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COMPLETE THERMODYNAMIC ANALYSIS OF THE IONIZATION OF *ORTHO*-METHOXYBENZOIC ACID. INFLUENCE OF THE MEDIUM ON THE *ORTHO* EFFECTS

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ABSTRACT

The ionization and solution enthalpies of *o*-methoxybenzoic 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 *ortho* effects by means of a linear combination of the ordinary polar, proximity polar, and steric effects was also performed. The CH_3O group seems to undergo a partial steric inhibition of resonance. Finally, the proton transfer process from the *ortho* derivative to benzoic acid, compared with the same process in the gaseous phase, is presented.

INTRODUCTION

The ionization and solution enthalpies of *p*-methoxybenzoic acid have been measured in water–dimethylsulfoxide(DMSO) mixtures [1]. 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, are also presented. Thus, a sufficiently complete thermodynamic analysis of the ionization of the above compound in water–DMSO mixtures at 25°C has been carried out.

In the present work the behaviour of *o*-methoxybenzoic acid is examined. The methoxy group in the *ortho* position shows the so-called *ortho* effect. It

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is interesting to ascertain if the equation used for the nitro, chloro [2], and hydroxy [3] *ortho* isomers also holds true for the *o*-methoxy compound.

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 [4], 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 0.0 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 *o*-methoxybenzoic acid (K and K) was purified by crystallization from water–ether mixtures and its melting point checked before use. The CH_3O–PhCOONa solutions were prepared by adding a NaOH solution of known molarity to the *o*-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^{-4}–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 of $Ch_3OPhCOOH$ in the various H_2O–DMSO mixtures of X mole fraction can be represented as

$$(CH_3OPhCOOH)_X \rightarrow (CH_3OPhCOO^-)_X + (H^+)_X \tag{1}$$

The molar enthalpy of ionization, $\Delta\bar{H}_1$, of $CH_3OPhCOOH$ was obtained by experimental measurement of:

(a) the molar enthalpy of reaction, $\Delta\bar{H}_2$, of $CH_3OPhCOONa$ dissolved in the mixed solvent of X' mole fraction, with 0.98 M HCl

$$(CH_3OPhCOO^-)_{X'} + (Na^+)_{X'} + (H^+)_{aq.} + (Cl^-)_{aq.} \rightarrow (CH_3OPhCOOH)_X + (Na^+)_X + (Cl^-)_X \tag{2}$$

(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

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

From the dissociation constants of water [5] and *o*-methoxybenzoic acid (this work) it can also be inferred that the salt undergoes very little hydrolysis ($\beta < 0.014\%$). 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] by subtracting the two values $\Delta\overline{H}_3$ and $\Delta\overline{H}_2$ and by adding to this difference the $\Delta\overline{H}_4$ values related to the molar transfer enthalpy of $CH_3OPhCOONa$ (at infinite dilution) from solvent X' to solvent X, viz.

$$(CH_3OPhCOO^-)_{X'} + (Na^-)_{X'} \rightarrow (CH_3PhCOO^-)_X + (Na^+)_X \tag{4}$$

It should be noted that the difference $(X' - X)$ turns out to be very small for each couple. In the most unfavorable case, it was 2×10^{-4} 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 each of the water–DMSO mixtures at x mole fraction, the $\Delta\overline{H}_1$ values refer to the ionization of 1 mole of $CH_3OPhCOOH$ dissolved at infinite dilution in 1000 g of the mixed solvent yielding 1 mole of protons and 1 mole of $CH_3OPhCOO^-$ ions solvated in the same amount of solvent. In order to refer process (1) to only one initial thermodynamic state, the solution enthalpies of the crystalline *o*-methoxybenzoic acid, $\Delta\overline{H}_S$, in the various solvent mixtures were measured

$$(CH_3OPhCOOH)_{cryst.} \rightarrow (CH_3OPhCOOH)_X \tag{5}$$

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

$$(CH_3OPhCOOH)_{cryst.} \rightarrow (H^+)_X + (CH_3OPhCOO^-)_X \tag{6}$$

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 ΔH^0 values [6]. All these 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 *o*-methoxybenzoic acid at 25°C, in the various mixtures, have been obtained from EMF measurements of the cell

$$\text{Ag, AgCl}|CH_3OPhCOOH_{(m_1)}, CH_3OPhCOONa_{(m_2)},$$

$$NaCl_{(m_3)}|\text{glass electrode}$$

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 $pK_{a/1}$ values have been described previously [5,7]. The $pK_{a/1}$ values obtained from potentiometric measurements were used to calculate ΔG^0. The initial thermodynamic state, to which ΔG^0 values of ionization refer, is defined as an ideal 1 m solution of $CH_3OPhCOOH$ behaving as an infinitely diluted solution. $T\Delta S^0$ values were calculated using the Gibbs–Helmholtz equation.

Again a study of the *ortho* effects and the entropic contribution to substituent effects was considered worthwhile. The effects of the medium on the substituent and reaction constants were explained in terms of solute–solvent interactions and a structure-breaking effect. The total *ortho* substituent effect can be expressed [2,3] in terms of the ordinary polar, proximity polar and steric effects, according to the equations

$$(\mathrm{CH_3OPhCOOH})_X + (\mathrm{PhCOO^-})_X = (\mathrm{CH_3OPhCOO^-})_X + (\mathrm{PhCOOH})_X \qquad (7)$$

$$-\frac{\delta\Delta G^0}{2.303\,RT} = \rho_o\sigma_o + fF^0 + \delta E_s^0 \qquad (8)$$

The ordinary polar effect would be imaginary [2,3] from *ortho* substituents without the proximity polar and steric effects. The ordinary polar effect is equal, by definition, to that of *para*-substituents, so that $\sigma_o \equiv \sigma_p$. The proximity polar effect, F^0, would account for the inductive and field effects. The steric effect would include the space-filling factor of the *ortho* substituent (primary steric effect) with a consequent steric hindrance to solvation for the functional group (E_s).

The secondary steric effect, such as steric inhibition of resonance in the substituent or the side-chain functional group, or both, significantly modifies the resonance effect of the *ortho* substituents. The extent of the resonance inhibition seems to depend on the steric dimension of the *ortho* substituents. If the secondary steric effect is significant in the substituent group, the σ_o values may be modified [2,3] as a function of the resonance inhibition. Equation (8) may also be written as [2,3]

$$-\frac{\delta\Delta G^0}{2.303\,RT} = \rho_H\sigma_H + \rho_s\sigma_s + fF^0 + \delta E_s^0 \qquad (9)$$

$\rho_H\sigma_H$ and $\rho_s\sigma_s$ being defined by the relations

$$-\frac{\delta\Delta H^0}{2.303\,RT} = \rho_H\sigma_H + \delta E_s^0 \qquad (9a)$$

$$\frac{\delta\Delta S^0}{2.303R} = \rho_s\sigma_s + fF^0 \qquad (9b)$$

The ρ_0, ρ_s and ρ_H values are assumed to be equal to 1 in water at 25°C and 1 atm. As previously shown [2,3] fF^0 values influence the entropic term while E_s values are related to the enthalpic term.

Finally, the proton transfer process from *ortho*-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 solvent x, referring to a gaseous initial state [8–11], i.e. $\delta\Delta P_i^{g\rightarrow x}$. 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

$$\begin{tikzcd}
\mathrm{CH_3OPhCOOH_{(g)}} \arrow[d, "\Delta P_s"] & + \mathrm{PhCOO^-_{(g)}} \arrow[d, "\Delta P_s"] \arrow[r, "\delta\Delta P_{i(g)}"] & \mathrm{CH_3OPhCOO^-_{(g)}} \arrow[d, "\Delta P_s"] & + \mathrm{PhCOOH_{(g)}} \arrow[d, "\Delta P_s"] \\
(\mathrm{CH_3OPhCOOH})_X & + (\mathrm{PhCOO^-})_X \arrow[r, "\delta\Delta P_{i(x)}"] & (\mathrm{CH_3OPhCOO^-})_X & + (\mathrm{PhCOOH})_X
\end{tikzcd}$$

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

$$\delta\Delta P_{i(x)} - \delta\Delta P_{i(g)} = \delta\Delta P_s^{g\to x} \qquad (10)$$

the right-hand term of eqn. [10] being assumed as the proton transfer, in solvent x, which refers to a gaseous initial thermodynamic state, so that

$$\delta\Delta P_s^{g\to x} = \delta\Delta P_i^{g\to x}$$

Again, according to Hepler [12] in eqn. (10) the solvent effects (external) can be separated from the intrinsic molecular effects (internal). We assume $\delta\Delta P_{i(x)}$ to be the "overall" interactions, $\delta\Delta P_i^{g\to x}$ are the "external" interactions, and $\delta\Delta P_{i(g)}$ are the "internal" ones. Using the values of McMahon and Kebarle [13], it is possible to calculate the $\delta\Delta G_{i(g)}$ values for *o*-methoxybenzoic acid. The $\delta\Delta G_{i(g)}$ and $\delta\Delta G_{i(x)}$ values (this work) are included in eqn. (10) and the $\delta\Delta G_i^{g\to x}$ values are calculated.

It is well known [14] that both the "external" and "internal" rotations in the half-process $HA_1 \rightarrow A_1^-$ 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 [13] $\delta\Delta S_i = 0$, then $\delta\Delta G_{i(g)}(600\ \text{K}) = \delta\Delta G_{i(g)}(298\ \text{K}) = \delta\Delta H_{i(g)}(298\ \text{K})$ 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 *ortho*-methoxybenzoic acid. 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 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 $CH_3OPhCOO^-$, respectively, from pure water to the mixed solvent. All these data are plotted against X_{DMSO} in Fig. 1, from which one may gather that in the $0 \leq X_{DMSO} \leq 0.4$ range desolvation plays a very important role both for the undissociated molecule and for the anion of the *o*-methoxybenzoic acid.

Using experimental ionization values for benzoic [7,15] and *o*-methoxybenzoic acid (this work), the standard free energy for reaction [8] is obtained

TABLE 1

Free energy, enthalpy and entropy values of the ionization of *o*-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^0	ΔH^0	$T\Delta S^0$
0.0	5.53	0.05	−5.48
0.1	6.48	0.84	−5.64
0.2	7.41	2.53	−4.88
0.3	8.38	4.81	−3.57
0.4	9.29	7.38	−1.91
0.5	10.25	9.95	−0.30
0.6	11.53	12.20	0.67
0.7	12.18	13.85	1.67
0.8	12.85	14.59	1.74

TABLE 2

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

X_{DMSO}	ΔH_5^0 (kcal $mole^{-1}$)	ΔH_6^0 (kcal $mole^{-1}$)
0.0	5.42	5.47
0.1	7.59	8.43
0.2	7.45	9.98
0.3	6.50	11.31
0.4	5.42	12.80
0.5	4.50	14.45
0.6	3.84	16.04
0.7	3.48	17.33
0.8	3.40	17.99

TABLE 3

Values of σ_o^1 calculated using eqn. (8) for *o*-methoxybenzoic acid and $\sigma_o^1 - \sigma_p$ values in water–DMSO mixtures at 25°C

X_{DMSO}	σ_o^1	$\sigma_o^1 - \sigma_p$
0.0	−0.472	−0.212
0.1	−0.535	−0.599
0.2	−0.489	−0.239
0.3	−0.461	−0.162
0.4	−0.421	−0.137
0.5	−0.409	−0.406
0.6	−0.526	−0.460
0.7	−0.380	−0.227
0.8	−0.329	−0.175

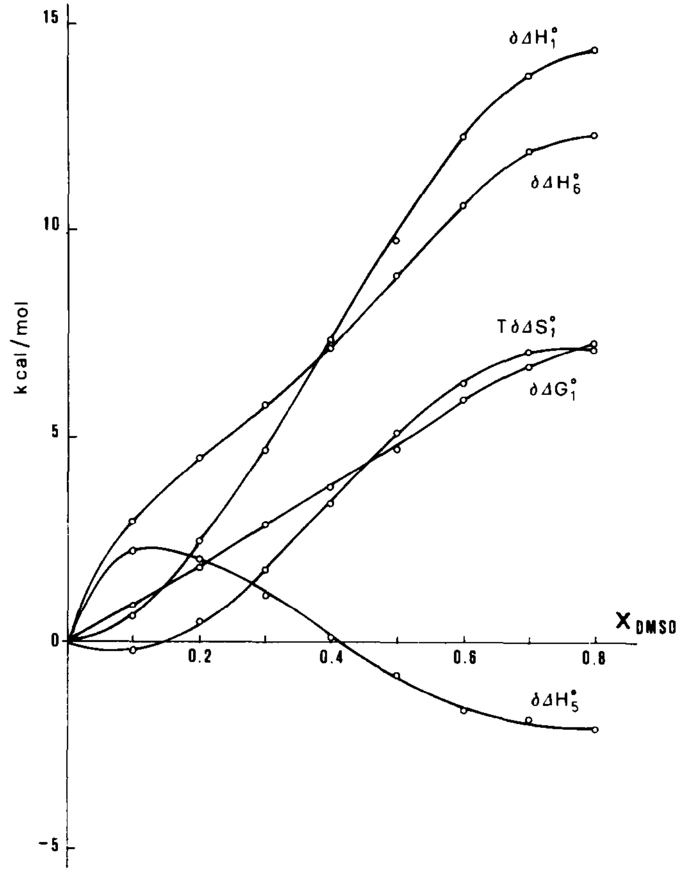

Fig. 1. Thermodynamic quantities for the transfer of *o*-methoxybenzoic acid from pure water to DMSO–water mixtures as a function of mole fraction at 25°C.

as $\delta\Delta G^0 = \Delta G^0_{\mathrm{CH_3OPhCOOH}} - \Delta G^0_{\mathrm{PhCOOH}}$. In the same way, the $\delta\Delta H_1^0$ and $\delta\Delta S^0$ values related to eqns. (9a) and (9b) can be obtained.

The ρ_0, f, F^0 and E_s^0 values for the dissociation of the *o*-benzoic acids in water–DMSO mixtures are reported in the literature [16]. If the above values are included in eqn. (9), σ_o^1 values are found in the same scale as σ_m and σ_p (Table 3).

It has to be remarked that for the chloro and nitro derivatives the σ_o^1 values [2] are very close to to the respective σ_p values [17,18]. Thus for these derivatives, the hypothesis, that the ordinary polar effect is equal to the *para* effect ($\sigma_o \simeq \sigma_p$) may be considered as valid. On the contrary, for *o*-hydroxybenzoic acid an additional term related to the internal hydrogen bond was included in eqn. (9) so that a better approximation for substituent constant values ($\sigma_o^2 \cong \sigma_p$) was found.

It is also known [19] that in water hydrogen bonding of the solvent to the

$-OCH_3$ group would contrast formation of the chelate structure and would modify the inductive and field effects of $-OCH_3$ on the $-COOH$ group. Therefore the hydration could increase the bulk of $-OCH_3$ to such a degree as to cause steric inhibition of resonance of $-COOH$ and $-OCH_3$ itself with the benzene ring.

If we assume that the secondary steric effect only occurs in the substituent group, then the $\sigma_o^1 - \sigma_p$ (Table 3) difference can be considered as a measure of steric inhibition of resonance and can be included in eqn. (9) as an additional term

$$-\frac{\delta\Delta G^0}{2.303\,RT} = \rho_o\sigma_o^2 + fF^0 + \delta E_s^0 + \sigma_o^1 - \sigma_p \qquad (11)$$

Thus a better approximation for the substituent constant values σ_o^2 (Table 4) was found.

It is interesting to note that eqn. (11) is consistent with the hypothesis that the ordinary polar effect is equal for *para* and *ortho* derivatives ($\sigma_o^2 = \sigma_p$). The σ_o^2 values lie on the same scale as σ_p and display a limited dependence on the medium effect. Thus, it seems reasonable to assume that the equation tested in water [20], viz. $\sigma = 0.91\sigma_s - 0.07$, which was used [17,18] for σ_p values over the whole mole fraction range, is also valid for σ_0^2 values. The σ_s values of *o*-methoxybenzoic acid (Table 5) are included in eqn. (9b) and the ρ_s values were also calculated (Table 5) and plotted against X_{DMSO} (Fig. 2).

The *o*-methoxy derivative shows negative σ_s values throughout the mole fraction range. This was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect. Thus it seems resonable to conclude that the $-CH_3O$ group undergoes a partial steric inhibition of resonance.

If one assumes that the inductive and field effects are the same for the hydroxy and methoxy derivatives, $\sigma_{o(OH)}^2 - \sigma_{o(CH_3O)}^2$ should be a measure of

TABLE 4

Values of σ_o^2 calculated using eqn. (11) for *o*-methoxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	σ_o^2
0.0	−0.248
0.1	−0.036
0.2	−0.309
0.3	−0.356
0.4	−0.336
0.5	−0.174
0.6	−0.304
0.7	−0.266
0.8	−0.248

TABLE 5

Values of σ_s and ρ_s calculated using entropic equations for *o*-methoxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	σ_s	ρ_s
0.0	−0.196	1.48
0.1	+0.037	−4.243
0.2	−0.262	−2.030
0.3	−0.314	−5.280
0.4	−0.292	−10.832
0.5	−0.114	−38.018
0.6	−0.257	−18.650
0.7	−0.215	−18.693
0.8	−0.196	−16.316

Fig. 2. Variation of ρ_s values for *o*-methoxybenzoic acid as a function of mole fraction at 25°C.

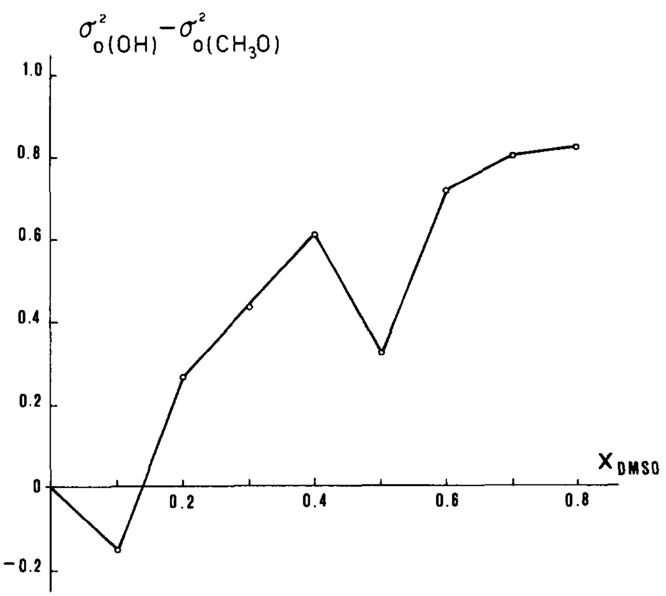

Fig. 3. Variation of the difference in the resonance effect of $\sigma^2_{o(\text{OH})} - \sigma^2_{o(\text{CH}_3\text{O})}$ as a function of mole fraction.

the difference of resonance effect of the two *ortho* derivatives as the DMSO content increases (Fig. 3). The CH_3O– group displays a greater electron-releasing resonance effect in the whole mole fraction range. An exception occurs in the water-rich solution ($0 \le X_{\text{DMSO}} \le 0.1$) where the steric inhibition of resonance is maximum [19].

The difference in solvation enthalpy between the hydroxy and methoxy *ortho* anions was calculated as

$$\begin{aligned}\Delta H^0_{(o\text{-OHPhCOO}^-)_x-(o\text{-CH}_3\text{OPhCOO}^-)_x} &= \delta\Delta H^0_{6(o\text{-OHPhCOOH})} \\ &\quad - \delta\Delta H^0_{6(o\text{-CH}_3\text{OPhCOOH})} \\ &\quad + \Delta H^0_{(o\text{-OHPhCOO}^-)_{\text{aq.}}-(o\text{-CH}_3\text{OPhCOO}^-)_{\text{aq.}}}\end{aligned} \quad , \quad (12)$$

while the difference in solvation enthalpy between the undissociated molecules is

$$\begin{aligned}\Delta H^0_{(o\text{-OHPhCOOH})_x-(o\text{-CH}_3\text{OPhCOOH})_x} &= \delta\Delta H^0_{5(o\text{-OHPhCOOH})} \\ &\quad - \delta\Delta H^0_{5(o\text{-CH}_3\text{OPhCOOH})} \\ &\quad + \Delta H^0_{(o\text{-OHPhCOOH})_{\text{aq.}}-(o\text{-CH}_3\text{OPhCOOH})_{\text{aq.}}}\end{aligned} \quad (13)$$

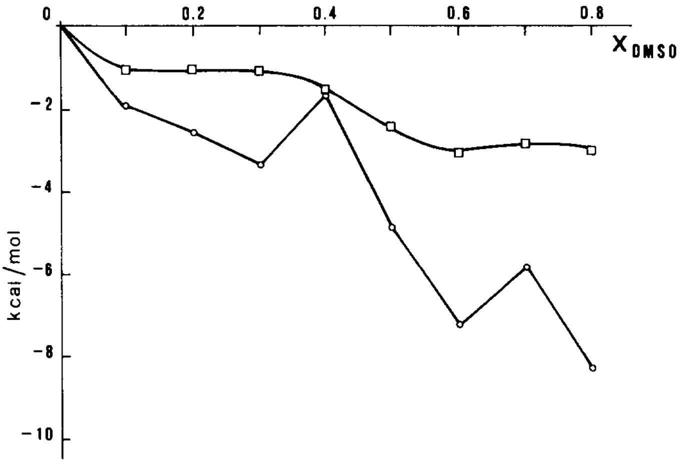

Fig. 4. Differences in the solvation enthalpy between the anions and the undissociated molecules of the hydroxy and methoxy derivatives in various DMSO–water solutions. The difference in the hydration enthalpy both between the anion couple and the undissociated molecule couple are arbitrarily set equal to zero. □, $\Delta\overline{H}_{o\text{-OHPhCOOH})-(o\text{-CH}_3\text{OPhCOOH})}$; ○, $\Delta\overline{H}_{(o\text{-OHPhCOO}^-)-(o\text{-CH}_3\text{OPhCOO}^-)}$.

The last term on the right-hand sides of eqns. (12) and (13) was arbitrarily assumed to be equal to zero and the resulting $\Delta H^0_{(o\text{-OHPhCOO}^-)_X-(o\text{-CH}_3\text{OPhCOO}^-)_X}$ and $\Delta H^0_{(o\text{-OHPhCOOH})_X-(o\text{-CH}_3\text{OPhCOOH})_X}$ are plotted in Fig. 4 as a function of the solvent composition. These values are supposed to closely approach the true values [21].

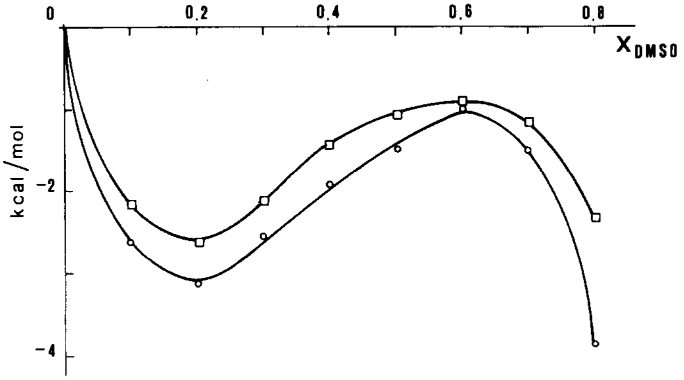

Fig. 5. Differences in solvation enthalpy between the anions and the undissociated molecules of the *para*- *p*- and *o*-methoxy derivatives in various DMSO–water solutions. The difference in the hydration enthalpy both between the anion couple and the undissociated molecule couple are arbitrarily set equal to zero. □, $\Delta\overline{H}_{(p\text{-CH}_3\text{OPhCOOH})-(o\text{-CH}_3\text{OPHCOOH})}$; ○, $\Delta\overline{H}$(*p*-$\text{CH}_3\text{OPhCOO}^-$)–(*o*-$\text{CH}_3\text{OCOO}^-$).

TABLE 6

Free energy, enthalpy and entropy values for the proton transfer process of *o*-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	0.35	0.50	0.15
0.1	0.66	0.91	0.25
0.2	0.85	1.87	1.02
0.3	0.94	3.48	2.54
0.4	0.91	5.50	4.59
0.5	0.93	7.12	6.19
0.6	1.28	9.45	8.17
0.7	0.99	10.11	9.12
0.8	0.91	9.06	8.15

For the methoxy and hydroxy derivatives the order of transfer both for the molecules and the anions is *o*-OH > *o*-CH_3O in the whole mole fraction range. This can be ascribed to the greater steric hindrance to solvation showed by the methoxy group. The steric hindrance to solvation also makes the anions and molecules of the *o*-methoxy compound more desolvated than those of the *p*-methoxy compound [1] (Fig. 5).

Finally, $\delta\Delta G_i^{g\to x}$, $\delta\Delta H_i^{g\to x}$ and $T\delta\Delta S_i^{g\to x}$ values were calculated and are reported in Table 6. They are also plotted against DMSO in Fig. 6, which represents the external interactions of the proton transfer with the medium.

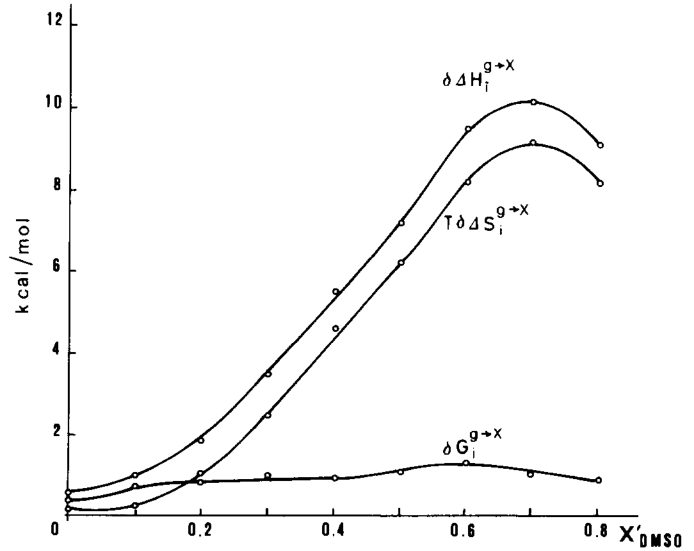

Fig. 6. Thermodynamic quantities for the proton transfer process of *o*-methoxybenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as reference.

As previously shown [8–11], $T_{\Delta}S_i^{g\to x}$ curves give a measure of the values of the solute–solvent interactions, while the ρ_s curves give only a trend. The ρ_s and $T\delta\Delta S_i^{g\to x}$ values are similar but symmetrical because of the negative values of σ_s which, in turn, make the ρ_s values negative too. The ρ_s curves confirm the larger desolvation showed by the molecules and anions of the *o*-methoxy derivative with respect to the hydroxy derivative [1].

Finally, the most favourable $\delta\Delta P_i^{g\to x}$ terms for the *p*-CH_3O [1] isomer with respect to the *o*-CH_3O isomer can be explained by the absence of the intramolecular hydrogen bond for the former in the gaseous phase.

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REFERENCES

1 F. Rodante, G. Ceccaroni and F. Fantauzzi, Thermochim. Acta, 59 (1982) 253.
2 F. Rodante, Thermochim. Acta, 34 (1979) 377.
3 F. Rodante and G. Pistoia, Thermochim. Acta, 43 (1981) 325.
4 J.C. Synnot and J.N. Butler, J. Phys. Chem., 73 (1969) 1470.
5 F. Fiordiponti, F. Rallo and F. Rodante, Z. Phys. N.F., 88 (1974) 149.
6 J. Chistensen, D.E. Smith, M.D. Slade and R.M. Izatt, Thermochim. Acta, 4 (1972) 17.
7 P. Fiordiponti, F. Rallo and F. Rodante, Gazz. Chim. Ital., 104 (1974) 649.
8 F. Rodante and M. Pasquali, Thermochim. Acta, 51 (1981) 191.
9 M.G. Bonicelli, G. Ceccaroni and F. Rodante, Thermochim. Acta, 52 (1982) 45.
10 F. Rodante and G. Pistoia, Thermochim. Acta, 52 (1982) 217.
11 F. Rodante and M. Pasquali, Thermochim. Acta, 52 (1982) 225.
12 L.G. Hepler, J. Am. Chem. Soc., 85 (1963) 3089.
13 J.B. McMahon and P. Kebarle, J. Am. Chem. Soc., 99 (1977) 2222.
14 J.B. Cumming and P. Kebarle, Can. J. Chem., 56 (1978) 1.
15 F. Rodante, F. Rallo and P. Fiordiponti, Thermochim. Acta, 9 (1974) 269.
16 T. Fujita and T. Nishiota, In R.W. Taft (Ed.), Progress in Physical Organic Chemistry, Interscience, New York, 1976, pp. 52, 53, 56, 58, 75, 82.
17 F. Rodante, Thermochim. Acta, 31 (1979) 221.
18 F. Rodante, Thermochim. Acta, 34 (1979) 29.
19 M.M. Davis and H.B. Hetzer, J. Res. Natl. Bur. Stand., 60 (1958) 569.
20 T.M. Krygoswki and R. Fawcett, Can. J. Chem., 53 (1974) 3622.
21 F. Rodante, Thermochim. Acta, 23 (1978) 311.