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CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,5-DINITROPHENOL IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The ionization and solution enthalpies of 2,5-dinitrophenol were measured calorimetrically at 25°C in water–DMSO mixtures ranging from 0.1 to 0.8 mole fraction of DMSO.

The effect of the nitro group in the *ortho* position seems to prevail over that of the nitro group in the *meta* position.

The greater acidity of dinitrophenol with respect to the mononitro isomers is explained on the basis of the interference of the nitro group in the *meta* position on the interactions between the nitro group in the *ortho* position and the hydroxyl group or phenolate oxygen.

INTRODUCTION

The ionization of phenol [1] and nitrophenol isomers [2], and the effect of the medium on the reaction constants of the dissociation of nitrophenols [3,4] in water–dimethylsulfoxide (DMSO) mixtures have been the subject of research carried out recently in our laboratory.

A study of the proton transfer processes from nitrophenols to nitrobenzoic acids and to benzoic acid in water–DMSO mixtures, compared with the same processes in the gaseous phase, has also been reported [5]. Thus, a sufficiently complete thermodynamic analysis of the ionization of the mononitro substituted phenols, as a function of the solvent composition, has been performed.

In the present work, the behaviour of 2,5-dinitrophenol in the same mixtures has been examined.

An attempt has also been made to study the effect of an additional nitro group in the *meta* position on the interactions between the first nitro substituent in the *ortho* position and the hydroxyl group or phenolate oxygen.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [2]. The thermograms were read using a computer program and the experimental values were obtained using a particular technique.

The DMSO–water mixtures were prepared by weight from purified DMSO [6] and CO_2-free twice-distilled water.

Aqueous solutions of 1N HCl and 0.1N NaOH were prepared from standard solutions; their concentrations were checked by potentiometric measurements. The 2,5-dinitrophenol(K & K) was purified by repeated crystallizations from ethanol to constant melting point.

Solutions of 2,5-dinitrophenol (2,5-NO_2PhOH) in water–DMSO mixtures were prepared in a nitrogen-filled dry box. Solutions of 2,5-NO_2PhONa were prepared by successive dilutions of a stock solution of 2,5-dinitrophenol and by adding NaOH solution of known molarity to the dinitrophenol dissolved in the mixed solvent. As a result of these operations, 100 g of the DMSO–water solutions at X' mole fraction were obtained. The concentration of the sodium salt was always in the range 2×10^{-3}–4×10^{-3} m (molal).

Approximately 4 or 5% of the original dinitrophenol content was not converted to the salt and remained as free dinitrophenol in order to avoid the presence of free alkali and to repress hydrolysis.

The ionization process of 2,5-NO_2PhOH in the various water–DMSO mixtures of X mole fraction can be represented as

$$(2{,}5\text{-}NO_2PhOH)_X \rightarrow (2{,}5\text{-}NO_2PhO^-)_X + (H^+)_X \qquad (1)$$

The molar enthalpy of ionization, $\Delta \overline{H}_1$, of 2,5-NO_2PhOH was obtained as described previously [1,2] by the experimental measurements of:

(a) the molar enthalpy of reaction, $\Delta \overline{H}_2$, of the sodium salt dissolved in the mixed solvent of X' mole fraction with 1N HCl, i.e.

$$(2{,}5\text{-}NO_2PhO^-)_{X'} + (Na^+)_{X'} + (H^+)_{aq.} + (Cl^-)_{aq.} \rightarrow (2{,}5\text{-}NO_2PhOH)_X + (Na^+)_X + (Cl^-)_X \qquad (2)$$

(b) the molar enthalpy of dilution, $\Delta \overline{H}_3$, of the same amount of 1N HCl in the same solvent mixture at X' mole fraction, i.e.

$$(H^+)_{aq} + (Cl^-)_{aq} \rightarrow (H^+)_X + (Cl^-)_X \qquad (3)$$

In eqns. (2) and (3), X' and X refer to the DMSO mole fraction in the solvent mixture before and after the process, respectively.

From the values of the dissociation constants of water [7] and 2,5-dinitrophenol predicted on the assumption of the additive effect of *ortho* and *meta*-nitrophenols [2], it can also be inferred that the salt undergoes, in the most unfavourable case ($X_{DMSO} = 0.8$), hydrolysis with $\beta < 0.01$. Therefore, it is not necessary to correct the $\Delta\overline{H}_2$ values measured experimentally in process (2) for hydrolysis.

The molar enthalpy of process (1) can be obtained by subtracting the two values $\Delta\overline{H}_3$ and $\Delta\overline{H}_2$ and adding to this difference the $\Delta\overline{H}_4$ values related to the molar transfer enthalpy of 2,5-NO_2PhONa (at infinite dilution) from solvent X' to solvent X, viz.

$$(2,5\text{-}NO_2PhO^-)_{X'} + (Na^+)_{X'} \rightarrow (2,5\text{-}NO_2PhO^-)_X + (Na^+)_X \qquad (4)$$

The difference ($X' - X$) turns out to be 2×10^{-4} in the most unfavourable case ($X_{DMSO} = 0.8$).

The thermal effect of process (4) was calculated using the experimental measurements reported in this work. For each of the water–DMSO mixtures at X_{DMSO} mole fraction, the $\Delta\overline{H}_1$ values refer to the ionization of one mole of 2,5-NO_2PhOH, dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of protons and one mole of 2,5-NO_2PhO^- ions solvated in the same amount of solvent. In order to refer process (1) to one initial thermodynamic state only, the solution enthalpies of the crystalline 3,5-dinitrophenol, $\Delta\overline{H}_s$, were measured in the various solvent mixtures.

$$2,5\text{-}NO_2PhOH_{cr.} \rightarrow (2,5\text{-}NO_2PhOH)_X \qquad (5)$$

so that $\Delta\overline{H}_6 = \Delta\overline{H}_5 + \Delta\overline{H}_1$ values obtained for the process

$$2,5\text{-}NO_2PhOH_{cr.} \rightarrow (H^+)_X + (2,5\text{-}NO_2PhO^-)_X \qquad (6)$$

refer to an identical initial thermodynamic state.

In processes (1) and (5), concentrations ranging from 2×10^{-3} to 4×10^{-3} m were used; therefore, the $\Delta\overline{H}$ values related to these processes were assumed to be equal to the ΔH^0 [8] values. All the measurements were carried out at 25°C, the average thermal jump in the cell during the experiments being about 2×10^{-3}°C.

RESULTS

Table 1 shows the ΔH^0 values of processes (1), (5) and (6) obtained for 2,5-NO_2PhOH in DMSO–water solutions as a function of the DMSO mole fraction. Due to the very limited solubility of the dinitrophenol in water, it is impossible to obtain reliable results for the enthalpic effects in aqueous solution.

So, it is convenient to express, for comparison purposes, the ionization

TABLE 1

Molar enthalpy of ionization (ΔH_1^0) and solution (ΔH_5^0) of 2,5-dinitrophenol in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_1^0 (kcal mole^{-1})	ΔH_5^0 (kcal mole^{-1})	ΔH_6^0 (kcal mole^{-1})
0.1	4.38	6.64	11.02
0.2	5.45	7.29	12.74
0.3	6.65	7.25	13.90
0.4	7.99	5.67	13.66
0.5	9.44	4.14	13.58
0.6	11.00	3.37	14.37
0.7	12.64	2.64	15.28
0.8	14.35	2.48	16.83

enthalpy as the difference between the values obtained in the mixed solvent at X mole fraction and those obtained in the mixed solvent at $X_{\mathrm{DMSO}} = 0.1$.

$$\delta\Delta H_1^0 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0.1}$$

These values are relative to the transfer of the ionization process, while $\delta\Delta H_5^0$ and $\delta\Delta H_6^0$ represent the transfer enthalpy of the undissociated molecule and of the H^+ and 2,5-NO_2PhO^- ions, respectively, from solution at $X_{\mathrm{DMSO}} = 0.1$ to mixed solvent. All these data are plotted vs. X_{DMSO} in Fig. 1.

DISCUSSION

From the curves in Fig. 1, it can be inferred that, from the enthalpic point of view, the desolvation of the 2,5-NO_2PhO^- anion plays a more important role than the solvation of the undissociated molecule, mostly in the water–rich solutions.

By comparing 2,5-dinitrophenol with 2-nitrophenol, 3-nitrophenol and to unsubstituted phenol, by means of the difference in ionization enthalpy (Fig. 2), it can be inferred that the first compound is a more effective acid in the whole mole fraction range. It is also noteworthy that the difference in the ionization enthalpy between the 2,5-dinitrophenol/2-nitrophenol couple is much smaller than the differences between the couples 2,5-dinitrophenol/3-nitrophenol and 2,5-dinitrophenol/phenol, which, in turn, show very close values. Thus, the effect of the nitro group in the *ortho* position should prevail over that of the nitro group in the *meta* position.

It is also clear that, in the DMSO–rich solutions, the different transfer solvation enthalpies of the anions play a major role in the differentiation of the acidity between the 2,5-dinitro and 2-nitro phenols. This difference, $\Delta H^0_{(2,5\text{-}NO_2PhO^-)-(2\text{-}NO_2PhO^-)_X}$, was calculated as shown previously [1,2]. In this case, however, the reference state is the DMSO–water solution with X_{DMSO}

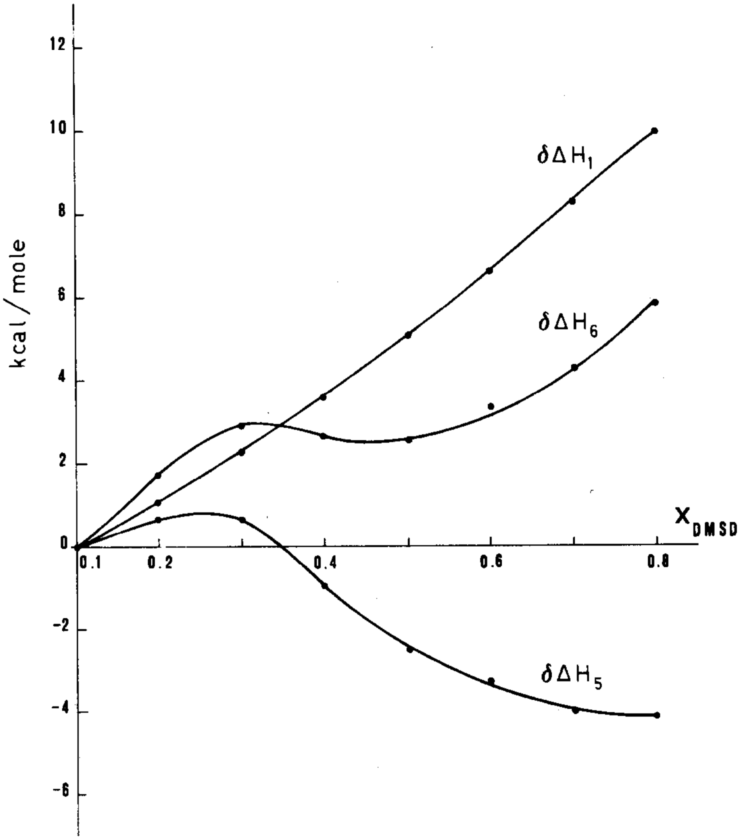


Fig. 1. Transfer enthalpy of the ionization process of 2,5-dinitrophenol and transfer enthalpies of the 2,5-dinitro anion and of the 2,5-dinitro undissociated molecule from $X_{\mathrm{DMSO}} = 0.1$ in DMSO–water mixtures as a function of the mole fraction at 25°C.

$= 0.1$. In the same way, the difference in solvation enthalpy between the undissociated molecules, $\Delta H^0_{(2,5\text{-NO}_2\text{PhOH})_X - (2\text{-NO}_2\text{PhOH})_X}$, was calculated.

Figure 3 shows that the dinitrophenol anion is solvated to a larger extent than the nitrophenol anion in DMSO-rich solutions, while in the water-rich solutions the contrary is true. The dinitro undissociated molecule is more desolvated than the nitro molecule in almost the whole mole fraction range. This can be related to the interference of the additional nitro group (*meta* position) on the interactions between the first nitro group (*ortho* position) and the hydroxyl group or phenolate oxygen.

As shown previously [2], there is a strong electrostatic interaction between the water molecules and the mono *ortho* anion, due, in turn, to the marked resonance between the phenolate oxygen and the oxygens in the neighbouring nitro group.

It is also well-known that the anions polarize the solvent molecules and

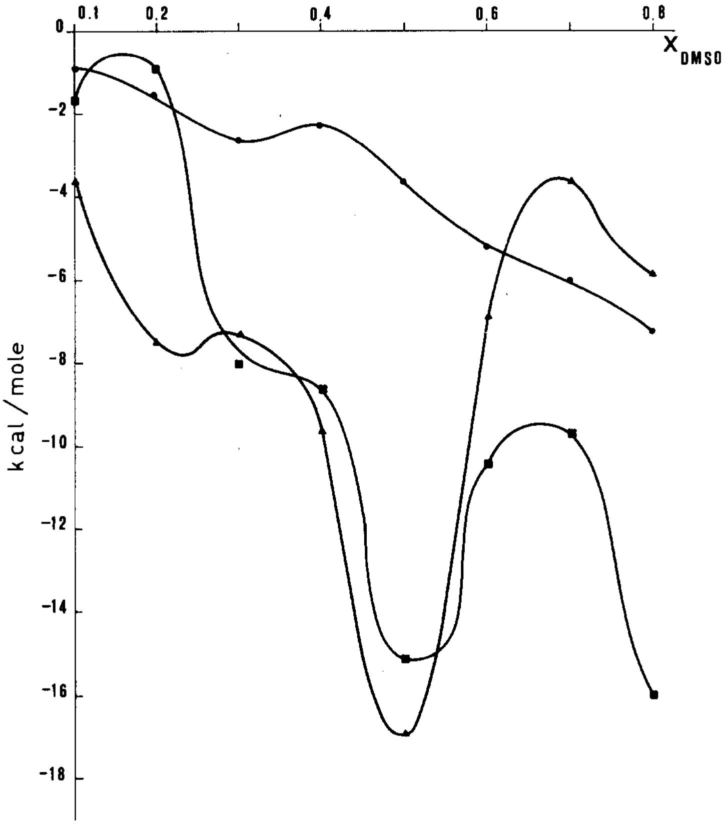
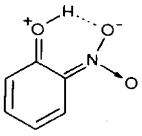


Fig. 2. Differences in the enthalpy of ionization for: ●, 2,5-NO_2PhOH/2-NO_2PhOH; ■, 2,5-NO_2PhOH/3-NO_2PhOH; ▲, 2,5-NO_2PhOH/PhOH couples.

the degree of this polarization strictly correlates with the stabilization of the anions. Thus the *ortho* anion stabilizes itself by dispersing its charge and surrounding itself with water molecules. For the dinitrophenol this is no longer possible due to the presence of the additive *meta*-nitro group which by means of the inductive electron-withdrawing effect, destabilizes the benzene ring. Furthermore, in the DMSO-rich solutions the large dipole of the 2,5-nitrophenol anion greatly interacts with the dipole of the DMSO molecules.

As for the undissociated molecules it is possible to admit [2] that the mono *ortho*-nitro form can be in resonance with the cyclic dipolar structure (I) which is mostly stable in water-rich mixtures where dipole–dipole interactions are allowed with the water molecules.



(I)

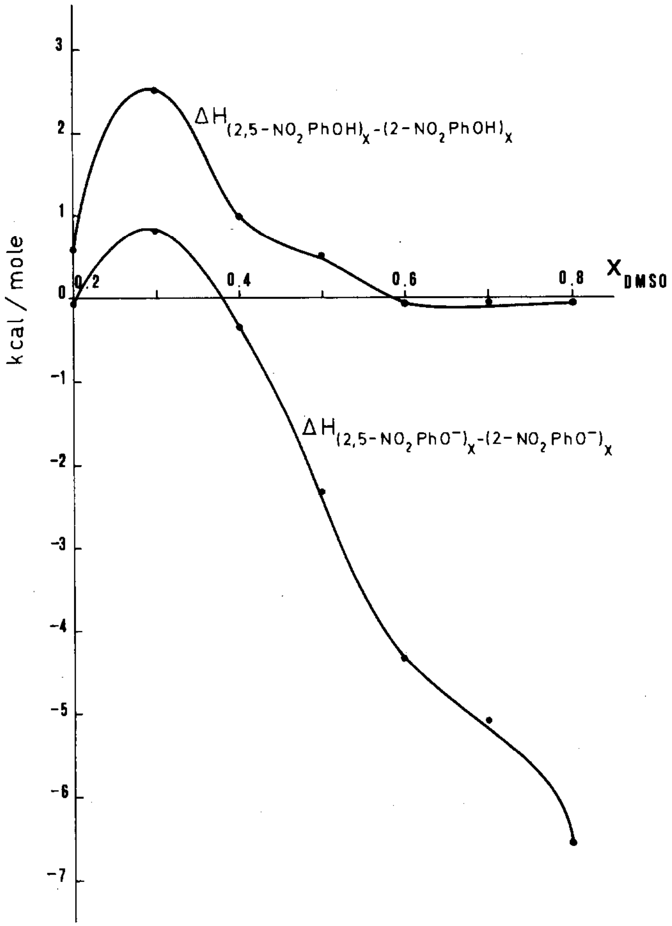


Fig. 3. Differences in the solvation enthalpies between the anions and the undissociated molecules of 2,5-NO_2PhOH and 2-NO_2PhOH in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couple and between the undissociated molecule couple are arbitrarily set equal to zero.

The introduction of a second nitro group in the *meta* position destabilizes the cyclic form and allows minor molecular interaction. When the DMSO content is increased the chelate ring structure is broken and the nitro group is forced out of the ring plane, so that the nitro and the dinitro phenols are desolvated in the same way.

Thus, we can conclude that the ring destabilization of both the ion and the undissociated molecule, due to the interference of the second nitro group, is the principal cause of the greater acidity of the 2,5-NO_2PhOH with respect to the mononitro isomers.

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