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THERMODYNAMIC ANALYSIS OF THE IONIZATION OF *ORTHO* AND *PARA* TOLUIC ACIDS : INFLUENCE OF THE MEDIUM ON THE HYPERCONJUGATIVE AND STERIC EFFECTS

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ABSTRACT

The hyperconjugative effect of the methyl group in the *para* and *ortho* position of the benzene ring is studied as a function of the medium. The ionization and solution enthalpies of *ortho* and *para* toluic acids have been measured in H_2O/DMSO mixtures. A study of the *ortho* effects by means of the linear combination of the ordinary polar, proximity polar and steric effects has also been performed.

The methyl group both in *ortho* and *para* position seems to be forced out by the benzene ring at $X_{DMSO} = 0.5$ mole fraction with a consequent decrease of hyperconjugation effect. A study of enthalpic and entropic contributions to substituent and reaction constants and the proton transfer process from *ortho* and *para* derivatives to benzoic acid, compared with the same process in the gaseous phase are also presented.

INTRODUCTION

Some substituted benzoic acids in water/dimethylsulphoxide (DMSO) mixtures have been the subject of extended research in this laboratory [1–10].

It was found that the substituent groups (Cl, NO_2, OH, CH_3O) influence the solvation processes of the undissociated molecules and ions differently, as a function of their inductive, resonance, field and steric effects, which in turn, are dependent on the position of the substituent with respect to the carboxylate group. The water/DMSO solutions constitute a very suitable system for studying the solvation of ions and undissociated molecules, which is the driving force of the ionization processes. Furthermore, water has always been considered a suitable solvent for most reactions. DMSO, in turn, has many uses as a medium for chemical reaction [11] since it is a powerful solvent for many organic and inorganic compounds.

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The proton transfer processes from the benzoic derivatives to benzoic acid in the liquid phase, compared with the same processes in the gaseous phase [12–14] also contribute to give a complete picture of the solvation phenomenon.

The methoxy group ($R^+ I^-$) as well as the hydroxyl group ($R^+ I^-$) in the *para* and (partially) *ortho* positions shows a large electron-releasing resonance effect. The difference between the two groups was shown to be related to the different degree of resonance [7,9,10]. For the methoxy and hydroxy *para* derivatives a greater electron-releasing resonance effect was found for the hydroxy derivative [7], while for the methoxy and hydroxy *ortho* derivatives the contrary is true [9]. The *ortho* methoxy derivative also shows a partial steric inhibition of resonance in water-rich solutions. It is well-known that the methyl group ($I^+ R^+$) shows the hyperconjugative effect. This is commonly regarded as a special kind of resonance effect primarily involving delocalization of electrons in C–H bonds adjacent to an unsaturated system. The actual nature of this substituent effect, however, must be regarded as a special effect of α-hydrogen atoms in the same sense as conjugative electron release.

The aim of this work is to study the influence of the medium on the hyperconjugative effect displayed by the methyl group in the *para* and *ortho* positions.

EXPERIMENTAL DETAILS AND PROCEDURE

The calorimetric measurements were performed by means of a Tronac 450 titration calorimeter and an LKB 8721-1 reaction and solution calorimeter.

DMSO (Carlo Erba, RP) was purified according to the procedure of Synnot and Butler [15]. DMSO/water 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. An aqueous solution of 0.098 M NaOH and solutions of 0.98 M HCl in various DMSO/water mixtures were prepared from standard solutions and their concentrations were checked by potentiometric titrations.

The *para*- and *ortho*-methyl benzoic acids (K and K) were purified by crystallization from water/ether mixtures and their melting points checked before use.

The $CH_3PhCOONa$ solutions were prepared by adding an NaOH solution of known molarity to the *para* and *ortho* methyl acids dissolved in the mixed solvent to give 100 g DMSO/water solution at X mole fraction. The concentration of the sodium salt was always in the range 2×10^{-3}–4×10^{-4} M.

A certain amount of acid (about 4–5% of the original content) was not converted into the salt and remained as free acid to avoid the presence of free alkali.

The ionization processes of CH_3 PhCOOH (*para* and *ortho* substituted) in the various H_2O/DMSO mixtures of X mole fraction can be represented as

$$(CH_3PhCOOH)_X \rightarrow (CH_3PhCOO^-)_X + (H^+)_X \tag{1}$$

The molar enthalpies of ionization, $\Delta\bar{H}_1$, of $CH_3PhCOOH$ acids were obtained by experimental measurements of:

(a) molar enthalpy of reaction, $\Delta\bar{H}_2$, of $CH_3PhCOONa$ dissolved in the mixed solvent of X mole fraction, with 0.98 M HCl (also dissolved in X mole fraction)

$$\begin{aligned}&(CH_3PhCOO^-)_X + (Na^+)_X + (H^+)_X + (Cl^-)_X\\ &\quad = (CH_3PhCOOH)_X + (Na^+)_X + (Cl^-)_X\end{aligned} \tag{2}$$

(b) the molar enthalpy of dilution, $\Delta\bar{H}_3$, of the same amount of 0.98 M HCl (dissolved in X mole fraction)

$$(H^+)_X + (Cl^-)_X = (H^+)_X + (Cl^-)_X \tag{3}$$

The molar enthalpy of process (1) can be obtained by subtracting the two values $\Delta\bar{H}_3$ and $\Delta\bar{H}_2$. For each of the water/DMSO mixtures at X mole fraction the $\Delta\bar{H}_1$ values refer to the ionization of 1 mole of $CH_3PhCOOH$ (*o*- or *p*-) dissolved at infinite dilution in 1000 g of mixed solvent, yielding 1 mole of protons and 1 mole of CH_3PhCOO^- ions solvated in the same amount of solvent.

In order to refer process (1) to only one initial thermodynamic state, the solution enthalpies of crystalline *o*- and *p*-methylbenzoic acids, $\Delta\bar{H}_S$, in the various solvent mixtures were measured

$$CH_3PhCOOH_{(cry)} \rightarrow (CH_3PhCOOH)_X \tag{4}$$

so that $\Delta H_5 = \Delta H_4 + \Delta H_1$ values obtained for the process

$$CH_3PhCOOH_{(cry)} \rightarrow (CH_3PhCOO^-)_X + (H^+)_X \tag{5}$$

refer to an identical initial thermodynamic state. In processes (1) and (4) concentrations ranging from 2×10^{-3} to 4×10^{-4} m were used. Therefore, the $\Delta\bar{H}$ values related to these processes were assumed to be equal to ΔH^0 values [16].

In the literature ΔG^0 values of process (1) for *o*- and *p*-methyl derivatives in some mole fractions are available [17], so the effects of the medium on the substituent and reaction constants for the methyl derivatives were explained in terms of solute–solvent interactions and structure-breaking effects according to the equations

$$(CH_3PhCOOH)_X + (PhCOO^-)_X = (CH_3PhCOO^-)_X + (PhCOOH)_X \tag{6}$$

$$-\delta\, \Delta G^0/2.303RT = \rho_{m,p}\sigma_{m,p} \tag{7a}$$

$$-\delta\, \Delta G^0/2.303RT = \rho_o\sigma_o + fF + \delta Es \tag{7b}$$

By separating substituent effects into enthalpic and entropic contributions [18], eqns. (7a) and (7b) may be written in the form

$$-\delta\, \Delta G^0/2.303RT = \rho_H\sigma_H + \rho_S\sigma_S \tag{8a}$$

$$-\delta\, \Delta G^0/2.303RT = \rho_H\sigma_H + \rho_S\sigma_S + \delta Es + fF \tag{8b}$$

$\rho_H\sigma_H$ and $\rho_S\sigma_S$ being defined by the relations

$$\rho_H\sigma_H = -\delta\, \Delta H^0/2.303RT \tag{9a}$$

$$\rho_S\sigma_S = \Delta S^0/2.303R \tag{9b}$$

The ρ, ρ_o, ρ_S and ρ_H values are assumed equal to unity in water at 25°C and 1 atm.

The total *ortho* substituent effect can be expressed in terms of the ordinary polar, proximity polar and steric effects. The ordinary polar effect would be imaginary [19] 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 $\sigma_o \cong \sigma_p$. The proximity polar 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 *Es*.

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* substituent. The extent of the resonance inhibition seems to depend on the steric dimensions of the *ortho* substituents. If the secondary steric effect is significant in the substituent group, the σ_o values may be modified [20,21] as a function of the resonance inhibition.

Finally, the proton transfer process from *ortho*- and *para*-methyl benzoic acids to benzoic acid in water/DMSO mixtures in comparison with the same processes in the gaseous phase have been examined. A thermodynamic cycle allows calculation of a proton transfer process in solvent X, referring to a gaseous initial state [12–14], i.e. $\delta\, \Delta Pi^{g \to X}$. 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.

$$\begin{tikzcd}
\mathrm{CH_3PhCOOH(g)} \arrow[d, "\Delta P_S"] & +\,\mathrm{PhCOO^-(g)} \arrow[r, "\delta\, \Delta Pi(g)"] \arrow[d, "\Delta P_S"] & \mathrm{CH_3PhCOO^-(g)} \arrow[d, "\Delta P_S"] & +\,\mathrm{PhCOOH(g)} \arrow[d, "\Delta P_S"] \\
(\mathrm{CH_3PhCOOH})_X & +\,(\mathrm{PhCOO^-})_X \arrow[r, "\delta\, \Delta Pi(x)"] & (\mathrm{CH_3PhCOO^-})_X & +\,(\mathrm{PhCOOH})_X
\end{tikzcd}$$

where $\delta\, \Delta Pi(g)$ is the gas-phase change of some thermodynamic properties

($Pi = G$, H, S) for the proton transfer process, and $\delta\,\Delta P\mathrm{i(X)}$ is the corresponding value in solvent X. Thus, this can be written as

$$\delta\,\Delta P\mathrm{i(X)} - \delta\,\Delta P\mathrm{i(g)} = \delta\,\Delta P\mathrm{s}^{\mathrm{g}\to\mathrm{X}} \qquad (10)$$

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 $\delta\,\Delta P\mathrm{s}^{\mathrm{g}\to\mathrm{X}} = \delta\,\Delta P\mathrm{i}^{\mathrm{g}\to\mathrm{X}}$.

Again according to Hepler [22] in eqn. (10) the solvent effects (external) can be separated from the intrinsic molecular effect (internal). We assume $\delta\,\Delta P\mathrm{i(X)}$ to be the "overall" interactions, $\delta\,\Delta P\mathrm{i}^{\mathrm{g}\to\mathrm{X}}$ the "external" interactions and $\delta\,\Delta P\mathrm{i(g)}$ the "internal" ones.

Using the values of McMahon and Kebarle [23] it is possible to calculate the $\delta\,\Delta G\mathrm{i(g)}$ values for *o*- and *p*-methyl benzoic acid (*ortho*, $\delta\,\Delta G\mathrm{i(g)} = -0.80$; *para*, $\delta\,\Delta G\mathrm{i(g)} = 1.1$ kcal mol^{-1}). The $\delta\,\Delta G\mathrm{i(g)}$ and $\delta\,\Delta G\mathrm{i(X)}$ values (this work) are included in eqn. (10) and $\delta\,\Delta G\mathrm{i}^{\mathrm{g}\to\mathrm{X}}$ values have been calculated.

It is well known [24] that both the "external" and "internal" rotations in the half-process $\mathrm{HA} \to \mathrm{A}^-$ occurring in the gaseous phase are responsible for the loss of entropy in the equation $\mathrm{HA}_1 + \mathrm{A}_2^- = \mathrm{A}_1^- + \mathrm{HA}_2$ so that $\delta\,\Delta S\mathrm{i(g)} \neq 0$. However, for reactions such as those considered here, symmetry numbers are small and almost cancel out, so if we put [22] $\delta\,\Delta S\mathrm{i(g)} = 0$, then $\delta\,\Delta G\mathrm{i(g)}$ (600 K) $= \delta\,\Delta G\mathrm{i(g)}$ (298 K) $= \delta\,\Delta H\mathrm{i(g)}$ (298 K) and it is possible to calculate $\delta\,\Delta H\mathrm{i(g)}^{\mathrm{g}\to\mathrm{X}}$ and $T\,\delta\,\Delta S\mathrm{i(g)}^{\mathrm{g}\to\mathrm{X}}$ 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 *o*- and *p*-methyl benzoic acids. Table 2 shows enthalpy values of processes (4) and (5).

TABLE 1

Enthalpy, entropy and free energy values of the ionization for *ortho*- and *para*-methyl benzoic acids in DMSO/water solutions at 25°C [a]

X_{DMSO}	*ortho*			*para*		
	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$
0.0	5.23	−1.40	−6.63	5.92	0.3	−5.62
0.1		−0.26			0.7	
0.2		1.12			1.11	
0.3		1.86			1.69	
0.4		2.98			2.62	
0.5	8.03	3.29	−4.74	8.05	3.23	−4.82
0.6		4.01			3.86	
0.7		5.83			5.10	
0.8	12.65	5.73	−6.92	12.80	5.99	−6.81

[a] All thermodynamic quantities are given in kcal mol^{-1}.

TABLE 2

Enthalpy values of solution (ΔH_4^0) and for process (5) (in kcal mol^{-1}) for *ortho*- and *para*-methyl benzoic acids in DMSO/water solutions at 25°C

X_{DMSO}	*ortho*		*para*	
	ΔH_4^0	ΔH_5^0	ΔH_4^0	ΔH_5^0
0.0	5.48	4.08	6.14	6.44
0.1	6.32	6.06	6.64	7.34
0.2	7.77	8.89	6.93	8.04
0.3	6.64	8.50	6.03	7.72
0.4	5.59	8.57	4.67	7.29
0.5	4.57	7.86	4.07	7.30
0.6	3.88	7.89	3.24	7.10
0.7	3.40	9.23	2.85	7.95
0.8	3.20	8.93	2.61	8.60

For comparison it is convenient to express the ionization enthalpy as the difference between the values obtained in a 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 $\delta\,\Delta H_4^0$ and $\delta\,\Delta H_5^0$ values represent the transfer enthalpy of the undissociated molecule, and the two ions H^+ and CH_3PhCOO^-, respectively, from pure water to the mixed solvent. All these data are plotted against X_{DMSO} in Figs. 1and 2. From these figures one may gather that in water-rich solutions ($0.0 < X_{DMSO} < 0.4$) desolvation plays a very important role both for the undissociated molecule and for the anions of the *o*- and *p*-methyl benzoic acids.

By comparing the ΔH_1^0 ionization values of the *para*- and *ortho*-methyl derivatives (Fig. 3), the calorimetric acid strength order $p > o$ is found over the whole mole fraction range, with the exception of water-rich solutions ($0 < X_{DMSO} < 0.2$) where the order is $o > p$.

The different ionization of the two methyl benzoic acids can be ascribed to the different solvation which the molecules and the ions undergo in the mixtures.

The difference in solvation between the *para* and *ortho* solvated ions was calculated as

$$\begin{aligned}&\Delta H^0(p\text{-}CH_3PhCOO^-)_X - (o\text{-}CH_3PhCOO^-)_X\\&\quad = \Delta H_5^0(p\text{-}CH_3PhCOOH)_X - \Delta H_5^0(o\text{-}CH_3PhCOOH)_X\\&\quad + \Delta H^0(p\text{-}CH_3COO^-)_{aq} - (o\text{-}CH_3COO^-)_{aq} \qquad (11)\end{aligned}$$

while the difference in the solvation enthalpy between the undissociated

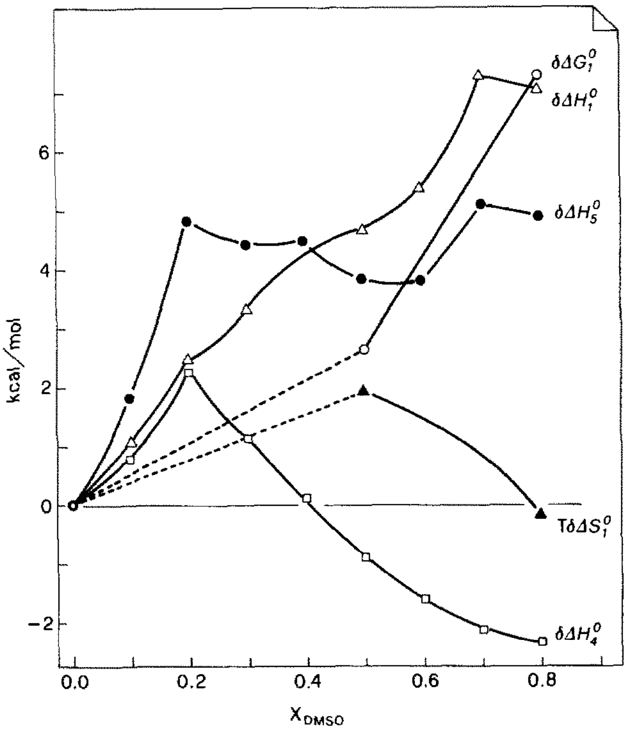

Fig. 1. Thermodynamic quantities for the transfer of *ortho*-methyl benzoic acid from pure water to DMSO/water mixtures as a function of the mole fraction at 25°C.

molecules is

$$\begin{aligned}\Delta H^0(p\text{-CH}_3\text{PhCOOH})_X - (o\text{-CH}_3\text{PhCOOH})_X &= \Delta H_4^0(p\text{-CH}_3\text{PhCOOH})_X \\ &- \Delta H_4^0(o\text{-CH}_3\text{PhCOOH})_X + \Delta H^0(\text{p-CH}_3\text{PhCOOH})_{aq} \\ &- (o\text{-CH}_3\text{PhCOOH})_{aq} \qquad (12)\end{aligned}$$

The last term on the right-hand side of eqns. (11) and (12) was arbitrarily assumed to equal zero and the resulting $\Delta H^0(p\text{-CH}_3\text{PhCOO}^-)_X - (o\text{-CH}_3\text{PhCOO}^-)_X$ and $\Delta H^0(p\text{-CH}_3\text{PhCOOH})_X - (o\text{-CH}_3\text{PhCOOH})_X$ values are plotted in Fig. 4 as a function of the solvent composition. These values are supposed to approach the true values very closely.

For the *ortho* and *para* methyl benzoic isomers the order of transfer both for the molecules and the ions is p-CH$_3$ > o-CH$_3$ in the whole mole fraction range. This can be ascribed to the greater hyperconjugative effect which, mostly for the anions, allows the formation of dipoles, with consequent greater degree of solvation.

The steric hindrance to solvation showed by the methyl group in the *ortho* position also makes the anions and the molecules of the o-methyl compound more desolvated than those of the p-methyl compound.

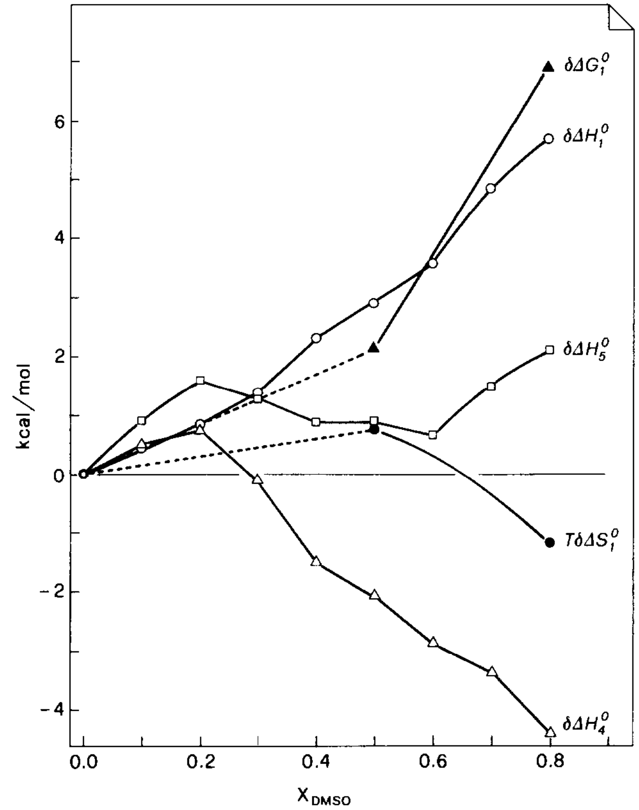

Fig. 2. Thermodynamic quantities for the transfer of *meta*-methyl benzoic acid from pure water to DMSO/water mixtures as a function of the mole fraction at 25 °C.

The relatively greater acid strength of the *ortho* isomer in water-rich solutions could also be attributed to the steric strain due to the large steric requirements of the methyl group which would conflict with the carboxylate group. This would favour proton dissociation and increase the apparent

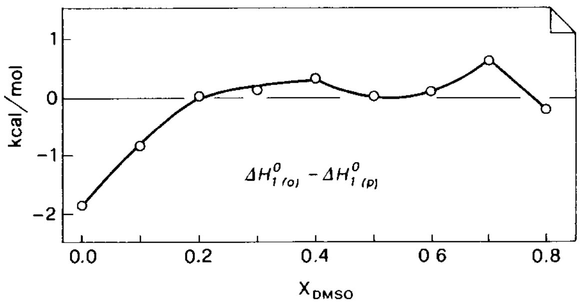

Fig. 3. Difference in ionization enthalpies of *ortho*- and *para*-methyl benzoic acids in various water/DMSO mixtures at 25 °C.

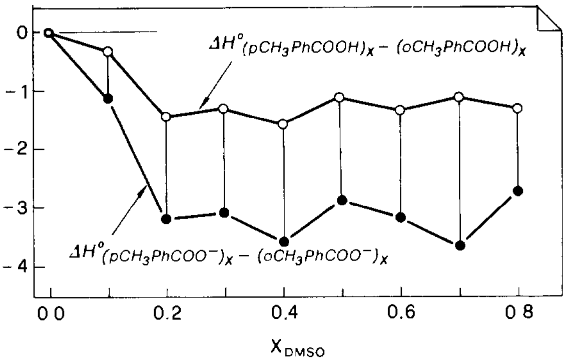

Fig. 4. Differences in the solvation enthalpy between the anions and the undissociated molecules of the *ortho* and *para* derivatives in various DMSO/water solutions. The differences in the hydration enthalpy both between the anion couple and the undissociated molecule are arbitrarily set equal to zero.

strength of the acid (as occurs in the gas phase where $\delta\ \Delta G\mathrm{i(g)}$, related to the proton transfer process from the *ortho* methyl to the benzoic acid, is negative).

It is also possible that the coplanarity of the $-COOH$ and $-CH_3$ groups can be reduced at high DMSO mole fraction. This seems to be attributable to the congestion of the *o*-methyl benzoic acid solvated with strong proton accepting solvent molecules. This could be confirmed by means of eqns. (7a) and (7b). Using experimental ionization values for benzoic [1] and *o*- and *p*-methyl benzoic acids (this work), the standard free energies are obtained as $\delta\ \Delta G^0 = \Delta G^0(CH_3PhCOOH) - \Delta G^0(PhCOOH)$. The ρ_o, $\rho_{m,p}$, f, F and Es values for the dissociation of *ortho*- and *para*-benzoic acids in water/DMSO mixtures are reported in the literature [19]. If the above values are included in eqns. (7a) and (7b), σ_m and σ_o (on the same scale as σ_m and σ_p) values are found (Table 3).

It has to be remarked that for the chloro and nitro derivatives the σ_o values are very close to the respective σ_p values [20]. Thus for these derivatives the hypothesis that the ordinary polar effect is equal to the *para* effect ($\sigma_o = \sigma_p$) may be considered as valid. On the contrary for hydroxy and

TABLE 3

Values of σ_o^1, σ_p, $\sigma_o - \sigma_p$ and σ_o^2, for *ortho*- and *para*-methyl derivatives in water/DMSO mixtures at 25°C

X_{DMSO}	σ_o^1	σ_p	$\sigma_o^1 - \sigma_p$	σ_o^2
0.0	−0.14(1)	−0.13(9)	−0.00(2)	−0.13(9)
0.5	0.51(9)	0.77(2)	−0.25(3)	0.67
0.8	−0.17	−0.10(7)	−0.06(2)	−0.20(3)

TABLE 4

Results of the application of the separate enthalpy–entropy equations to the ionization of *ortho*- and *para*-methyl benzoic acids in DMSO/water mixtures at 25°C

X_{DMSO}	*ortho*		*para*	
	$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	0.46(7)	−0.60(1)	−0.14(6)	0.06(6)
0.5	−0.42	1.28(9)	0.11	1.22(4)
0.8	−0.23(7)	−0.34(6)	0.11(7)	−0.34(5)

methoxy *ortho* derivatives this is not true [9,21]. The difference $\sigma_o - \sigma_p$ was assumed as a measure of the internal hydrogen bond and also as a measure of steric inhibition of resonance.

The differences $\sigma_o - \sigma_p$ for the methyl derivatives are given in Table 3. If we assume that the secondary steric effect only occurs in the substituent group, then the $\sigma_o - \sigma_p$ difference can be considered a measure of steric inhibition of resonance and can be included in eqn. (7b) as an additional term

$$-\delta\,\Delta G^0/2.303RT = \rho_o\sigma_o^2 + fF + \delta Es + \sigma_0^1 - \sigma_p \qquad (13)$$

Thus a better approximation for the substituent constant values σ_o^2 was found (Table 3). As would be expected only at $X = 0.5$ is there a significantly correction for the σ_o^1 value. In pure water both the substituent constant values ($\sigma_o = -0.139$, $\sigma_p = -0.139$) are negative; at $X = 0.5$ the values become positive and at $X = 0.8$ again negative. This could be explained by virtue of the weakening of the hyperconjugative effect due to the fact that the –COOH and CH_3 groups are forced out from the benzene ring at $X = 0.5$. The σ_H and σ_S values could also confirm such behaviour. The $\delta\,\Delta H^0$ [2] and $\delta\,\Delta S^0$ values of reaction (6) for *o*- and *p*-methyl benzoic acids are included in eqns. (9a) and (9b) and the values $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are calculated and reported in Table 4.

Using equations tested in water [18] $\sigma = 0.91\sigma_S - 0.07$ and $\sigma_S = -3.6\sigma_H + 0.15$ together with eqns. (9a) and (9b) it is possible to calculate σ_H, σ_S, ρ_H, ρ_S values (Table 5). We observe that σ_o and σ_p values are greatly affected by the solvent composition at $X = 0.5$; thus we believe that only approximate values for the above cited quantities are found at this mole fraction.

In order to assess the relative contributions of enthalpy and entropy to the substituent effect the following equations are used.

$$f_H = |\sigma_H|/(|\sigma_H| + |\sigma_S|)$$

$$f_S = |\sigma_S|/(|\sigma_S| + |\sigma_H|)$$

The f_H and f_S values are reported in Table 6. In pure water it was noted that for *p*-CH_3 the enthalpic contribution ($f_H = 0.74$) prevails. This clearly

TABLE 5

σ_S, σ_H, ρ_S and ρ_H values calculated using entropic and enthalpic equations for *ortho-* and *para-*methyl benzoic acids in water/DMSO mixtures at 25°C

X_{DMSO}	*ortho*				*para*			
	σ_S	ρ_S	σ_H	ρ_H	σ_S	ρ_S	σ_H	ρ_H
0.0	−0.60(1)	1	0.46(7)	1	0.06(6)	1	−0.33(9)	1
0.5	0.81(3)	1.58	−0.18(4)	2.28	0.92(5)	1.32	−0.21(5)	1.51
0.8	−0.14(6)	2.37	0.08(2)	−2.88	−0.11(5)	2.92	0.07	1.5

TABLE 6

f_H and f_S values for *ortho-* and *para-*methyl benzoic acids in DMSO/water mixtures at 25°C

X_{DMSO}	*ortho*		*para*	
	f_H	f_S	f_H	f_S
0.0	0.43(7)	0.56	0.74	0.26
0.5	0.18	0.82	0.19	0.81
0.8	0.36	0.64	0.39	0.61

shows [18] that the resonance contribution (hyperconjugative effect) to the substituent effects is prevalent in this compound.

In DMSO rich solutions, the resonance contribution decreases (mostly at $X_{DMSO} = 0.5$), thus confirming the fact that the CH_3 and –COOH groups are forced out from the benzene ring, with consequent decrease of hyperconjugative effect. Finally $\delta\,\Delta H\mathrm{i}^{g\rightarrow X}$, $\delta\,\Delta G\mathrm{i}^{g\rightarrow X}$ and $T\,\delta\,\Delta S\mathrm{i}^{g\rightarrow X}$ were calculated and values are reported in Table 7. They are also plotted against DMSO in Fig. 5 which represents the "external" interactions of the proton transfer with the medium.

The most favourable $\delta\,\Delta P\mathrm{i}^{g\rightarrow X}$ terms for the *p*-CH_3 isomers with respect to the *o*-CH_3 isomers can be explained by the presence of the dipole in the gaseous phase (due to the greater hyperconjugative effect), this being con-

TABLE 7

Enthalpy, entropy and free energy values (kcal mol^{-1}) for the proton transfer process of *ortho-* and *para-*methyl benzoic acids in DMSO/water mixtures calculated by assuming a gaseous initial thermodynamic state

X_{DMSO}	*ortho*			*para*		
	$\delta\,\Delta G\mathrm{i}^{g\rightarrow X}$	$\delta\,\Delta H\mathrm{i}^{g\rightarrow X}$	$T\,\delta\,\Delta S^{g\rightarrow X}$	$\delta\,\Delta G\mathrm{i}^{g\rightarrow X}$	$\delta\,\Delta H\mathrm{i}^{g\rightarrow X}$	$T\,\delta\,\Delta S^{g\rightarrow X}$
0.5	3.5	5.49	1.99	1.03	1.83	0.8
0.8	8.12	7.93	−0.19	5.78	4.59	−1.19

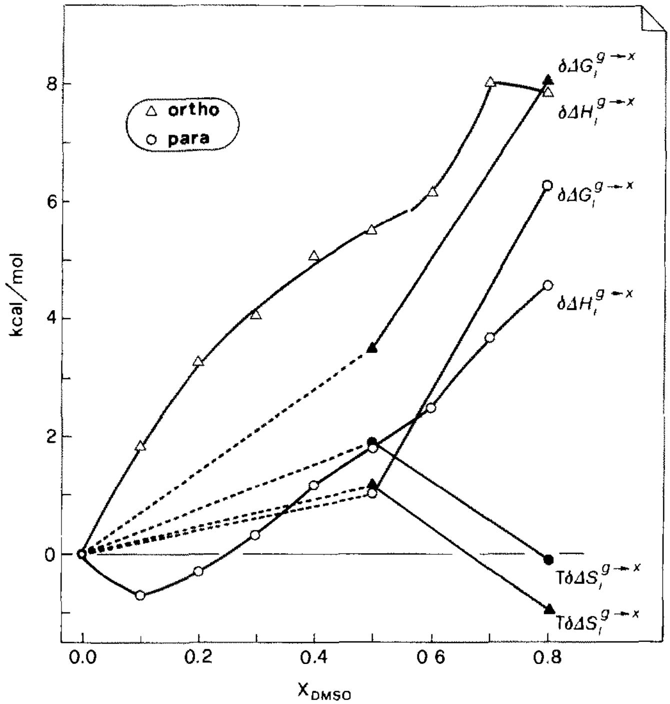

Fig. 5. Thermodynamic quantities for the proton transfer process of *ortho*- and *para*-methyl benzoic acid derivatives in DMSO/water solutions, obtained by assuming a gaseous state as reference.

firmed by the positive value of the proton transfer process in the gaseous phase from the *para* substituent to the benzoic acid.

The greater extent of the effect of the σ_S with respect to the σ_H values indicates the external contributions are entropy controlled and therefore chiefly inductive in character [18], so that the solute–solvent interactions are exclusively discussed in terms of ρ_S change (Fig. 6). But as previously shown [12–14], $T\,\delta\,\Delta S^{g\to X}$ curves give a measure of the value of the solute–solvent

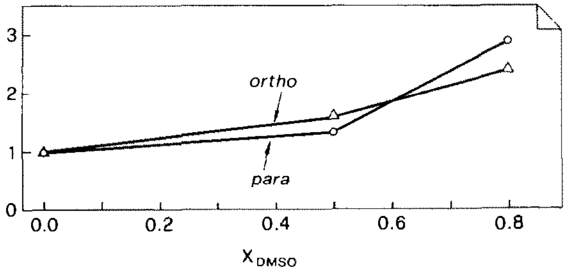

Fig. 6. Variation of the ρ_S values for *ortho*- and *para*-methyl benzoic acids as a function of mole fraction at 25°C.

interactions, while the ρ_S curves give only a trend. The ρ_S and $T\,\delta\,\Delta S^{g\rightarrow X}$ values are similar until $X = 0.5$; beyond this mole fraction the curves become symmetrical because of the negative values of σ_S, which in turn make ρ_S positive. The ρ_S curves confirm that in DMSO-rich solutions, the solvent–solution interactions are greater for the *para*-methyl derivatives, this being due to the (partially) re-established hyperconjugative effect.

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