

## THERMODYNAMICS OF PROTON-LIGAND DISSOCIATION OF SOME FLUORINATED $\beta$ -DIKETONES IN DIOXANE-WATER MIXTURES

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### ABSTRACT

The thermodynamic proton-ligand dissociation constants ( $TpK_a$ ) of the three fluorinated  $\beta$ -diketones namely 1,1,1-trifluoro-2,4-hexanedione, 1,1,1-trifluoro-5-methyl-2,4-hexanedione and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione have been determined pH-metrically in various dioxane-water mixtures at 25 and  $35 \pm 0.1^\circ\text{C}$  by applying an empirical pH correction for mixed organo-aqueous media. Both extrapolation and the least-squares methods were used to obtain  $TpK_a$  in pure water (0%). All the compounds investigated are weak monoprotic acids. The  $TpK_a$  values do not vary linearly with the reciprocal of the dielectric constant of the medium whereas a plot of dioxane mole fraction ( $n_2$ ) versus  $TpK_a$  is linear at a given temperature. An expression relating the solvation number and 'true ionization constant' has been mathematically evaluated. The values of changes in the standard free energy, enthalpy and entropy associated with their proton-ligand dissociation have been calculated. Temperature and medium as well as substituent effects are briefly discussed.

### INTRODUCTION

$\beta$ -Diketones constitute a class of the most important reagents which have been extensively employed from the beginning of this century [1,2]. They exhibit a great variety of coordination modes besides the usual bidentate behaviour of the monoanion [3]. Numerous studies have unambiguously established that their fluorinated derivatives have advantages over the non-fluorinated analogues and are indispensable in organic, inorganic and analytical chemistry, and biochemistry [4–6]. Various aspects of the coordination chemistry of  $\beta$ -diketones have been recently reviewed [7–12]. Of considerable interest were the observations that the introduction of the trifluoromethyl ( $-\text{CF}_3$ ) group into  $\beta$ -diketone molecules appreciably enhanced the extracting abilities of such compounds, particularly for Zr and Hf from acidic media and, in addition, improved the separation efficiency of these

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elements [13]. Moreover, many workers confirmed that such a substitution increased the volatility of the metal chelates which can be eluted with ease using gas chromatography [14–16].  $\beta$ -Diketones have a promising future as versatile chelating extractants and attempts are being vigorously pursued to enhance their acidic strength to the point where they can be applied in acidic solutions [17]. Previous studies [15,16] have established that 1,1,1-trifluoro-2,4-hexanedione (TFHD), 1,1,1-trifluoro-5-methyl-2,4-hexanedione (TFMH) and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (TFDH) are excellent tools in metal-chelate gas-chromatography. Surprisingly, no systematic work seems to have been carried out on the evaluation of their acid dissociation constants, which prompted this detailed study of the thermodynamic proton–ligand dissociation constants ( $\text{Tp}K_a$ ) of these three closely related fluorinated  $\beta$ -diketones and the determination of other thermodynamic parameters.

Values of  $\text{Tp}K_a$  for TFHD, TFMH and TFDH have been determined pH-metrically in 10–50 vol.% dioxane–water mixtures at 25 and  $35 \pm 0.1^\circ\text{C}$ , and the changes in the standard thermodynamic functions ( $\Delta G^\ominus$ ,  $\Delta H^\ominus$ ,  $\Delta S^\ominus$ ) associated with their dissociation were computed following the standard equations.

The  $\beta$ -diketones studied here are sparingly soluble in water, hence the use of dioxane–water mixed media for these experiments. Also, the determination of  $\text{Tp}K_a$  in binary mixed solvents provides useful data for the theoretical understanding of the ionization process in systems where two dipoles (dioxane and water), as well as the anion, can compete for the proton. The dioxane–water system is a good model system because it covers a very wide range of dielectric constant, from 78 for pure water to 2.2 for pure dioxane, and consists of a polar hydrogen-bonding component and a relatively non-polar component. Values of solvation number and the true ionization constant for their protonation were also mathematically evaluated.

## EXPERIMENTAL

### *Materials*

The  $\beta$ -diketones, procured from K and K Labs (U.S.A.), and were used as received. The *p*-dioxane used was purified as recommended [18]. A 0.1 M solution of tetramethylammonium hydroxide (TMAH) (A.R.) was used as the titrant. It was standardized against potassium hydrogen phthalate. All other chemicals used were of A.R. or G.R. grade.

### *TpK<sub>a</sub> determination*

A Beckman Research pH meter with a glass combination electrode was used for all pH measurements which could be read up to  $\pm 0.002$  pH units.

It was standardized with phthalate and borax buffers before starting the titrations. Constant temperature was maintained (to an accuracy of  $\pm 0.1^\circ\text{C}$ ) by circulating water from a thermostat through the annular space of the double-walled titration vessel.

The titration procedure for determining the  $\text{Tp}K_a$  was essentially the same as that outlined by Albert and Serjeant [19]. 47.5 ml of the appropriate dioxane–water mixture, containing 0.50 mM of the  $\beta$ -diketone, was put into a thermostated titration vessel equipped with a magnetic stirring bar, a glass combination electrode and a 5.0 ml microburet. This initial volume allowed for the change in total volume of the solution on titrant addition [20]. For practical purposes, the error caused by volume correction is almost negligible [21]. After 10 min, the titration was started by adding 0.50 ml aliquots of 0.10 M TMAH and recording the highest stable pH value. Further titrant additions were made in the same fashion. Titrations were conducted in duplicate and values were reproducible within  $\pm 0.01$  pH unit.

## CALCULATIONS

Two methods, the non-logarithmic (N) and the logarithmic (L), were followed to calculate the  $\text{Tp}K_a$  of these ligands.

### *Method N*

The  $\text{Tp}K_a$  of an acid in an aqueous medium can be written

$${}^{\text{T}}K_a = [\text{H}^+][\text{A}^-]\gamma_{\pm}^2 / [\text{HA}] \quad (1)$$

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 [HA] from eqn. (2) into (1) and rearranging

$$[\text{A}^-] = -1/{}^{\text{T}}K_a([\text{A}^-][\text{H}^+]\gamma_{\pm}^2) + C_a \quad (3)$$

which is a straight line equation ( $y = mx + C$ ) having slope  $m$  and intercept  $C$  equal to  $-1/K_a$  and  $C_a$  respectively,  $x = ([\text{A}^-][\text{H}^+]\gamma_{\pm}^2)$  and  $y = ([\text{A}^-])$ . The least-squares method was used to evaluate the slope and intercept given by the above equation. Values of  $[\text{A}^-]$  and  $[\text{H}^+]$  were obtained analytically. The relationship of van Uitert and Haas [21] was used to evaluate the hydrogen ion concentration from the values on the pH-meter  $B$

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

Values of the correction factor,  $\log U_{\text{H}}^{\ominus}$ , were obtained experimentally [22] and those of the mean activity coefficients  $\gamma_{\pm}$  were computed by interpolation of the data given by Harned and Owen [23] assuming that the mean activity coefficients are the same on both molal and molar scales.

### Method L

The following equation is used to determine the  $\text{Tp}K_{\text{a}}$

$$\text{Tp}K_{\text{a}} = B + \log U_{\text{H}}^{\ominus} + \log\left(\frac{[\text{HA}]}{[\text{A}^{-}]}\right) + \log(1/\gamma_{\pm}) \quad (4)$$

Details of this method are given elsewhere [24]. The thermodynamic functions ( $\Delta G^{\ominus}$ ,  $\Delta H^{\ominus}$  and  $\Delta S^{\ominus}$ ) associated with the proton–ligand dissociation were calculated employing the standard equations [24].

## RESULTS AND DISCUSSION

The  $\text{Tp}K_{\text{a}}$  values obtained by Method L usually showed either an upward or a downward trend as the titration progressed which is probably caused by an impurity in the substance undergoing determination so that less of it was present than had been supposed. On this account, Method N is superior to Method L as the former does not involve the total concentration term and the accuracy of this method depends on the ability of the pH meter to read

TABLE 1

Thermodynamic proton–ligand dissociation constants ( $\text{Tp}K_{\text{a}}$ ) of fluorinated  $\beta$ -diketones <sup>a</sup>

Ligand	Temp. (°C)	Solvent medium (vol.% dioxane)				
		10 $n_2 \neq 0.023$	20	30	40	50
TFHD	25	Ins. <sup>b</sup>	6.80	6.96	7.16	7.46
		Ins.	6.83	6.93	7.13	7.48
	35	Ins.	6.53	6.72	6.92	7.21
		Ins.	6.54	6.68	6.90	7.26
TFMH	25	6.80	6.96	7.11	7.21	7.54
		6.76	6.92	7.07	7.18	7.53
	35	6.50	6.61	6.80	6.97	7.29
		6.48	6.57	6.78	6.93	7.32
TFDH	25	7.36	7.51	7.72	7.87	8.28
		7.33	7.47	7.65	7.96	8.27
	35	7.07	7.20	7.39	7.58	7.99
		7.07	7.17	7.39	7.69	7.99

<sup>a</sup> The average  $\text{Tp}K_{\text{a}}$  value generally falls within a spread of  $\pm 0.03$  units but not beyond  $\pm 0.04$  in any case. Second-row values are evaluated using Method L.

<sup>b</sup> Ins., insoluble.

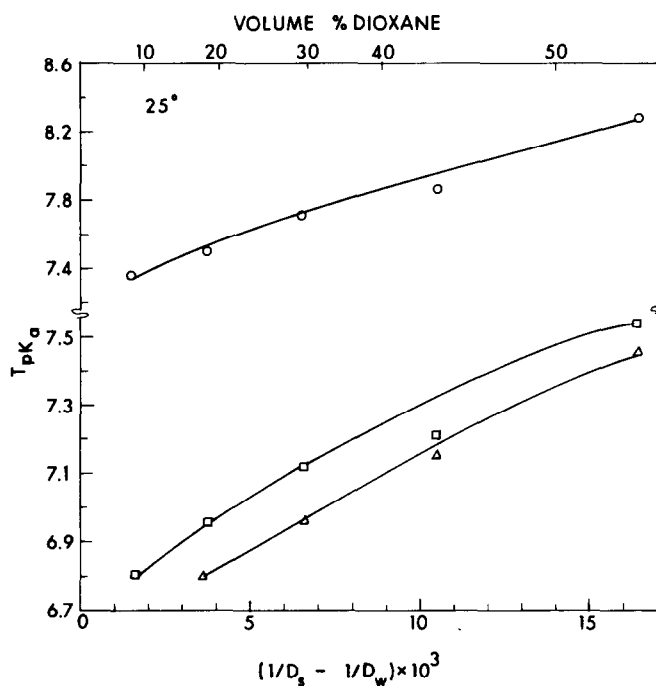


Fig. 1. Variation of  $TpK_a$  with  $(1/D_s - 1/D_w)$  of the medium (temperature, 25°C). Compounds: ○—○, TFDH; □—□, TFMH; △—△, TFHD.

correctly. Values of  $TpK_a$ , for the three substituted  $\beta$ -diketones in various dioxane–water mixtures at 25 and 35°C are summarized in Table 1. Interestingly, the values obtained by the N and L methods are in fair agreement. However, the values obtained by Method N were used for all other calculations and plots. The  $TpK_a$  values of all the ligands slightly decreased with temperature increase which is as expected as the enol content decreases with the rise in temperature [25]. Values of  $TpK_a$  are plotted

TABLE 2

Empirical relation between  $TpK_a$  and mole fraction of dioxane ( $n_2$ )

Ligand	Temp. (°C)	Graphical		Least-squares		$r^a$
		$TpK_a = mn_2 + C$		$TpK_a = mn_2 + C$		
		$m$	$c$	$m$	$c$	
TFHD	25	5.27	6.53	5.25	6.53	0.999
	35	5.50	6.26	5.48	6.25	0.999
TFMH	25	4.70	6.69	4.67	6.70	0.990
	35	5.30	6.35	5.21	6.36	0.997
TFDH	25	5.92	7.22	5.93	7.21	0.993
	35	5.99	6.90	5.98	6.90	0.994

<sup>a</sup>  $r$  is the correlation coefficient.

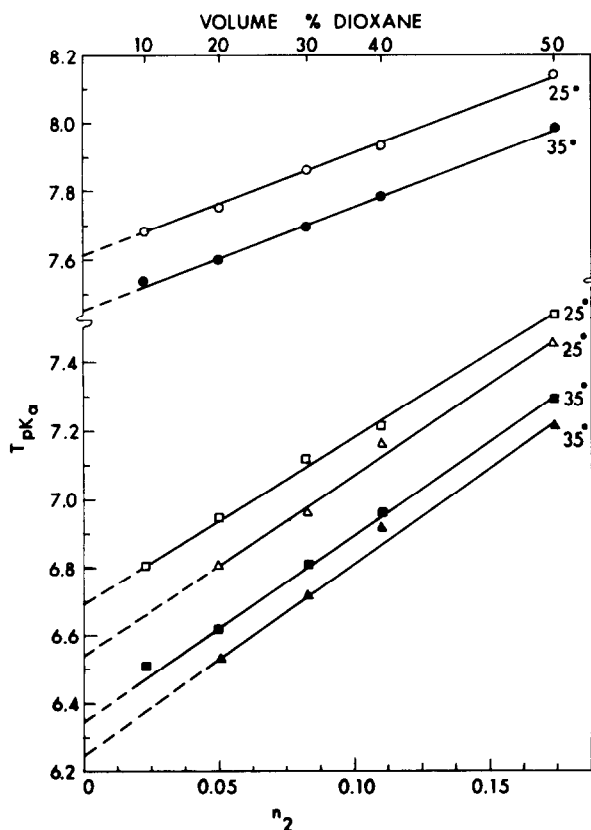


Fig. 2. Variation of  $TpK_a$  with  $n_2$  (mole fraction of dioxane). Compounds:  $\circ$ — $\circ$ , TFDH, 25°C;  $\square$ — $\square$ , TFMH, 25°C;  $\triangle$ — $\triangle$ , TFHD, 25°C;  $\bullet$ — $\bullet$ , TFDH, 35°C;  $\blacksquare$ — $\blacksquare$ , TFMH, 35°C;  $\blacktriangle$ — $\blacktriangle$ , TFHD, 35°C.

against  $(1/D_s - 1/D_w)$  (Fig. 1) and mole fraction of dioxane ( $n_2$ ) (Fig. 2). Empirical relations derived therefrom are given in Table 2. Such relations between  $TpK_a$  and  $n_2$  were also calculated by subjecting the  $TpK_a$  data to least-squares analysis (Table 2). Table 3 records the thermodynamic functions computed by the temperature variation method.

### Medium effects

In a mixed solvent, the proton–ligand dissociation equilibria may be influenced by different solvent characteristics. These effects can be due to: (1) the dielectric constant of the mixed solvent; (2) the change in the hydrogen-bonding of water caused by the presence of an organic solvent; and (3) the proton solvation of the organic solvent.

Bates et al. [26] and Rorabacher et al. [27] have explained the changes in  $TpK_a$  with solvent composition considering both electrostatic and non-electrostatic effects and concluded that the non-electrostatic phenomenon be-

TABLE 3

Calculation of "true proton-ligand dissociation constant",  $pK_a^\ominus$ , for fluorinated  $\beta$ -diketones

$\beta$ -Diketones	$pK_a^*$ (found)		$\log S$		$pK_a$ (Calc.)		$pK_a$ (Graph)	
	25°C	35°C	25°C	35°C	25°C	35°C	25°C	35°C
Vol. % dioxane, 10								
TFHD	Ins. <sup>a</sup>	Ins.	1.694	1.693	Ins.	Ins.	Ins.	Ins.
TFMH	6.80	6.50			6.80	6.47	6.80	8.47
TFDH	7.36	7.07			7.34	7.07	7.34	7.06
Vol. % dioxane, 20								
TFHD	6.80	6.53	1.635	1.634	6.79	6.52	6.79	6.51
TFMH	6.96	6.61			6.94	6.63	6.95	6.63
TFDH	7.51	7.20			7.51	7.21	7.51	7.21
Vol. % dioxane, 30								
TFHD	6.96	6.72	1.568	1.567	6.97	6.71	6.96	6.72
TFMH	7.11	6.80			7.10	6.80	7.11	6.80
TFDH	7.72	7.39			7.71	7.41	7.72	7.40
Vol. % dioxane, 40								
TFHD	7.16	6.92	1.490	1.488	7.18	6.93	7.17	6.92
TFMH	7.21	6.97			7.28	7.01	7.20	6.99
TFDH	7.87	7.58			7.95	7.65	7.88	7.64
Vol. % dioxane, 50								
TFHD	7.46	7.21	1.394	1.392	7.44	7.20	7.44	7.21
TFMH	7.54	7.29			7.51	7.26	7.53	7.29
TFDH	8.28	7.99			8.23	7.94	8.24	7.96

Ins., insoluble.

TFHD:

at 25°C,  $n = 2.70 \pm 0.04$  (calc.); 2.68 (graph);  $pK_a^\ominus = 11.20 \pm 0.03$ ; 11.23 (graph);at 35°C,  $n = 2.80 \pm 0.03$  (calc.); 2.83 (graph);  $pK_a^\ominus = 11.11 \pm 0.04$ ; 11.13 (graph).

TFMH:

at 25°C,  $n = 2.35 \pm 0.03$  (calc.); 2.38 (graph);  $pK_a^\ominus = 10.79 \pm 0.03$ ; 10.82 (graph);at 35°C,  $n = 2.61 \pm 0.02$  (calc.); 2.59 (graph);  $pK_a^\ominus = 10.90 \pm 0.03$ ; 10.87 (graph).

TFDH:

at 25°C,  $n = 2.99 \pm 0.04$  (calc.); 2.96 (graph);  $pK_a^\ominus = 12.40 \pm 0.04$ ; 12.33 (graph);at 35°C,  $n = 3.00 \pm 0.04$  (calc.); 2.96 (graph);  $pK_a^\ominus = 12.11 \pm 0.03$ ; 12.10 (graph).

comes increasingly important in solvents containing a higher proportion of the organic component.

Gurney [28] and Sagar et al. [29] 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 environment and a non-electrostatic term (non.) insensitive to the environment and independent of temperature

$$\Delta G_{\text{diss.}}^\ominus = \Delta G_{\text{el.}}^\ominus + \Delta G_{\text{non.}}^\ominus \quad (5)$$

If the electrostatic part is expressed by Born's formula [30]

$$\Delta G_{\text{el.}}^\ominus = - (Ne^2/2)(1 - 1/D)(1/r^+ + 1/r^-) \quad (6)$$

where  $r^+$  and  $r^-$  denote the radii of the solvated ions, for the simultaneous transfer of the ions from water to an aquo-organic mixed medium, eqn. (5) takes the form

$$\Delta G_{\text{diss.}}^{\ominus} = \Delta G_{\text{non.}}^{\ominus} - (Ne^2/2)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \quad (7)$$

where  $D_s$  and  $D_w$  are the dielectric constants of the mixed medium and pure water respectively. Further, as  $\Delta G_{\text{diss.}}^{\ominus} = 2.303 RT \text{p}K_a$ , the equation simplifies as

$$\text{p}K_a = (\Delta G_{\text{non.}}^{\ominus}/2.303RT) - (Ne^2/4.606RT)(1/D_s - 1/D_w)(1/r^+ + 1/r^-) \quad (8)$$

Conventionally,  $\text{p}K_a$  is plotted against the inverse of the dielectric constant assuming  $\Delta G_{\text{non.}}^{\ominus}$  to be independent of the solvent. Both types of relationships, the linear for water-rich media ( $D_s > 30$ ) [31,32] and the non-linear [33], have been reported. The plots of  $\text{Tp}K_a$  as a function of  $(1/D_s - 1/D_w)$  for most of the ligands, do not obey a strict linear relationship and their curvatures vary (Fig. 1). For brevity, only plots at 25°C are shown in Fig. 1. When there is no change in the solvation of an acid and its anion in a binary mixed solvent, such a plot should give a straight line. The  $\text{Tp}K_a$  values of all the compounds, when plotted against  $(1/D_s - 1/D_w)$  showed some distinct curvature which can be primarily attributed to two facts. (1) Dioxane is a non-polar basic solvent. Although intermolecular interactions between dioxane molecules are weak, interaction between dioxane molecules and water molecules are rather strong due to the basicity of the etheral oxygen atoms of dioxane. Therefore, dioxane can form hydrogen bonds with water and is miscible at any proportion of dioxane and water. As dioxane forms associates with water molecules in aqueous dioxane, hydrogen bonds between water molecules originally existing in pure water are partly replaced by those between dioxane and water molecules in the mixture. On the other hand, as dioxane has a very poor acidity, dioxane molecules cannot interact with the oxygen atom of the water molecule. As a result, dioxane acts as a breaker of the water structure. According to Braude and Stern [34], the tetrahedral lattice structure of the water gradually breaks down with addition of organic solvent. On decreasing the extent of hydrogen bonding in water by the organic solvent, the proton-accepting property of water increases. Hence, the  $\text{p}K_a$  of the ligand decreases. (2) When the proportion of the organic component becomes sufficiently large in a water-organic mixture, proton solvation of the organic solvent molecules takes place. Thus increasing proton solvation by the organic solvent decreases the  $\text{p}K_a$  of an acid and vice versa.

#### *Mole fraction of dioxane*

Consideration of the direct participation of the solvent in the acid dissociation should lead to a better understanding of the compositions of the



solvent as well as of the solvates [35]. For example, such a participation is apparent from the straight-line  $pK_a$  versus  $n_2$  plots in several instances [36].

When the mole fraction of dioxane is altered, an appreciable change in the  $TpK_a$  is evident for all the three compounds. Thus on plotting  $TpK_a$  versus  $n_2$ , linear relationships were obtained (Fig. 2). The experimental values of  $TpK_a$  here showed a maximum deviation from linearity of the order of  $\pm 0.04$  in  $TpK_a$ . These plots gave slopes equivalent to about 5–6 which is as expected for  $\beta$ -diketones [37]. The fit was judged by calculating the correlation coefficient,  $r$ , as given elsewhere [24]. Linear proportionality between two variables is quite evident from the values of  $r$  which are approximately  $\pm 1.0$  (Table 2) in all the cases. A similar behaviour is found for some other mixed solvents, e.g. acetic, propionic, butyric and benzoic acids in methanol–water mixtures [38], dimedone in ethanol–water [39] and also for a number of  $\beta$ -diketones in aqueous–dioxane mixtures [25,37].

#### *Evaluation of $pK_a$ and $n$*

The acid dissociation constant ( $K_a^\ominus$ ) of an acid, HA, in a mixed medium can be expressed as



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

$$(xSH^+)(ySA^-)/(S)^n(HA) = K_a^\ominus \quad (10)$$

where parentheses denote activity. Equation (10) is usually written as

$$(H^+)(A^-)/(HA) = K_a^\ominus(S)^n = K_a^\star \quad (11)$$

where it is understood that the ions are solvated and  $K_a^\star$  includes the solvent term  $(S)^n$ . By taking logarithms of eqn. (11)

$$\log K_a^\star = \log K_a^\ominus + n \log(S)$$

or

$$pK_a^\star = pK_a^\ominus - n \log(S) \quad (12)$$

Since  $pK_a^\star$ , defined in eqn. (12), is the thermodynamic constant,  $pK_a^\ominus$  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. (12)

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

The  $pK_a^\ominus$  and  $n$  values listed in Table 3 have been computed by least-squares fitting of eqn. (12) and from the plot of  $pK_a^\star$  (or  $TpK_a$ ) against

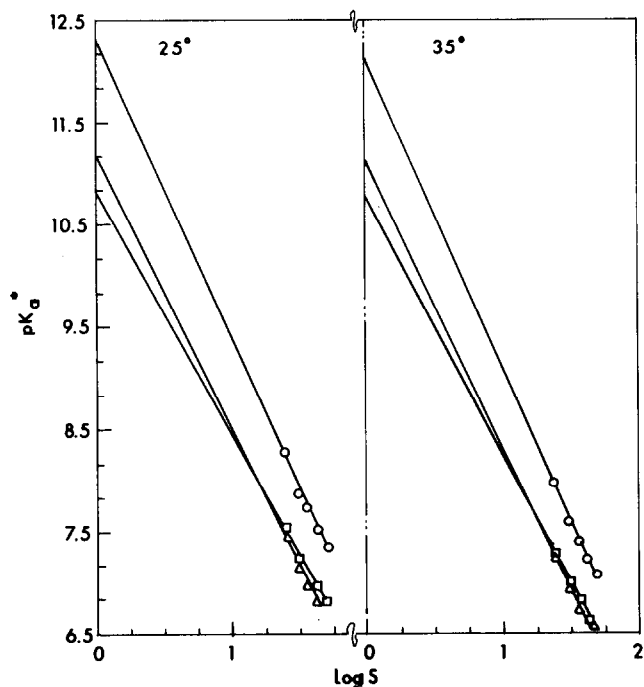


Fig. 3. Plots of  $\text{Tp}K_a^*$  versus  $\log S$  at 25 and 35°C. Compounds: ○—○, TFDH; □—□, TFMH; △—△, TFHD.

$\log(S)$  (Fig. 3). Slight deviations of graphical values from experimental ones are seen. It is of interest to note that there is excellent agreement between the two sets of values of  $\text{Tp}K_a$  calculated independently via eqns. (3) and (12).

#### *Thermodynamic functions*

The  $\text{Tp}K_a$  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  $\pm 0.03$  and  $\pm 0.04$  kcal mol<sup>-1</sup>. The procedure followed here to evaluate  $\Delta H^\ominus$  is subject to some error because the enthalpy change is small and values were not obtained at different temperatures which would have allowed use of a more precise method [40]. However, the positive values of  $\Delta H^\ominus$  obtained in dioxane–water solutions for these  $\beta$ -diketones indicate that their dissociation is accompanied by absorption of heat and that the process is endothermic. Further, the change in  $\Delta H^\ominus$  with change in medium is relatively small and negligible within experimental error. It is because of this that the slopes of the straight lines in the plot of  $\text{Tp}K_a$  versus  $n_2$  (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

TABLE 4

Standard free energy, enthalpy and entropy change for proton–ligand dissociation of fluorinated  $\beta$ -diketones

Thermodynamic functions <sup>a</sup>	Solvent medium (vol.% dioxane)				
	10	20	30	40	50
<b>TFHD</b>					
$\Delta G^\ominus$ 25°C	Ins.	9.28	9.50	9.77	10.17
$\Delta G^\ominus$ 35°C	Ins.	9.20	9.47	9.75	10.17
$\Delta H^\ominus = 10.94$					
$-\Delta S^\ominus$ 25°C	Ins.	5.55	4.81	3.93	2.56
$-\Delta S^\ominus$ 35°C	Ins.	5.63	4.75	3.84	2.49
<b>TFMH</b>					
$\Delta G^\ominus$ 25°C	9.28	9.49	9.71	9.84	10.29
$\Delta G^\ominus$ 35°C	9.16	9.32	9.60	9.82	10.28
$\Delta H^\ominus = 12.41$					
$-\Delta S^\ominus$ 25°C	10.50	9.78	9.66	8.61	7.10
$-\Delta S^\ominus$ 35°C	10.54	10.01	9.13	8.39	6.91
<b>TFDH</b>					
$\Delta G^\ominus$ 25°C	10.04	10.24	10.53	10.74	11.30
$\Delta G^\ominus$ 35°C	9.97	10.16	10.42	10.69	11.27
$\Delta H^\ominus = 13.46$					
$-\Delta S^\ominus$ 25°C	11.46	10.79	9.81	9.13	7.24
$-\Delta S^\ominus$ 35°C	11.33	10.71	9.86	8.98	7.12

<sup>a</sup>  $\Delta H^\ominus$  and  $\Delta G^\ominus$  are in kcal mol<sup>-1</sup>,  $\Delta S^\ominus$  is in cal mol<sup>-1</sup>K<sup>-1</sup>.

over the range investigated. On this assumption, a new value of  $\Delta H^\ominus$  was calculated. Numerically, this is equal to 42.06 times the difference in the intercepts of the parallel lines on the  $\text{Tp}K_a$  axis (Fig. 2) and this is the value given in Table 4.

The slightly decreasing trend in  $\Delta S^\ominus$  with increasing dioxane content suggests that the dissociation of these compounds is primarily an entropy-controlled process. As dissociation diminishes, the entropy of the system also decreases; this is favoured in higher dielectric solvents, i.e. at lower values of  $n_2$ . The fairly large negative values of  $\Delta S^\ominus$  encountered here can be explained as being due to the dissociation of the ligand as the sum total of the "bound" water molecules is more than the water molecules originally accompanying the undissociated reagent. These facts are thus in accordance with the assumption that the decrease of the  $\text{Tp}K_a$  in dioxane–water mixtures is chiefly due to a statistical effect. For any definite explanation, extensive data for mixed solutions would be needed.

It is interesting to note that  $\Delta G^\ominus$  becomes increasingly positive, with increase in dioxane content in the case of ionization processes such as  $\text{HA} = \text{H}^+ + \text{A}^-$ . This is not necessarily correlated with the change in water structures i.e., the structure of water is enhanced due to addition of dioxane

or due to the increase in basicity of the solvents. The results could be explained in terms of ionic solvations and the consequent change in entropy and enthalpy values. This also shows that the dielectric constant is not the only factor affecting the dissociation, the main factor being solute-solvent interactions [41,42].

### *Substituent effects*

$\beta$ -Diketones generally exist as an equilibrium mixture of the tautomeric keto and enol forms. Therefore the  $\text{Tp}K_a$  values given in Table 1 should, in principle, refer to the twin process of enolization and ionization [43]

$$K_a = [\text{H}^+][\text{A}^-]/([\text{keto}] + [\text{enol}]) \quad (13)$$

The replacement of one of the terminal methyl groups in acetylacetone (HAcAc), a typical non-fluorinated  $\beta$ -diketone, by an electron-withdrawing group such as  $-\text{CF}_3$  shifts the equilibrium in favour of the enol tautomer thereby considerably decreasing the  $\text{Tp}K_a$  of all three compounds as compared to HAcAc in all solvent media. On the other hand, further replacement of the H atoms of the terminal methyl group in TFHD by electron-repelling methyl groups (TFMH and TFDH) would decrease the acid dissociation, resulting in an increased  $\text{Tp}K_a$  of TFDH and TFMH relative to that of TFHD. Their  $\text{Tp}K_a$  falls in the expected sequence and follows the order  $\text{TFHD} < \text{TFMH} < \text{TFDH}$ .

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