

## Short Communications

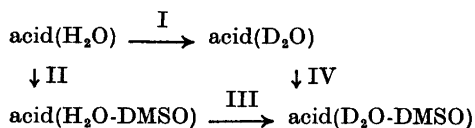
Transfer and Exchange Effects in the Dissociation of 3-Nitrobenzoic Acid in H<sub>2</sub>O and D<sub>2</sub>O and in Their DMSO Mixtures

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The effect of including the transfer terms in the equations of the simple equilibrium theory of acetic acid dissociation in H<sub>2</sub>O and D<sub>2</sub>O has been studied by Gold<sup>1</sup> applying the so-called transfer activity factors. The free energy of transfer amounts to about 10% of the total effect in this case. Salomaa<sup>2</sup> has separated the transfer and exchange effects in the dissociation of picric acid using the assumption that the free energy of transfer of undissociated picric acid from H<sub>2</sub>O to D<sub>2</sub>O equals that of 1,3,5-trinitrobenzene. The magnitude of the transfer effect is about 15% of the total change in the free energy in this case. The study of carbonic and sulfurous acids made by Salomaa *et al.*<sup>3</sup> has also revealed a transfer contribution of 15–25%.

The dissociation constants of 3-nitrobenzoic acid have been determined by potentiostatic titration.<sup>4</sup> Because of the scarce solubility of the acid in water, the titrations were carried out in water–DMSO mixtures. Therefore, it is possible to study and compare the transfer effects when the acid and its dissociation products are transferred in the following cyclic process:



The mol fractions of DMSO in H<sub>2</sub>O and D<sub>2</sub>O were chosen in such a way that the total change in the acid dissociation had the magnitude of  $(pK_{\text{D}_2\text{O}} - pK_{\text{H}_2\text{O}}) = \Delta pK$  also in processes II, III, and IV. The mol fractions of DMSO in the aqueous solutions are 0.096 and 0.090 in H<sub>2</sub>O and D<sub>2</sub>O, respectively, when the conditions mentioned above are fixed.

The transfer and exchange effects cannot be separated by measuring only the  $pK$  values.

Therefore, the free energies of transfer of methyl ester and the barium salt of 3-nitrobenzoic acid from one solvent to another have been determined. The former compound represents the undissociated acid and the latter the dissociation products of the acid in the transfer from one solvent to another. These assumptions seem to be relevant, although the barium salt in itself is a rather crude model for H<sup>+</sup>A<sup>-</sup>. On the other hand there are enough previous data, especially concerning the transfer free energies from H<sub>2</sub>O to D<sub>2</sub>O, making it quite possible to use the barium salt for this purpose.<sup>3,5a</sup>

The barium salt of 3-nitrobenzoic acid was prepared by mixing equal amounts of Ba(OH)<sub>2</sub> and the acid in water. The product was twice recrystallized from water. The methyl ester of 3-nitrobenzoic acid was prepared by the standard method.<sup>6</sup> The product was treated with charcoal and recrystallized three times from absolute methanol. The treatment of other chemicals and reagents has been described earlier.<sup>4</sup>

The free energies of transfer of barium 3-nitrobenzoate were determined by solubility measurements. The solubility was analyzed conductometrically using a method described elsewhere.<sup>5b</sup> The solubility products were then extrapolated to zero ionic strength by the aid of the Debye-Hückel equation (1).

$$\log y_{\pm} = \frac{2 \times 3^{1/2} A c^{1/2}}{1 + 3^{1/2} B a c^{1/2}} \quad (1)$$

In this equation  $A$  is calculated as described in the previous paper,<sup>4</sup>  $c$  is the concentration of the salt, and the ionic size parameter  $Ba$  was assumed to be of the same magnitude in all solutions ( $=1.81$ ).<sup>7</sup> The solubility product at zero ionic strength is calculated by eqn. (2). The  $K_s$  values are

$$K_s = 4(y_{\pm})^3 c^3 \quad (2)$$

seen in Table 1.

The free energies of transfer of methyl 3-nitrobenzoate were determined by distributing the ester between cyclohexane and aqueous phases. The concentration in the two phases were analyzed spectrophotometrically. The free energies of transfer of methyl ester and barium salt in processes I, II, III, and IV are tabulated in Table 2.

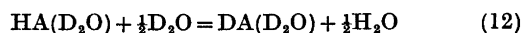
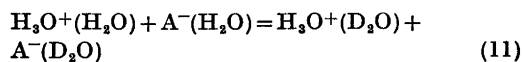
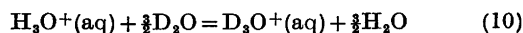
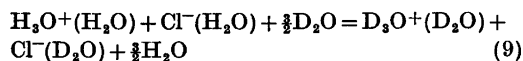
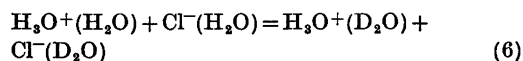
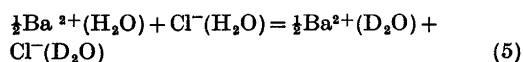
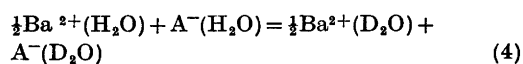
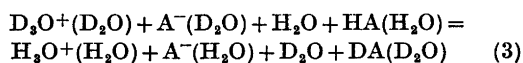
Table 1. Solubilities and solubility products of Ba 3-nitrobenzoate in H<sub>2</sub>O and D<sub>2</sub>O and their DMSO mixtures.

Solvent	$c/\text{mol dm}^{-3} \cdot 10^{-3}$	$-\log y_{\pm}$	$K_s/10^{-7}$	$\Delta G^{\ominus}/\text{kJ mol}^{-1}$
H <sub>2</sub> O	6.322	0.1126	4.644	36.153
D <sub>2</sub> O	5.177	0.1045	2.696	37.501
H <sub>2</sub> O-DMSO	6.447	0.1161	4.808	36.068
D <sub>2</sub> O-DMSO	5.728	0.1110	3.492	36.861

Table 2. Free energies of transfer of methyl 3-nitrobenzoate and Ba 3-nitrobenzoate and transfer contributions of total  $\Delta G^{\ominus}$  in the dissociation of 3-nitrobenzoic acid for processes I, II, III, and IV (for assumptions, see text).

Process	$\Delta G_t^{\ominus} \text{ J mol}^{-1}$ for Me-ester (for HA)	$\Delta G_t^{\ominus} \text{ J mol}^{-1}$ for Ba-salt (for 2H <sup>+</sup> A <sup>-</sup> )	Total transfer contribution
I	110	1350	560
II	-2010	-85	1970
III	550	795	-150
IV	-1570	-640	1250

A procedure analogous to that described by Salomaa was applied when transfer and exchange effects in the H<sub>2</sub>O-D<sub>2</sub>O system were evaluated.<sup>2</sup> The following equilibria are included in this procedure (concentration scale is applied throughout):



The corresponding free energies are reported in Table 3. The transfer free energy for the

Table 3. Free energies for equilibria (3)-(12).

Eqn.	$\Delta G^{\ominus}/\text{J mol}^{-1}$	Ref.
(3)	-2280	This work
(4)	675	This work
(5)	1040	5a
(6)	840	8
(7)	110	This work
(8)	110	This work
(9)	3610	8
(10)	2770	8,9
(11)	475	This work
(12)	855	This work

dissociation products of the acid (eqn. 11) calculated from the basis of eqns. (4), (5), and (6) is  $\Delta G_t^{\ominus} = 475 \text{ J mol}^{-1}$ . The total transfer free energy is obtained if eqn. (8) is taken into account and is  $475 - 110 = 365 \text{ J mol}^{-1}$ . The total reaction of isotopic exchange is formed by adding eqn. (10) and the reverse of eqn. (12). The free energy for eqn. (12) is obtained from the free energies of eqns. (3), (4), (9), (5), and (8). The total free energy of isotopic exchange equilibrium is thus  $2770 - 855 = 1915 \text{ J mol}^{-1}$ . Thus the contribution of the transfer effect is  $(365/2280)100 = 16\%$  from the total effect. This is of the same magnitude as that for picric acid which is reasonable.

The transfer and exchange effects may also be studied in the whole cyclic process in the

following rather naive way. It is assumed that the free energies of transfer for  $H^+A^-$  and  $\frac{1}{2}Ba^{2+}A^-$  and for HA and methyl ester are equal when passing from one solvent to another. The  $\Delta G^\ominus$  values as well as the transfer free energy contributions calculated therefrom are reported in Table 2.

It is difficult to conclude whether the deviations from total  $\Delta G^\ominus$  in passing from  $H_2O$  or  $D_2O$  to their DMSO mixtures are due to experimental errors or some structural features of the system. Anyway, the  $\Delta G^\ominus$  values are clearly lower when the exchange effects are included (processes I and III). The liquid structure of the DMSO mixtures where the mol fraction of DMSO is low, deviates somewhat from that of pure water although there are some controversial opinions on that. The effect of experimental errors on the determined  $\Delta G^\ominus$  values is considerable, especially in distribution measurements. More extensive investigation has to be made especially at different temperatures and solvent compositions.

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