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COMPLETE THERMODYNAMIC ANALYSIS OF THE IONIZATION OF ANISIC ACID IN WATER–DIMETHYLSULPHOXIDE MIXTURES AT 25°C

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ABSTRACT

The ionization and solution enthalpies of *para*-methoxybenzoic (anisic) acid have been measured in H_2O–DMSO mixtures. In the same solutions, the ΔG^0 values for the ionization process have been determined by potentiometric measurements. A study of the enthalpic and entropic contributions to substituent and reaction constant effects, and the proton transfer process from the methoxy derivative to benzoic acid, compared with the same process in the gaseous phase, is also presented.

INTRODUCTION

The ionization of benzoic acid and phenol derivatives in H_2O–DMSO mixtures has been the subject of extended research in this laboratory [1–4]. For the same compounds the enthalpic and entropic contributions to substituent and reaction effects and the proton transfer process from the derivatives to benzoic acid compared with the same process in the gaseous phase have been studied [5–7].

Thus, a sufficiently complete picture of the solute–solvent interactions has been obtained. In the present work, the behaviour of *para*-methoxybenzoic (anisic) acid has been examined. The methoxy group (R^+I^-), as well as the hydroxyl group (R^+I^-), in the *para* position shows a large electron-releasing resonance effect. The difference in behaviour between the two groups can be related to the different degree of resonance.

EXPERIMENTAL AND PROCEDURE

The calorimetric measurements were performed by means of (a) a Tronac 450 titration calorimeter, and (b) an L.K.B. 8721-1 reaction and solution calorimeter.

DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot and Butler [8]. DMSO–H_2O mixtures were prepared by weighing purified DMSO and CO_2-free, twice distilled water. The mole fraction of DMSO in these mixtures ranged from 0.1 to 0.8. Aqueous solutions of 0.98 M HCl and 0.098 M NaOH were prepared from standard solutions and their concentrations were checked by potentiometric titrations.

The *p*-methoxybenzoic acid (K and K) was purified by crystallization from water–ether mixtures and its melting point checked before use. The $NaBzO_s$ solutions (where the subscript indicates the substituted acid) were prepared by adding a NaOH solution of known molarity to the *p*-methoxybenzoic acid dissolved in the mixed solvent. As a result of this addition, 100 g of the DMSO–water solution at X' mole fraction were obtained. The concentrations of the sodium salt were always in the range 2×10^{-3}–4×10^{-4} m. An amount of acid, about 4–5% of the original content, was not converted to the salt and remained as free acid to avoid the presence of free alkali.

The ionization process in $HBzO_s$ of the various H_2O–DMSO mixtures of X mole fraction can be represented as

$$(HBzO_s)_X \rightarrow (H^+)_X + (BzO_s^-)_X \qquad (1)$$

The molar enthalpy of ionization, $\Delta\bar{H}_1$, of $HBzO_s$ was obtained by experimental measurement of (a) the molar enthalpy of reaction, $\Delta\bar{H}_2$, of $NaBzO_s$ dissolved in the mixed solvent of X' mole fraction, with 0.98 M HCl

$$(BzO_s^-)_{X'} + (Na^+)_{X'} + (H^+)_{aq.} + (Cl^-)_{aq.} \rightarrow (HBzO_s)_X + (Na^+)_X + (Cl^-)_X \qquad (2)$$

(b) the molar enthalpy of solution, $\Delta\bar{H}_3$, of the same amount of 0.98 M HCl in the same solvent mixture at X' mole fraction

$$(H^+)_{aq.} + (Cl^-)_{aq.} \rightarrow (H^+)_X + (Cl^-)_X \qquad (3)$$

From the dissociation constants of water [9] and *p*-methoxybenzoic acid (this work), it can also be inferred that the salt undergoes very little hydrolysis ($\beta < 0.02\%$). Therefore, it is not necessary to correct the experimental $\Delta\bar{H}_2$ values for hydrolysis.

The molar enthalpy process (1) can be obtained [1–4] by subtracting the two values $\Delta\bar{H}_3$ and $\Delta\bar{H}_2$ and by adding to this difference the $\Delta\bar{H}_4$ values related to the molar transfer enthalpy of $NaBzO_s$ (at infinite dilution) from solvent X' to solvent X, viz.

$$(BzO_s^-)_{X'} + (Na^+)_{X'} \rightarrow (BzO_s^-)_X + (Na^+)_X \qquad (4)$$

It should be noted that the difference ($X' - X$) turns out to be very small for each couple. In the most unfavourable case, it was 2×10^{-4} m when the DMSO final mole fraction was 0.8. The thermal effect of process (4) was calculated using the data obtained in this work. For every one of the water–DMSO mixtures at X_{DMSO} mole fraction, the $\Delta\overline{H}_1$ values refer to the ionization of 1 mole of $HBzO_s$ dissolved at infinite dilution in 1000 g of the mixed solvent, yielding 1 mole of BzO_s^- ions solvated in the same amount of the solvent. In order to refer process (1) to only one initial thermodynamic state, the solution enthalpies of the crystalline *p*-methoxybenzoic acid $\Delta\overline{H}_s$ in the various solvent mixtures were measured

$$HBzO_{s(\text{cryst.})} \rightarrow (HBzO_s)_X \tag{5}$$

so that $\Delta\overline{H}_6 = \Delta\overline{H}_5 + \Delta\overline{H}_1$ values obtained for the process

$$HBzO_{\text{cryst.}} \rightarrow (H^+)_X + (BzO_s^-)_X \tag{6}$$

refer to an identical initial thermodynamic state.

In processes (1) and (5), concentrations ranging from 2×10^{-3} to 4×10^{-4} m were used. Therefore the $\Delta\overline{H}$ values related to these processes were assumed to be equal to the ΔH^0 values [10]. All the measurements were carried out at 25°C, the average thermal jump in the cell during the experiments being about 2×10^{-2}°C.

The ionization constants of the *p*-methoxybenzoic acid at 25°C, in the various mixtures, have been obtained from EMF measurements of the cell

$$\text{Ag, AgCl}|HBzO_{s(m_1)},\ NaBzO_{s(m_2)},\ NaCl_{(m_3)}|\text{Glass electrode}$$

Potential measurements were made with an Orion 801 digital pH meter; an Orion 91-01-00 glass electrode was used. Details of the potentiometric measurements and the technique for obtaining the pK_a values have been described previously [11,12]. The pK_a values obtained from potentiometric measurements were used to calculate ΔG^0.

The initial standard state, to which ΔG^0 values of ionization refer, is defined as an ideal 1 m solution of $HBzO_s$ behaving as an infinitely dilute solution. $T\Delta S^0$ values were calculated using the Gibbs–Helmholtz equation. Again, a study of the enthalpic and entropic contributions to substituent effects was considered worthwhile. The effect of the medium on the substituent and reaction constants was explained in terms of solute–solvent interactions and structure-breaking effect.

According to Hammett [13] and others [14,15], the following may be written

$$(CH_3O\text{–}PhCOOH)_X + (PhCOO^-)_X = (CH_3O\text{–}PhCOO^-)_X + (PhCOOH)_X \tag{7}$$

$$-\delta\Delta G^0 = 2.303RT\rho\sigma \tag{8}$$

where X (ranging from 0.0 to 0.8) is the mole fraction of the solvent. The ρ and σ values are affected in different ways by the variation of the solvent composition.

Using experimental ionization values of benzoic [16] and *para*-methoxybenzoic acid (this work) the standard enthalpy change for eqn. (7) is obtained as

$$\delta\Delta H^0 = \Delta H^0_{\mathrm{CH_3OPhCOOH}} - \Delta H^0_{\mathrm{PhCOOH}}$$

in the same way, the $\delta\Delta G^0$ and $\delta\Delta S^0$ values related to process (7) can be obtained.

By separating substituent effects into enthalpic and entropic contributions [17] eqn. (7) may be written in the form

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_{\mathrm{H}}\sigma_{\mathrm{H}} + \rho_{\mathrm{S}}\sigma_{\mathrm{S}} \tag{9}$$

$\rho_{\mathrm{H}}\sigma_{\mathrm{H}}$ and $\rho_{\mathrm{S}}\sigma_{\mathrm{S}}$ being defined by the relations

$$\rho_{\mathrm{H}}\sigma_{\mathrm{H}} = -\frac{\delta\Delta H^0}{2.303RT} \tag{10a}$$

$$\rho_{\mathrm{S}}\sigma_{\mathrm{S}} = \frac{\delta\Delta S^0}{2.303R} \tag{10b}$$

The ρ, ρ_{H} and ρ_{S} values are assumed equal to 1 in water at 25°C and 1 atm.

Finally, the proton transfer process from *para*-methoxybenzoic acid to benzoic acid in water–DMSO mixtures in comparison with the same process in the gaseous phase has been examined. A thermodynamic cycle allows calculation of a proton transfer process in a solvent x, referring to a gaseous initial state [18–21], i.e. $\delta\Delta P_{\mathrm{i}}^{g\to x}$. These thermodynamic quantities have been assumed to be a measure of "external" solute–solvent interactions. The thermodynamic cycle used to calculate the "external" interactions employs benzoic acid as reference

$$\begin{array}{ccccccc}
\mathrm{CH_3O{-}PhCOOH_{(g)}} & + \mathrm{PhCOO^-(g)} & \overset{\delta\Delta P_{\mathrm{i(g)}}}{\rightarrow} & \mathrm{CH_3OPhCOO^-_{(g)}} & + \mathrm{PhCOOH_{(g)}} \\
\downarrow \Delta P_{\mathrm{S}} & \downarrow \Delta P_{\mathrm{S}} & & \downarrow \Delta P_{\mathrm{S}} & \downarrow \Delta P_{\mathrm{S}} \\
(\mathrm{CH_3O{-}PhCOOH})_X & + (\mathrm{PhCOO^-})_X & \overset{\delta\Delta P_{\mathrm{i(x)}}}{\rightarrow} & (\mathrm{CH_3OPhCOO^-})_X & + (\mathrm{PhCOOH})_X
\end{array}$$

where $\delta\Delta P_{\mathrm{i(g)}}$ is the gas-phase change of some thermodynamic properties ($P_{\mathrm{i}} = \mathrm{G, H, S}$), for the proton transfer process, and $\delta\Delta P_{\mathrm{i(x)}}$ is the corresponding values in solvent x. Thus, this can be written

$$\delta\Delta P_{\mathrm{i(x)}} - \delta\Delta P_{\mathrm{i(g)}} = \delta\Delta P_{\mathrm{s}}^{g\to x} \tag{11}$$

the right-hand term of eqn. (11) being assumed as the proton transfer, in solvent x, which refers to a gaseous initial thermodynamic state, so that

$$\delta\Delta P_{\mathrm{s}}^{g\to x} = \delta\Delta P_{i}^{g\to x}.$$

Again, according to Hepler [22], in eqn. (11) the solvent effects (external) can be separated from the intrinsic molecular effects (internal). We assume $\delta\Delta P_{\mathrm{i(x)}}$ to be the "overall" interactions, $\delta\Delta P_{\mathrm{i(g)}}$ are the "internal" interactions and $\delta\Delta P_{\mathrm{i}}^{g\to x}$ the "external" interactions.

Using the values of McMahon and Kebarle [23], it is possible to calculate the $\delta\Delta G_{i(g)}$ values for *p*-methoxybenzoic acid. The $\delta\Delta G_{i(g)}$ and $\delta\Delta G_{i(x)}$ values (this work) are included in eqn. (11) and the $\delta\Delta G_i^{g\to x}$ values are calculated.

It is well known [24] that both the "external" and "internal" rotations in the half-process $HA_1 \to A_1^-$ occurring in the gaseous phase are responsible for the loss of entropy in the equation

$$HA_1 + A_2^- = A_1^- + HA_2$$

so that $\delta\Delta S_i \neq 0$.

However, for reactions such as those considered here, symmetry numbers are small and almost cancel out. So, if we put [24] $\delta\Delta S_1 \simeq 0$, then $\delta\Delta G_{i(g)}$ (600 K) $\simeq \delta\Delta G_{i(g)}$ (298 K) $= \delta\Delta H_{i(g)}$ and it is possible to calculate $\delta\Delta H_i^{g\to x}$ and $T\delta\Delta S_i^{g\to x}$ at 298 K.

RESULTS AND DISCUSSION

Table 1 shows the ΔG^0, ΔH^0 and $T\Delta S^0$ values of process (1) obtained for *para*-methoxybenzoic acid.

For the ΔH^0 values, each number reported for process (1) is the difference between an average of at least six values relative to process (2) and a similar average for process (3); the standard deviations are indicated next to the tabulated values. The average standard deviation of the pK_a values is 0.02 pK unit; the corresponding accuracy for the ΔG^0 values is ±28 cal. Table 2 shows the enthalpy values of processes (5) and (6).

For comparison, it is convenient to express the ionization enthalpy as the difference between the values obtained in the mixed solvent of X mole

TABLE 1

Free energy, enthalpy and entropy values of the ionization of *p*-methoxybenzoic acid in DMSO–water solutions of various mole fractions at 25°C (all thermodynamic quantities are given in kcal mole^{-1})

X_{DMSO}	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$
0.0	6.09 ± 0.03	0.60 ± 0.01	-5.49 ± 0.03
0.1	6.26 ± 0.03	0.91 ± 0.02	-5.35 ± 0.04
0.2	7.57 ± 0.03	2.58 ± 0.02	-4.30 ± 0.04
0.3	8.62 ± 0.03	4.89 ± 0.03	-3.74 ± 0.04
0.4	9.56 ± 0.03	7.23 ± 0.02	-2.33 ± 0.04
0.5	9.88 ± 0.03	10.08 ± 0.04	0.20 ± 0.05
0.6	10.97 ± 0.03	12.76 ± 0.03	1.79 ± 0.04
0.7	12.17 ± 0.03	14.13 ± 0.05	1.96 ± 0.06
0.8	13.10 ± 0.03	13.60 ± 0.04	0.50 ± 0.05

TABLE 2

Enthalpy values of solution ΔH_5^0 and process (6) for *p*-methoxybenzoic acid in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_5^0 (kcal mole^{-1})	ΔH_6^0 (kcal mole^{-1})
0.0	7.91±0.02	8.51±0.03
0.1	7.99±0.02	8.90±0.02
0.2	7.30±0.01	9.88±0.02
0.3	6.84±0.02	11.73±0.03
0.4	6.50±0.01	13.73±0.04
0.5	5.86±0.01	15.94±0.03
0.6	5.42±0.01	18.18±0.01
0.7	4.77±0.01	18.89±0.02
0.8	3.55±0.01	17.15±0.03

fraction and in pure water so that $\delta\Delta H_1^0=(\Delta H_1^0)_X-(\Delta H_1^0)_{X=0}$. In a similar way the values of $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ can be defined and calculated. These three values are relative to the transfer of the ionization process, while the $\delta\Delta H_5^0$ and $\delta\Delta H_6^0$ values represent the transfer enthalpy of the undissociated molecules, and the two ions H^+ and BzO_s^-, respectively, from pure water to mixed solvent. All these data are plotted against X_{DMSO} in Fig. 1.

The $\delta\Delta H^0$, $\delta\Delta G^0$ and $\delta\Delta S^0$ values of reaction (7) for methoxybenzoic acid are included in eqns. (8), (10a) and (10b) and the values of $\rho\sigma$, $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are reported in Table 3.

It is possible to calculate the σ values using the $\rho_{p,m}$ values [25] for the dissociation of benzoic acids at various mole fractions (see Table 4). The *para*-methoxy derivative shows negative σ values throughout the mole fraction range. This was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect. We observe that the σ values (Table 4 and Fig. 2) are greatly affected by the solvent composition in the 0.2–0.45 molar fraction range. Thus we believe that [17]

$$\sigma=0.91\sigma_S-0.07 \tag{12}$$

and eqn. (10b) give an approximate trend for σ_S (Table 4 and Fig. 2) and ρ_S (Table 4 and Fig. 3) in the above-mentioned mole fractions.

The substituents with negative values exhibit an "abnormal" enthalpy–entropy relationship and so σ_H can not be calculated. In order to assess the relative contributions of enthalpy and entropy to the substituent effects the following equations are used

$$f_H=\frac{|\sigma_H|}{|\sigma_H|+|\sigma_S|} \qquad f_s=\frac{|\sigma_S|}{|\sigma_S|+|\sigma_H|}$$

For the *p*-methoxy derivative the enthalpic contribution $f_H=0.79$ prevails.

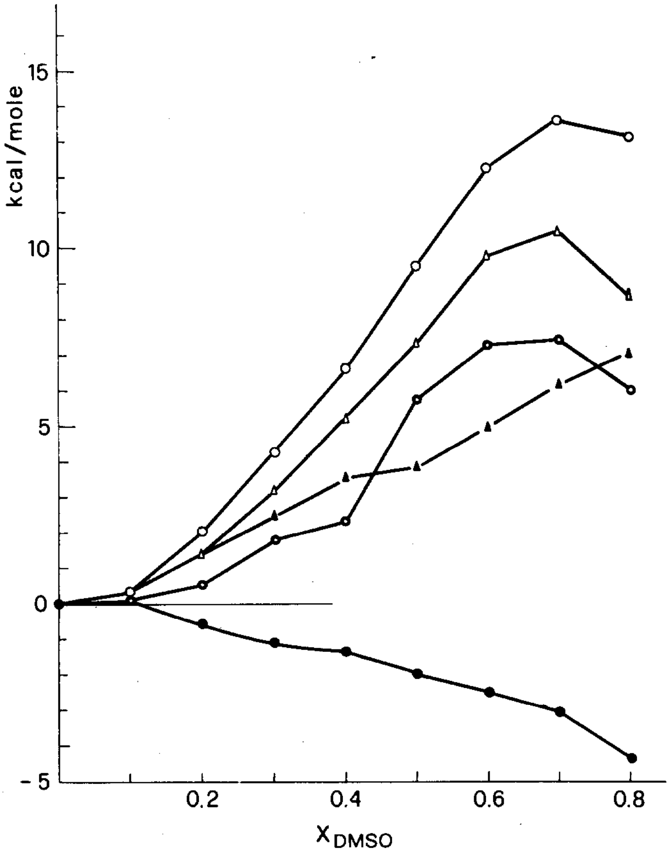


Fig. 1. Thermodynamic quantities for the transfer of *p*-methoxybenzoic acid from pure water to DMSO–water mixtures as a function of mole fraction at 25°C. ○, $\delta\Delta H_1^0$; △, $\delta\Delta H_6^0$; **O**, $T\delta\Delta S_1^0$; ▲, $\delta\Delta G_1^0$; ●, $\delta\Delta H_5^0$.

TABLE 3

Results of the application of the normal Hammett equation and separate enthalpy–entropy equations to the ionization of *p*-methoxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	−0.260	−0.366	0.087
0.1	0.078	0.316	0.396
0.2	−0.339	1.003	0.662
0.3	−0.464	2.202	1.737
0.4	−0.465	3.520	3.055
0.5	−0.006	4.910	4.903
0.6	−0.125	6.930	6.808
0.7	−0.315	7.210	6.895
0.8	−0.466	5.51	7.050

TABLE 4

σ Values calculated using the Hammett equation, and σ_S and ρ_S values calculated using entropic equations for *p*-methoxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	σ	σ_S	ρ_S
0.0	−0.260	0.087	1
0.1	0.064	0.147	2.694
0.2	−0.250	−0.198	−3.343
0.3	−0.299	−0.252	−6.893
0.4	−0.284	−0.235	−13.000
0.5	−0.003	0.074	
0.6	−0.066	0.004	
0.7	−0.153	−0.091	−75.76
0.8	−0.154	−0.092	−52.33

This clearly shows that the resonance contribution to the substituent effect is large. $\delta\Delta G_i^{g\to x}$, $\delta\Delta H_i^{g\to x}$ and $T\delta\Delta S_i^{g\to x}$ are reported in Table 5 and are plotted against DMSO mole fraction in Fig. 4, which represents the "external" interactions of the proton transfer with the medium.

If it is assumed that the inductive and field effects are the same for the hydroxy and methoxy derivatives, $\sigma_{p(OH)} - \sigma_{p(CH_3O)}$ should be a measure of the difference of the resonance effect for the two derivatives as the content of DMSO increases (Table 6 and Fig. 5). At $X_{DMSO} = 0.5$ where the solution displays the maximum structure breaking effect, this difference shows a maximum. The difference in the resonance can be confirmed by the dif-

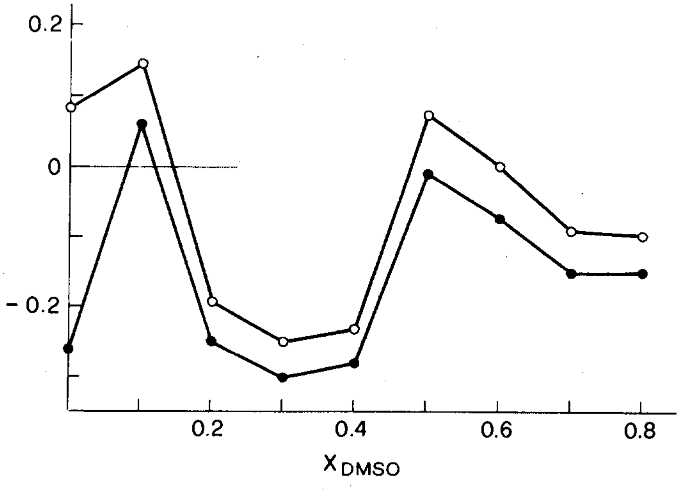


Fig. 2. Variation of the σ and σ_S values for *p*-methoxybenzoic acid as a function of the mole fraction at 25°C. ○, σ_S; ●, σ.

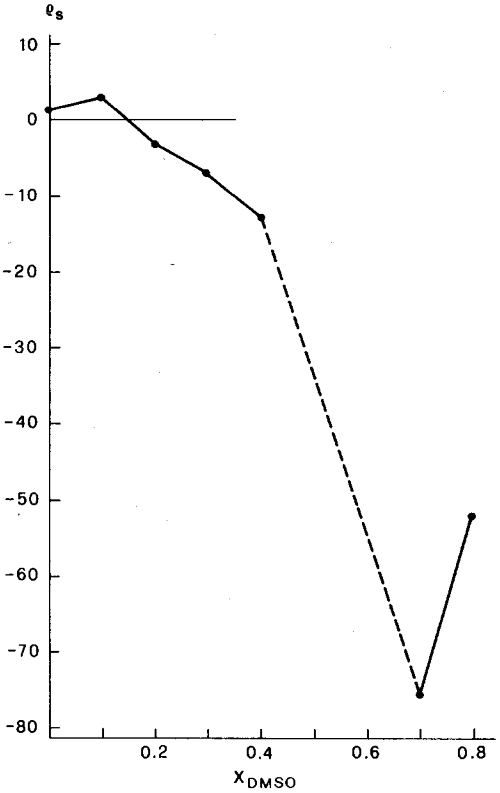


Fig. 3. Variation of the ρ_S values for *p*-methoxybenzoic acid as a function of mole fraction at 25°C.

TABLE 5

Free energy, enthalpy and entropy for the proton transfer process of *p*-methoxybenzoic acid in water–DMSO mixtures calculated by assuming a gaseous initial thermodynamic state

X_{DMSO}	$\delta\Delta G_i^{g\to x}$	$\delta\Delta H_i^{g\to x}$	$T\delta\Delta S_i^{g\to x}$
0.0	−0.45	−0.30	0.15
0.1	−0.91	−0.40	0.51
0.2	−0.34	0.57	0.91
0.3	−0.17	2.21	2.38
0.4	−0.17	4.61	4.78
0.5	−0.80	5.90	6.70
0.6	−0.63	8.66	9.29
0.7	−0.37	9.03	9.37
0.8	−0.19	6.72	6.91

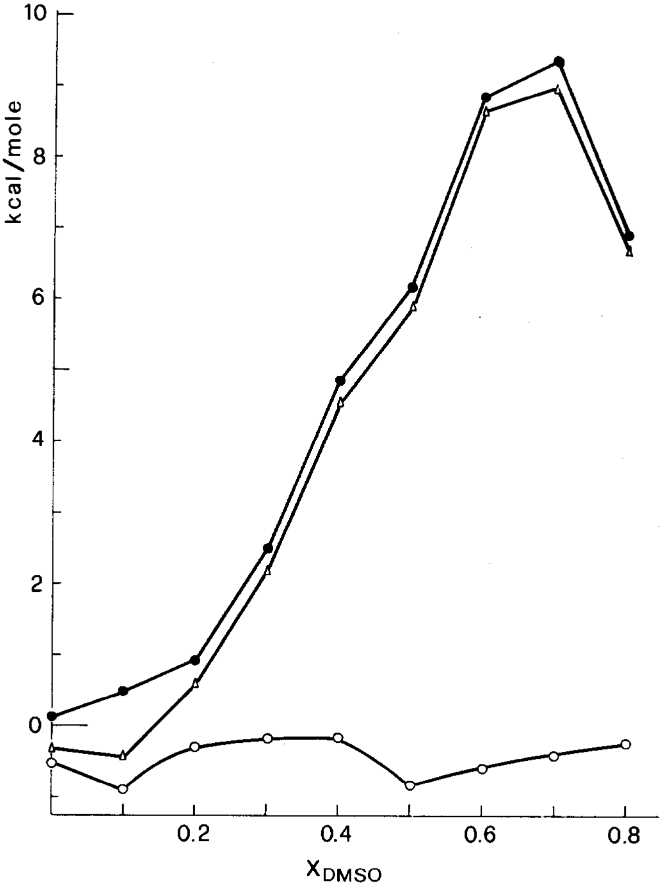


Fig. 4. Thermodynamic quantities for the proton transfer process of *p*-methoxybenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as reference. ●, $T\delta\Delta S_i^{g\to x}$; △, $\delta\Delta H_i^{g\to x}$; ○, $\delta\Delta G_i^{g\to x}$.

TABLE 6

Variation of the difference of the resonance effect $\sigma_{p(\mathrm{OH})} - \sigma_{p(\mathrm{CH_3O})}$ as a function of mole fraction at 25°C

X_{DMSO}	$\sigma_{p(\mathrm{OH})} - \sigma_{p(\mathrm{CH_3O})}$
0.0	−0.121
0.1	−0.414
0.2	−0.113
0.3	−0.139
0.4	−0.047
0.5	−0.661
0.6	−0.310
0.7	−0.220
0.8	−0.145

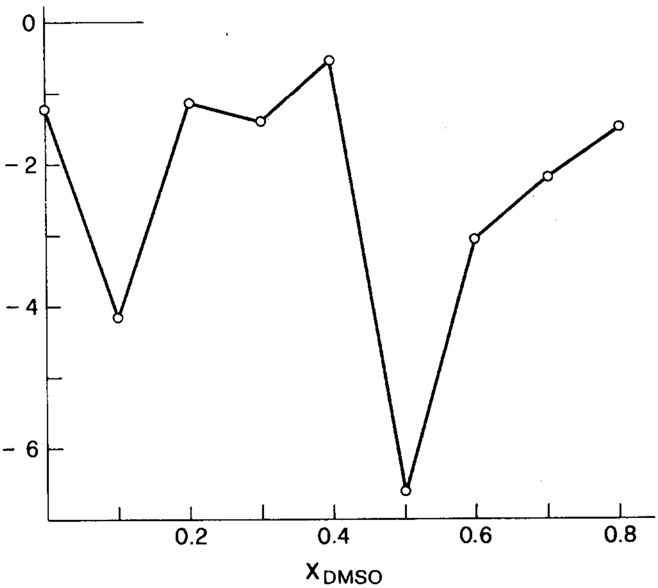


Fig. 5. Variation of the difference of the resonance effect $\sigma_{P_{(OH)}} - \sigma_{P(CH_3O)}$ as a function of mole fraction.

ference in solvation enthalpy between the hydroxy and methoxy compounds. The difference in solvation enthalpy between the anions was calculated as

$$\Delta \overline{H}_{(pCH_3OBzO^-)_x-(pOHBzO^-)_x} = \delta\Delta H^0_{6(pCH_3OHBzO)} - \delta\Delta H^0_{6(pOHHBzO)} + \Delta \overline{H}_{(pCH_3OBzO^-)_{aq.}-(OHBzO^-)_{aq.}} \tag{13}$$

while the difference in solvation enthalpy between the undissociated molecules is

$$\Delta \overline{H}_{(CH_3OHBzO)_x-(OHHBzO)_x} = \delta\Delta H^0_{5(pCH_3OHBzO)} - \delta\Delta H^0_{5(pOHHBzO)} + \Delta \overline{H}_{(pCH_3OHBzO)_{aq.}-(pOHHBzO)_{aq.}} \tag{14}$$

The last term on the right-hand sides of eqns. (13) and (14) was arbitrarily assumed to be equal to zero and the resulting $\Delta \overline{H}_{(pCH_3OBzO^-)_x-(pOHBzO^-)_x}$ and $\Delta \overline{H}_{(pCH_3OHBzO)_x-(pOHHBzO)_x}$ are plotted in Fig. 6 as a function of the solvent composition. These values are supposed to closely approach the true values [2].

For the methoxy and hydroxy derivatives the order of transfer both for the molecules and the anions is p-OH $>$ p-CH_3O in the whole mole fraction range, with the exception of the interval 0.1–0.35 for the anions.

Beyond $X_{DMSO} = 0.5$ the dipolar structure (I) can interact with the dipole of the DMSO molecules but to a lesser extent than the dipolar structure of

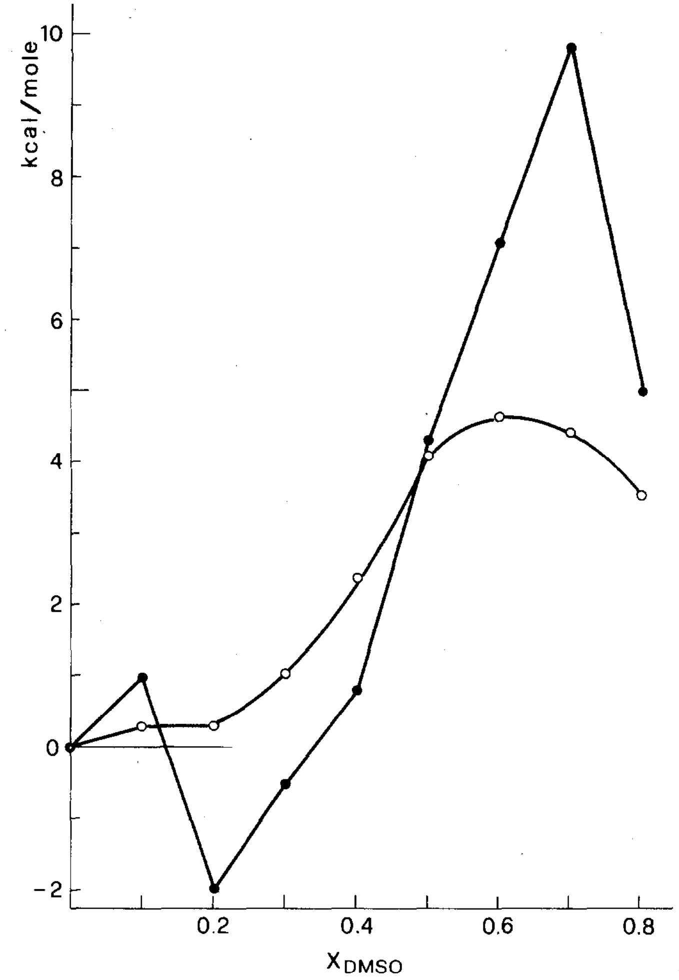
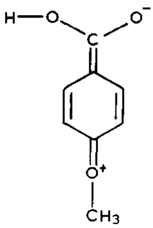


Fig. 6. Differences in the solvation enthalpy between the anions and the undissociated molecules of the hydroxy and methoxy derivatives in various DMSO–water solutions. The differences in the hydration enthalpy both between the anion couple and the undissociated molecule couple are arbitrarily set equal to zero. ●, $\Delta\bar{H}_{p\mathrm{CH_3OBzO^-}-p\mathrm{OHBzO^-}}$; ○, $\Delta\bar{H}_{p\mathrm{CH_3OHBzO}-p\mathrm{OHHBzO}}$.

the hydroxy derivative.



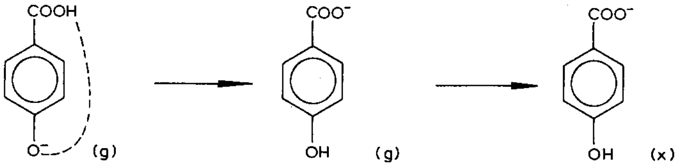
(I)

For the anions the hydroxyl group in the *para* position attracts the negative charge of the carboxylate group more weakly than the methoxy group because of the greater resonance. For this reason, the *para* hydroxy anion interacts with the solution molecules to a greater extent than the methoxy anion.

In the plot of ρ_S vs. X_{DMSO} (Fig. 3) the dotted line represents a hypothetical trend for those values of ρ_S which are most uncertain because of the greater influence of the solvent. It is also interesting to compare the ρ_S values with the $T\delta\Delta S_i^{g\to x}$ term. The last curve is very close (but symmetrical) to that of the reaction constants ρ_S because of the negative values of σ, which, in turn, make the ρ_S values negative too.

It can be observed that the $T\delta\Delta S_i^{g\to x}$ values confirm the trend of the ρ_S values. Moreover, the negative ρ_S values of *p*-methoxybenzoic acid increase as the H_2O content decreases more markedly than the ρ_S values of the *p*-hydroxy derivative [7]. This can be related to a larger desolvation showed (Fig. 6) by the molecules and the anions of the methoxy derivative.

Finally, the most favourable $\delta\Delta P_i^{g\to x}$ terms for the *p*-methoxy isomer in the solution from the gas phase can be explained by the absence of the intramolecular transfer process. Indeed the *p*-hydroxy derivative [21] in the gas phase behaves as phenol, thus in the $\delta\Delta P_i^{g\to x}$ terms the intramolecular proton transfer process must be included



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