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STUDY OF THE PROTON TRANSFER PROCESSES OF HYDROXY-SUBSTITUTED BENZOIC ACIDS IN WATER–DIMETHYLSULFOXIDE MIXTURES COMPARED WITH THE SAME PROCESSES IN THE GASEOUS PHASE

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ABSTRACT

A study of the proton transfer processes from the hydroxy substituted benzoic acids to benzoic acid in water–DMSO mixtures in comparison with the same processes in the gaseous phase is presented

A thermodynamic cycle was used to calculate in solvent X a proton transfer process which refers to an initial gaseous thermodynamic state, i e $\delta\Delta P_1^{g\rightarrow X}$

By using these values, it is possible to calculate the "external" interactions of the above cited processes

As the *o*- and *p*-hydroxybenzoic acids behave, in the gas phase, as phenols, an intramolecular proton transfer process hinders the solvation process

Solvation in the *ortho*-anions is made much more difficult by the internal hydrogen bond

INTRODUCTION

The proton transfer processes from chloro- and nitrobenzoic acids to benzoic acid in water–dimethylsulfoxide (DMSO) mixtures in comparison with the same processes in the gaseous phase have recently been examined [1,2].

A thermodynamic cycle allows the calculation of a proton transfer process in a solvent X, referring to a gaseous initial state [1,2] i.e. $\delta\Delta P_1^{g\rightarrow X}$. These thermodynamic quantities have been assumed as a measure of "external" solute–solvent interactions.

A comparison between the chloro and nitro isomers shows that the proton transfer process is easier for the nitro isomers in the gaseous phase while the opposite is true in solution.

The different effect of the two groups can be related to the resonance, the greater size and the different inducive effect of the nitro group.

The equations used to illustrate the substituent effect in solvent X were the following

$$(\text{R-PhCOOH})_X + (\text{PhCOO}^-)_X = (\text{R-PhCOO}^-)_X + (\text{PhCOOH})_X \quad (1)$$

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$$-\frac{\delta\Delta G^\circ}{2.303\,RT}=\rho\sigma=\rho_{\mathrm{H}}\sigma_{\mathrm{H}}+\rho_s\sigma_s \tag{2}$$

$$-\frac{\delta\Delta G^\circ}{2.303\,RT}=\rho_o\sigma_o+fF+\delta E_s=\rho_H\sigma_H+\rho_s\sigma_s+fF+\delta E_s \tag{3}$$

$$\rho_H\sigma_H=-\frac{\delta\Delta H^\circ}{2.303\,RT} \tag{4a}$$

$$\rho_s\sigma_s=\frac{\delta\Delta S^\circ}{2.303\,RT} \tag{4b}$$

$$\rho_H\sigma_H=-\frac{\delta\Delta H^\circ}{2.303\,RT}-\delta E_s \tag{5a}$$

$$\rho_s\sigma_s=\frac{\delta\Delta S^\circ}{2.303\,RT}-f\bar{F} \tag{5b}$$

the symbols R and X representing, respectively, the substituent group and the mole fraction of the solvent.

In the present paper we intend to study the behaviour of the proton transfer process of the hydroxybenzoic acids in both the liquid and gaseous phase.

It is noteworthy that in the gaseous phase the *o*- and *p*-hydroxybenzoic acids behave as phenols [3].

In the liquid phase a strong influence on the transfer process was shown by intermolecular and intramolecular hydrogen bonds [4–6].

The latter are so important in the *ortho* isomers that an additional term $\sigma_o^1-\sigma_p$ for the field effect is included in the general equation [6] of the *ortho* compounds

$$-\frac{\delta\Delta G^\circ}{2.303\,RT}=\rho_o\sigma_o^2+fF+\sigma_o^1-\sigma_p+\delta E_s^\circ \tag{6}$$

EXPERIMENTAL PROCEDURE

The calorimetric apparatus, the preparation of the DMSO–water mixtures and the technique for obtaining the thermodynamic values for the hydroxybenzoic [4] and benzoic [7] acids have been described previously.

RESULTS AND DISCUSSION

The aim of this paper is to calculate the "external" interactions of the proton transfer process for the hydroxybenzoic acid derivatives and to examine the substituent effects mostly in terms of hydrogen bonding.

This involves the assembly of various types of data as shown by the following thermodynamic cycle

$$\begin{tikzcd}
\mathrm{OH{-}PhCOOH_{(g)}} \arrow[d, "\Delta P_s"] & +\,\mathrm{PhCOO^-_{(g)}} \arrow[d, "\Delta P_s"] \arrow[r, "\delta\Delta P_{t(g)}"] & \mathrm{OH{-}PhCOO^-_{(g)}} \arrow[d, "\Delta P_s"] & +\,\mathrm{PhCOOH_{(g)}} \arrow[d, "\Delta P_s"] \\
(\mathrm{OH{-}PhCOOH})_X & +\,(\mathrm{PhCOO^-})_X \arrow[r, "\delta\Delta P_{t(X)}"] & (\mathrm{OH{-}PhCOO^-})_X & +\,(\mathrm{PhCOOH})_X
\end{tikzcd}$$

Following previous conventions [1,2], $\delta\Delta P_{i(g)}$ is the gas-phase change of some thermodynamic properties ($P_i = G, H, S$) for the proton transfer process, while $\delta\Delta P_{i(X)}$ is the corresponding value in a solvent X.

So one can write

$$\delta\Delta P_{i(X)} - \delta\Delta P_{i(g)} = \delta\Delta P_s^{g\rightarrow X} \tag{7}$$

the right-hand term of eqn. (7) being assumed as the proton transfer, in solvent X, which refers to the initial gaseous thermodynamic state, i.e.

$$\delta\Delta P_s^{g\rightarrow X} = \delta\Delta P_i^{g\rightarrow X}$$

Again, according to Hepler [8–10], we can separate in eqn. (7) the solvent effects (external) from the intrinsic molecular effect (internal). We assume the $\delta\Delta P_{i(X)}$ as the "overall" interactions, $\delta\Delta P_{i(g)}$ as the "internal" interactions and $\delta\Delta P_i^{g\rightarrow X}$ as the "external" ones.

It is well-known [11,12] that for these reactions it is possible to assume $\delta\Delta S_{i(g)} \simeq 0$, so that

$$\delta\Delta G_{i(g)\ 600\ \mathrm{K}} \simeq \delta\Delta G_{i(g)\ 300\ \mathrm{K}} \simeq \delta\Delta H_{i(g)}$$

By including $\delta\Delta G_{i(g)}$ values (available in the literature) and $\delta\Delta G_{i(X)}$ values (by means of ionization values previously calculated [4.7]) in eqn. (7) it is possible to calculate $\delta\Delta G_i^{g\rightarrow X}$. In the same way $\delta\Delta H_i^{g\rightarrow X}$ values may be calculated. Finally, by means of $\delta\Delta H_i^{g\rightarrow X}$ and $\delta\Delta G_i^{g\rightarrow X}$ terms, the $T\delta\Delta S_i^{g\rightarrow X}$ term can be calculated.

All thermodynamic values are reported in Tables 1–3 and are plotted against DMSO mole fraction in Figs. 1–3.

As previously shown [3], in the gas phase the *o*- and *p*-hydroxy isomers behave as phenols. The greater acidity of the hydroxyl group can be justified by the stabilization of the phenoxide ion [1] while no equivalent form is available for the *p*-hydroxybenzoate ion.

TABLE 1

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

X_{DMSO}	$\delta\Delta G_i^{g\rightarrow X}$ (kcal mole^{-1})	$\delta\Delta H_i^{g\rightarrow X}$ (kcal mole^{-1})	$T\delta\Delta S_i^{g\rightarrow X}$ (kcal mole^{-1})
0.0	11.67	13.93	2.26
0.1	15.23	13.61	−1.61
0.2	15.71	14.01	−1.68
0.3	10.48	14.68	4.20
0.4	9.99	19.02	9.03
0.5	9.62	18.17	8.55
0.6	9.62	18.17	8.55
0.7	8.91	20.59	11.68
0.8	8.71	17.19	8.48

TABLE 3

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

X_{DMSO}	$\delta\Delta G_t^{g-x}$ (kcal mole^{-1})	$\delta\Delta H_t^{g-x}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g-x}$ (kcal mole^{-1})
0.0	4.52	4.27	−0.25
0.1	4.58	4.68	0.10
0.2	4.67	7.71	3.03
0.3	4.93	8.26	3.33
0.4	4.74	10.15	5.41
0.5	5.65	11.56	5.91
0.6	4.97	10.74	5.77
0.7	5.05	8.26	3.27
0.8	5.18	9.82	4.64

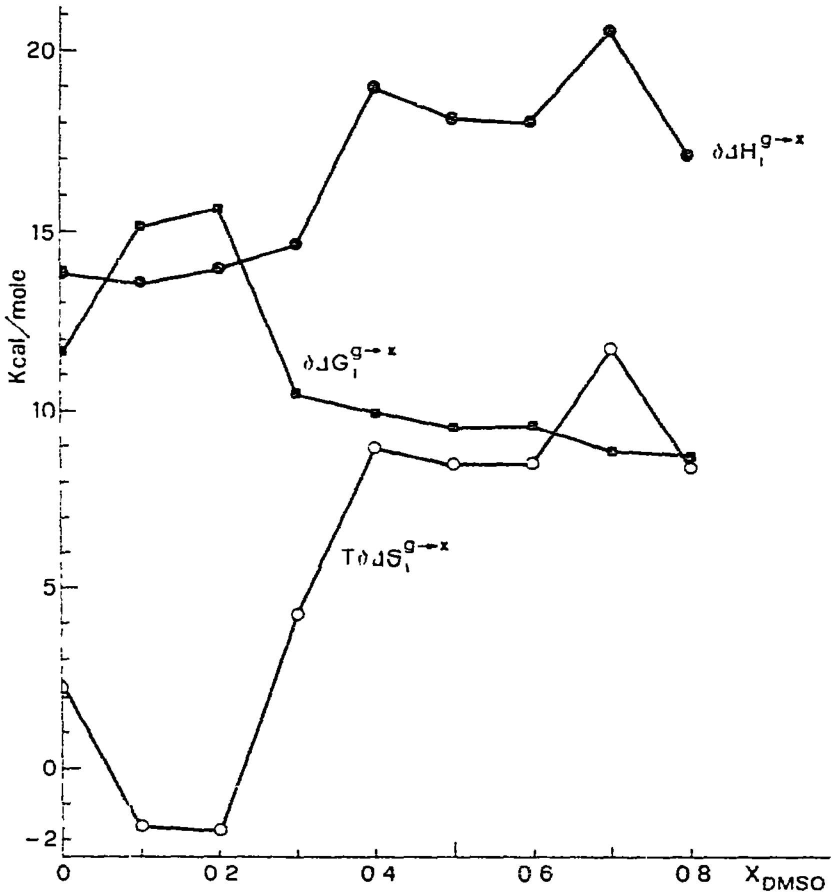


Fig. 1. Thermodynamic quantities for the proton transfer process of *o*-hydroxybenzoic acid in DMSO—water solutions, obtained by assuming a gaseous state as a reference.

TABLE 3

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

X_{DMSO}	$\delta\Delta G_{i}^{g-X}$ (kcal mole^{-1})	$\delta\Delta H_{i}^{g-X}$ (kcal mole^{-1})	$T\delta\Delta S_{i}^{g-X}$ (kcal mole^{-1})
0 0	4 52	4 27	−0 25
0 1	4 58	4 68	0 10
0 2	4 67	7 71	3 03
0 3	4 93	8 26	3 33
0 4	4 74	10 15	5 41
0.5	5 65	11.56	5 91
0 6	4 97	10 74	5 77
0 7	5 05	8 26	3 27
0 8	5 18	9 82	4 64

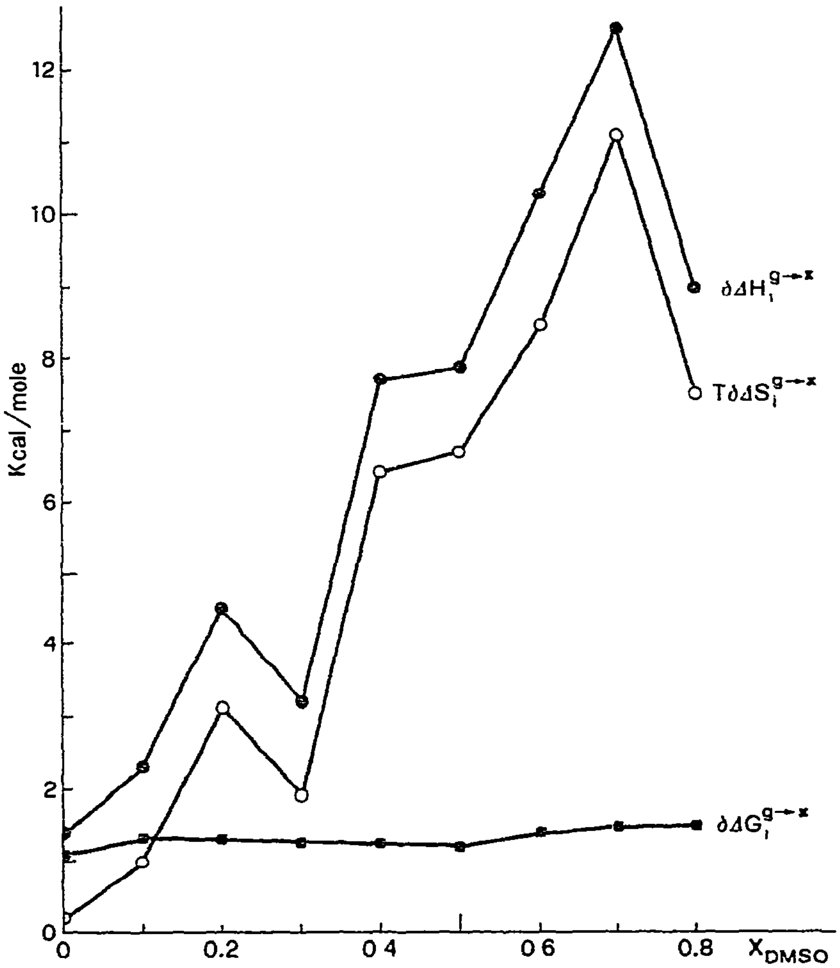


Fig. 2 Thermodynamic quantities for the proton transfer process of the *m*-hydroxybenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as a reference.

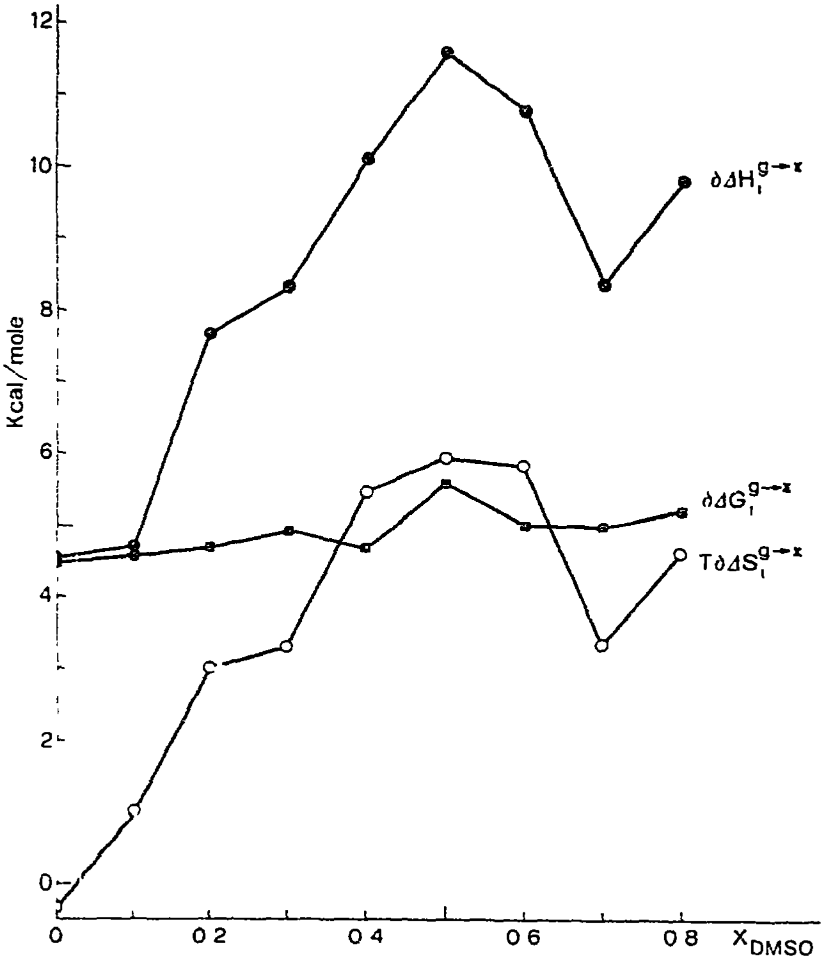
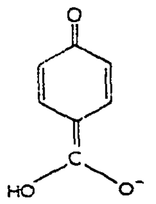


Fig 3 Thermodynamic quantities for the proton transfer process of *p*-hydroxybenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as a reference



(I)

The *ortho*-hydroxy isomer behaves as the *para*-isomer. This can be related to a stabilization of the *ortho*-anion by an internal hydrogen bond between the –COOH group and the $-O^-$. This is confirmed by the $\delta\Delta G_{t(g)}$ of the three isomers

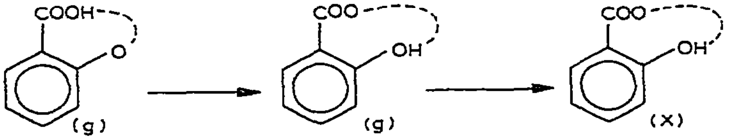
ortho $\delta\Delta G_t = -13.3$ kcal mole^{-1}

meta $\delta\Delta G_t = -\ 1.3$ kcal mole^{-1}

para $\delta\Delta G_t = -\ 4.0$ kcal mole^{-1}

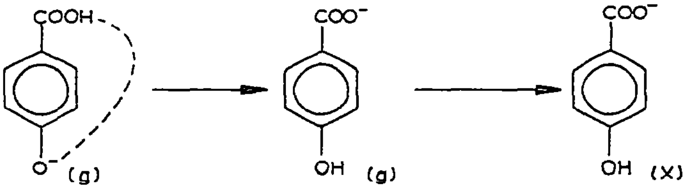
In the liquid phase, the *o*-hydroxybenzoic acid, from the enthalpic point of view, undergoes solvation from the gas phase with more difficulty than the *m*- and *p*-hydroxybenzoic acids. Indeed, in the gas phase the *o*-hydroxy isomer behaves like phenol. This allows a strong internal hydrogen bond between the $-$COOH group and the -0^-.

Thus, in the $\delta\Delta P_s^{g\rightarrow X} = \delta\Delta P_t^{g\rightarrow X}$ term the intramolecular proton transfer process must be included.



Both the intramolecular transfer process and the strong intramolecular hydrogen bond make the $\delta\Delta H_t^{g\rightarrow X}$ change unfavourable in the whole mole fraction.

The same intramolecular proton transfer process can be assumed for the *p*-hydroxybenzoic acid.



The less unfavourable $\delta\Delta H_t^{g\rightarrow X}$ values showed by the *p*-hydroxy compound can be related to the weak electron withdrawing effect of the hydroxyl group in the *para* position. Moreover, the resonance effect (R^+) in the *para* position decreases the inductive effect. For these reasons, in the water-rich mixtures, the *p*-hydroxy anion is strongly solvated by the water molecules.

It is also interesting to compare the entropic reaction constants of the proton transfer process with the entropic $T\delta\Delta S_t^{g\rightarrow X}$ term.

It is noteworthy that the shape of the $T\delta\Delta S_t^{g\rightarrow X}$ curve, for the *p*-hydroxy isomer, is very close (but symmetrical) to that [5] of the entropic reaction constants ρ_s.

This can be related to the negative values of p-σ_{OH} which, in turn, make negative the ρ_s values too, by increasing and thus localizing the negative charge on the carboxylate group.

It can be observed that in the 0.3–0.4 mole fraction range where the p-σ_{OH} values are greatly affected [5] by the solvent composition, the $T\delta\Delta S_t^{g\rightarrow X}$ values are very different from the ρ_s ones. This means that the σ_s-0.91σ–0.07 equation gives bad approximate values.

The most favourable $\delta\Delta H_t^{g\rightarrow X}$ term for the *m*-hydroxy isomer can be explained with the absence of the intramolecular transfer process, of the intramolecular hydrogen bond and of the resonance. All this contributes to a great localization [9] of the charge on the carboxylate group, so that an easier solvation of the anions from the gas phase is possible. Comparing the nitro-, chloro- and hydroxybenzoic acids the ease of solvation from the gas phase for the *ortho* isomers is as follows:

o-Cl > *o*-NO$_2$ > *o*-OH, while for the *meta*, the sequence is *m*-Cl > *m*-OH > *m*-NO$_2$. Finally, for the *para* isomers one has *p*-Cl > *p*-OH > *p*-NO$_2$. It is apparent that with the exception of the *o*-hydroxy isomer the nitro isomers experience the greatest difficulty in undergoing solvation from the gas phase.

This fact can be further explained. by taking into account the "volume" of the nitro group which would show the greatest difficulty in creating a cavity in the medium. Indeed, it has to be noted [13] that the radius of the cavity in a solvent is given as a function of the sum of the solvent and solute diameters.

Furthermore, while the variation [13] of the free energy of the cavity with the diameter of solvent, for the same molecule of the solute, is very close in water and DMSO, the variation in the enthalpy of the cavity is much greater in DMSO. This is in keeping with our results.

REFERENCES

1 M G Bonicelli, G Ceccaroni and F Rodante, Thermochim Acta, 52 (1982) 45
2 F Rodante and M Pasquali, Thermochim Acta, 51 (1981) 191
3 T B McMahon and P Kebarle, J Am Chem Soc, 99 (1977) 222
4 F Rodante, G Ceccaroni and M G Bonicelli, Thermochim Acta 42 (1980) 223
5 F Rodante, M G Bonicelli and G Ceccaroni, Thermochim Acta, 43 (1981) 199
6 F Rodante and G Pistoia, Thermochim Acta, 43 (1981) 325
7 F Rodante, F Rallo and P Fiordiponti, Thermochim Acta, 9 (1974) 269
8 L G Hepler and W F O'Hara, J Phys Chem, 65 (1961) 811
9 L G Hepler, Can J Chem, 49 (1971) 2809
10 T Matsui and L G Hepler, Can J Chem, 54 (1977) 1296
11 R. Yamdagni, T B McMahon and P Kebarle, J Am Chem Soc, 96 (1974) 4035
12 J B Cumming and P Kebarle, Can J Chem, 56 (1978) 1
13 N Morel-Desrosiers and J P Morel, Can J Chem, 59 (1981) 1