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STUDY OF THE PROTON TRANSFER PROCESSES OF NITROPHENOLS TO NITROBENZOIC ACIDS AND TO BENZOIC ACID IN WATER–DIMETHYLSULFOXIDE MIXTURES COMPARED WITH THE SAME PROCESSES IN THE GASEOUS PHASE

F. RODANTE AND M PASQUALI

Istituto di Chimica, Facolta di Ingegneria, Università di Roma, Rome (Italy)

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ABSTRACT

A study of the proton transfer processes from the nitrophenols to nitrobenzoic acids in water–DMSO mixtures compared with the processes in the gaseous phase is presented

By means of two thermodynamic cycles which refer to a gaseous initial thermodynamic state, it has been possible to calculate the "external" interactions of the cited processes

The internal hydrogen bond plays a very important role, in the gas and in the liquid phase, for the *ortho* isomers

In the *para* derivatives the resonance effect prevails in the solvation of the phenols over the whole mole fraction, while in the *meta* derivatives the inductive effect influences the solvation of the phenols only in water-rich solutions

INTRODUCTION

The proton transfer processes from chloro-, nitro- and hydroxybenzoic acids to benzoic acid in water–dimethylsulfoxide (DMSO) mixtures, in comparison with the same processes in the gaseous phase have been studied [1–3].

By using a thermodynamic cycle we have calculated, in the solvent X, a proton transfer process which refers to a gaseous initial thermodynamic state.

The thermodynamic values $\delta\Delta P_1^{g\to X}$ calculated in this way have been assumed as a measure of the "external" interactions of the above processes.

The ease of solvation from the gaseous phase to various solutions was as follows: chloro isomers > hydroxy isomers > nitro isomers, except for the *ortho* derivatives for which the greatest difficulty of solvation was shown by the hydroxy isomer.

This general trend of solvation from the gas phase could be accounted for mostly by the site of the molecule—the greatest being that of the nitro group.

It seemed that it would be interesting to compare the influence of the nitro group in the corresponding phenol and benzoic acid.

Furthermore, this study can explain the influence, with respect to solvation from

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the gas phase, of the internal hydrogen bond in the undissociated molecules and in the ions.

In a previous work [4], some linear free energy relationships between the dissociation of nitrophenols and nitrobenzoic acids in various water–DMSO mixtures have been studied.

The following equations have been considered.

$$(NO_2\text{-}PhOH)_X + (PhO^-)_X = (NO_2\text{-}PhO^-)_X + (PhOH)_X \qquad (1)$$

$$(NO_2\text{-}PhCOOH)_X + (PhCOO^-)_X = (NO_2\text{-}PhCOO^-)_X + (PhCOOH)_X \qquad (2)$$

$$-\delta\Delta G^\circ = 2.303\,RT\rho\sigma \qquad (3)$$

$$-\delta\Delta G = 2.303\,RT\rho(\sigma + R\Delta\sigma_p^-) \qquad (4)$$

$$-\delta\Delta G = \rho_o\sigma_o + fF + \delta E_s + rR \qquad (5)$$

where X (ranging from 0.0 to 0.8) represents the mole fraction of the solvent.

In the above equations the inductive, resonance, steric effect and the electrostatic effect related to the internal hydrogen bond were factored in the various terms and coefficients.

The trends of the entropic reaction constants ρ_s, show that the stabilization of the negative charge on the phenate ion reduces the number of intermolecular hydrogen bonds among the anions of the phenol isomers and the water molecules as compared with those of the benzoic acid. This fact allows the solvent to interfere, to a minor extent, with the interactions between the reaction site and the substituent group.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, the preparation of the DMSO–water mixtures and the technique for obtaining the thermodynamic values for the nitrobenzoic acids [5], the nitrophenols [6] and benzoic acid [7] have previously been described.

RESULTS AND DISCUSSION

The thermodynamic cycle used to calculate the "external" interactions employs this time the isomers of the nitrobenzoic acid as reference compounds.

$$\begin{tikzcd}
NO_2\text{-}PhOH_{(g)} \arrow[d, "\Delta P_s"] & +NO_2\text{-}PhCOO^-_{(g)} \arrow[r, "\delta\Delta P_{t(g)}"] \arrow[d, "\Delta Ph_s"] & NO_2\text{-}PhO^-_{(g)} \arrow[d, "\Delta P_s"] & +NO_2\text{-}PhCOOH_{(g)} \arrow[d, "\Delta P_s"] \\
(NO_2\text{-}PhOH)_X & +(NO_2\text{-}PhCOO^-)_X \arrow[r, "\delta\Delta P_{t(X)}"] & (NO_2\text{-}PhO^-)_X & +(NO_2\text{-}PhCOOH)_X
\end{tikzcd} \qquad (6)$$

where $\delta\Delta P_{t(g)}$ is, following previous conventions [1–3], the gas phase change of some thermodynamic properties ($P_t = G, H, S$), for the proton transfer process, while

$\delta\Delta P_{i(X)}$ is the corresponding value in solvent X. Thus one can write

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

the right-hand side of the eqn. (7) being assumed as the proton transfer process, in solvent X, which refers to a gaseous initial thermodynamic state, i.e. $\delta\Delta P_s^{g\rightarrow X} = \delta\Delta P_i^{g\rightarrow X}$. Again we assume the $\delta\Delta P_i^{g\rightarrow X}$ term as a measure of the "external" interactions, so that it is reasonable to suppose that the $\delta\Delta P_{i(X)}$ term represents the "overall" interactions and $\delta\Delta P_{i(g)}$ the "internal" ones. By using the values [8] of McMahon and Kebarle, it is possible to calculate $\delta\Delta G_{i(g)}$ values for the *o*-, *m*- and *p*-nitro isomers of the phenols with respect to the nitrobenzoic acids.

The $\delta\Delta G_{i(X)}$ values can be calculated by means of the ionization values previously calculated [5,6]. So, by using eqn. (7). it is possible to calculate $\delta\Delta G_i^{g\rightarrow X}$ values.

As previously shown [1–3], for such reactions as those considered here, the symmetry numbers are small and almost cancel out. So $\delta\Delta G_{i(g)}$ can be put $\simeq 0$ and then $\delta\Delta G_{i(g)600\ K} \simeq \delta\Delta G_{i(g)300\ K} \simeq \delta\Delta H_{i(g)}$.

From this, it is also possible to calculate the $\delta\Delta H_i^{g\rightarrow X}$ values. The $T\delta\Delta S_i^{g\rightarrow X}$ term can be calculated by means of the enthalpic and free energy terms.

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

In the gas phase it can be seen that the proton transfer process shows an unfavourable $\delta\Delta G_i^{g\rightarrow X}$ term for the *ortho* and *meta* isomers. Indeed for the *ortho* derivatives, the internal hydrogen bond of the nitrophenol is stronger than that of the nitrobenzoic acid.

In the *meta* derivatives, the nitro group influences the hydroxyl group to a lesser extent than the carboxylate group. For the *para* isomers, the contrary is true. Indeed, in the latter isomers, the nitro group disperses and thus stabilizes the negative charge developed in the phenate ion much more than in the carboxylate ion.

In the solvation from the gas to the liquid phase the $\delta\Delta H_i^{g\rightarrow X}$ term for the *ortho* derivatives is unfavourable mostly beyond $X_{\mathrm{DMSO}} > 0.6$, again because of the

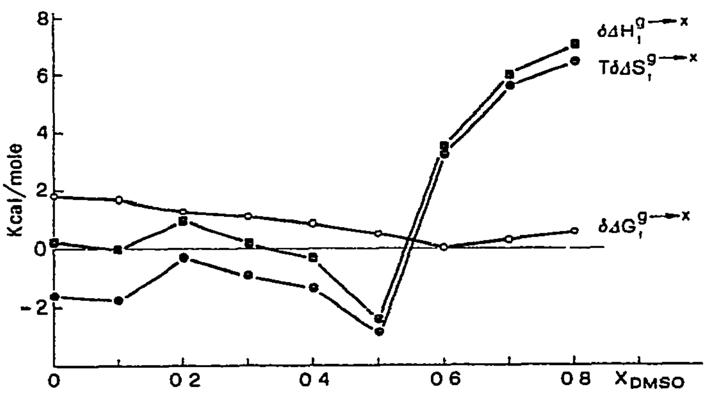

Fig. 1. Thermodynamic quantities for the proton transfer process of *o*-nitrophenol to *o*-nitrobenzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

TABLE 1

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

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	1.78	0.23	−1.55
0.1	1.67	−0.02	−1.69
0.2	1.31	1.01	−0.30
0.3	1.09	0.19	−0.90
0.4	0.94	−0.29	−1.33
0.5	0.54	−2.40	−2.94
0.6	0.13	3.48	3.35
0.7	0.28	6.02	5.74
0.8	0.57	7.11	6.54

TABLE 2

Free energy, enthalpy and entropy values for the proton transfer process from *m*-nitrophenol to *m*-nitrobenzoic acid in water–DMSO mixtures calculated by assuming a gaseous initial thermodynamic state

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	3.19	0.96	−2.23
0.1	3.12	0.40	−2.72
0.2	3.40	−3.79	−7.19
0.3	3.13	0.78	−2.35
0.4	3.14	−1.58	−4.72
0.5	2.63	5.00	2.37
0.6	2.58	1.37	−1.21
0.7	2.73	6.91	4.18
0.8	3.37	14.32	10.95

TABLE 3

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

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	9.56	8.72	−0.84
0.1	5.39	9.76	4.07
0.2	9.94	12.06	2.12
0.3	9.61	9.18	−0.43
0.4	9.20	19.57	10.37
0.5	8.71	21.96	13.26
0.6	8.58	14.73	6.15
0.7	8.51	19.61	11.10
0.8	9.04	12.63	3.59

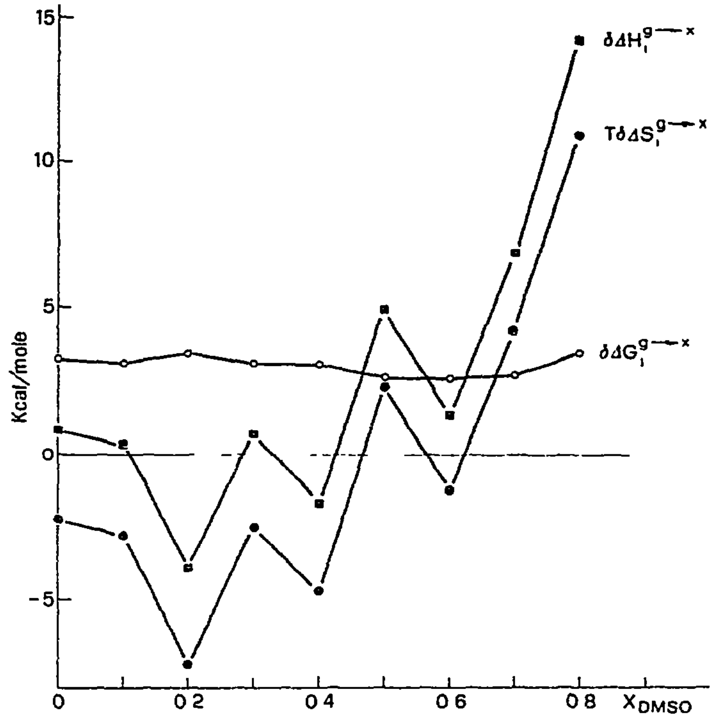

Fig 2 Thermodynamic quantities for the proton transfer process of *m*-nitrophenol to *m*-nitrobenzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

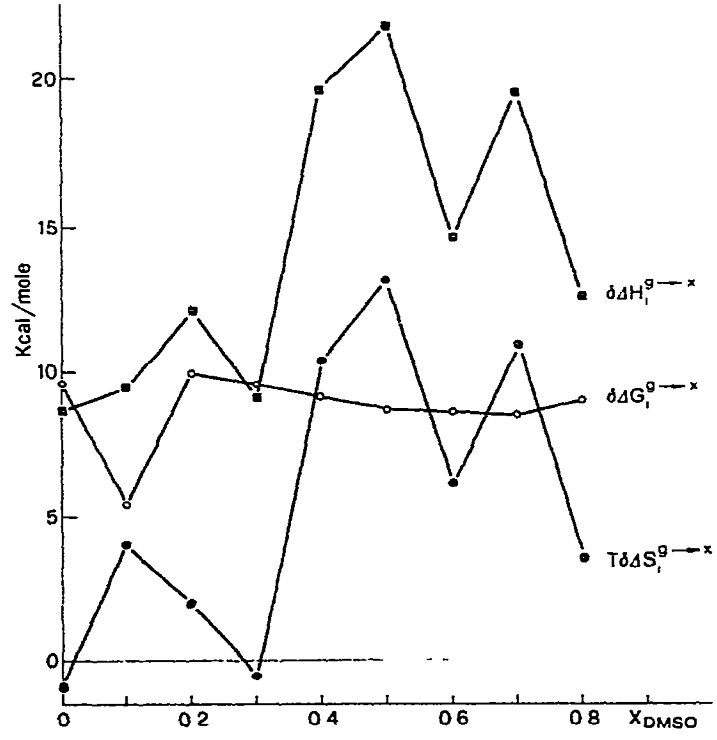

Fig 3 Thermodynamic quantities for the proton transfer process of *p*-nitrophenol to *p*-nitrobenzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

stronger internal hydrogen bond of the phenol. In the 0.4–0.5 mole range this term is favourable. This will be explained later.

For the *para* derivatives, the $\delta\Delta H_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}}$ term is very unfavourable. This is due to the drastic delocalization of the negative charge on the oxygen atom of the phenate ion.

Finally, for the *meta* derivatives, the smaller inductive effect of the nitro group on the hydroxyl group localizes the negative charge developed in the phenate ion much more than in the carboxylate ion. So, in the mole fraction where a sufficient number of water molecules is present, there are favourable $\delta\Delta H_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}}$ values.

For a better understanding of these curves, it is useful to take into account another cycle, which employs the benzoic acid as a reference compound.

$$\begin{tikzcd}
\mathrm{NO_2{-}PhOH_{(g)}} \arrow[d, "\Delta P_s"] & +\,\mathrm{PhCOO^-_{(g)}} \arrow[r, "\delta\Delta P_{i(g)}"] \arrow[d, "\Delta P_s"] & \mathrm{NO_2{-}PhO^-_{(g)}} \arrow[d, "\Delta P_s"] & +\,\mathrm{PhCOOH_{(g)}} \arrow[d, "\Delta P_s"] \\
(\mathrm{NO_2{-}PhOH})_X & +\,(\mathrm{PhCOO^-})_X \arrow[r, "\delta\Delta P_{i(X)}"] & (\mathrm{NO_2{-}PhO^-})_X & +\,(\mathrm{PhCOOH})_X
\end{tikzcd}$$

Then, we can calculate, as previously shown, the "internal", "external" and "overall" interactions $\delta\Delta P_{\mathrm{i}}$ which are related to each other by the relation

$$\delta\Delta P_{\mathrm{i(X)}} - \delta\Delta P_{\mathrm{i(g)}} = \delta\Delta P_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}} \tag{8}$$

These values are reported in Tables 4–6 and are plotted against DMSO mole fraction in Figs. 4–6 Equation (7) can be considered as the difference of eqn. (8)

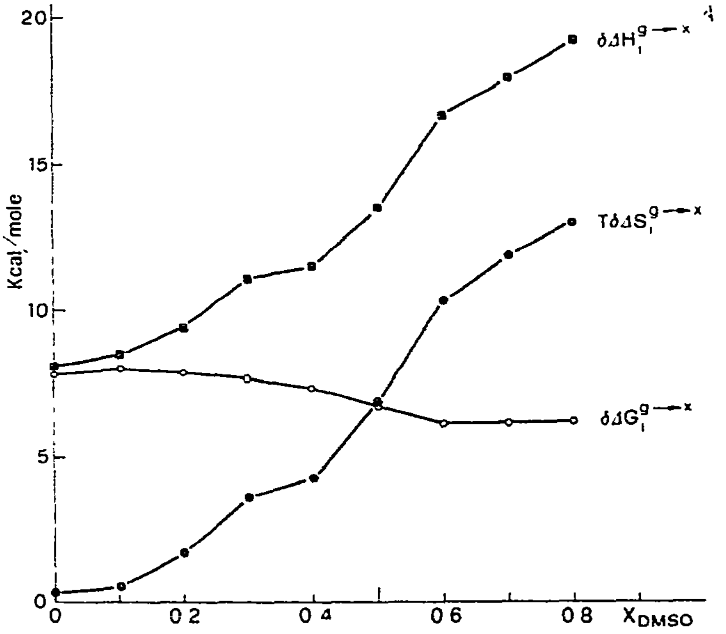

Fig 4 Thermodynamic quantities for the proton transfer process of *o*-nitrophenol to benzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

TABLE 4

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

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	7.81	8.15	0.34
0.1	8.01	8.54	0.53
0.2	7.79	9.47	1.68
0.3	7.55	11.15	3.60
0.4	7.28	11.56	4.28
0.5	6.71	13.51	6.80
0.6	6.14	16.55	10.41
0.7	6.11	18.05	11.94
0.8	6.25	19.33	13.08

TABLE 5

Free energy, enthalpy and entropy values for the proton transfer process from *m*-nitrophenol to benzoic acid in water–DMSO mixtures calculated by assuming a gaseous initial thermodynamic state

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	11.20	10.30	−0.90
0.1	10.90	11.02	0.12
0.2	10.97	10.67	−0.30
0.3	10.50	18.33	7.83
0.4	10.34	19.60	9.26
0.5	9.67	26.74	17.07
0.6	9.48	23.60	14.12
0.7	9.48	23.60	14.08
0.8	10.04	29.75	19.71

TABLE 6

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

X_{DMSO}	$\delta\Delta G_t^{g\to X}$ (kcal mole^{-1})	$\delta\Delta H_t^{g\to X}$ (kcal mole^{-1})	$T\delta\Delta S_t^{g\to X}$ (kcal mole^{-1})
0.0	19.63	20.15	−0.52
0.1	19.72	20.73	1.01
0.2	19.60	23.45	3.85
0.3	22.10	25.15	3.06
0.4	18.57	35.39	16.82
0.5	18.00	36.84	18.84
0.6	17.72	30.47	12.75
0.7	17.48	36.60	19.12
0.8	17.85	33.56	15.71

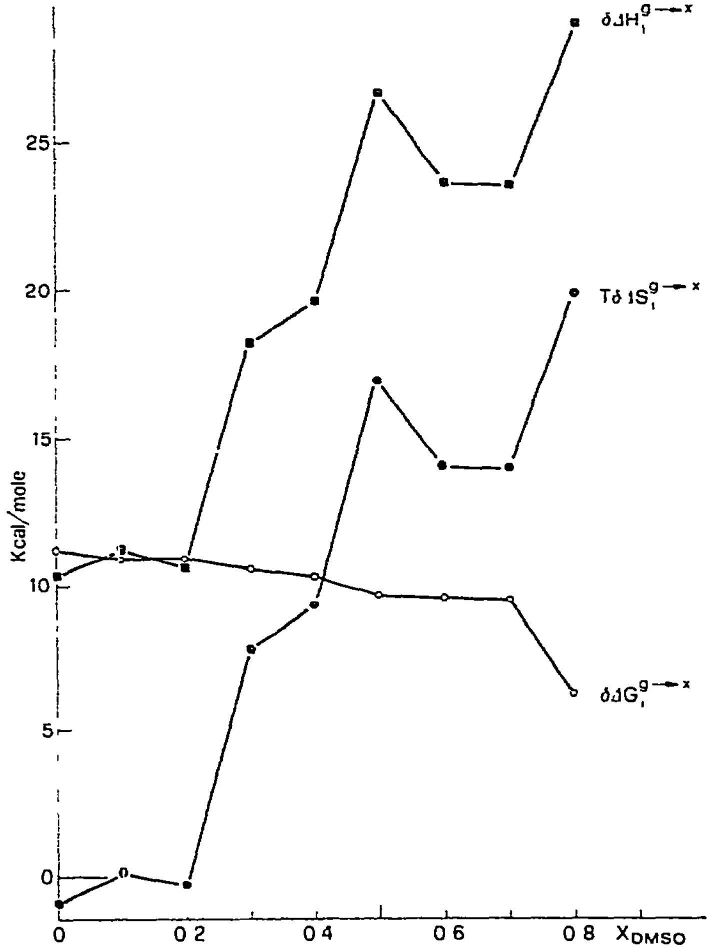

Fig. 5. Thermodynamic quantities for the proton transfer process of *m*-nitrophenol to benzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

and the similar equation in ref. 2 related to the transfer proton process from nitrobenzoic acids to benzoic acid.

Comparing Fig. 1 with Fig. 4 and with Fig. 1 of ref. 2 (related to the transfer proton process of the nitrobenzoic acid) the minimum at $X_{DMSO} = 0.5$ can be ascribed to the greater difficulty of solvation, at the same mole fraction, shown by the undissociated molecule of the *o*- nitrobenzoic compared with the benzoic acid.

Conversely, the term unfavourable to solvation $\delta\Delta H_t^{g\to X}$ increases linearly for the nitrophenol/benzoic acid couple.

The comparison between Fig. 5 and Fig. 2 of ref. 2 (nitrobenzoic acid) shows that the curves of the nitrophenol/benzoic acid and nitrobenzoic/benzoic acid for the *meta* derivatives are similar.

In the mole fraction range 0.1–0.3 the solvation from gas phase is easier for the phenol curve, whereas in the remaining mole fraction the contrary is true.

Finally, a comparison of the curves of the *para* isomers (Fig. 6 and Fig. 3 of ref. 2) shows that for the couple nitrophenol/benzoic acid the $\delta\Delta H_t^{g\to X}$ values are very

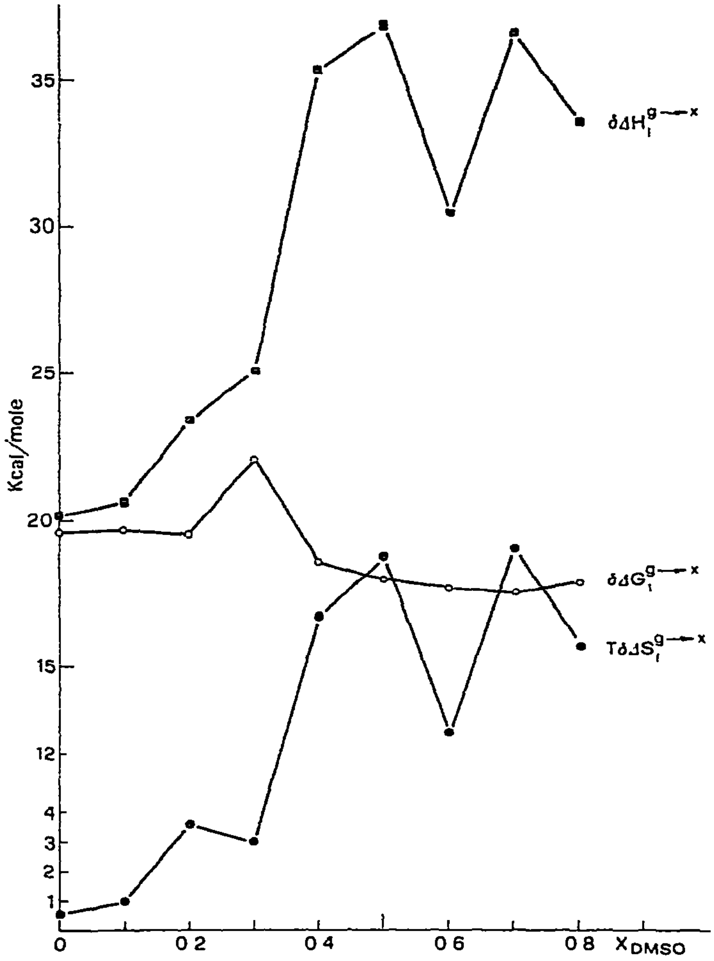

Fig 6 Thermodynamic quantities for the proton transfer process of *p*-nitrophenol to benzoic acid in water–DMSO solutions, obtained by assuming a gaseous state as a reference

unfavourable and they greatly influence the shape of the nitrophenol/nitrobenzoic acid curve.

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