1/{}^T K_{a(\text{aq})}$  and  $C_a$ , respectively, where  $x = ([\text{A}^-] [\text{H}^+] \Gamma_{\pm}^2)$  and  $y = [\text{A}^-]$ . The quantities  $[\text{HA}]$ ,  $[\text{H}^+]$  and  $[\text{A}^-]$  were calculated at each point in a titration. Details of the calculations have been published previously.<sup>18</sup>

The relationship of Van Uiter and Haas<sup>19</sup> was used to evaluate the hydrogen ion concentration from the values read on the pH meter ( $B$ ) in aqueous dioxane medium:

$$-\log[\text{H}^+] = B + \log U_{\text{H}}^0 - \log(1/\Gamma_{\pm})$$

Values of the correction factor,  $\log U_{\text{H}}^0$ , were obtained experimentally<sup>20</sup> and those of the mean activity coefficient,  $\Gamma_{\pm}$ , were computed by interpolation of the data given by Harned and Owen<sup>21</sup> assuming that the mean activity coefficients are the same on both molal and molar scales. Values of dielectric constants for different

dioxane–water mixtures were taken from the literature.<sup>22</sup>

#### Method L

The following equation is used to determine  ${}^T\text{p}K_a$  in aqueous dioxane:

$${}^T\text{p}K_a = B + \log U_{\text{H}}^0 + \log([\text{HA}]/[\text{A}^-]) + \log(1/\Gamma_{\pm})$$

Details of this method are given elsewhere.<sup>23</sup>

The thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) associated with the acid ionization were calculated employing the following standard equations:

$$\Delta G^\circ (25^\circ\text{C}) = 5.71 {}^T\text{p}K_a (25^\circ\text{C}) \text{ (kJ)} \quad (4)$$

$$\Delta G^\circ (35^\circ\text{C}) = 5.90 {}^T\text{p}K_a (35^\circ\text{C}) \text{ (kJ)} \quad (5)$$

$$\Delta H^\circ = 176.06 [{}^T\text{p}K_a (25^\circ\text{C}) - {}^T\text{p}K_a (35^\circ\text{C})] \text{ (kJ)} \quad (6)$$

$$-T\Delta S^\circ (25^\circ\text{C}) = [\Delta G^\circ (25^\circ\text{C}) - \Delta H^\circ] \text{ (kJ)} \quad (7)$$

$$-T\Delta S^\circ (35^\circ\text{C}) = [\Delta G^\circ (35^\circ\text{C}) - \Delta H^\circ] \text{ (kJ)} \quad (8)$$

### RESULTS AND DISCUSSION

Values of  ${}^T\text{p}K_a$  for HPMTFP, HPMAP and HPMHP in various dioxane–water mixtures at  $25$  and  $35^\circ\text{C}$  are summarized in Table 2.  ${}^T\text{p}K_a$  values for HPMBP, reported previously,<sup>13</sup> are also listed for comparison. Values obtained by method N were used for all other calculations and plots, since it is superior to method L as the former does not involve the total concentration term. Further, the accuracy of this method depends on the ability of the pH meter to read correctly. The  ${}^T\text{p}K_a$  values of HPMAP and HPMHP increased slightly with increase in temperature whereas for HPMTFP it decreased slightly with increase in temperature.

Figures 1 and 2 depict the plots of  ${}^T\text{p}K_a$  values against  $1/D_s - 1/D_w$  (where  $D_s$  is the dielectric constant of the solvent and  $D_w$  that of water) and the mole fraction of dioxane ( $n_2$ ), respectively. Empirical relationships derived from the latter are given in Table 3. Such relationships were also calculated by least-squares treatment of  ${}^T\text{p}K_a$  and  $n_2$  data (Table 3). Table 4 summarizes the thermodynamic functions calculated by the temperature variation method.

#### Medium effects

Considerable attention has been paid to the ionization behaviour of acids and bases in mixed media consisting of water and a dipolar protophilic organic solvent such as dioxane. This has led to the elucidation of the complex nature of the solute–solvent and solvent–solvent interactions in media containing two types of solvent species. Acid strength and hence  ${}^T\text{p}K_a$  values of proton acids are influenced by the intrinsic basicity of the solvent. The protolytic equilibrium

Table 2. Thermodynamic proton ionization constants,  $\log K_a$ , of 4-acylpyrazol-5-ones.<sup>a</sup>

Ligand	Temperature (°C)	Solvent medium [% (v/v) dioxane]										
		10 ( $n_2 = 0.023$ )	20 ( $n_2 = 0.050$ )	30 ( $n_2 = 0.083$ )	40 ( $n_2 = 0.123$ )	45 ( $n_2 = 0.147$ )	50 ( $n_2 = 0.174$ )	60 ( $n_2 = 0.240$ )	70 ( $n_2 = 0.330$ )			
HPMTFP	25	Ins.	Ins.	2.83 ±0.01	3.02 ±0.01	ND	3.24 ±0.01	3.54 ±0.01	ND	ND	ND	
		Ins.	Ins.	2.87 ±0.04	3.06 ±0.04	ND	3.25 ±0.01	3.59 ±0.05	ND	ND	ND	
		Ins.	Ins.	2.79 ±0.01	2.95 ±0.01	ND	3.14 ±0.01	3.43 ±0.01	ND	ND	ND	
HPMAP	25	Ins.	Ins.	2.83 ±0.04	3.00 ±0.05	ND	3.20 ±0.06	3.48 ±0.05	ND	ND	ND	
		3.94 ±0.01	4.01 ±0.03	4.19 ±0.01	4.37 ±0.01	ND	4.63 ±0.01	ND	ND	ND	ND	
		4.00 ±0.06	4.06 ±0.05	4.22 ±0.03	4.41 ±0.04	ND	4.68 ±0.05	ND	ND	ND	ND	
HPMHP	35	3.96 ±0.02	4.06 ±0.02	4.22 ±0.03	4.49 ±0.03	ND	4.72 ±0.01	ND	ND	ND	ND	
		4.00 ±0.04	4.10 ±0.04	4.25 ±0.03	4.54 ±0.05	ND	4.78 ±0.04	ND	ND	ND	ND	
		Ins.	Ins.	Ins.	Ins.	4.87 ±0.01	5.05 ±0.01	5.56 ±0.01	6.22 ±0.01	6.25 ±0.03	6.25 ±0.01	
HPMBP <sup>b</sup>	25	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	4.73 ±0.03	5.15 ±0.05	5.82 ±0.05	6.82 ±0.04
		Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	5.14 ±0.06	5.46 ±0.01	6.10 ±0.05	7.12 ±0.03
		Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.

<sup>a</sup> Obtained by using at least ten values of a titration set. Lower sets of values evaluated using method L. ND, Not determined; Ins., insoluble.<sup>b</sup> Data from Ref. 13.

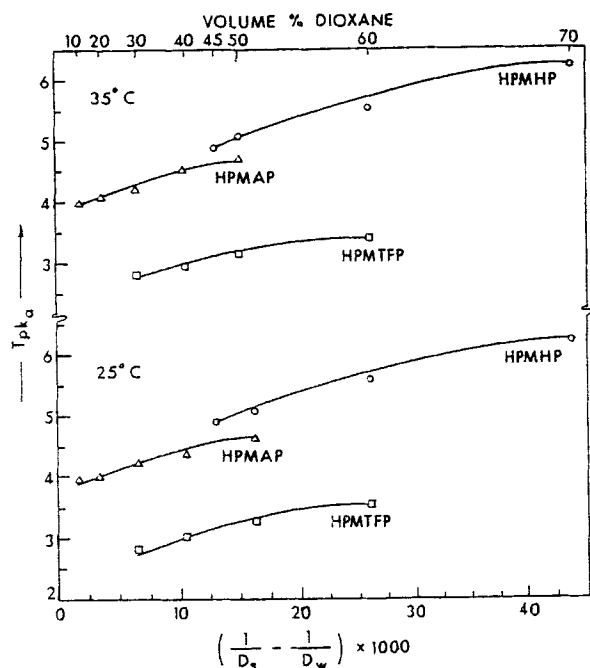


Figure 1. Variation of  $TpK_a$  with the dielectric constant of the medium

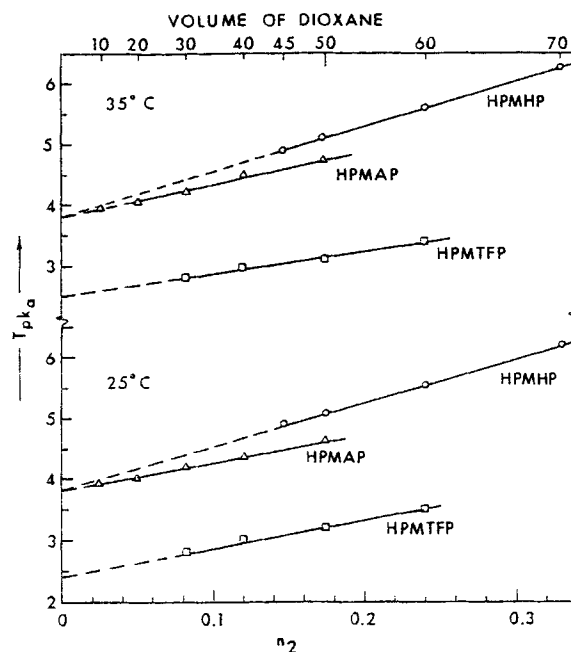
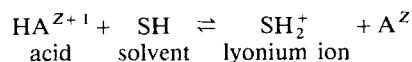


Figure 2. Variation of  $TpK_a$  with  $n_2$  (mole fraction of dioxane)

of pyrazolones is an ionogenic reaction and, therefore, the changes in  $TpK_a$  with dioxane should be accounted for by the electrostatic and specific solvation effects. Considering their acid ionization, represented by



it is seen that the acid ionization depends on the basicity of the solvent. In other words, the effective strength of an acid is greater the higher is the proton affinity of the

medium. However, the ionization of the acid depends not only on the basicity of the solvent, but also on its dielectric constant and its ion-solvating ability. An increase in the organic content of the solvent system results in a decrease in the dielectric constant of the medium. This will increase the electrostatic (ion-ion) interaction between a proton and a negatively charged oxygen atom to a greater extent than the ion-dipole interaction between the proton and the solvent. Thus, as the dielectric constant decreases, the  $pK_a$  increases

Table 3. Empirical relationship between  $TpK_a$  and mole fraction of dioxane ( $n_2$ ) for 4-acylpyrazol-5-ones

Ligand	Temperature (°C)	Graphical: $TpK_a = mn_2 + c$		Least-squares: $TpK_a = mn_2 + c$		$r^a$
		$m$	$c$	$m$	$c$	
HPMTFP	25	4.44	2.48	4.59	2.45	0.999
	35	3.93	2.48	4.03	2.45	0.998
HPMAP	25	4.45	3.83	4.44	3.83	0.999
	35	5.20	3.82	4.95	3.84	0.998
HPMHP	25	7.42	3.77	7.23	3.81	0.998
	35	7.37	3.83	7.57	3.79	0.998
HPMBP	25	9.29	3.60	10.06	3.46	0.998
	35	9.38	3.85	10.41	3.65	0.998

<sup>a</sup> Correlation coefficient.

Table 4. Standard free energy, enthalpy and entropy changes for acid ionization of 4-acylpyrazol-5-ones<sup>a</sup>

Compound	Thermodynamic function <sup>b</sup>	Solvent medium [% (v/v) dioxane]							
		10	20	30	40	45	50	60	70
HPMTPF	$\Delta G^\circ$ (25 °C)	Ins.	Ins.	16.18	17.27	ND	18.53	20.25	ND
	$\Delta G^\circ$ (35 °C)	Ins.	Ins.	16.47	17.44	ND	18.57	20.25	ND
	$\Delta H^\circ$	Ins.	Ins.	7.04	12.32	ND	17.61	19.37	ND
	$-T\Delta S^\circ$ (25 °C)	Ins.	Ins.	9.14	4.95	ND	0.92	0.88	ND
	$-T\Delta S^\circ$ (35 °C)	Ins.	Ins.	9.43	5.12	ND	0.96	0.88	ND
HPMAP	$\Delta G^\circ$ (25 °C)	22.55	22.93	23.98	24.98	ND	26.49	ND	ND
	$\Delta G^\circ$ (35 °C)	23.39	23.98	24.94	26.49	ND	27.88	ND	ND
	$-\Delta H^\circ$	3.52	8.80	5.28	21.13	ND	15.85	ND	ND
	$-T\Delta S^\circ$ (25 °C)	26.07	31.73	29.26	46.11	ND	42.34	ND	ND
	$-T\Delta S^\circ$ (35 °C)	26.91	32.78	30.22	47.62	ND	43.73	ND	ND
HPMHP	$\Delta G^\circ$ (25 °C)	Ins.	Ins.	Ins.	Ins.	27.83	28.88	31.78	35.55
	$\Delta G^\circ$ (35 °C)	Ins.	Ins.	Ins.	Ins.	28.97	30.26	33.20	36.93
	$-\Delta H^\circ$	Ins.	Ins.	Ins.	Ins.	5.28	12.32	10.56	5.28
	$-T\Delta S^\circ$ (25 °C)	Ins.	Ins.	Ins.	Ins.	33.11	41.20	42.34	40.83
	$-T\Delta S^\circ$ (25 °C)	Ins.	Ins.	Ins.	Ins.	34.25	42.58	43.76	42.21

<sup>a</sup>ND, Not determined; Ins., insoluble.<sup>b</sup> $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  in kJ mol<sup>-1</sup>.

for proton–ligand systems, as borne out in Table 2 for all 4-acylpyrazol-5-ones. This prediction has been amply confirmed for two analogous 4-acylpyrazol-5-ones, namely, HPMBP and HMPP, on the basis of a previous similar study.<sup>13</sup>

The variation in  ${}^1pK_a$  [ $\Delta {}^1pK_a = {}^1pK_{a(w)} - {}^1pK_{a(s)}$ ] with the dielectric constant of the medium can be simply represented by the Born equation:<sup>24</sup>

$$\Delta {}^1pK_a = (-N_A e^2 / 2RT)(1/r_{H_2^+} + Z_A^2/r_A - Z_{HA}^2/r_{HA}) \times (1/D_s - 1/D_w)$$

where  $D_s$  and  $D_w$  are the dielectric constants of the mixed medium and pure water, respectively, and  $r_A$  and  $r_{HA}$  denote the radii of the ionized and unionized acid respectively. Conventionally,  ${}^1pK_a$  values are plotted against  $1/D_s - 1/D_w$ . Both types of relationship, the linear for water-rich media ( $D_s > 30$ )<sup>25,26</sup> and the non-linear,<sup>27</sup> have been reported. When  ${}^1pK_a$  values of HPMTPF, HPMAP and HPMHP are plotted versus  $1/D_s - 1/D_w$ , it is seen that the plots possess a distinct curvature (Figure 1). This suggests that the change in  ${}^1pK_a$  with the proportion of dioxane, although mainly governed by the dielectric constant, are also influenced by solvent basicity and by the solvation of the solute by organic solvent molecules.

For all 4-acylpyrazol-5-ones, the change in  ${}^1pK_a$  with  $n_2$  is of a considerable magnitude, as is seen from the difference in the  ${}^1pK_a$  values in aqueous medium ( $n_2 = 0$ ) and 70% aqueous dioxane ( $n_2 = 0.330$ ), which is of the order of 2–3  ${}^1pK_a$  units. When the  ${}^1pK_a$  values of these ligands are plotted against  $n_2$ , linear relationships are obtained (Figure 2). The experimental values of  ${}^1pK_a$  here indicate a maximum deviation from

linearity of the order of 0.05 or about 0.5% in  ${}^1pK_a$ . These plots gave slopes in the range 4–7. Similar behaviour is observed in other mixed solvents, such as acetic, propionic, butyric and benzoic acid in aqueous methanol<sup>28</sup> and  $\beta$ -diketones in aqueous dioxane mixtures.<sup>29</sup>

#### Thermodynamic functions for protolytic equilibria

The  ${}^1pK_a$  values were determined with a precision of  $\pm 0.02$ – $0.03$  and hence the error in  $\Delta G^\circ$  is estimated to be between  $\pm 0.13$  and  $\pm 0.17$  kJ mol<sup>-1</sup>. The method used to evaluate  $\Delta H^\circ$  is subject to some error as the enthalpy change is small and  ${}^1pK_a$  values were not obtained at several temperatures, which would have allowed the use of a more precise method.<sup>30</sup> Nevertheless, the negative values of  $\Delta H^\circ$  found in dioxane–water solutions for HPMAP and HPMHP indicate that their ionization is accompanied by the liberation of heat and the process is exothermic. In contrast, the ionization of HPMTPF is found to be an endothermic process at least up to 35 °C in dioxane–water mixtures.

The slightly decreasing trend in  $T\Delta S^\circ$  with increasing dioxane content evidently indicates that the ionization of these pyrazol-5-ones is primarily an entropy-controlled process. Since the ionization diminished, the entropy of the system also decreased; the same is favoured in solvents with higher dielectric constants, i.e. lower values of  $n_2$ . The fairly large negative values of  $T\Delta S^\circ$  encountered here can be explained as being due to ionization of the ligands, since the sum total of the ‘bound’ water molecules is more than the total number of molecules originally accompanying the non-ionized reagent. These facts are thus in accord with

the assumption that the decrease in ionization in the dioxane-water mixtures is mainly due to a statistical effect. For a more definite explanation, extensive data in mixed solutions would be needed.

It is interesting that  $\Delta G^\circ$  becomes increasingly positive with increasing amounts of dioxane, indicating that the transfer of these ligands from water to the hydro-organic media is not spontaneous. This also shows that the dielectric constant is not the only factor affecting the ionization, the main factor being solute-solvent interactions.<sup>31,32</sup>

### Substituent effects

A comparison of the  ${}^T pK_a$  values (Table 2) shows clearly the marked effect of acyl substitution on the acidity of the 4-substituted pyrazol-5-ones. The influence of substituents with HPMBP as a standard reagent was compared. Their  ${}^T pK_a$  values decrease in the expected order, HPMTFP < HPMAP  $\leq$  HPMHP, at least in pure aqueous medium ( $n_2 = 0$ ).

Qualitatively, factors that modify  $pK_a$  values mainly include inductive, electrostatic and electron delocalization (mesomeric effects), together with contributions from hydrogen bonding, conformational differences and steric factors. Comparison of the  ${}^T pK_a$  value of a 4-acylpyrazol-5-one (HPMBP) with that of two unfluorinated 4-alkanoyl-substituted pyrazol-5-ones (HPMAP and HPMHP) revealed that both the acyl substituents tend to stabilize an ionic species more than the corresponding neutral molecule, or a neutral molecule than the anion derived from it, and the  ${}^T pK_a$  value of the resulting acids is raised as expected from theoretical considerations. Hence both these 4-acyl substitutions prove to be acid-weakening or base-strengthening and follow the  ${}^T pK_a$  order HPMHP > HPMAP in 50% aqueous-dioxane media. The  ${}^T pK_a$  order for these ligands particularly in water ( $c$  values in Table 3), i.e. R = CF<sub>3</sub> (2.45) < Ph (3.46) < Me = pentyl (3.83, 3.81), can be simply explained by an inductive effect; this is compatible with a good linear correlation between  ${}^T pK_a$  and the Hammett  $\sigma$  value for R = substituted phenyls,<sup>12</sup> suggestive of a minor contribution of resonance effect of phenyl groups. Trifluoroacetyl substitution (R = CF<sub>3</sub>) considerably lowers the  ${}^T pK_a$  as compared with the other two 4-acyl derivatives and also HPMBP, which is primarily caused by increased stabilization of the anion relative to the neutral species, leading to considerably acid strengthening or base weakening. A trifluoromethyl group strongly withdraws electrons between the H<sup>+</sup> ion and the acyl pyrazolone, whereas an aromatic group as in HPMBP gives a resonance effect to  $\pi$ -electrons of the chelate ring.

Pyrazolones in solution usually exist as equilibrium mixtures of the keto-enol forms. The  ${}^T pK_a$  values in Table 2 should therefore, in principle, refer to their

twin processes of enolization and ionization,<sup>33</sup> viz.

$$K_a = [H^+][A^-]/([keto] + [enol])$$

The results of this investigation revealed that all the three 4-acylpyrazol-5-ones are weak acids with  $pK_a$  values of the order of 3-4. Consideration of the factors that modified the relative stabilities of these ionized species could therefore provide an insight into why the acidity constants varied in a systematic manner, in addition to a quantitative indication of how acyl substitutions affected the  $pK_a$  values.

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