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STUDY OF THE EFFECT OF THE MEDIUM ON THE REACTION CONSTANTS FOR THE DISSOCIATION OF NITROPHENOLS IN WATER—DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The effect of the medium on the reaction constants of the dissociation of nitrophenols in water—dimethylsulfoxide mixtures ranging from 0.0 to 0.8 mole fraction of DMSO is presented. In this study, use has been made of some linear free energy relationships. For standard reactions, the ionization processes of nitrobenzoic acids, at the same mole fractions, are used. The trend of the three reaction constants is very similar and their values are quite close.

INTRODUCTION

The linear free energy relationship between the dissociation of *meta*- and *para*-substituted phenols and the dissociation of *meta*- and *para*-substituted benzoic acids is well-known and has been extensively investigated in water [1].

In the present research, some linear free energy relationships between the dissociation of nitrophenols and nitrobenzoic acids in various water—DMSO mixtures are examined.

In order to study these relationships, the following [2—6] equations have been considered.

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

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

$$-\delta\Delta G^0 = 2.303RT\rho\sigma \quad (3)$$

$$-\delta\Delta G^0 = 2.303RT\rho\,(\sigma + R\Delta\sigma_p^-);\ \sigma_p^- - \sigma_p = \Delta\sigma_p^- \quad (4)$$

$$-\delta\Delta G^0 = \rho_0\sigma_0 + fF + \delta E_s + r\mathcal{R} \quad (5)$$

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

By using experimental ionization values of phenol [7] and nitrophenols

[8], the standard free energy change for eqn. (1) is obtained as

$$\delta \Delta G^0 = \Delta G^0_{NO_2-PhOH} - \Delta G^0_{PhOH} \tag{6}$$

The σ_m, σ_p and σ_0 values for nitrobenzoic acids were previously calculated [9,10] in the various mole fractions. The f, F, $\mathcal{R}$, r, δ and E_s values, in the same mole fractions are reported in the literature [6].

Equation (3) was used for *meta* derivatives and eqn. (5) for *ortho* derivatives. For the *para* derivatives, eqn. (4), with R ranging from 1 in pure water [6] to 0.804 in pure DMSO [11], was used. The *p*-nitro group has a much greater influence on the substitutent constant of the phenol than it does on that of benzoic acid. Indeed, when the reaction center involves an atom with unshared electron pairs and it is also directly conjugated with a strong electron-withdrawing group, the resonance effect is very enhanced.

Furthermore, in pure water *o*-nitrophenol has been shown to take part in a strong internal hydrogen bond [6].

The aim of this work is to study the effect of the medium on the reaction constants of the dissociation of nitrophenols.

The standard reactions are the ionization processes of the nitrobenzoic acids at the various mole fractions.

PROCEDURE

The free energy values for the ionization of the nitrophenols have been previously calculated [8], in the various mole fractions, at 25°C and the $pK_{a/I}$ values for the ionization of the phenol, at the same mole fractions, are reported at 20°C in the literature [7]. Unfortunately, no $\Delta\overline{H}_{ion}$ values for the ionization of phenol in the various water—DMSO mixtures at 25°C are found. In order to use the well-known equation

$$pK_{25°C} = pK_{20°C} - \frac{\Delta\overline{H}_{ion}\ \Delta T}{1.987\ T_1 T_2\ 2.303} \tag{7}$$

it seems reasonable to use the $\Delta\overline{H}_{ion}$ values at 25°C of the *m*-nitrophenol. So the $\Delta\overline{G}_{ion}$ value for the ionization of the phenol in pure water was calculated from eqn. (7) using $\Delta\overline{H}_{ion}$. The $\Delta\overline{G}_{ion}$ value calculated in this way differed from the experimental $\Delta\overline{G}_{ion}$ value of 28 cal [12].

DISCUSSION

The $\delta\Delta G^0$ values for *m*-, *p*- and *o*-nitrophenol and also the f, F, E_s, δ, R, $\mathcal{R}$, r values for nitrobenzoic acids at various mole fractions, are included in eqns. (3)—(5). Thus the reaction constants for the nitrophenol isomers, in the whole range of mole fractions, are obtained and reported in Table 1.

The values for the reaction constants are plotted against X_{DMSO} in Fig. 1.

For *o*-nitrophenol, the internal hydrogen bond is most stable in water-rich mixtures [8]. This internal hydrogen bond is due to the strong electrostatic attraction between the negative charge on the oxygen of the nitro

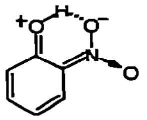
TABLE 1

ρ Values calculated by using eqns. (3)—(5) for *m*-, *p*- and *o*-nitrophenols in water—DMSO mixtures at 25°C

X_{DMSO}	ρ		
	m-Nitrophenol	*p*-Nitrophenol	*o*-Nitrophenol
0.0	2.17	2.28	1.91
0.1	2.77	2.39	2.22
0.2	2.80	2.61	2.43
0.3	3.21	2.89	2.89
0.4	3.19	3.23	3.17
0.5	3.69	3.62	3.67
0.6	4.17	4.00	4.57
0.7	4.07	4.10	4.48
0.8	3.64	3.85	4.41

group and the positive charge on the hydroxyl hydrogen.

It is also possible that the *ortho* form can be in resonance with the cyclic dipolar structure (I) [8].



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Because of this, the steric effect for the *ortho*-compound in pure water can be represented by the E_s value with the maximum dimension, while the term $r\mathcal{R}$ represents the resonance effect.

Finally, the electrostatic effect related to the internal hydrogen bond was factored in terms of proximity polar effect. This fact results from the large f value [6] for eqn. (5) in pure water.

The positive ρ values measure the sensitivity of the phenol derivatives to the electron-withdrawing effect of the nitro group with respect to the nitrobenzoic acids in the same solvent.

The values of the reaction constants exceed those found in pure water over the whole range of mole fraction with a maximum at $X_{DMSO} = 0.6$.

Indeed, the nitro groups disperse and thus stabilize the negative charge developed in the phenate anion much more than that in the carboxylate anion. Thus the trend of the ρ values can be related to the reduced number of intermolecular hydrogen bonds between the anions and the water molecules. This fact allows the solvent to interfere, to a minor extent, with the interactions between the reaction site and the substituent group.

In the mixtures where the percentage of the DMSO is much larger, the interactions between the dipolar DMSO molecules and the negative charge dispersed on the large anions decrease the ρ values.

The trend of the three reaction constants is similar and their values are quite close. This fact was to be expected, because it seems reasonable to

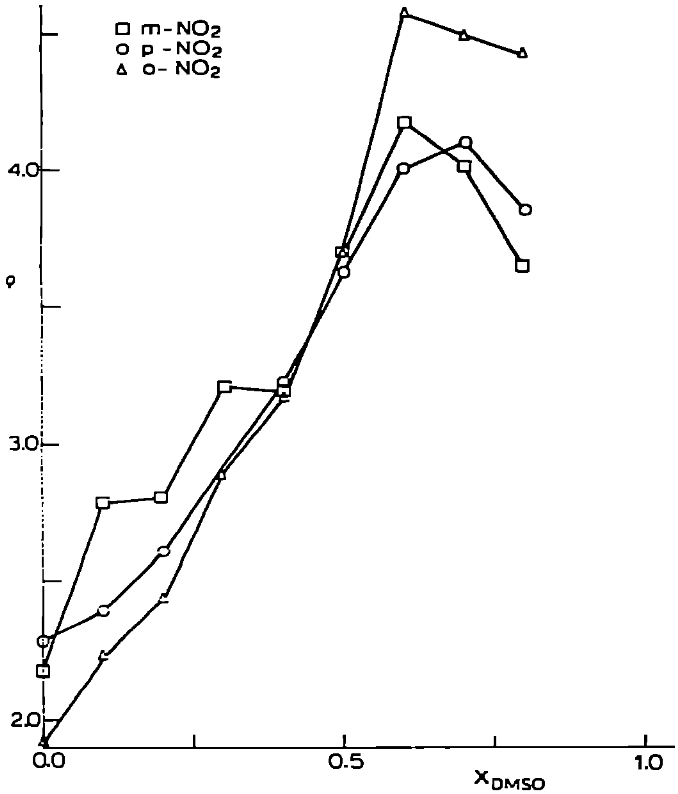

Fig. 1. Variation of the ρ values for *m*-, *p*- and *o*-nitrophenols as a function of the mole fraction of DMSO at 25°C.

assume the same mechanism of dissociation for the three nitro isomers.

It is interesting to note that eqn. (5) represents very well the trend of the *ortho* derivatives, which are affected by the so-called "*ortho*-effects" and by the intramolecular hydrogen bond.

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