

## Short Communications

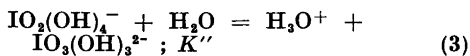
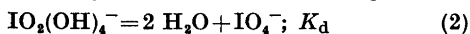
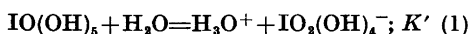
## Mixed Solvent Deuterium Isotope Effects on the Dissociation of Periodic Acid

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Various aspects of the equilibrium theory of deuterium solvent isotope effects on the acid-base equilibria and kinetics were recently discussed by Salomaa, Schaleger and Long<sup>1</sup> and by Kresge.<sup>2</sup> It was shown that, although the general validity of excluding the free energy contributions arising from the transfer of the species involved from light to heavy water could not be experimentally assessed, the equations derived were good approximations by virtue of their insensitivity to such transfer effects and were therefore found to hold for all the existing data within the limits of experimental error.

In the present paper we wish to report a particular example in which the transfer effects do not cancel leading to a failure of the simple equilibrium theory, *viz.* the first and second dissociation of periodic acid in H<sub>2</sub>O-D<sub>2</sub>O mixtures. In dilute solutions in light water the following equilibria are involved:<sup>3</sup>



The apparent first and second dissociation constants  $K_1$  and  $K_2$  which are directly measured are therefore  $K'(1 + K_d)$  and  $K''/(1 + K_d)$ , respectively. The conclusion of Crouthamel *et al.*,<sup>3</sup> according to which the divalent anion is substantially in the hydrated form  $\text{IO}_3(\text{OH})_3^{2-}$ , is further

supported, apart from the measurements discussed below, by recent IR studies.<sup>4</sup>

Reagent grade chemicals were used throughout. The purification and analysis of the heavy water employed took place as described elsewhere.<sup>5</sup> The technique of the pK measurements was that of Salomaa, Schaleger and Long.<sup>1</sup> The apparent pK values extrapolated to infinite dilution were for the first and second dissociation of periodic acid in light water at 25°C 1.61 and 8.25, respectively, which compare well with the literature values.<sup>3,6</sup>

Equilibrium (2) was studied by spectrophotometry following the method of Crouthamel *et al.*,<sup>3</sup> by measuring the optical density of sodium periodate solutions up to relatively high temperatures. The measurements were made on a Beckman DU Quartz Spectrophotometer equipped with a thermostated cell housing. The results for solutions in light water are illustrated in Fig. 1, which gave  $\Delta H = 11.4$  kcal/mole and  $\Delta S = 44.0$  E. U. for the reaction (2), in good agreement with the values reported by Crouthamel *et al.*:<sup>3</sup>  $\Delta H = 10.0$  kcal/mole and  $\Delta S = 44.0$  E. U.

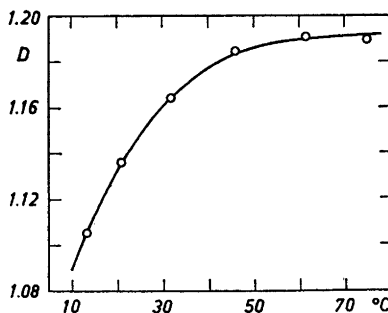


Fig. 1. Optical density  $D$  of  $1.150 \times 10^{-4}$  M sodium metaperiodate solution in light water in a 1.000 cm cell at  $221.5 \text{ m}\mu$  as the function of temperature.

The apparent relative pK values for the first and second dissociation in H<sub>2</sub>O-D<sub>2</sub>O mixtures are given in Table 1. The value of  $K_H/K_D$  calculated for the first dissociation, 1.20, is abnormally low. This is, however, an obvious result from the fact that periodic acid is fivebasic itself, whereas its monovalent anion is substantially in the form IO<sub>4</sub><sup>-</sup> containing no exchangeable hydrogens. Therefore the relative dissociation constant contains a fractionation factor term of the undissociated acid in the fifth power,<sup>1</sup> which is not compensated by a fractionation term relating to the product of the dissociation.

Table 1. Relative pK values for the first and second dissociation of periodic acid in H<sub>2</sub>O-D<sub>2</sub>O mixtures at 25°C.  $\Delta pK = pK_n - pK_H$ , in which the subscripts refer to a solution of deuterium atom fraction  $n$  and to pure protium oxide, respectively.

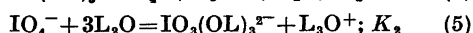
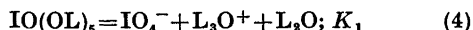
1st dissociation		2nd dissociation	
$n$	$\Delta pK$	$n$	$\Delta pK$
0.100	0.002	0.100	0.035
0.199	0.020	0.200	0.075
0.299	0.031	0.299	0.137
0.398	0.050	0.399	0.212
0.498	0.051	0.499	0.266
0.597	0.050	0.599	0.347
0.697	0.052	0.699	0.408
0.797	0.063	0.798	0.476
0.896	0.070	0.898	0.558
0.996	0.083	0.998	0.647
1.000	0.079 <sup>a</sup>	1.000	0.657 <sup>a</sup>

<sup>a</sup>) extrapolated

Table 2. Spectrophotometric values for the equilibrium constant  $K_d$ .

$n$	°C	$K_d$
0.000	5	9
»	15	15
»	25	27
»	35	57
»	45	163
0.200	25	29
0.399	»	31
0.798	»	58

Neglecting as the first approximation the portions of the monovalent anions that are in the hydrated form, which according to Table 2 are 1/30 or less, the equilibria relating to the measured 1st and 2nd dissociation constants are (L = H, D):



The equilibrium theory of the deuterium solvent isotope effects,<sup>1</sup> now predicts the following behavior of the values of  $K_1$  and  $K_2$  in H<sub>2</sub>O-D<sub>2</sub>O mixtures:

$$(K_1)_H/(K_1)_n = (1 - n + n\varphi_0)^5 (1 - n + n l)^{-2}; (K_1)_H/(K_1)_D = \varphi_0^5 l^{-2} \quad (6)$$

$$(K_2)_H/(K_2)_n = (1 - n + n\varphi_2)^{-3} (1 - n + n l)^{-2}; (K_2)_H/(K_2)_D = \varphi_2^{-3} l^{-2} \quad (7)$$

Here the subscripts H, D, and  $n$  refer to H<sub>2</sub>O, D<sub>2</sub>O, and to a mixture of deuterium atom fraction  $n$ , respectively, and  $\varphi_0$  and  $\varphi_2$  are the isotopic fractionation factors for hydrogens in the undissociated acid and in its divalent anion, which can be calculated from the values of  $K_H/K_D$  with the known value of the fractionation factor  $l$  for the hydronium ion. The results of such calculations are shown in Fig. 2. In the calculations we have used the recent value<sup>7</sup> of 9.0 for  $L = l^{-1/6}$  at 25°C. Owing to the insensitivity of the equations to the particular choice of  $L$ , the values calculated for

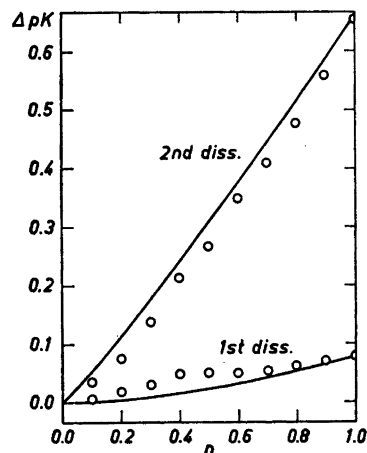


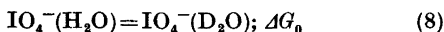
Fig. 2. Observed and calculated values of  $\Delta pK$  for the first and second dissociation of periodic acid in H<sub>2</sub>O-D<sub>2</sub>O mixtures at 25°C. The solid lines are those calculated from eqns. (6) and (7).

$K_H/K_n$  are experimentally indistinguishable from those obtained with the earlier value of 11.0.

It is seen from the figure that the values calculated for the first dissociation are too small and those for the second too large, the relative deviations in  $K_H/K_n$  being of the same magnitude but opposite in sign. The maximum deviations are in the both cases approximately 6%. It might be suggested that the neglect of the dehydration equilibria of  $\text{IO}_2(\text{OL})_4^-$  could cause such a behavior. In the more general equations that would account for these equilibria the values of  $K_H/K_D$  for the first dissociation should be multiplied by  $(1 + 1/(K_d)_H)/(1 + 1/(K_d)_n)$  and those for the second dissociation divided by the same factor. Calculations based on these more general equations indicate, however, that because of the relatively high values of  $K_d$  the equations become very insensitive to variations in this constant and no essentially better fits can be obtained.

As the deviations are approximately of the same magnitude but opposite in sign it may be concluded that they arise mainly from the product of the first dissociation and from the initial reactant of the second, viz. from the metaperiodate anion  $\text{IO}_4^-$ . It is reasonable to assume that, unlike acids and ions containing OL-groups that are hydrogen-bonded to the water structure, considerable free energy changes are involved in the transfer of species like  $\text{IO}_4^-$  from light to heavy water, the influence of which is incorporated into the measured values of  $K_H/K_n$ .

If the differences between the observed and calculated values are wholly ascribed to the transfer free energy of the periodate ion:



and if it is assumed that the corresponding transfer free energy from  $\text{H}_2\text{O}$  to a solvent of another isotopic composition varies approximately linearly with the deuterium atom fraction  $n$ , eqns. (6) and (7) should be replaced by

$$(K_1)_H/(K_1)_n = (1 - n + n \varphi_0)^5 / (1 - n + n l)^{-3} \times \exp(-n\Delta G_0/RT) \quad (9)$$

$$(K_2)_H/(K_2)_n = (1 - n + n \varphi_2)^{-3} (1 - n + n l)^{-3} \times \exp(+n\Delta G_0/RT) \quad (10)$$

Calculations based on these equations show that an excellent fit to the experimental data is found with the following set of the

parameters:  $\varphi_0 = 0.71$ ,  $\varphi_2 = 0.67$ ,  $\Delta G_0 = +460$  cal/mole.

Although the above estimation of  $\Delta G_0$  assumes a linear dependence of the transfer free energy on the deuterium atom fraction, the validity of which is difficult to assess experimentally, its value is seen to be of expected magnitude, as the corresponding transfer free energy for the considerably smaller chloride ion is about +210 cal/mole.<sup>7</sup> Another independent check can be made using the data for the dehydration equilibrium (2) (Table 2). Here the equilibrium theory of deuterium solvent isotope effects gives, when corrected for the transfer free energy of the  $\text{IO}_4^-$  ion, the following equation:

$$(K_d)_H/(K_d)_n = (1 - n + n \varphi_1)^4 \times \exp(-n\Delta G_0/RT) \quad (11)$$

in which the fractionation factor  $\varphi_1$  refers to the hydrated form of the monoanion  $\text{IO}_2(\text{OL})_4^-$ . Because the values calculated above for  $\varphi_0$  and  $\varphi_2$  were approximately of the same magnitude, viz. 0.71 and 0.67, it follows that the value of  $\varphi_1$  should also be of this magnitude. In fact, when eqn. (11) is applied to the data of Table 2, one obtains with  $\Delta G_0 = 460$  cal the values 0.7, 0.7, and 0.6 for  $\varphi_1$  at  $n = 0.200$ , 0.399, and 0.798, respectively. Although the values of  $K_d$  can be determined much less accurately than those of  $K_1$  and  $K_2$ , it is seen that the behavior of the dehydration equilibrium in  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$  mixtures is satisfactorily represented by eqn. (11). More detailed knowledge of the dependence of the transfer free energies on the isotopic composition of the solvent were necessary to allow more accurate calculations to be made.

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