THERMODYNAMICS OF PROTON DISSOCIATION OF ACETYLACETONE AND 3-METHYLACETYLACETONE IN DIOXANE—WATER MIXTURES

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ABSTRACT

Thermodynamic ionization constants ($^T pK_a$) of acetylacetone and 3-methylacetyl-acetone have been determined potentiometrically in aqueous and aqueous-dioxane media at 25 and 35 ±0.01°C applying an empirical pH correction for mixed aqueous media. The $^T pK_a$ values do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of $^T pK_a$ vs. the mole fraction of dioxane is linear at a given temperature. Temperature as well as medium effects are briefly discussed. Values of ΔG^0, ΔH^0, and ΔS^0 are tabulated.

INTRODUCTION

β-Diketones, represented by the general formula

$$R_1 \!-\! \underset{\underset{O}{\|}}{C} \!-\! CH_2 \!-\! \underset{\underset{O}{\|}}{C} \!-\! R_2$$
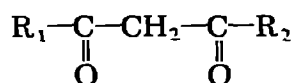
have found immense analytical applications [1—7]. However, such applications necessitate a precise knowledge of their ionization constants. Recently, several analogous compounds have been synthesized by the introduction of substituent groups in different positions for improved analytical characteristics. This empirical approach, although sometimes inescapable, is generally wasteful and it is more fruitful to determine the physico-chemical properties of the reagents and their resulting metal complexes, and in particular their ionization constants, which could lead to a better understanding of the cause of specificity and selectivity of relevant analytical reactions.

Acetylacetone, a β-diketone, possesses remarkable versatility as a reagent for solvent extraction of numerous metals [8,9]. Data on its acid dissociation constants would be of great importance in various analytical procedures and also in the elucidation of the structure of the resulting metal complexes. With this in view, the thermodynamic acid dissociation constant, $^T pK_a$, of acetylacetone (AcAc) in aqueous as well as 10, 20, 30, 40 and 50

vol.% dioxane—water media at 25 and 35 ±0.01°C have been determined and the thermodynamic functions associated with the acid dissociation evaluated. Similar studies were carried out with 3-methylacetylacetone (3M-AcAc) to assess the relative effect of methyl substitution. The noteworthy characteristic of these β-diketones is their relatively higher aqueous solubility.

Studies with higher concentrations of dioxane were avoided because of possible association of solutes, which may be expected in solvents of low dielectric constant; also, activity coefficient corrections would be considerably more in such solutions. In addition, experimental errors might be introduced in the $^{T}pK_a$ measurements due to the higher pH meter correction necessary.

EXPERIMENTAL

Reagents

Acetylacetone (AcAc) and 3-methylacetylacetone (3M-AcAc) procured from Riedel—De Haen, A.G., Hannover, were used as supplied. All other chemicals employed were of A.R. or G.R. grade from B.D.H. or E. Merck, unless otherwise specified.

Titrant

An aqueous solution (10%) of tetramethylammonium hydroxide titrant was obtained from Hopkin and Williams Ltd. This was standarized against analytical grade potassium hydrogenphthalate [10] and diluted to 0.1 M, the proportions of dioxane and water being the same as used in preparing the titre solutions.

Dioxane

B.D.H. "AnalaR" p-dioxane was purified by the procedure of Weissberger and Proskauer [11].

pH metric titration

The titration procedure for determining the ionization constants was essentially the same as that outlined by Albert and Sergeant [12]. Generally, a 0.01 M solution of β-diketone was titrated without the addition of inert salt. Measurements of pH were made on a Beckmann Research pH meter which can be read to 0.002 unit of pH. The instrument was standardized against phthalate and borax buffers before and after each titration.

In the 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 β-diketone in the appropriate dioxane—water composition was taken and the contents were 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 [13]. For practical purposes, the error caused by volume correction is almost negligible (less than 0.01 pH unit for the inner five readings of a set of pH titrations) with a maximum error of 0.018 pH unit [14]. About 10 min after the settings, the titration was started by adding 0.5 ml aliquots of 0.1 M tetramethyl-ammonium hydroxide at a time and noting the highest drift-free reading in the pH meter. Titrations, carried out in duplicate, were reproducible within ±0.01 pH unit.

CALCULATIONS

The $^T pK_a$'s have been determined by the pH titration method employing a pH meter cell of the type

Glass electrode	β-Diketone in aqueous or aqueous dioxane mixture (0.01 M)	Aqueous saturated KCl (salt bridge)	Calomel electrode (saturated KCl)

To make the pH meter reading meaningful using a glass and saturated calomel electrode in cells with liquid junction potential in mixed aqueous dioxane medium, Van Uitert and Haas [15] have established the following empirical relation between the stoichiometric hydrogen ion concentration, $[H^+]$ in such media and the pH meter reading (B)

$$-\log[H^+] = B + \log U_H^0 + \log y_\pm \tag{1}$$

The ionization of β-diketone (HA) in aqueous solution gives hydrogen ion $[H^+]$ and diketonate ion $[A^-]$ and the equilibrium constant is given by eqn. (2) in aqueous medium.

$$^T K_a(aq.) = ([H^+][A^-]/[HA])(y_{H^+} y_{A^-}/y_{HA}) \tag{2}$$

or

$$^T pK_a(aq.) = -\log[H^+] + \log([HA]/[A^-]) + 2\log\left(\frac{1}{y_\pm}\right) \tag{3}$$

Assuming y_{HA}, the activity coefficient of unionized acid is unity, the final form of the equation for calculating the ionization constant in the dioxane—water media is obtained by eqns. (1 and 3).

$$^T pK_a = B + \log U_H^0 + \log([HA]/[A^-]) + \log\left(\frac{1}{y_\pm}\right)$$

Hydrolysis of the salt, appreciable above pH 10, in a given medium was taken into consideration via eqns. (5) and (6).

$$^T pK_a(aq.) = -\log[H^+] + \log \frac{[HA] + \{OH^-\}}{[A^-] - \{OH^-\}} + \log\left(\frac{1}{y_\pm}\right) \tag{5}$$

and for mixed aqueous media by

$$^T pK_a = B + \log U_H^0 + \log \frac{[HA] + \{OH^-\}}{[A^-] - \{OH^-\}} + \log\left(\frac{1}{y_\pm}\right) \tag{6}$$

Hydroxyl ion activity, $\{OH^-\}$, was computed from the relationship [16]

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

Ionic product of water, pK_w, has been obtained from the data of Harned and Owen [17] in various dioxane—water mixtures. The numerical equations expressed for the linear relationship are as under [18].

At 25°C: $pK_w = 11.93 \ n_2 + 14.00$ $\qquad\qquad\qquad\qquad\qquad$ (7)

At 35°C: $pK_w = 12.01 \ n_2 + 13.68$ $\qquad\qquad\qquad\qquad\qquad$ (8)

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

Values of mean activity coefficients ($y_\pm$) of HCl of different molalities in water and dioxane—water mixtures at several temperatures are available [19, 20]. However, as these data at the desired temperature, mole fractions of dioxane, and molalities of 1 : 1 electrolyte were not available, the same were computed by the interpolation of appropriate data available in the cited references. Values of log U_H^0, the correction factor at $\mu \to 0$, are published elsewhere [21].

Finally, the thermodynamic functions (ΔG^0, ΔH^0 and ΔS^0) were calculated in the usual way.

RESULTS AND DISCUSSION

The values of $^T pK_a$ of AcAc and 3M-AcAc in aqueous and aqueous-dioxane media at 25 and 35°C are presented in Tables 1 and 2, respectively. Values of $^T pK_a$ for AcAc at 25°C, reported earlier by us [22], have been redetermined under the present set of conditions. The average $^T pK_a$ generally falls within a spread of ±0.02 but not beyond ±0.03 in any case. The $^T pK_a$'s were plotted against mole fraction of dioxane (n_2) in Fig. 1 and the empirical relations derived therefrom are given in Table 3. The empirical relationship between $^T pK_a$ and n_2 for both the β-diketones was also obtained by subjecting the data to a least-squares analysis (Table 3). Thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0, associated with these proton—ligand reactions computed by adopting the temperature variation method are given in Table 4.

The β-diketones are very weak acids [22] and their acidity may be attri-

TABLE 1

Thermodynamic ionization constants of acetylacetone

Vol. % dioxane	Mole fraction of dioxane (n_2)	$^T pK_a$ at 25°C				$^T pK_a$ at 35°C			
		Found *	Calcd. **	Graphical	$\Delta \times 10^2$ (col. 3—col. 4)	Found *	Calcd. **	Graphical	$\Delta \times 10^2$ (col. 7—col. 8)
1	2	3	4	5	6	7	8	9	10
0	0	9.13	9.07	9.08	+6	8.97	8.91	8.95	+6
10	0.023	9.28	9.26	9.27	+2	9.16	9.12	9.14	+4
20	0.050	9.50	9.49	9.50	+1	9.34	9.35	9.37	−1
30	0.083	9.72	9.77	9.78	−5	9.61	9.65	9.65	−4
40	0.123	10.13	10.10	10.12	+3	9.96	9.99	9.98	−3
50	0.174	10.53	10.53	10.55	0	10.49	10.45	10.41	+4
Total:					17				22
Ave. deviation:					2.83×10^{-2} ~0.03				3.7×10^{-2} ~0.04

* $^T pK_a$ obtained using all nine values of a set.
** Calculated values of $^T pK_a$ obtained by subjecting the experimental data to a least-squares analysis.

TABLE 2

Thermodynamic ionization constants of 3-methylacetylacetone

Vol. % dioxane	Mole fraction of dioxane (n_2)	$^{T}pK_a$ at 25°C				$^{T}pK_a$ at 35°C			
		Found *	Calcd. **	Graphical	$\Delta \times 10^2$ (col. 3−col. 4)	Found *	Calcd. **	Graphical	$\Delta \times 10^2$ (col. 7−col. 8)
1	2	3	4	5	6	7	8	9	10
0	0	10.38	10.40	10.40	+2	10.30	10.28	10.30	+2
10	0.023	10.63	10.62	10.63	+1	10.54	10.50	10.52	+4
20	0.050	10.91	10.89	10.90	+2	10.75	10.77	10.77	−2
30	0.083	11.19	11.21	11.23	−2	11.08	11.08	11.09	0
40	0.123	11.58	11.60	11.63	−2	11.43	11.47	11.47	−4
50	0.174	12.12	12.10	12.14	+2	12.00	11.96	11.96	+4
Total:					11				16
Ave. deviation:					1.83×10^{-2} ~0.02				2.67×10^{-2} ~0.03

* $^{T}pK_a$ obtained using all nine values of a set.
** Calculated values of $^{T}pK_a$ obtained by subjecting the experimental data to a least-squares analysis.

TABLE 3

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

β-Diketone	$^{T}pK_a = mn_2 + C$, at 25°C						$^{T}pK_a = mn_2 + C$, at 35°C					
	Graphical		Least-squares				Graphical		Least-squares			
	m	C	m	C	r	b	m	C	m	C	r	b
AcAc	8.44	9.08	8.38	9.07	+0.999	8.36	8.39	8.95	8.83	8.91	+0.999	8.73
3M-AcAc	10.00	10.40	9.78	10.40	+0.996	9.74	9.54	10.30	9.67	10.28	+0.998	9.65

r and b refer to the correlation coefficient and regression coefficient (actual slope), respectively.
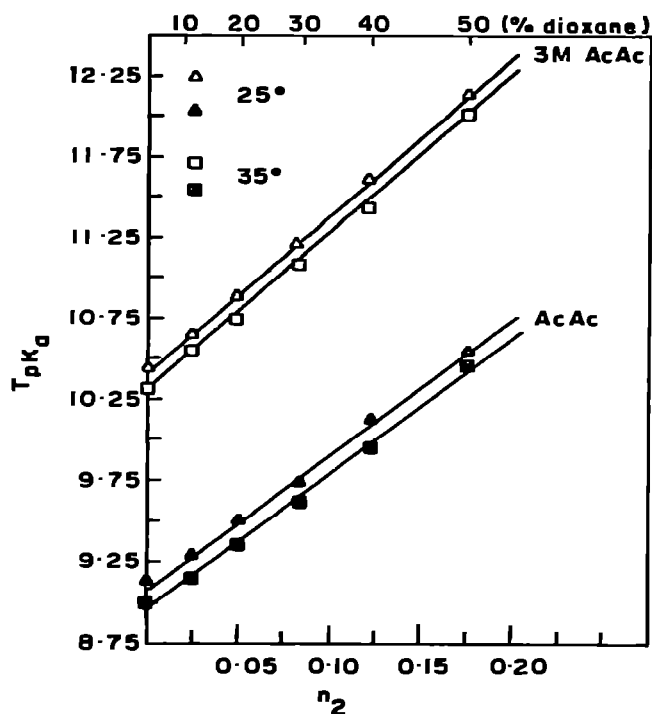
Fig. 1. Variation of $^{T}pK_a$ with n_2 (mole fraction of dioxane).

TABLE 4

Thermodynamic parameters for ionization of acetylacetone and 3-methylacetylacetone *

Function **	Solvent medium, % (v/v) dioxane					
	0	10	20	30	40	50
	Acetylacetone					
ΔG°	12.46	12.66	12.96	13.26	13.82	14.37
	12.65	12.92	13.17	13.55	14.05	14.79
$\Delta H^{\circ} = 6.06$						
$-\Delta S^{\circ}$	21.46	22.13	23.14	24.15	26.02	27.87
	21.38	22.26	23.07	24.30	25.92	28.33
	3-Methylacetylacetone					
ΔG°	14.17	14.51	14.89	15.27	15.80	16.54
	14.53	14.86	15.16	15.63	16.12	16.92
$\Delta H^{\circ} = 4.98$						
$-\Delta S^{\circ}$	30.82	31.96	33.23	34.51	36.28	38.77
	30.99	32.06	33.03	34.56	36.15	38.74

* First and second row values at 25 and 35°C, respectively.
** ΔG° and ΔH° in kcal mol^{-1}, ΔS° in cal mol^{-1} K^{-1}.

buted essentially to the —OH group. The suppression of acidic character may be ascribed to the intramolecular hydrogen bonding as shown by IR spectroscopic studies [23].

For studying the protonation of β-diketones, (i) 0.01 M HClO$_4$, and (ii) 0.01 M HClO$_4$ in the presence of 0.01 M of AcAc or 3M-AcAc, were titrated separately with 0.1 M (CH$_3$)$_4$NOH. The two sets of pH titration curves were superimposable up to strong acid end point. From these observations, it is inferred that the protonation of the β-diketones is essentially negligible.

Temperature effects

From the data given in Tables 1 and 2, it is evident that the ^TpK_a of these β-diketones in aqueous as well as aqueous dioxane media are consistently lower at 35°C compared to 25°C.

Medium effects

Acid strength and thus ^TpK_a values of the β-diketones are influenced by the intrinsic basicity of the solvent. A solvent of low dielectric constant (D) increases the electrostatic forces between the ions and facilitates formation of molecular species which should increase the ^TpK_a, as borne out for AcAc and 3M-AcAc by Tables 1 and 2. This prediction has been amply confirmed for other β-diketones on the basis of similar studies [24,25].

As shown by Gurney [26] and others [27,28], the standard free energy change associated with the proton transfer, $\Delta G^0_{diss.}$, may be split into two distinct parts, electrostatic (el.) and nonelectrostatic (nonel.).

$$\Delta G^0_{diss.} = \Delta G^0_{el.} + \Delta G^0_{nonel.} \tag{9}$$

The electrostatic contribution to free energy change is often estimated by using the Born equation [29]

$$\Delta G^0_{el.} = W = \frac{Ne^2}{2D}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{10}$$

where R_+ and R_- are the radii of the solvated ions and D is the dielectric constant of the medium [30,31]. Hence

$$\Delta G^0_{diss.} = \Delta G^0_{nonel.} + \frac{Ne^2}{2D}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{11}$$

Further, as $\Delta G^0_{diss.} = 2.303\,RTpK_a$ [30], the equation simplifies as

$$pK_a = \frac{\Delta G^0_{nonel.}}{2.303\,RT} + \frac{Ne^2}{4.606\,RTD}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{12}$$

Conventionally, pK_a is plotted against $1/D$ assuming $\Delta G^0_{nonel.}$ to be independent of the solvent. In general, linear relationships, particularly in
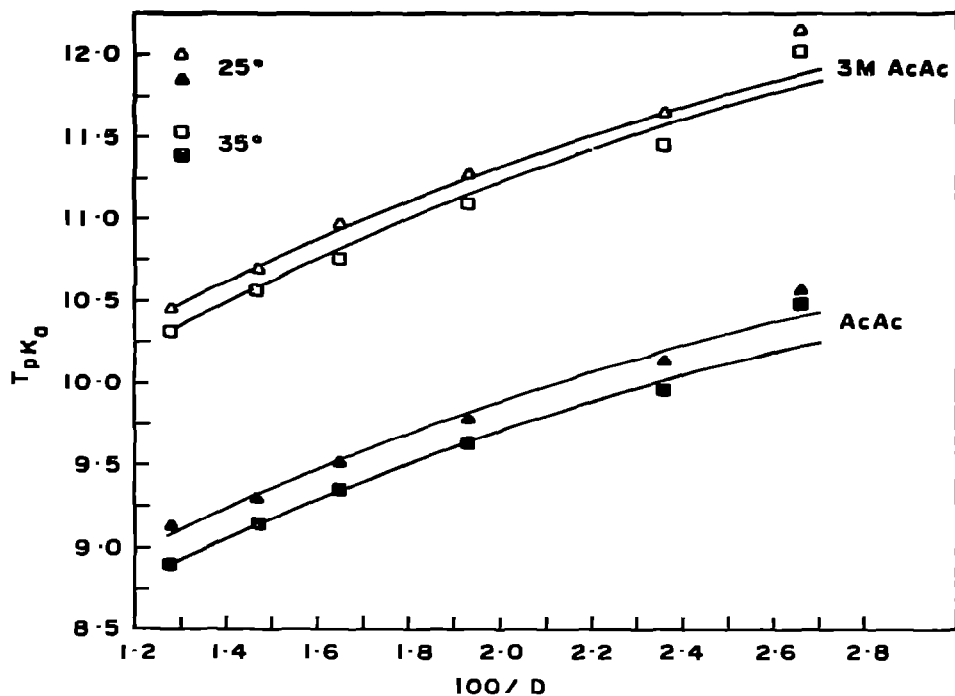
Fig. 2. Variation of $^{T}pK_a$ with the dielectric constant (D) of the medium.

the water-rich portions of the medium $(D > 30)$, are encountered [32—35], while instances of failure from linearity have also not been uncommon [36]. When the $^{T}pK_a$ values of the β-diketones are plotted against $1/D$, it is seen that the plots possess distinct curvature (Fig. 2). This points that nonelectrostatic factors exert a considerable influence in the acid dissociation of β-diketones.

Mole fraction of dioxane

For AcAc and 3M-AcAc the change in $^{T}pK_a$ with mole fraction of dioxane (n_2) is of considerable magnitude. Generally, the difference in $^{T}pK_a$ in aqueous medium $(n_2 = 0)$ and 50% aqueous dioxane $(n_2 = 0.174)$ is of the order of 2—3 $^{T}pK_a$ units. When the $^{T}pK_a$'s of these β-diketones are plotted against n_2, straight line relationships are encountered (Fig. 1). The experimental values of $^{T}pK_a$ here indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% in $^{T}pK_a$.

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

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

where $\bar{x}$ and $\bar{y}$ are the mean values of $x(^{T}pK_a)$ and $y(n_2)$, respectively. The summations are extended to all pairs (x, y) available. Linear proportionality is readily indicated between the two variables when the value of r is $+1.0$

[37]. The value of b, "regression coefficient" or actual slope of the lines, is finally given by

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

Since the value of r is approximately +1.0 at 25 and 35°C for both β-diketones (Table 3), it implies that there is quite a high probability of a linear relationship between $^{T}pK_a$ and n_2. A similar behaviour is found for several other acids such as benzoic, acetic, propionic and formic acids [38] and a number of β-diketones in aqueous dioxane [24,25]. Likewise, linear proportionality is also obtained for some other mixed water solvents, e.g. acetic, propionic, butyric and benzoic acids in methanol—water mixtures [39] and dimedone in ethanol—water [40].

It is of interest to compare the accuracy of the experimentally determined values of $^{T}pK_a$ of these β-diketones in aqueous media with the extrapolated values at zero dioxane concentration ($n_2 = 0$). The data given in Tables 1 and 2 show that there is excellent agreement in two sets of values, proving the validity of the extrapolation method for evaluating $^{T}pK_a$ of β-diketones in aqueous media.

Thermodynamic functions for acid dissociations

The $^{T}pK_a$ values have been determined with a precision of ±0.02 to ±0.03 and hence the error in ΔG^0 is believed to be close to ±0.03 and ±0.04 kcal mole^{-1}.

The temperature coefficient method employed here for the computation of ΔH^0 is subject to some error because (i) the enthalpy change associated with acid dissociation is relatively small, and (ii) the $^{T}pK_a$ at several temperatures has not been obtained which would otherwise have made it possible to follow a more accurate graphical method [41] for its computation. In this study an error of 0.01 in $^{T}pK_a$ determination causes an error of 0.42 kcal in ΔH^0, while the magnitude of error in $\Delta^{T}pK_a$ depends on the cancellation or addition of error of an individual set of $^{T}pK_a$'s determined at two temperatures.

Although the temperature coefficient method affords a value of ΔH^0 with relatively large errors, the thermodynamic parameters thus obtained are still of great significance for arriving at certain valuable conclusions. In any case, the positive value of ΔH^0 found in aqueous as well as aqueous dioxane mixtures for both β-diketones proves that their ionization at temperatures up to 35°C is endothermic. The positive value of ΔH^0 encountered here may be ascribed to the breakage of the covalent bond present in the enolic form of the β-diketones. Further, it is evident that the magnitude of change in ΔH^0 with solvent composition is relatively small and falls within the range of experimental error. It is because of this that the slopes of straight lines in the plots of $^{T}pK_a$ vs. n_2 (Fig. 1) do not differ markedly and are nearly the same and parallel at the two temperatures for these two β-diketones (Table 3).

In the light of the findings referred to above it is justifiable, as a first approximation, to assume that ΔH^0 is independent of solvent media at least

in the narrow range of the 0—0.174 mole fraction of dioxane. With this assumption, a fresh value of ΔH^0 for AcAc and 3M-AcAc was calculated. Numerically, it is equal to 42.06 times the difference in the intercepts of the parallel lines on the $^T pK_a$ axis (Fig. 1). Values of ΔH^0 thus calculated are given in Table 4, while the values computed at each n_2 are omitted for the reasons cited previously.

Values of ΔS^0 at different concentrations of dioxane are found to be essentially the same for both AcAc and 3M-AcAc, thereby proving that it is independent of solvent composition. At the outset, the negative value of ΔS^0 observed in the present work would appear surprising in view of the larger number of particles produced on the ionization of the β-diketones. However, each proton liberated on dissociation will be associated with four molecules of water [42] $(H_9O_4^+)$ and the negatively charged enolate ion will also be associated with an appreciable number of water molecules. It would, therefore, appear that the sum total of the number of water molecules "bound" is more than the water molecules originally accompanying the undissociated β-diketone. This probably gives rise to the large negative entropy observed here.

When the acid dissociates in two media, the free energy change for the transfer reaction from one medium to the other is given by $2.303\, RT\, \Delta^T pK_a$. For instance with AcAc, $\Delta G^0_{(aq.)}$ and $\Delta G^0_{(n_2=0.174)}$ are 12.46 and 14.37 kcal mol^{-1}, respectively, and ΔG^0 changes by 1.91 kcal mol^{-1} in the transfer reaction

$$HA_{(dioxane)} + H^+_{(aq.)} + A^-_{(aq.)} \rightleftharpoons HA_{(aq.)} + H^+_{(dioxane)} + A^-_{(dioxane)}$$
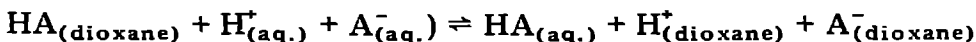
and this results in a change of 6.41 cal K^{-1} mol^{-1} in entropy.

$\Delta^T pK_a(S—W)$, i.e. $^T pK_a(S) - {}^T pK_a(W)$ (where "S" and "W" refer to mixed solvents and water, respectively) of AcAc and 3M-AcAc at 25 and 35°C are given in Table 5. The change in $^T pK_a(S—W)$ is found to be greater in 3M-AcAc than in AcAc for the same percentage of dioxane. Temperature change from 25 to 35°C has almost negligible effect on $\Delta^T pK_a(S—W)$ for either of these β-diketones. Small variations in $\Delta^T pK_a(S—W)$ in the range 0—0.174 mole fraction of dioxane for both AcAc and 3M-AcAc are likely to be due to the hydrogen bonding capability of these compounds.

TABLE 5

$\Delta^T pK_a(S—W) = {}^T pK_a(S) - {}^T pK_a(W)$

Dioxane (Vol. %)	Acetylacetone		3-Methylacetylacetone	
	25°C	35°C	25°C	35°C
10	0.15	0.19	0.25	0.24
20	0.37	0.37	0.53	0.45
30	0.59	0.64	0.81	0.78
40	1.00	0.99	1.20	1.13
50	1.40	1.52	1.74	1.70

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Substituent effect

The introduction of substituents into the molecule of an organic chelating agent often results in changes in the chelating ability of the proton or metal in addition to changes in other chemical and physical properties.

β-diketones in solution generally exist as equilibrium mixtures of the keto-enol forms. Values of $^T pK_a$ given in Tables 1 and 2 should, therefore, in principle refer to the twin processes of enolization and ionization of the β-diketones [43], viz.

$$K = [H^+][A^-]/[keto] + [enol]$$

The acid strength of these compounds is affected by the nature and structure of the substituent. Values of $^T pK_a$ for 3M-AcAc are consistently higher than those of AcAc in all solvent media. The positive inductive effect $(+I)$ of the $-CH_3$ group present in the former compound is responsible for the acid weakening effect, thereby decreasing its ionization, i.e. higher $^T pK_a$.

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