Thermochimica Acta, 51 (1981) 191—197 191
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

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

F. RODANTE and M. PASQUALI

Istituto di Chimica, Facoltà di Ingegneria, Università di Roma, via del Castro Laurenziano 7, Rome (Italy)

(Received 12 May 1981)

ABSTRACT

A study of the proton transfer process from nitro-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 allows calculation of a transfer process in solvent X which refers to a gaseous initial state, i.e. $\delta\Delta P_i^{g\to x}$. These thermodynamic quantities have been assumed as a measure of "external" solute—solvent interactions. It may be noted that in solution the resonance effect appears in the *ortho*-anion, while in the gaseous phase the resonance is effective for the *para*-compound. A comparison with the chloro-isomers shows that the proton transfer process is easier for the nitro-isomers in the gas phase while the contrary is true in solution.

INTRODUCTION

The proton transfer process from chlorobenzoic acids to benzoic acid in water—dimethylsulfoxide (DMSO) mixtures has recently been compared with the same process in the gaseous phase [1]. Using a thermodynamic cycle we have calculated, in DMSO—Water mixtures, a proton transfer process which refers to a gaseous initial thermodynamic state. The thermodynamic quantities ($\delta\Delta P_i^{g\to x}$) calculated have been assumed as a measure of the "external" interactions of the proton transfer process among molecules, anions and solvent.

It has also been shown that the respective shapes of the entropic and free energy terms are very close to those of the previously calculated [2,3] entropic reaction constants and substituent constants. The entropic reaction constants, giving only a trend of the "external" solute—solvent interactions, were found to be chiefly inductive in character. In contrast, the $T\,\delta\Delta S_i^{g\to x}$ curve gives a measure of the values of the solute—solvent interactions.

In the present work, the behavior of the nitro benzoic acids in the same transfer proton process has been examined. The effect of these two substituents on the above-mentioned process is quite different. This is related to the resonance, the greater size and the different inductive effect of the nitro-group.

The following equations have been used [2,3] to illustrate the substituent effect

$$(\mathrm{NO_2{-}PhCOOH})_X + (\mathrm{PhCOO^-})_X = (\mathrm{NO_2{-}PhCOO^-})_X + (\mathrm{PhCOOH})_X \tag{1}$$

where X is the mole fraction of the solvent

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho\sigma = \rho_\mathrm{H}\sigma_\mathrm{H} + \rho_\mathrm{S}\sigma_\mathrm{S} \tag{2}$$

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_0\sigma_0 + fF + \delta E_s = \rho_\mathrm{H}\sigma_\mathrm{H} + \rho_\mathrm{S}\sigma_\mathrm{S} + fF + \delta E_s \tag{3}$$

in eqn. (2) $\rho_\mathrm{H}\sigma_\mathrm{H}$ and $\rho_\mathrm{S}\sigma_\mathrm{S}$ are defined by the relations

$$\rho_\mathrm{H}\sigma_\mathrm{H} = -\frac{\delta\Delta H^0}{2.303RT} \tag{4a}$$

$$\rho_\mathrm{S}\sigma_\mathrm{S} = \frac{\delta\Delta S^0}{2.303R} \tag{4b}$$

while in eqn. (3) $\rho_\mathrm{H}\sigma_\mathrm{H}$ and $\rho_\mathrm{S}\sigma_\mathrm{S}$ are defined as

$$\rho_\mathrm{H}\sigma_\mathrm{H} = -\frac{\delta\Delta H^0}{2.303RT} - \delta E_\mathrm{S} \tag{5a}$$

$$\rho_\mathrm{S}\sigma_\mathrm{S} = \frac{\delta\Delta S^0}{2.303R} - fF \tag{5b}$$

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO—water mixtures, and the technique to determine the thermodynamic values for benzoic and nitrobenzoic acids have been described [4,5].

RESULTS AND DISCUSSION

The thermodynamic cycle used to calculate the "external" interactions employs, as already shown [1], benzoic acid as a reference compound

$$\begin{tikzcd}
\mathrm{NO_2{-}PhCOOH_{(g)}} \arrow[d, "\delta\Delta P_\mathrm{S}"] & + & \mathrm{PhCOO^-_{(g)}} \arrow[r, "\delta\Delta P_{\mathrm{i(g)}}"] \arrow[d, "\delta\Delta P_\mathrm{S}"] & \mathrm{NO_2{-}PhCOO^-_{(g)}} \arrow[d, "\delta\Delta P_\mathrm{S}"] & + & \mathrm{PhCOOH_{(g)}} \arrow[d, "\delta\Delta P_\mathrm{S}"] \\
(\mathrm{NO_2{-}PhCOOH})_X & + & (\mathrm{PhCOO^-})_X \arrow[r, "\delta\Delta P_{\mathrm{i(X)}}"] & (\mathrm{NO_2{-}PhCOO^-})_X & + & (\mathrm{PhCOOH})_X
\end{tikzcd} \tag{6}$$

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

Thus, this can be written

$$\delta\Delta P_{i(X)} - \delta\Delta P_{i(g)} = \delta\Delta P_S^{g\to x} \tag{7}$$

the right-hand term of eqn. (7) being assumed as the proton transfer, in solvent X, which refers to a gaseous intial thermodynamic state, so that $\delta\Delta P_s^{g\to x} = \delta\Delta P_i^{g\to x}$.

Further, according to Hepler et al. [6—8] in eqn. (1) the solvent effects can be separated from the intrinsic molecular effects as

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

It is assumed that the $\delta\Delta P_{i(X)}$ values are the total interactions, and $\delta\Delta P_{i(g)}$ and $\delta\Delta P_i^{g\to x}$ are the "internal" and "external" interactions, respectively.

It is well known (1,9—11) that for reactions such as those considered here, it is possible to assume $\delta\Delta S_{i(g)} \approx 0$, so that $\delta\Delta G_{i(g)}$ (600 K) $\approx \delta\Delta G_{i(g)}$ (298 K) $\approx \delta\Delta H_{i(g)}$.

$\delta\Delta G_{i(g)}$ values are available in the literature [10] and $\delta\Delta G_{i(X)}$ values have been calculated [3,12]. By including these values in eqn. (8) it is possible to calculate $\delta\Delta G_i^{g\to x}$. Similarly, $\delta\Delta H_i^{g\to x}$ may be calculated. Finally, the entropic term $T\ \delta\Delta S_i^{g\to x}$ can be calculated by means of the enthalpic $\delta\Delta H_i^{g\to x}$ and free energy $\delta\Delta G_i^{g\to x}$ terms. All thermodynamic values are reported in Tables 1—3 and are plotted against DMSO mole fraction in Figs. 1—3.

As shown in previous works [3,12], the solute—solvent interactions are expressed by means of the entropic reaction constants ρ_s. The curves of the $T\ \delta\Delta S_i^{g\to x}$ term have shapes very close to those of the reaction constants, and give a measure of the values of solute—solvent interactions, while the ρ_s curves give only a trend.

It is interesting to note that the behavior of the nitro-isomers in the gaseous phase is quite different from that which occurs in solution. Indeed, in the former phase the (negative) values of the free energy term, related to the proton transfer process, decrease according to the sequence p-$NO_2 > m$-$NO_2 > o$-NO_2. This order can be justified bearing in mind that, in the gaseous phase, the intramolecular bond is acid-weakening the *ortho*-isomer, while the resonance effect is acid-strengthening the *para*-isomer. In contrast, in the latter phase the unfavorable effect of the "external" thermodynamic terms is ordered as: m-$NO_2 > p$-$NO_2 > o$-NO_2. It may be noted that, for the three isomers, the enthalpic term clearly prevails.

As previously shown [5], in the mixed solvent the two —CH_3 groups of DMSO interfere with the approach of the negative group of the *ortho*-anion to the dipole. This allows the *ortho*-anion to re-establish the resonance between the phenyl and carboxyl groups. The effective dipole—dipole interactions with the DMSO molecule stabilize the *ortho*-anion, thus increasing the acid-strengthening effect.

Contrary to what happens in the gas phase, the resonance effect for the *para*-anion is very poor, so that the negative charge is mainly localized on the —COO^- group and the solvation effect is strongest. Therefore, in solution the resonance effect appears for the *ortho*-anion only, while in the gaseous phase the resonance is effective for the *para*-isomer.

TABLE 1

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

X_{DMSO}	$\delta\Delta G_t^{g\to x}$	$\delta\Delta H_t^{g\to x}$	$T\delta\Delta S_t^{g\to x}$
0	6.03	7.92	1.89
0.1	6.34	8.36	2.22
0.2	6.48	8.46	1.98
0.3	6.46	10.86	4.40
0.4	6.34	11.85	5.51
0.5	6.17	15.89	9.72
0.6	6.01	13.06	7.06
0.7	5.83	12.02	6.19
0.8	5.68	12.21	6.53

TABLE 2

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

X_{DMSO}	$\delta\Delta G_t^{g\to x}$	$\delta\Delta H_t^{g\to x}$	$T\delta\Delta S_t^{g\to x}$
0	8.01	9.34	1.33
0.1	7.78	10.62	2.84
0.2	7.53	14.46	6.93
0.3	7.40	17.46	10.06
0.4	7.20	21.19	13.99
0.5	7.04	21.72	14.68
0.6	6.90	22.22	15.32
0.7	6.75	16.64	9.89
0.8	6.67	15.43	8.76

TABLE 3

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

X_{DMSO}	$\delta\Delta G_t^{g\to x}$	$\delta\Delta H_t^{g\to x}$	$T\delta\Delta S_t^{g\to x}$
0	10.07	11.43	1.36
0.1	9.83	11.27	1.44
0.2	9.66	11.40	1.74
0.3	9.49	15.88	6.39
0.4	9.37	15.82	6.45
0.5	9.29	14.28	6.99
0.6	9.14	15.73	6.59
0.7	8.99	16.98	7.99
0.8	8.81	20.93	12.12

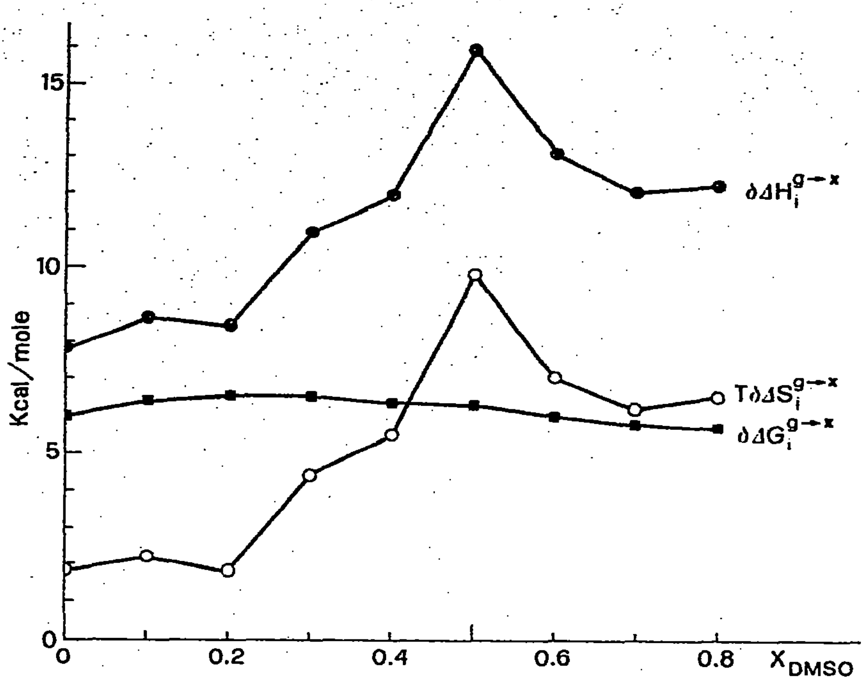

Fig. 1. Thermodynamic quantities for the proton transfer process of *ortho*-nitrobenzoic acid in DMSO—water solutions, obtained by assuming a gaseous state as reference.

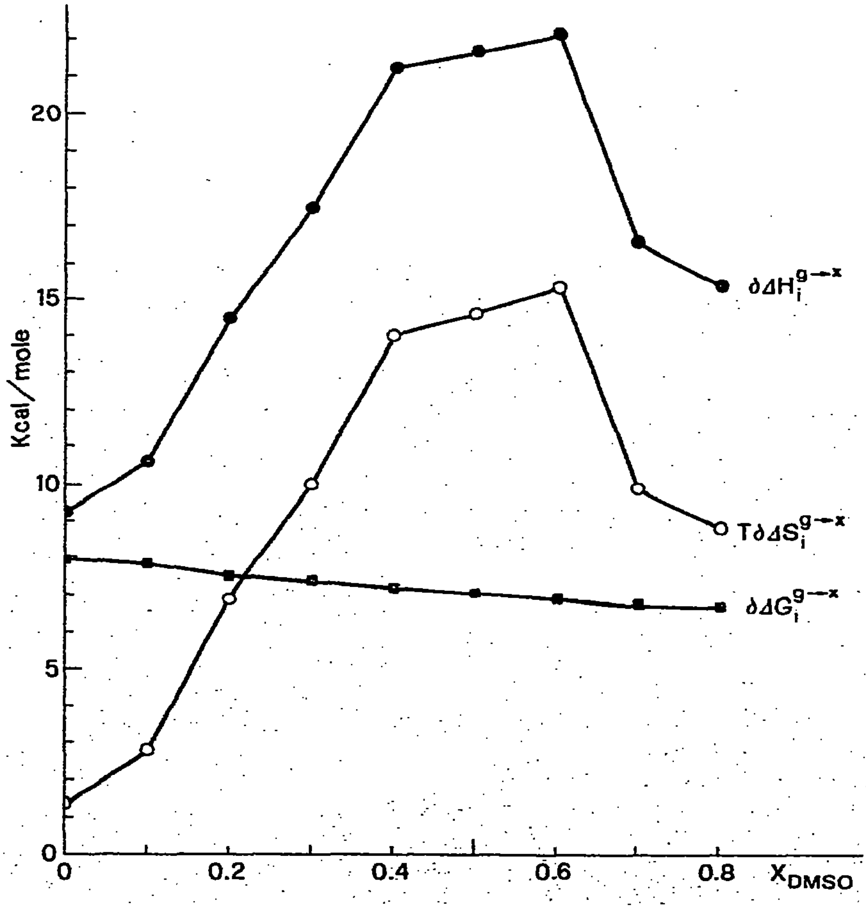

Fig. 2. Thermodynamic quantities for the proton transfer process of *meta*-nitrobenzoic acid in DMSO—water solutions, obtained by assuming a gaseous state as reference.

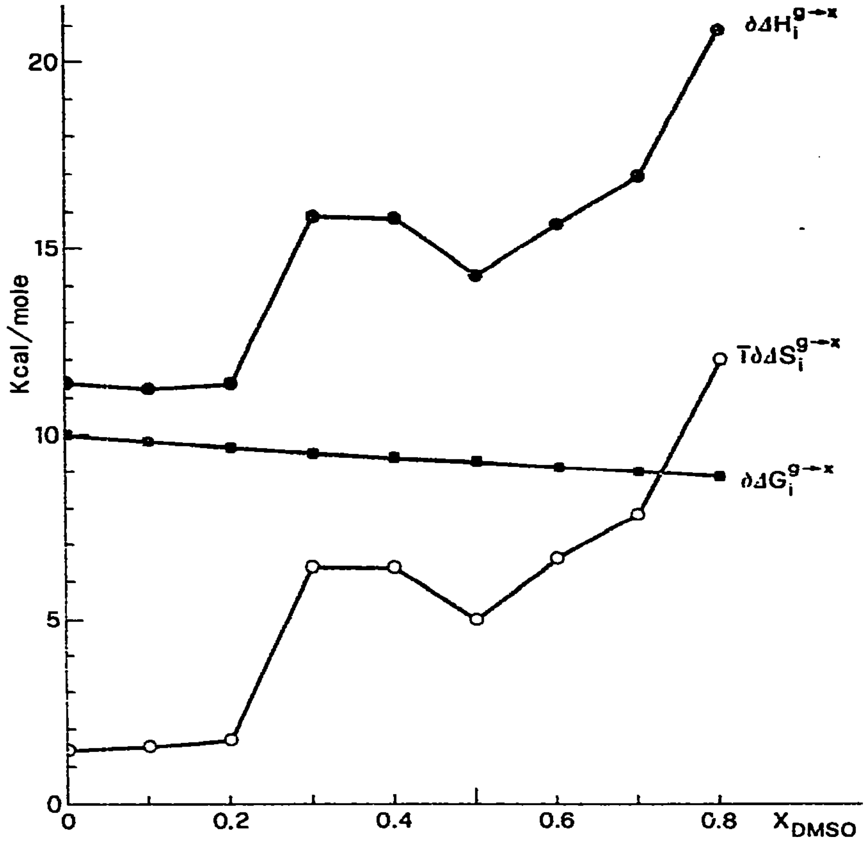

Fig. 3. Thermodynamic quantities for the proton transfer process of *para*-nitrobenzoic acid in DMSO—water solutions, obtained by assuming a gaseous state as reference.

In solution the *meta*-compound shows the greatest unfavorable effect to proton transfer. This can be related to the drastic desolvation of the *meta*-anion with respect to *para*- and *ortho*-anions.

In the gaseous phase the proton transfer process is easier for the nitro- than for the chloro-isomers, while in solution the contrary is true. Indeed, in the gas phase the inductive effect of the nitro-group is stronger than that of the chloro-group. Consequently, in the liquid phase the nitro-anions are more desolvated than the chloro-anions. Furthermore, the *ortho*-anion exhibits a steric inhibition of solvation on the carboxylate group.

REFERENCES

1 M.G. Bonicelli, G. Ceccaroni and F. Rodante, Thermochim. Acta, 52 (1982) 45.
2 F. Rodante, Thermochim. Acta, 31 (1979) 221.
3 F. Rodante, Thermochim. Acta, 34 (1979) 377.
4 F. Rodante, F. Rallo and P. Fiordiponti, Thermochim. Acta, 9 (1974) 269.
5 F. Rodante, Thermochim. Acta, 32 (1979) 293.
6 L.G. Hepler and W.F. O'Hara, J. Phys. Chem., 65 (1961) 811.
7 L.G. Hepler, Can. J. Chem., 49 (1971) 2809.

8 T. Matsui and L.G. Hepler, Can. J. Chem., 54 (1977) 1296.
9 R. Yamdagni. T.B. McMahon and P. Kerbale, J. Am. Chem. Soc., 96 (1974) 4035.
10 T.B. McMahon and P. Kerbale, J. Am. Chem. Soc., 99 (1977) 222.
11 J.B. Cumming and P. Kerbale, Can. J. Chem., 56 (1978) 1.
12 F. Rodante, Thermochim. Acta, 34 (1979) 29.