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A STUDY OF THE PROTON TRANSFER OF CHLORO-SUBSTITUTED BENZOIC ACIDS IN WATER–DIMETHYLSULFOXIDE MIXTURES COMPARED WITH THE SAME PROCESS IN THE GASEOUS PHASE

M G BONICELLI, G CECCARONI and F RODANTE *

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

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ABSTRACT

A study of the proton transfer process from chloro-substituted benzoic acids to benzoic acid in H_2O–DMSO mixtures compared with the same process in the gaseous phase is presented. A thermodynamic cycle was used to calculate, in solvent X, a proton transfer process which refers to a gaseous initial thermodynamic state, i.e. $\delta\Delta P_i^{g\to x}$. Values of this term have been assumed as a measure of "external" interactions of the proton transfer process among molecules, anions and solvent. It has been shown that the shapes of $T\delta\Delta S_i^{g\to x}$ and $\delta\Delta G_i^{g\to x}$ curves are very close to those of the entropic reaction constants and of the substituted constants calculated for the same acids in previous works.

INTRODUCTION

The ionization processes of benzoic and chlorobenzoic acids in water–dimethylsulfoxide (DMSO) mixtures ranging from 0.0 to 0.8 mole fractions have been examined [1,2]. Again, the enthalpic and entropic contributions to substituent effects on the dissociation of the *ortho*, *meta* and *para* chlorobenzoic acids in the same solutions have been investigated [3,4].

The following equations have been used to illustrate the substituent effects

$$(\text{Cl–PhCOOH})_X + (\text{PhCOO}^-)_X = (\text{Cl–PhCOO}^-)_X + (\text{PhCOOH})_X \tag{1}$$

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho\sigma = \rho_H\sigma_H + \rho_S\sigma_S \tag{2}$$

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_O\sigma_O + fF + \delta E_S = \rho_H\sigma_H + \rho_S\sigma_S + fF + \delta E_S \tag{3}$$

In eqn. (2) $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are defined by the relations

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303RT} \tag{4a}$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303R} \tag{4b}$$

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* To whom correspondence should be addressed

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while in eqn. (3) $\rho_H\sigma_H$ and $\rho_S\sigma_S$ are defined as

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303RT} - \delta E_S \tag{5a}$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303R} - fF \tag{5b}$$

X (ranging from 0.0 to 0.8) represents the mole fraction of the solvent and f, F, δ and E_S values in the same mole fractions are reported in the literature [5].

The effects of the medium on the substituent and on reaction constants were explained in terms of solute–solvent interactions. These interactions were regarded as "external" interactions and were found to be chiefly inductive in character.

Hepler [6–9] has supposed the usefulness of expressing thermodynamic functions of reactions of type (1) in terms of "internal" and "external" contributions as in the following

$$\delta\Delta H^0 = \delta\Delta H_{in} + \delta\Delta H_{ex}$$

$$\delta\Delta S^0 = \delta\Delta S_{in} + \delta\Delta S_{ex}$$

"Internal" effects are those intrinsic to the molecule and the anion of the acid, whereas "external" ones derive from solvent interactions with molecules and anions. To separate the solvent effects from the intrinsic molecular effects in eqn. (1) it is necessary to know the thermodynamics for the same process occurring in the gaseous phase.

Information regarding the intrinsic acidities is obtained from the gas phase proton transfer reactions

$$A_1H + A_2^- = A_1^- + HA_2 \tag{6}$$

These studies were carried out by means of ICR mass spectrometry [10], high-pressure pulsed ions sources [11] and flowing afterglow apparatus measurements [12].

The free energy changes $\delta\Delta G^0$ for the proton transfer process in eqn. (6) were determined by measuring $\delta\Delta G^0 = -RT \ln K$. The values obtained by McIver and Silvers [13] at 25°C with ICR measurements are in good agreement with those of Yamdagni et al. [14], at 327°C, obtained with high-pressure mass spectrometry. Furthermore, the entropy terms for such processes in the gaseous phase are assumed to be negligible [14,15] so that $\delta\Delta G_{i(g)} \approx \delta\Delta H_{i(g)}$. In some cases changes of rotational symmetry numbers may lead to a small entropy change which causes a difference of about [16] 1–2 kcal between the enthalpy change in reaction (6) and the measured free energy. For the same reasons, an uncertainty of the same magnitude between $\delta\Delta G^0_{600\,K}$ and $\delta\Delta G^0_{300\,K}$ is possible [16].

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO–water mixtures and the technique for obtaining the thermodynamic values for benzoic and chlorobenzoic acid have been described previously [1,2].

RESULTS AND DISCUSSION

The cycle used to calculate the "external" interactions employs the benzoic acid as a reference compound as follows

$$\begin{tikzcd}
\text{Cl-PhCOOH}_{(g)} \arrow[d, "\Delta P_s"] & + & \text{PhCOO}^-_{(g)} \arrow[r, "\Delta P_{i(g)}"] \arrow[d, "\Delta P_s"] & \text{Cl-PhCOO}^-_{(g)} \arrow[d, "\Delta P_s"] & + & \text{PhCOOH}_{(g)} \arrow[d, "\Delta P_s"] \\
\text{Cl-PhCOOH}_{(X)} & + & \text{PhCOO}^-_{(X)} \arrow[r, "\Delta P_{i(X)}"] & \text{Cl}-\text{PhCOO}^-_{(X)} & + & \text{PhCOOH}_{(X)}
\end{tikzcd}$$

So we can write

$$\delta\Delta P_{i(X)} - \delta\Delta P_{i(g)} = [\Delta P_s(\text{Cl-PhCOO}^-) - \Delta P_s(\text{ClPhCOOH})] - \\ - [\Delta P_s(\text{PhCOO}^-) - \Delta P_s(\text{PhCOOH})]$$

and again

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

where $\delta\Delta P_{i(g)}$ will be the gaseous phase change of any thermodynamic property ($P_i = G, H, S$) for the proton transfer from the substituted acid to benzoic acid. The corresponding value in solvent X is $\delta\Delta P_{i(X)}$. The right-hand term of eqn. (7) can be assumed as the proton transfer, 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 assume that in the equation

$$\delta\Delta P_{i(X)} = \delta\Delta P_{i(g)} + \delta\Delta P_i^{g\rightarrow x} \qquad (8)$$

the $\delta\Delta P_{i(X)}$ term represents the total interactions, $\delta\Delta P_{i(g)}$ the "internal" interactions and $\delta\Delta P_i^{g\rightarrow x}$ the "external" ones.

By using the values of McMahon and Kerbale [15], it is possible to calculate the $\delta\Delta G_{i(g)}$ values for the *o*-, *m* and *p*-chlorobenzoic acid. The $\delta\Delta G_{i(g)}$ and $\delta\Delta G_{i(X)}$ values [3,4] are included in eqn. (8) and the $\delta\Delta G_i^{g\rightarrow x}$ values are calculated.

It is well known [16] that both the "external" and "internal" rotations in the half-process $HA_i \rightarrow A_i^-$ occurring in the gaseous phase are responsible for the loss of entropy in eqn. (6), so that $\delta\Delta S_{i(g)} \neq 0$. However, for reactions such as those considered here, symmetry numbers are small and almost cancel out. So, if we put [15] $\delta\Delta S_{i(g)} \approx 0$, then $\delta\Delta G_{i(g)}$ (600 K) $\approx \delta\Delta G_{i(g)}$ (298 K) $\approx \delta\Delta H_{i(g)}$ and it is possible to calculate the $\delta\Delta H_i^{g\rightarrow x}$ and $T\delta\Delta S_i^{g\rightarrow x}$ values at 298 K. All these values are reported in Tables 1–3 and are plotted against DMSO mole fraction in Figs. 1–3. These figures represent the "external" interactions of the proton transfer of the chloro-derivatives with the medium. It is interesting to compare the reaction and substituent constants for the proton transfer with the entropic $T\delta\Delta S_i^{g\rightarrow x}$ and free energy $\delta\Delta G_i^{g\rightarrow x}$ terms of these figures. In previous works [3,4], the solute–solvent interactions were expressed as entropic reaction constants.

It is worth noting that the shape of $T\delta\Delta S_i^{g\rightarrow x}$ curves, for the *ortho* chloro isomer, is very close to that of the entropic reaction constant ρ_S [4], which is derived by eqns.

TABLE 1

Enthalpy, entropy and free energy values for the proton transfer process of *ortho* chlorobenzoic acid in DMSO–water mixtures calculated by assuming a gaseous initial thermodynamic state (all thermodynamic quantities are given in kcal mole^{-1})

x_{DMSO}	$\delta\Delta G_t^{g\to s}$	$\delta\Delta H_t^{g\to s}$	$T\delta\Delta S_t^{g\to s}$
0.0	2.08	1.2	−0.88
0.1	2.38	2.06	−0.32
0.2	2.64	5.55	2.91
0.3	2.63	4.64	1.99
0.4	2.52	4.49	1.97
0.5	2.18	4.57	2.39
0.6	2.41	8.22	5.81
0.7	2.22	12.22	10.01
0.8	2.23	9.68	7.45

TABLE 2

Enthalpy, entropy and free energy values for the proton transfer process of *meta* chlorobenzoic acid in DMSO–water mixtures calculated by assuming a gaseous initial thermodynamic state (all thermodynamic quantities are given in kcal mole^{-1})

x_{DMSO}	$\delta\Delta G_t^{g\to s}$	$\delta\Delta H_t^{g\to s}$	$T\delta\Delta S_t^{g\to s}$
0.0	4.20	4.63	0.43
0.1	4.05	4.48	0.43
0.2	3.97	5.66	1.69
0.3	3.94	6.57	2.63
0.4	3.99	4.73	0.74
0.5	3.61	6.88	3.27
0.6	3.60	8.36	4.76
0.7	3.49	7.54	3.75
0.8	3.32	10.52	7.20

TABLE 3

Enthalpy, entropy and free energy values for the proton transfer process of *para* chlorobenzoic acid in DMSO–water mixtures, calculated by assuming a gaseous initial thermodynamic state (all thermodynamic quantities are given in kcal mole^{-1})

x_{DMSO}	$\delta\Delta G_t^{g\to s}$	$\delta\Delta H_t^{g\to s}$	$T\delta\Delta S_t^{g\to s}$
0.0	1.54	4.55	3.01
0.1	3.81	4.33	0.52
0.2	3.73	5.22	1.49
0.3	3.76	7.51	3.75
0.4	3.91	7.24	3.33
0.5	3.69	4.20	0.51
0.6	3.69	5.30	1.61
0.7	3.46	7.35	3.89
0.8	3.51	9.99	6.48

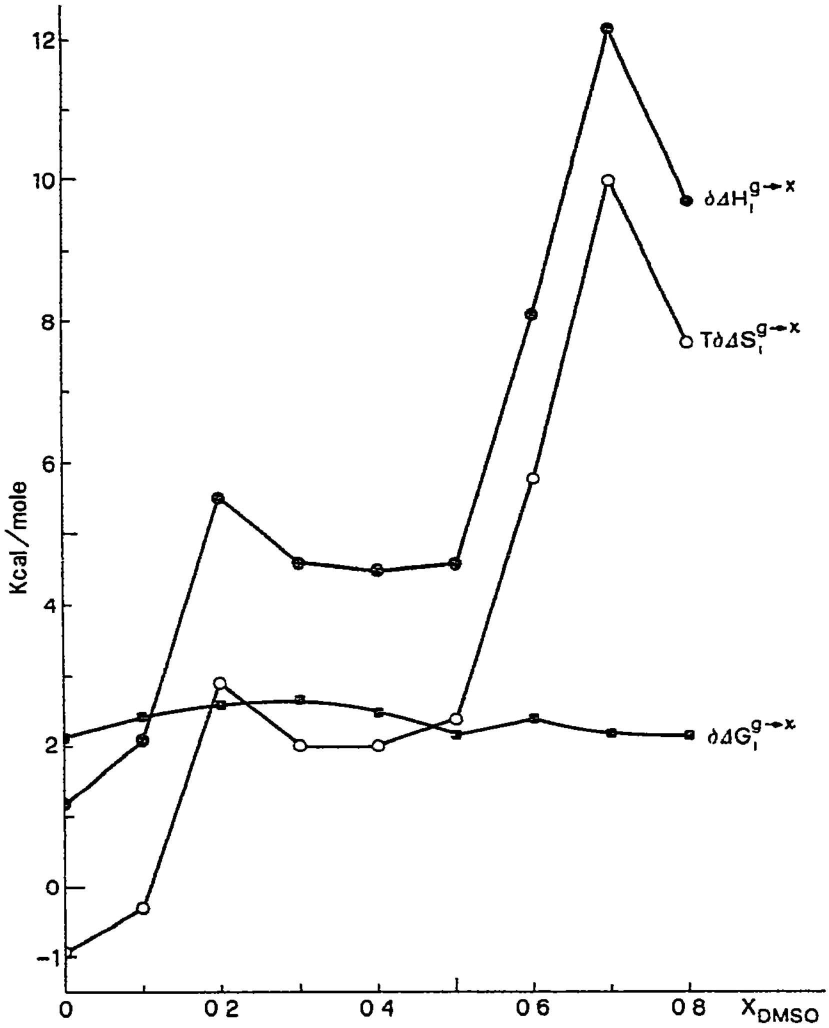

Fig 1 Thermodynamic quantities for the proton transfer process of *ortho* chlorobenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as reference

(3) and (5b). Yet the $T\delta\Delta S_i^{g\rightarrow x}$ curve gives a measure of the values of the solute–solvent interactions, while the ρ_S curve gives only a trend.

Keeping in mind that the $\delta\Delta S_i$ term in the gaseous phase is nearly equal to zero, it can be seen that in the water-rich solutions the entropic term $T\delta\Delta S_i^{g\rightarrow x}$ turns out to be unfavorable to proton transfer. Therefore, the last process is more "order forming" and thus more anti-entropic in these solutions than it was in the gas phase. This can be related, in pure water, to the appearance of the hydrogen bond $A^- \ldots H^+\!-\!OH$. The intramolecular hydrogen bond, which in the gas phase decreases the acidity of the *ortho* compound, in water-rich solutions hinders the solvation of the undissociated molecule, so favoring the transfer of the proton. Furthermore, the chlorine atom in the *ortho* position keeps a portion of the negative charge away from the $-COO^-$ group, thus decreasing the H_2O–anion hydrogen

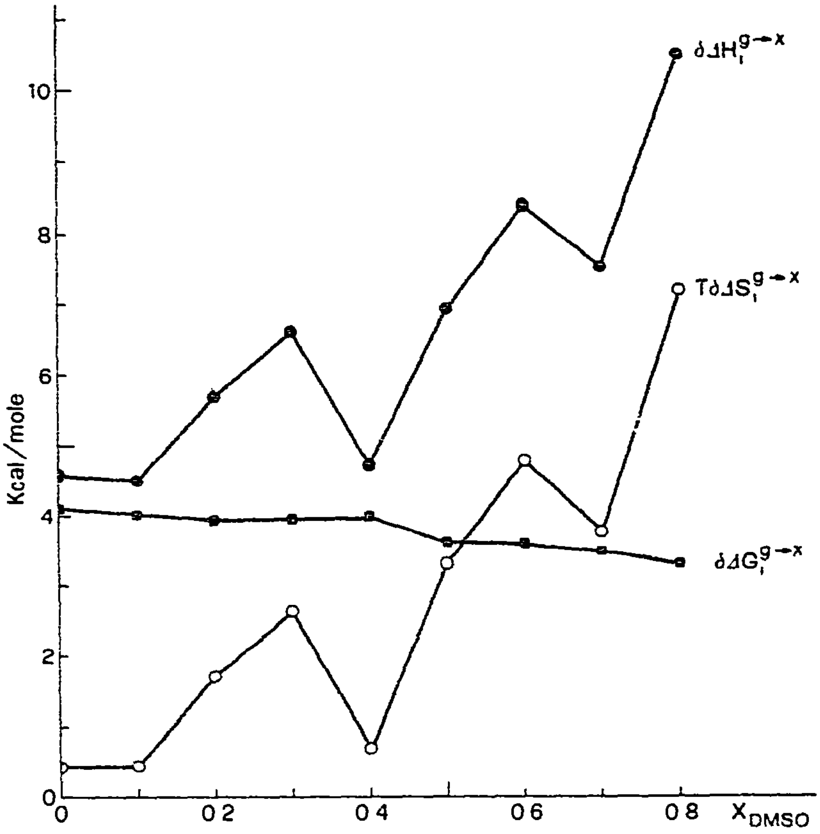

Fig 2 Thermodynamic quantities for the proton transfer process of *meta* chlorobenzoic acid in DMSO-water solutions, obtained by assuming a gaseous state as reference

bond. So the solvation of the *ortho* anion is very sensitive to decreasing H_2O content. In the mole fraction range 0.1–0.2 the greater disorder of the solvent in the neighborhood of the substituted anion (due to a diminished number of hydrogen bonds $A^- \ldots H^- {-} OH$, which in turn is related to a drastic decrease in $H_2O/DMSO$ molar ratio) causes a sharp increase of a favorable entropy change. From 0.2 to 0.5 mole fraction, where the ratio $H_2O/DMSO$ decreases slowly, the hydrogen bonds are able to offset the increasing solvent disorder [2].

Beyond the 0.5 mole fraction there is a sharp increase in the entropy term, due to the large percentage of DMSO, highly associated by itself, so that the last term is favorable to a proton transfer process.

In DMSO-rich mixtures both the anions are desolvated and there is a similarity between the behavior in DMSO and in the gas phase, i.e. the substituent effect is contained predominantly in the enthalpy change.

In the water-rich solutions the $\delta\Delta G_t^{g-x}$ term is somewhat greater than the enthalpic term so that the substituent effect is in part reflected in the entropy term. The favorable $\delta\Delta H_{t(g)}$ change in the gas phase, due to an acidifying substituent, is wiped out in solution by an unfavorable effect of the same substituent exerted mostly on the anion. This effect makes unfavorable the $\delta\Delta H_t^{g-x}$ change in the whole

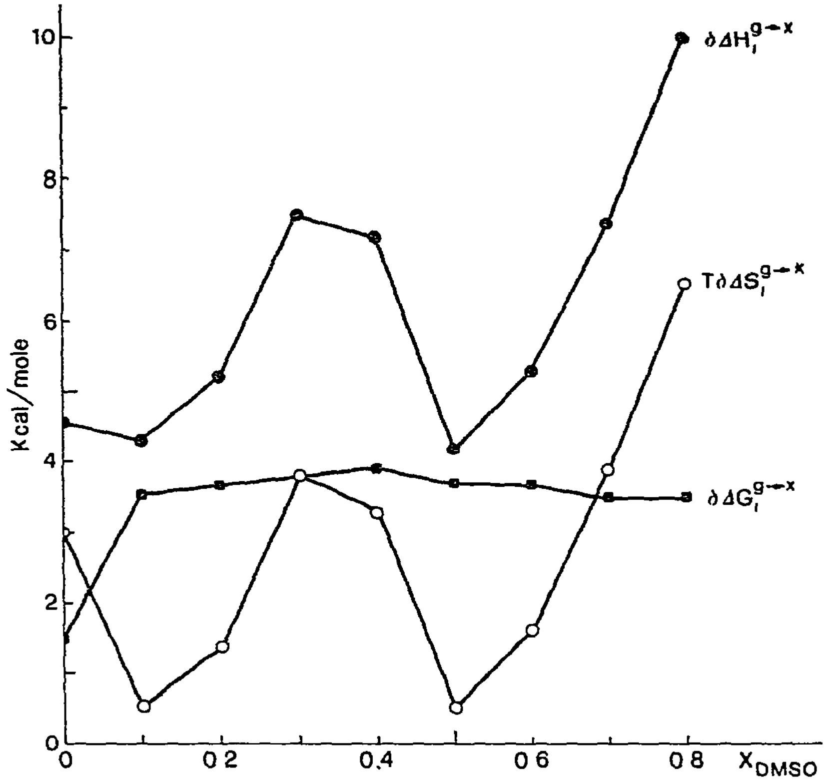

Fig 3 Thermodynamic quantities for the proton transfer process of *para* chlorobenzoic acid in DMSO–water solutions, obtained by assuming a gaseous state as reference

of the mole fraction range. Keeping as a reference the free energy transfer process in the gaseous state it is possible to see that in solutions, the free energy exhibits a very limited dependence on the medium effect. There is also clear evidence that the shape of the $\delta\Delta G_t^{g\to x}$ curve is similar to that of the substituent constant [4] σ_O. Thus $\delta\Delta G_t^{g\to x}$ values give a measure of the effect of the medium on the structure variation caused by the substituent group.

From the free energy point of view, the transfer process is easier in the DMSO-rich solutions, this behavior being similar to that observed in the gaseous phase. For the *meta* and *para* chloro-derivatives too, the shape of the entropic terms $T\delta\Delta S^{g\to x}$ are identical to those of the respective entropic reactions [3], with a minimum at $X_{DMSO} = 0.4$ and 0.5, respectively. This may be explained by an increased solvating power of the mixture towards the anions, at $X_{DMSO} = 0.5$, which, in turn have a more localized charge on the carboxylate group than the *ortho* anion.

In the DMSO-rich solutions the behavior is similar to that observed in the gas phase. The $\delta\Delta G_t^{g\to x}$ values also show that the transfer process is easier in the DMSO-rich solutions but not so much as for the *ortho* derivative.

For the *para* anion, the negative charge is more tightly localized on the carboxylate group, owing the weaker electron-withdrawing effect of the chlorine atom.

Therefore, in pure water, the numerous hydrogen bonds decrease the $\delta\Delta G_{t}^{\beta\to x}$ of the *para* derivative with respect to those of the *meta* and *ortho* derivatives. Beyond $X_{DMSO} = 0.05$ the $\delta\Delta G_{t}^{\beta\to x}$ values of the *ortho* derivative are smaller than those of the *meta* and *para* derivatives.

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