*Journal of Molecular Structure*, 161 (1987) 193—204
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

# β-DIKETONE INTERACTIONS

## Part 5. Solvent effects on the keto ⇋ enol equilibrium

JOHN EMSLEY* and NEVILLE J. FREEMAN
*Department of Chemistry, King's College, Strand, London WC2R 2LS (Great Britain)*

(Received 20 March 1987)

ABSTRACT

The keto ⇋ enol equilibrium of pentane-2,4-dione (PD) has been measured in 21 solvents at infinite dilution and a linear free energy relationship (LFER) tested against four solvent polarity vectors: $\epsilon$, $E_T$, $\pi^*$ and $A + B$. The best correlation coefficient is found for $A + B$. Similarly 3-methyl-pentane-2,4-dione (MePD) has been studied in 14 solvents and 3-ethylpentane-2,4-dione (EtPD) in six. The results suggest that the cyclic hydrogen bonding of the enol remains intact in all the solvents studied.

INTRODUCTION

The complexity of solvent—solute interactions is reflected in the variety of parameters devised to explain and predict the effects of solvents on spectra, reactions and equilibria. Polarity and protonicity are the two aspects of a solvent which are judged to be most important, and it is the former which has proved particularly difficult to quantify. The most commonly used, and directly measurable, polarity parameter is relative permittivity, $\epsilon$ (dielectric constant), and this has proved most enduring despite its limitations for solvents such as dioxan and ethanoic acid whose low $\epsilon$ values betray their solvent abilities.

Several alternatives to $\epsilon$ have been put forward. These include DN (donor numbers), based on Lewis basicities towards $SbCl_5$ [1]; $Y$ values based on rate constants [2—4]; $Z$ values based on the charge transfer absorption band of 1-ethyl-4-methoxycarbonyl-pyridinium iodide [5—7]; and $E_T$ values similarly based on the dye molecule pyridinium-*N*-phenol betaine [8, 9]. All these parameters are derived from a single physical property, but recently more complex relationships have been introduced which attempt to quantify both protonicity and polarity and combine them into a single solvent vector.

The best known approach is that of Kamlet and Taft [10, 11] which started out with three parameters, $\pi^*$ (polarity), $\alpha$ (hydrogen bond donor ability) and $\beta$ (hydrogen bond acceptor ability). The property being observed, $P_{obs}$, is related to the property out of solution, $P_0$, according to eqn. (1) where $s$, $a$ and $b$ are factors determined experimentally [10]

0022-2860/87/$03.50

$$P_{obs} = P_0 + s\pi^* + a\alpha + b\beta \tag{1}$$

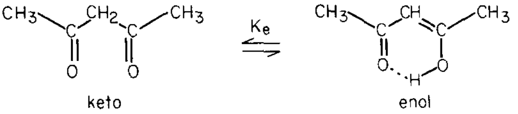
Later this equation was expanded to include a further three parameters with associated factors [11].

A similar approach has been advocated by Swain et al. [12] who criticised eqn. (1) on the grounds that $\pi^*$, $\alpha$ and $\beta$ were not independent variables. Instead they split polarity and protonicity between two variables $A$ (termed "acity") and $B$ ("basity") and used the relationship (2)

$$P_{obs} = P_0 + aA + bB \tag{2}$$

In this approach acity is related to hydrogen bond donor ability, anion solvation and nucleophilicity, and basity to hydrogen bond acceptor ability, cation solvation and electrophilicity. $A$ and $B$ were calculated for 61 solvents using data from 77 systems [12] and the solvent polarity vector is defined as $A + B$.

In our studies [13—15] of the hydrogen bonding of the enol tautomer of $\beta$-diketones such as pentane-2,4-dione (PD) we have been aware of the well-known sensitivity of the keto ⇋ enol equilibrium (3) to solvent.



(3)

Polar solvents favour the keto side of the equilibrium.

The anomalous behaviour of amine solvents, which were claimed to give 100% enol tautomer [16—19] has been explained as due to NMR limitations [14] and not to strong enol—amine hydrogen bonding. In studying these systems we made use of IR spectroscopy to analyse $\beta$-diketone concentrations. We have now extended these studies to other solvents and $\beta$-diketones, the object being to see if any solvent behaved anomalously and whether the percentage of enol tautomer could be closely related to one of the polarity parameters.

## EXPERIMENTAL

### *Instruments*

NMR spectra were run on a Bruker WM250 (250 MHz) spectrometer. IR spectra were run on a Perkin-Elmer 983G spectrometer using $BaF_2$ 0.1 mm cells.

### *Materials*

Pentane-2,4-dione (PD) was purified by the method of Fujinaga and Lee [20] and refluxed over $P_2O_5$ before use.

### *Synthesis of 3-methylpentane-2,4-dione (MePD) and 3-ethyl-pentane-2,4-dione (EtPD)*

PD (33 g, 0.33 mol), iodomethane (57 g, 0.4 mol) or iodoethane (62 g, 0.4 mol) and $K_2CO_3$ (42 g, 0.3 mol) were heated in refluxing acetone (70 $cm^3$) for 24 h. The products were extracted with 40—60 petroleum-ether, stripped of solvent on a rotary evaporator, and fractionally distilled to give MePD (30 g, 0.26 mol, 66% yield), b.p. 170°C or EtPD (36 g, 0.28 mol, 70% yield), b.p. 179°C.

### *Solvents*

(1) Cyclohexane (hereafter $C_6H_{12}$) was distilled and stored over Na wire; (2) carbon tetrachloride ($CCl_4$) was BDH Spectrosol grade, used as supplied; (3) 1,4-dioxane (dioxan) was purified according to the method in ref. 21; (4) triethylamine (TEA) was shaken with $CaH_2$, fractionally distilled, and stored over $CaH_2$; (5) propanoic acid (PA) was purified according to the method in ref. 22; (6) diethylether ($Et_2O$) was purified according to the method in ref. 21; (7) trichloromethane ($CHCl_3$) was distilled and stored over anhydrous $CaCl_2$; (8) ethanoic acid (AcOH) was purified according to the method in ref. 22; (9) $d_8$-tetrahydrofuran ($d_8$THF) and (10) dimethyl-diethylene glycol (diglyme) were purified according to the method in ref. 21; (11) ethanol (EtOH) and (12) methanol (MeOH) was James Burroughs plc analytical grade used as supplied; (13) $d_3$-nitromethane (NM) and (14) acetonitrile (AN) were Aldrich Gold Label, stored over 4A molecular sieves and used as supplied; (15) *N*,*N*-dimethylformamide (DMF) was shaken over 4A molecular sieves for seven days then fractionally distilled under reduced pressure; (16) *N*,*N*-dimethylacetamide (DMA) was shaken with BaO for five days then fractionally distilled under reduced pressure; (17) $d_6$-dimethylsulfoxide (DMSO) was shaken over 4A molecular sieves for seven days then fractionally distilled; (18) methanoic acid ($HCO_2H$) was purified according to the method in ref. 23; (19) propylene carbonate (PC) from Lancaster Synthesis Ltd was dried over 4A molecular sieves and used as supplied; (20) water ($H_2O$) was BDH Analytical grade; (21) formamide ($HCONH_2$) was dried over 3A molecular sieves for seven days then fractionally distilled; (22) benzene ($C_6H_6$) was distilled and stored over Na wire; (23) pyridine ($C_5H_5N$) was shaken with $CaH_2$, fractionally distilled and stored over $CaH_2$.

### *Method*

A solution of PD can be analysed for its tautomer composition by IR analysis provided its spectrum clearly displays the keto and enol carbonyl stretching modes at 1709 and 1618 $cm^{-1}$ respectively. The former band is the out-of-phase vibration of the keto form; the in-phase mode is at 1727 $cm^{-1}$ but less intense.

Accurate calibration is necessary if the IR method is to be used. Diglyme was chosen as the solvent for this purpose since NMR studies showed that

PD in this medium is constant in tautomer composition over a wide range of concentrations, unlike other solvents. Solutions of PD in diglyme (1—5% w/w) were left to attain tautomer equilibrium for several days at room temperature. Temperature equilibrium was assumed to have been reached after 4 h in the sample compartment of the IR spectrometer at 25°C.

Absorbance spectra gave linear plots of carbonyl absorbance versus mole fraction for both the enol and keto bands. The ratio of the slopes of these plots was 0.287 from which the percentage of enol tautomer is calculated to be 77.8 ± 0.8, in good agreement with the value of 79.6 ± 0.2% obtained by $^1$H NMR signal integration of the $CH_3$ resonances at $\delta$ 1.99 (enol) and 2.16 (keto).

The IR method assumes that enol and keto carbonyl bands have the same extinction coefficient. Calculation of these, using the $^1$H NMR results gave $\epsilon$(keto) = 724 ± 45 and $\epsilon$(enol) = 727 ± 24 dm$^3$ mol$^{-1}$ cm$^{-1}$.

Once the PD—diglyme system has been used to calibrate the concentration of the respective species against absorbance peak areas, the QUANT software package of the PE 983G spectrometer was used to determine the enol composition of those solvents which had a window in the IR spectrum above 1500 cm$^{-1}$. The results are shown in Table 1 where they are compared with those obtained by $^1$H NMR analysis.

The NMR results were obtained by serial dilution experiments. Solutions were made up and allowed to reach tautomer equilibrium over a period of days. Spectra were run on samples over the mole fraction range 0.25 and below. The average of several plots were used in order to compensate for the significant degree of variation observed with these systems. In some solvents the composition can be determined by the integration of both $CH_3$ (keto) and $CH_3$ (enol) resonances. A typical plot is shown in Fig. 1 for the middle polarity solvent DMF. The positive slope for this system is typical of most solvents but some have negative slopes (see Table 1, Gradients column).

Data in Table 1 was computed from percentage of enol determinations projected to infinite dilution using a simple weighted linear regression program, which was also used to obtain the correlation coefficients of Table 2. The data in this Table is based on the NMR results of Table 1 with the exceptions of TEA and DMSO whose IR data gives better correlations (see Discussion section). The plots of Figs. 2—5 show these correlation graphs for PD against the solvent parameters $\epsilon$ (Fig. 2), $E_T$ (Fig. 3), $\pi^*$ (Fig. 4) and $A + B$ (Fig. 5). Similarly for MePD the results are recorded in Tables 3 and 4 and for EtPD in Tables 5 and 6.

## DISCUSSION

IR was the original spectroscopic technique used in 1949 to study the keto $\leftrightharpoons$ enol equilibrium of ethyl acetoacetate [24]. Powling and Bernstein [25] extended the method to PD in various solvents and chose the concentration of 0.1 mol dm$^{-3}$ to express their results. However IR techniques were

TABLE 1

Solvents, polarity data, tautomeric composition and thermodynamic data for pentane-2,4-dione

| Solvent[a] | $\epsilon$[b] | $E_T$[c] | $\pi^*$[d] | $A + B$[e] | % enol (IR) | % enol (NMR) | Gradient[f] | $K_e$[g] | $-\Delta G$ (kJ mol$^{-1}$)[h] |
|---|---|---|---|---|---|---|---|---|---|
| 1. $C_6H_{12}$ | 2.0 | 30[i] | 0.00 | 0.09 | 97.7 (±0.2) | 97.0 (±1.2) | −37 | 32.3 | 8.99 |
| 2. $CCl_4$ | 2.2 | 32.5 | 0.28 | 0.43 | 96.8 (±0.3) | 94.6 (±0.3) | −14 | 17.5 | 7.40 |
| 3. dioxan | 2.2 | 36.0 | 0.55 | 0.86 | 82.6 (±0.3) | 82.4 (±0.4) | −23 | 4.68 | 3.99 |
| 4. TEA | 2.3 | n.a.[j] | 0.14 | 0.27 | 91.9 (±0.3) | [100][k] | +52 | 11.3[l] | 6.27[l] |
| 5. PA | 3.4 | n.a.[j] | n.a.[j] | n.a.[j] | —[m] | 73.0 (±0.8) | +53 | 2.70 | 2.57 |
| 6. $Et_2O$ | 4.2 | 34.6 | 0.27 | 0.46 | 96.1 (±0.1) | 91.9 (±0.2) | −19 | 10.1 | 5.98 |
| 7. $CHCl_3$ | 4.7 | 39.1 | 0.58 | 1.15 | 85.3 (±0.7) | 82.6 (±0.4) | −1 | 4.75 | 4.03 |
| 8. AcOH | 6.2 | n.a.[j] | 0.64 | 1.06 | —[m] | 73.4 (±0.2) | +14 | 2.76 | 2.62 |
| 9. THF-$d_8$ | 7.6 | 37.4 | 0.58 | 0.84 | 86.2 (±0.1) | 87.5 (±0.3) | −9 | 7.00 | 5.03 |
| 10. diglyme | n.a.[j] | n.a.[j] | 0.64 | n.a.[j] | 77.8 (±0.8) | 79.6 (±0.2) | 0 | 3.90 | 3.52 |
| 11. EtOH | 24.3 | 51.9 | 0.54 | 1.11 | 72.1 (±1.1) | 74.4 (±0.9) | +17 | 2.91 | 2.76 |
| 12. MeOH | 32.6 | 55.5 | 0.60 | 1.25 | 69.8 (±0.4) | 68.0 (±0.2) | +25 | 2.13 | 1.95 |
| 13. NM-$d_3$ | 35.9 | 46.3 | 0.85 | 1.31 | —[m] | 54.0 (±2.3) | +39 | 1.17 | 0.415 |
| 14. AN | 36.2 | 46.0 | 0.75 | 1.22 | 55.0 (±0.3) | 52.9 (±0.5) | +84 | 1.12 | 0.300 |
| 15. DMF | 36.7 | 43.8 | 0.88 | 1.23 | —[m] | 64.8 (±0.3) | +25 | 1.84 | 1.58 |
| 16. DMA | 37.8 | 41.0 | 0.88 | 1.23 | —[m] | 65.7 (±0.8) | +30 | 1.92 | 1.68 |
| 17. DMSO-$d_6$ | 46.7 | 45.0 | 1.00 | 1.41 | 43.0 (±0.5) | 57.4 (±0.7) | +74[l] | 0.763[l] | −0.710[l] |
| 18. $HCO_2H$ | 58.5 | n.a.[j] | n.a.[j] | 1.69 | —[m] | 40.1 (±0.6) | +91 | 0.669 | −1.42 |
| 19. PC | 65.1 | 46.6 | 0.83 | n.a.[j] | —[m] | 50.6 (±1.5) | +50 | 1.024 | 0.0621 |
| 20. $H_2O$ | 78.5 | 63.1 | 1.09 | 2.00 | —[m] | 12.9 (±0.4) | +267 | 0.148 | −4.94 |
| 21. $HCONH_2$ | 109.5 | 56.6 | 0.97 | 1.65 | —[m] | 32.5 (±0.9) | +86 | 0.481 | −1.90 |

[a] For full names see experimental. [b] Relative permittivity (dielectric constant), ref. J. A. Riddick and W. B. Bunger, Organic Solvents, Wiley-Interscience, New York, 1970. [c] Taken from C. Reichardt, Angew. Chem. Int. Edn. Engl., 4 (1965) 29. [d] Taken from M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, J. Org. Chem., 48 (1983) 2877. [e] See ref. 12. [f] Slope of plot of percentage enol versus mole fraction of PD. [g] $K_e$ = [enol]/[keto] based on NMR data. [h] From $K_e$ (NMR). [i] Estimated from $E_T(CCl_4) \times \epsilon(C_6H_2)/\epsilon(CCl_4)$. [j] Not available. [k] See ref. 14. [l] Based on IR data. [m] Unmeasureable.

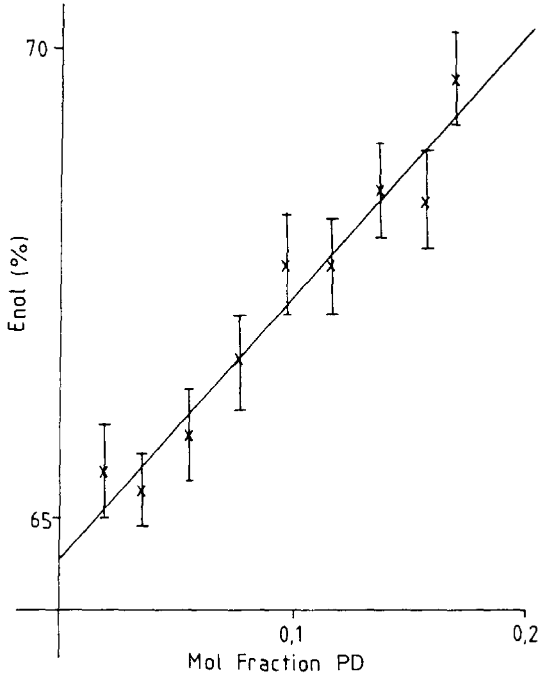


Fig. 1. Percentage of enol of PD versus mole fraction PD in DMF.

TABLE 2

LFER of $-\Delta G$ (kJ mol$^{-1}$) and polarity parameters ($S$) for PD: $-\Delta G = x + yS$

| Polarity parameter | $x$ | $y$ | Correlation coefficient |
|---|---|---|---|
| $\epsilon$ | 5.36 (±0.63) | −0.0982 (±0.0150) | +0.839 |
| $E_T$ | 18.58 (±0.83) | −0.368 (±0.050) | +0.890 |
| $\pi^*$ | 9.71 (±0.71) | −11.06 (±1.01) | +0.936 |
| $A + B$ | 10.13 (±0.54) | −7.08 (±0.46) | +0.968 |

rapidly superseded by NMR methods which has remained the method of choice ever since [16, 17, 26–28].

This was not always a change for the better. For instance studies of PD in TEA by NMR show no keto resonances under normal conditions, a fact that was invariably taken to mean that there was 100% enol present [16, 19]. However IR analysis reveals 8.2% keto [14]. Because of this difference we have returned to the quantitative IR method [29] as an independent measure of enol composition. Another advantage is that IR allows more dilute solutions to be measured giving points closer to the ordinate (infinite dilution). A disadvantage is that fewer solvents can be studied because of the prerequisite of a "window" in the 1600–1800 cm$^{-1}$ region.

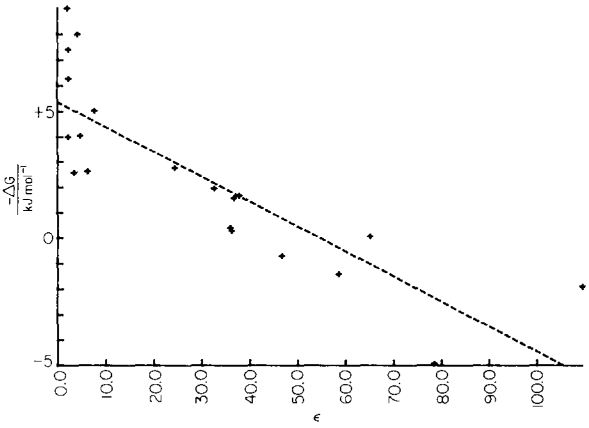


Fig. 2. LFER of $-\Delta G$ (keto ⇌ enol) versus $\epsilon$.

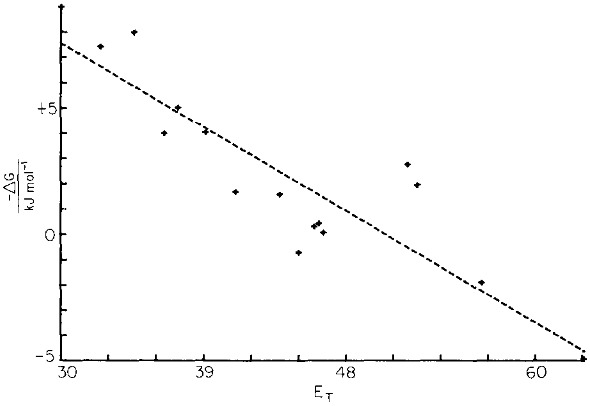


Fig. 3. LFER of $-\Delta G$ (keto ⇌ enol) versus $E_T$.

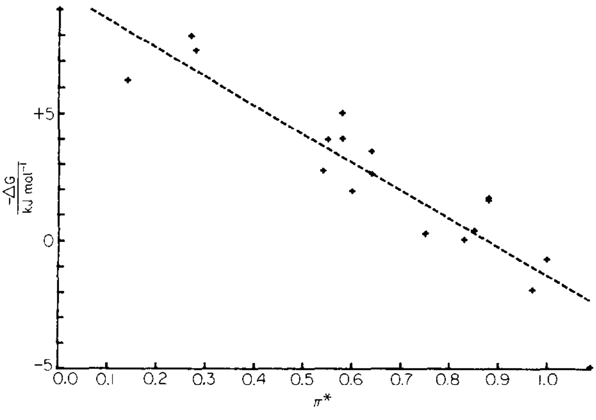


Fig. 4. LFER of $-\Delta G$ (keto ⇌ enol) versus $\pi^*$.

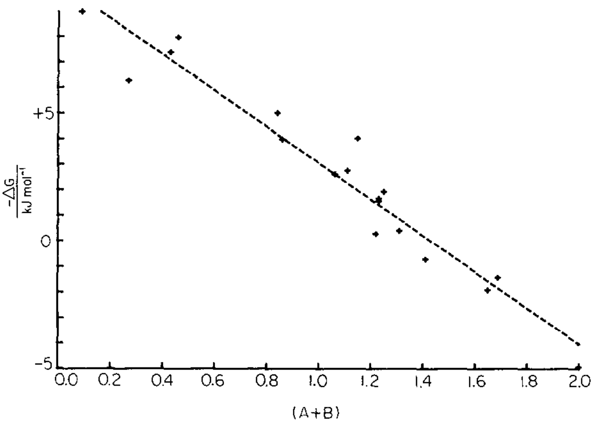


Fig. 5. LFER of $-\Delta G$ (keto ⇋ enol) versus $A + B$.

TABLE 3

Solvents, tautomeric composition and thermodynamic data for 3-methylpentane-2,4-dione

| Solvent[a] | | % Enol[b] | Gradient[c] | $K_e$[d] | $-\Delta G$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 2. | $CCl_4$ | 47.7 ± 1.3[e] | −72 | 0.912 | −0.238 |
| 3. | dioxan | 38.7 ± 1.1 | −140 | 0.631 | −1.191 |
| 6. | $Et_2O$ | 78.3 ± 2.5 | −532 | 3.608 | 3.318 |
| 7. | $CHCl_3$ | 34.7 ± 0.4 | +6 | 0.531 | −1.635 |
| 9. | THF-$d_8$ | 46.1 ± 6.3 | −109 | 0.855 | −0.404 |
| 10. | diglyme | 30.9 ± 0.7 | 0 | 0.447 | −2.081 |
| 11. | EtOH | 50.3 ± 4.3 | −774 | 1.012 | 0.031 |
| 12. | MeOH | 34.4 ± 1.6 | −590 | 0.524 | −1.669 |
| 17. | DMSO-$d_6$ | 18.0 ± 0.1[f] | +2 | 0.220 | −3.921 |
| 18. | $HCO_2H$ | 11.8 ± 0.5[g] | +29 | 0.134 | −5.198 |
| 20. | $H_2O$ | 3.1 ± 0.3[g] | +62 | 0.032 | −8.902 |
| 21. | $HCONH_2$ | 13.2 ± 0.2[g] | +12 | 0.152 | −4.870 |
| 22. | $C_6H_6$[h] | 45.0 ± 0.8[g] | −44 | 0.818 | 0.519 |
| 23. | $C_5H_5N$[i] | 33.6 ± 0.9[g] | −21 | 0.506 | −1.762 |

[a] For full names see experimental. [b] IR results unless otherwise indicated. [c] Slope of plot of percentage of enol versus mole fraction of 3-MePD. [d] $K_e$ = [enol]/[keto]. [e] NMR analysis gave 50.7 ± 0.5. [f] NMR results. IR gave 24.6 ± 0.9%. [g] NMR data. [h] Solvent parameters: $\epsilon$, 2.27%; $E_T$, 34.5; $\pi^*$, 0.59; $A + B$, 0.73. [i] Solvent parameters: $\epsilon$, 12.3; $E_T$, 40.2; $\pi^*$, 0.87; $A + B$, 1.20.

Table 1 for PD shows that for most solvents the IR method confirms the NMR data. Two solvents, TEA and DMSO, show disparate results, one of which TEA, has previously been explained [14]. The NMR signals of the DMSO solution were somewhat broad, probably due to its high vicosity, and consequently the IR-determined value has been preferred in calculating correlation coefficients for the various solvent parameters of Table 2.

TABLE 4

LFER of $-\Delta G$ (kJ mol$^{-1}$) and polarity parameters ($S$) for 3-methylpentane-2,4-dione: $-\Delta G = x + yS$

| Polarity parameter | $x$ | $y$ | Correlation coefficient |
|---|---|---|---|
| $\epsilon$ | 0.00 (±0.72) | −0.0699 (±0.0162) | +0.793 |
| $E_T$ | 8.19 (±1.03) | −0.299 (±0.062) | +0.762 |
| $\pi^*$ | 4.72 (±1.14) | −9.95 (±1.62) | +0.880 |
| $A + B$ | 4.62 (±0.94) | −5.89 (±0.77) | +0.918 |

TABLE 5

Solvents, tautomeric composition and thermodynamic data for 3-ethylpentane-2,4-dione

| Solvent[a] | | % enol[b] | Gradient[c] | $K_e$[d] | $-\Delta G$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 2. | $CCl_4$ | 46.7 ± 1.7 | −36 | 0.876 | −0.342 |
| 17. | DMSO-$d_6$ | 20.3 ± 1.2 | −11 | 0.254 | −3.54 |
| 18. | $HCO_2H$ | 4.1 ± 1.2 | +84 | 0.043 | −8.15 |
| 21. | $HCONH_2$ | 6.8 ± 2.9 | +84 | 0.073 | −6.77 |
| 22. | $C_6H_6$ | 42.6 ± 3.3 | −61 | 0.742 | −0.771 |
| 23. | $C_5H_5N$ | 28.8 ± 1.1 | −20 | 0.404 | −2.34 |

[a] For full names see experimental. [b] NMR results. [c] Slope of plot of percentage of enol versus mole fraction 3-EtPD. [d] $K_e$ = [enol]/[keto].

TABLE 6

LFER of $-\Delta G$(kJ mol$^{-1}$) and polarity parameters ($S$) for 3-ethylpentane-2,4-dione: $\Delta G = x + yS$

| Polarity parameter | $x$ | $y$ | Correlation coefficient |
|---|---|---|---|
| $\epsilon$ | −1.16 (±1.09) | −0.064 (±0.0020) | +0.849 |
| $E_T$ | 8.44 (±0.05) | −0.268 (±0.003) | +0.999 |
| $\pi^*$ | 2.20 (±2.38) | −6.68 (±3.01) | +0.788 |
| $A + B$ | 3.18 (±1.56) | −5.76 (±1.23) | +0.920 |

Substitution of an alkyl group on the middle carbon of PD favours the keto tautomer. In the pure compounds the percentage of enol is 29 for MePD and 26 for EtPD [28, 30]; solvent studies on these β-diketones have not been reported to date. The affects of various solvents are given in Tables 3 and 5, and although there are spectral limitations which reduce the range of systems that can be studied, it can be seen that they follow the same trends as PD. For EtPD only NMR data was obtainable.

### *Infinite dilution*

The results in Tables 1, 3 and 5 are calculated for extrapolation to infinite dilution. Previous workers with PD have used merely dilute solutions [28, 31, 32] as an approximation. The effect of dilution on the keto $\rightleftharpoons$ enol equilibrium has not been reported in detail except in one instance [7] where extrapolation has been over a large distance from the ordinate.

For low polarity solvents the percentage of enol increases with dilution, but for the more polar solvents it decreases with dilution. This we believe is as a consequence of the solute's polarity and its effect on the medium. Neat PD has $\epsilon = 25.7$ and it is seen that in general solvents of lower $\epsilon$ have a negative gradient and those of higher $\epsilon$ show a positive gradient for percentage of enol versus mole fraction enol. Yet there are exceptions to this generality, e.g. TEA, PA, AcOH and, possibly, EtOH.

The observation that diglyme does not have a gradient implies that its polarity is the same as PD itself. Unfortunately a value of $\epsilon$ values for diglyme cannot be found in the literature, but about 26 would seem likely in view of its nature. For MePD and EtPD the gradients are also in line with PD except that some anomalously large deviations occur for $Et_2O$, EtOH and MeOH with MePD. Why these systems are so sensitive to concentration cannot be explained.

Linear free energy relationships of $-\Delta G$ ($=RT\ln K_e$) and four parameters which claim to measure solvent polarity have been tested: $\epsilon$, $E_T$, $\pi^*$ and $A + B$. The numerical values of these parameters are listed in Table 1. Tables 1, 3 and 5 also give $K_e$ and $\Delta G$ which are calculated from the measured percentage of enol at infinite dilution. Tables 2, 4 and 6 give the results of LFERs for the $-\Delta G$ and polarity scales (4), calculated using the linear regression program.

$$\Delta G = x + yS \ (S = \text{solvent parameter}) \qquad (4)$$

Table 2 for PD shows that the highest correlation coefficient is obtained for Swain's [12] $A + B$ scale. Since the solvent effect of the keto $\rightleftharpoons$ enol equilibrium of PD was not one of the systems used in constructing any of these solvent scales, it can be used as an independent assessment of their ability to measure "polarity". Table 4 for MePD also shows $A + B$ as the best guide but in Table 6 EtPD shows a perfect correlation with $E_T$, albeit on a much narrower range of data.

Because of the good correlation with polarity we are tempted to conclude that none of these solvents behaves anomalously with PD, MePD or EtPD insofar as the keto $\rightleftharpoons$ enol equilibrium at infinite dilution is concerned. There is no good evidence that the solvents weight either side of the equilibrium by hydrogen bonding more favourable with the keto or enol tautomers. Previous assessments of the strength of the hydrogen bonding in the enol ring of PD of 75 KJ $mol^{-1}$ [14] would tend to rule out enol—solvent hydrogen bonding unless this were really strong.

Spencer et al. [32] explained the deviations from linearity of their percentage of enol versus the Onsager—Kirkwood solvent parameter [33, 34] as being due to PD—solvent interactions. This deviation is however probably simply a reflection of the inadequacy of the model. The other example, in PD—TEA, in which it was assumed that enol—hydrogen bonding was responsible [16—18] has been shown to be an artefact of the method of measurement [4]. We are thus led to conclude that there is no special solvent interaction with either side of the keto $\rightleftharpoons$ enol equilibrium in any solvent so far studied, and that the point of balance is influenced solely by the polarity of the medium.

### *Water*

This solvent is often anomalous in its behaviour and with its propensity to hydrogen bond this might be expected to deviate most. However recalculating the correlation coefficients of Table 2 with the $H_2O$ data omitted gave slightly poorer results: +0.8 ($\epsilon$); +0.86 ($E_T$) and +0.96 ($A + B$). For $\pi^*$ the correlation was marginally better, +0.93. Clearly $H_2O$ is no different from the other solvents.

Inspection of Fig. 4 shows three solvents that deviate most from the DG versus $A + B$ graph: TEA, $CHCl_3$ and AN. The first of these has already been mentioned. $CHCl_3$ is notoriously difficult to purify and Swain et al. [12] acknowledged the fact. Indeed their $A + B$ value of 1.15 is notably high for such a solvent. Assuming this to be the case then our $\Delta G$ value can be used to recalculate a better value for $A + B$ ($CHCl_3$) and gives 0.87. Whether this reduction is due to $A$ (0.42) or $B$ (0.73) being originally overestimated cannot be decided. AN too is difficult to purify, and applying the same criterion to reassess its $A + B$ value gives 1.40, slightly more polar than the 1.22 normally quoted.* Excluding these three solvents from the analysis gives a correlation coefficient of 0.990 for $-\Delta G$ versus $A + B$.

### *Other polarity parameters*

The Onsager—Kirkwood parameter [33, 34], $(\epsilon - 1)e/(2\epsilon + 1)M_R$ where $e$ = density and $M_R$ = relative molecular mass, showed no LFER with $-\Delta G$. Other parameters tested were DN, $Y$-values, and Brownstein's $S$ numbers [35] but no correlation was observed. Kamlet and Taft's [10, 11] $\alpha$ and $\beta$ terms were also checked but gave no correlation, nor did Swain's [12] $A$ and $B$ quantities when considered separately. The absence of a LFER relationship with these would support there being no strong hydrogen bonding component to the solvation of $\beta$-diketone tautomers. The keto $\rightleftharpoons$ enol equilibrium of PD, MePD and EtPD appears to be influenced only by solvent polarity.

---

*By the same token the $A + B$ values missing from Table 1 can also be computed: PA = 1.08 (cf. AcOH = 1.06), diglyme = 0.94 and PC = 1.44.

## ACKNOWLEDGEMENT

We thank Conoco for a grant (to N. J. F.) and K. Spiers for the linear regression program.

## REFERENCES

1 V. Gutman, Coordination Chemistry in Non-aqueous Solutions, Springer-Verlag, Berlin, 1968.
2 E. Grundwald and S. Winstein, J. Am. Chem. Soc., 70 (1948) 846.
3 S. Winstein, E. Grunwald and H. W. Jones, J. Am. Chem. Soc., 73 (1951) 2700.
4 A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78 (1956) 2770.
5 E. M. Kosower, J. Am. Chem. Soc., 80 (1958) 3253.
6 E. M. Kosower, Molecular Biochemistry, McGraw-Hill, London, 1962 p. 180.
7 E. M. Kosower, J. Chem. Phys., 61 (1964) 230.
8 K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, Liebig Ann. Chem., 661 (1983) 1.
9 K. Dimroth, C. Reichardt and A. Schweig, Liebig Ann. Chem., 669 (1963) 95.
10 M. J. Kamlet and R. W. Taft, J. Am. Chem. Soc., 98 (1976) 337, 2886.
11 R. W. Taft, M. H. Abrahams, R. M. Doherty and M. J. Kamlet, J. Am. Chem. Soc., 107 (1985) 3105.
12 C. G. Swain, M. S. Swain, A. L. Powell and S. Alunni, J. Am. Chem. Soc., 105 (1983) 502.
13 J. Emsley, N. J. Freeman, R. J. Parker, H. M. Dawes and M. B. Hursthouse, J. Chem. Soc. Perkin Trans. I, (1986) 471.
14 J. Emsley, N. J. Freeman, R. J. Parker and R. E. Overill, J. Chem. Soc. Perkin Trans. II, (1986) 1479.
15 J. Emsley, N. J. Freeman, P. Bates and M. B. Hursthouse, J. Mol. Struct., 161 (1987) 181.
16 L. W. Reeves, Can. J. Chem., 35 (1957) 1351.
17 L. W. Reeves and W. G. Schneider, Can. J. Chem., 36 (1958) 793.
18 T. K. Leipert, Org. Mag. Reson., 9 (1977) 157.
19 M. Raban and G. Yamamoto, J. Org. Chem., 42 (1977) 2549.
20 T. Fujinaga and H. L. Lee, Talanta, 24 (1977) 395.
21 A. I. Vogel, Textbook of Practical Organic Chemistry, 4th edn., Longmans, London, 1976 p. 264.
22 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, 2nd edn., Pergamon Press, Oxford, 1980.
23 K. J. P. Orton and A. E. Bradfield, J. Chem. Soc., (1927) 983.
24 R. J. W. Le Fevre and M. Welsh, J. Chem. Soc., (1949) 2230.
25 J. Powling and H. J. Bernstein, J. Am. Chem. Soc., 73 (1951) 2353.
26 J. L. Burdett and M. T. Rogers, J. Am. Chem. Soc., 86 (1964) 2105.
27 M. T. Rogers and J. L. Burdett, Can. J. Chem., 43 (1965) 1516.
28 G. Allen and R. A. Dwek, J. Chem. Soc. B, (1966) 161.
29 N. S. Isaacs, Experiments in Physical Organic Chemistry, Macmillan, New York, 1969 p. 132.
30 Yu. N. Mollin, S. T. Yoffe, E. E. Zaev, E. K. Solov'eva, E. E. Kuchneva, V. V. Voevodskii and M. I. Kabachnik, Izv. Akad. Nauk. SSSR, Ser. Khim., (1965) 1556.
31 D. W. Thompson and A. L. Allred, J. Phys. Chem., 73 (1971) 433.
32 J. N. Spencer, E. S. Holmboe, M. R. Kirshenbaum, D. W. Frith and P. B. Pinto, Can. J. Chem., 60 (1982) 1178.
33 L. Onsager, J. Am. Chem. Soc., 58 (1936) 1486.
34 J. G. Kirkwood, J. Chem. Phys., 2 (1934) 351.
35 S. Brownstein, Can. J. Chem., 38 (1960) 1590.