

## CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,4-DINITROPHENOL IN WATER–DIMETHYLSULPHOXIDE MIXTURES AT 25°C

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(Received 20 April 1983)

### ABSTRACT

The ionization and solution enthalpies of 2,4-dinitrophenol were measured calorimetrically at 25°C in water–DMSO mixtures ranging from 0.1 to 0.8 mole fraction of DMSO.

The greater acidity of 2,4-dinitrophenol with respect to 2,5-dinitrophenol is explained on the basis of the observation that in the anion the  $\pi$ -withdrawing resonance effect of the *para* nitro group stabilizes the benzene ring while in the undissociated molecule the contrary is true.

### INTRODUCTION

The thermodynamic study of the ionization process [1,2], the medium effect on the reaction constants [3,4], and the proton transfer process in water–dimethylsulphoxide (DMSO) mixtures compared with the same process in the gaseous phase [5] for the phenol and nitrophenol isomers have been the subject of extended research in our laboratory.

A calorimetric study of the ionization of 2,5-dinitrophenol was also performed [6]. The greater acidity of 2,5-dinitrophenol with respect to the mono-nitro isomers was 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 the phenolate oxygen.

In the present work, the behaviour of 2,4-dinitrophenol is examined. In this case, the interference of the additional nitro group in the *para* position

on the interactions between the *ortho*-nitro group and the hydroxyl group or phenolate oxygen is studied.

An attempt is also made to compare the  $\sigma$ -inductive electron-withdrawing effect of the *meta*-nitro group [6] to the  $\pi$ -resonance electron-withdrawing effect of the *para*-nitro group (both) on the benzene ring stabilization.

#### EXPERIMENTAL AND PROCEDURE

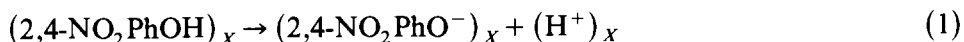
The calorimetric apparatus has been described previously [1,2]. The thermograms were read using a computer program and the experimental values were obtained using a particular technique.

The DMSO-water mixtures were prepared by weight from purified DMSO [7] and CO<sub>2</sub>-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 2,4-dinitrophenol (K&K) was purified by repeated crystallizations from ethanol to constant melting point.

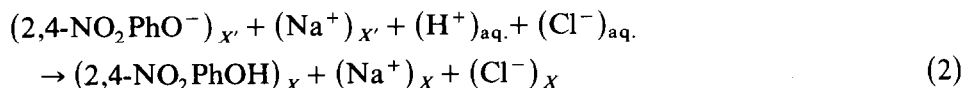
Solutions of 2,4-dinitrophenol (2,4-NO<sub>2</sub>PhOH) in water-DMSO mixtures were prepared in a nitrogen-filled dry box. Solutions of 2,5-PhONa were prepared by successive dilutions of a stock solution of 2,4-dinitrophenol and by adding an NaOH solution of known molarity to the dinitrophenol dissolved 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  $2 \times 10^{-3}$ – $4 \times 10^{-4}$  m(molal). Approximately 4 or 5% of the original dinitrophenol content was not converted to the salt and remained as the free dinitrophenol in order to avoid the presence of free alkali and to repress hydrolysis.

The ionization process of 2,4-NO<sub>2</sub>PhOH in the various water-DMSO mixtures of  $X$  mole fraction can be represented by

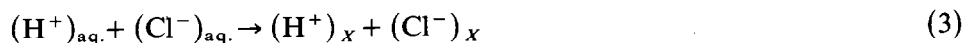


The molar enthalpy of ionization,  $\Delta\bar{H}_1$ , of 2,4-NO<sub>2</sub>PhOH was obtained as described previously [1,2] by the experimental measurements of:

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



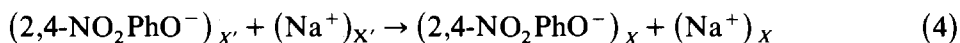
(b) the molar enthalpy of dilution,  $\Delta\bar{H}_3$ , of the same amount of 1N HCl in the same solvent mixture at  $X'$  mole fraction, given by



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

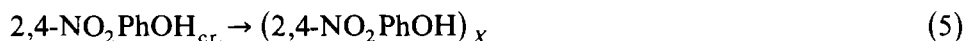
From the values of the dissociation constants of water [8] and 2,4-NO<sub>2</sub>PhOH (calculated on the assumption of the additive effect of *ortho* and *para*-nitrophenols [2]), it can also be inferred that the salt undergoes, in the most unfavourable case ( $X_{\text{DMSO}} = 0.8$ ), hydrolysis with  $\beta < 0.013\%$ . Therefore, it is not necessary to correct the  $\Delta\bar{H}_2$  values measured experimentally in process (2) for hydrolysis.

The molar enthalpy of process (1) can be obtained by subtracting the two values  $\Delta\bar{H}_3$  and  $\Delta\bar{H}_2$  and adding to this difference the  $\Delta\bar{H}_4$  values related to the molar transfer enthalpy of 2,4-NO<sub>2</sub>PhONa (at infinite dilution) from solvent  $X'$  to solvent  $X$ , viz.

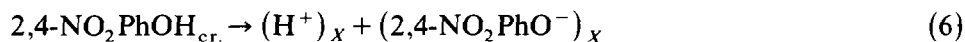


The difference ( $X' - X$ ) turns out to be  $2 \times 10^{-4}$  in the most unfavourable case ( $X_{\text{DMSO}} = 0.8$ ).

The thermal effect of process (4) was calculated using the experimental measurements reported in this work. For each of the water-DMSO mixtures at  $X$  mole fraction, the  $\Delta\bar{H}_1$  values refer to the ionization of one mole of 2,4-NO<sub>2</sub>PhOH dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of protons and one mole of 2,4-NO<sub>2</sub>PhO<sup>-</sup> ions solvated in the same amount of solvent. In order to refer process (1) to one initial thermodynamic state only, the solution enthalpies of crystalline 2,4-dinitrophenol,  $\Delta\bar{H}_5$ , were measured in the various solvent mixtures.



Therefore,  $\Delta\bar{H}_6 = \Delta\bar{H}_5 + \Delta\bar{H}_1$  values obtained for the process



refer to an identical initial thermodynamic state.

In processes (1) and (5), concentrations ranging from  $2 \times 10^{-3}$  to  $4 \times 10^{-3}$  m were used; therefore, the  $\Delta\bar{H}$  values related to these processes were assumed to be equal to the  $\Delta H^0$  [9] values. All the measurements were carried out at 25°C, the average thermal jump in the cell during the experiments being about  $2 \times 10^{-3}$ °C.

## RESULTS

Table 1 shows the  $\Delta H^0$  values of processes (1), (5) and (6) obtained for 2,4-NO<sub>2</sub>PhOH in DMSO-water solutions as a function of the DMSO mole fraction. Due to the very limited solubility of dinitrophenol in water, it is impossible to obtain reliable results for the enthalpic effects in aqueous solutions.

So, it is convenient to express, for the purpose of comparison, the ionization enthalpy as the difference between the values obtained in the

TABLE I

Molar enthalpy of ionization ( $\Delta H_1^0$ ) and solution ( $\Delta H_5^0$ ) of 2,4-dinitrophenol in DMSO–water solutions of various mole fractions at 25°C  
All enthalpic quantities are given in kcal mole<sup>-1</sup>.

$X_{\text{DMSO}}$	$\Delta H_1^0$	$\Delta H_5^0$	$\Delta H_6^0$
0.1	2.68	6.80	9.48
0.2	2.80	8.99	11.79
0.3	3.34	8.25	11.59
0.4	4.71	6.04	10.75
0.5	7.03	4.68	11.71
0.6	9.04	3.89	12.93
0.7	12.19	3.18	15.37
0.8	13.10	2.92	16.02

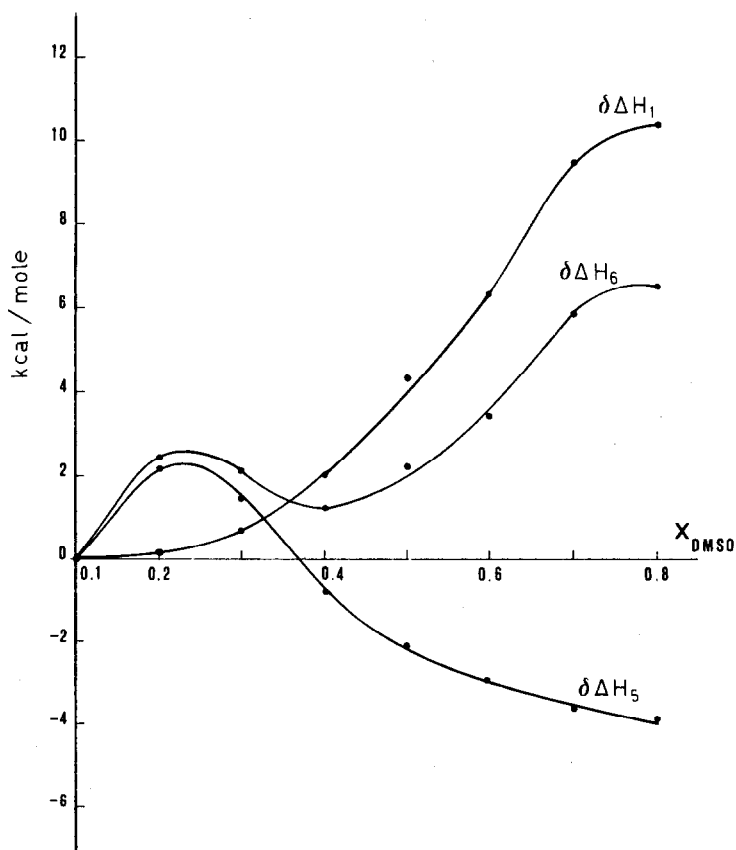


Fig. 1. Transfer enthalpy of the ionization process of 2,4-dinitrophenol and transfer enthalpies of the 2,4-dinitro anion and of the 2,4-dinitro undissociated molecule from  $X_{\text{DMSO}} = 0.1$  in DMSO–water mixtures as a function of the mole fraction at 25°C.

mixed solvent at  $X$  mole fraction and those obtained in the mixed solvent at  $X_{\text{DMSO}} = 0.1$ , i.e.

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

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  $\text{H}^+$  and  $2,4\text{-NO}_2\text{PhO}^-$  ions, respectively, from solution at  $X_{\text{DMSO}} = 0.1$  to mixed solvent. All these data are plotted against  $X_{\text{DMSO}}$  in Fig. 1.

## DISCUSSION

Figure 1 shows that from the enthalpic point of view the desolvation of the  $2,4\text{-NO}_2\text{PhO}^-$  anion plays a more important role than the solvation of the undissociated molecule in the DMSO-rich solutions ( $0.38 < X_{\text{DMSO}} < 0.8$ ).

In the water-rich solutions, the anion and undissociated molecule are both desolvated. It is noteworthy that in  $0.1 < X_{\text{DMSO}} < 0.2$  the desolvation values are identical.

By comparing 2,4-dinitrophenol and 2,5-dinitrophenol [6] by means of the difference in the enthalpy of ionization,  $\Delta H_{1(2,4\text{-NO}_2\text{PhOH})}^0 - \Delta H_{1(2,5\text{-NO}_2\text{PhOH})}^0$ , (Fig. 2) it can be inferred that the former is a more effective acid in the whole mole fraction range, this being more evident in the water-rich solutions.

It is also clear that, in the water-rich solutions, the transfer solvation enthalpies of anions and undissociated molecules play an equivalent role in the differentiation of the acidity between the 2,4-dinitro and 2,5-dinitrophenols.

These differences,  $\Delta H_{(2,4\text{-NO}_2\text{PhOH})_X}^0 - \Delta H_{(2,5\text{-NO}_2\text{PhOH})_X}^0$  and  $\Delta H_{(2,4\text{-NO}_2\text{PhO}^-)_X}^0 - \Delta H_{(2,5\text{-NO}_2\text{PhO}^-)_X}^0$ , were calculated as shown previously [1,2,6].

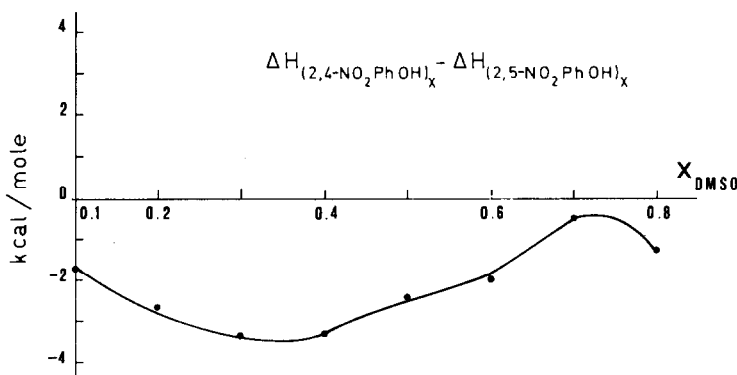


Fig. 2. Differences in the enthalpy of ionization between 2,4-dinitrophenol and 2,5-dinitrophenol.

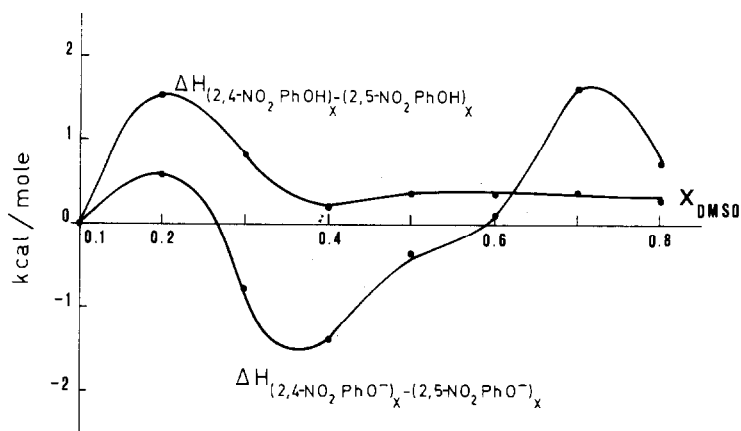


Fig. 3. Differences in the solvation enthalpies between the anions and the undissociated molecules of 2,4-NO<sub>2</sub>PhOH and 2,5-NO<sub>2</sub>PhOH in various DMSO–water mixtures. The differences in the hydration enthalpies both between the anion couple and between the undissociated molecule couple are arbitrarily set equal to zero.

In this case, however, the reference state is the DMSO–water solution with  $X_{\text{DMSO}} = 0.1$ .

Figure 3 shows that the 2,4-dinitro anion is solvated to a larger extent than the 2,5-dinitro anion in the range  $0.25 < X_{\text{DMSO}} < 0.6$  while, as regards the undissociated molecules, 2,4-dinitrophenol is more desolvated than 2,5-dinitrophenol in the whole mole fraction range.

This behaviour can be ascribed to a larger 2,4-dinitro anion stabilization, due, in turn, to the additivity of the resonance effect of the two nitro groups. Then, in this case, the interference of the additional NO<sub>2</sub> group (in the *para* position) on the interactions between the first NO<sub>2</sub> group (*ortho* position) and the phenolate oxygen stabilizes the benzene ring.

The anions polarize the solvent molecules and the degree of this polarization strictly correlates with the stabilization of the anions. Thus, the 2,4-dinitro anion stabilizes itself by dispersing its charge and surrounding itself with water molecules, in greater degree than the 2,5-dinitro anion. For the latter compound, the ring-stabilization is hindered by the  $\sigma$ -inductive electron-withdrawing effect [6]. Furthermore, in the DMSO-rich solutions, the large dipole of the 2,5-dinitrophenol anion interacts to a great extent with the DMSO molecules [6].

As regards the undissociated molecules, the introduction of an NO<sub>2</sub> group in the *para* position diminishes the dipole between the hydroxyl group and the *ortho* nitro group of the cyclic form [2,6] more than the NO<sub>2</sub> group in the *meta* position does, thus allowing less molecular solvation. So, it can be concluded that the greater acidity of 2,4-dinitrophenol with respect to 2,5-dinitrophenol is due to the fact that the interference of the *para* nitro group, in the anion and the undissociated molecule, behaves in the opposite way. Therefore, in the former, a  $\pi$ -electron-withdrawing resonance effect

stabilizes the benzene ring while in the latter  $\pi$ -resonance destabilizes the dipolar cyclic form. Instead, both the anion and the undissociated molecule of 2,5-dinitrophenol are ring-destabilized [6] by means of the  $\sigma$ -electron-withdrawing inductive effect.

#### ACKNOWLEDGEMENT

This work was carried out with the financial support of the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy.

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