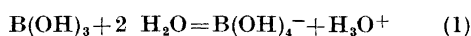# The Structure of Boric Acid in Aqueous Solution

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The Raman spectra of borate solutions [1] indicate that the aqueous borate ion exists in the form $B(OH)_4^-$. The dissociation of boric acid is thus usually written as

$$B(OH)_3 + 2 \ H_2O = B(OH)_4^- + H_3O^+ \qquad (1)$$

which represents boric acid as a Lewis acid. However, as pointed out by Bell,[2] aqueous boric acid itself may be in monohydrated form, in which case its dissociation scheme would involve proton transfer from a Brønsted acid:

$$H_2\overset{+}{O} - \overset{-}{B}(OH)_3 + H_2O = B(OH)_4^- + H_3O^+ \quad (2)$$
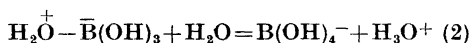
The dissociation schemes (1) and (2) were discussed recently by Gold and Lowe [3] in connection with their study of the solvent deuterium isotope effect on the acidity constant of boric acid in $H_2O - D_2O$ mixtures. They found that an equation based on scheme (2) could be fitted by the experimental values slightly better than an equation based on scheme (1). However, it was recognized that the differences were too small to allow firm conclusions to be made. In addition, the transfer free energy effects associated with going from one solvent to another within the $H_2O - D_2O$ system, though probably small in this case, could affect the results.

In the present paper we wish to report about some preliminary results which have a close bearing on the problem in question. Our data refer to the kinetics of proton transfer from various acids, including boric acid, to an unsaturated system. More specifically, the data relate to the acid-catalyzed hydrolysis of a vinyl ether, methyl isopropenyl ether, in water solution. As discussed earlier,[4] the reaction exhibits general acid catalysis, and its overall rate is determined by concurrent proton transfers to the substrate from the various Brønsted acids present in the solution.

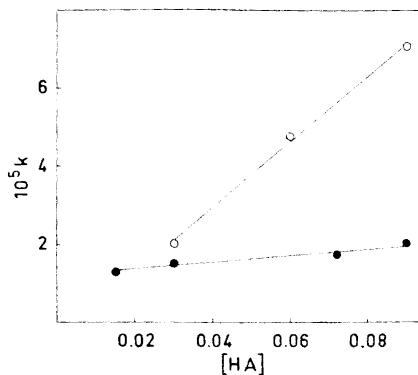Fig. 1 shows some of the determined values of the overall rate coefficients in

Fig. 1. First-order rate coefficients k (in s^{-1}) for the hydrolysis of methyl isopropenyl ether in carbonate-bicarbonate (O) and in borate-boric acid (●) buffers of constant ionic strength at 35°C. [HA]=concentration of the acid component of the buffer in moles per liter. The buffer ratios, [HA]:[A$^-$], were 1:1 throughout.

borate and carbonate buffers. The primary interest herein is the slopes of the lines shown, *i.e.*, the catalytic coefficients of the bicarbonate ion and boric acid, which are, respectively, $(0.85 \pm 0.04) \times 10^{-3} \ M^{-1} s^{-1}$ and $(0.087 \pm 0.014) \times 10^{-3} \ M^{-1} s^{-1}$ (the intercepts represent catalysis by water and by the hydronium ion, the concentration of the latter being about tenfold in the borate solutions). The magnitudes of the standard deviations indicate that the 90 % confidence limits for the catalytic coefficients are $(0.85 \pm 0.25) \times 10^{-3} \ M^{-1} \ s^{-1}$ for the bicarbonate ion, and $(0.087 \pm 0.041) \times 10^{-3} \ M^{-1} \ s^{-1}$ for boric acid, respectively (t-test). It is thus seen that boric acid is quite an ineffective catalyst compared to the bicarbonate ion, notwithstanding the fact that the apparent acidity of boric acid ($pK = 9.2$) is clearly higher than that of the bicarbonate ion ($pK = 10.2$). Statistical corrections based on molecular symmetry do not alter this situation.

The fact that the proton-donating ability of boric acid is much less than that expected from the value of its apparent acidity constant is readily understood if the latter constant is actually that of equilibrium (1) and not that of a proton transfer from aqueous boric acid (in any molecular form) to the solvent water.

Bell[5] has emphasized, in connection with this particular problem, that the kinetics of proton transfer reactions often give more information about the state of dissolved species than equilibrium studies do, although he regretted the scarcity of relevant experimental studies. One reason for the latter may be the lack of suitable model reactions that could be conveniently studied under widely varying conditions. The hydrolysis of vinyl ethers seems to offer certain experimental advantages. First, the reaction is catalyzed by general acids only, which avoids the complications due to simultaneous catalysis by general bases encountered in many classical examples of general acid-base catalysis. Second, the sensitivity of the rate to the structure of the vinyl ether[4] makes it possible to choose a compound the kinetics of which can be conveniently studied under the conditions of interest.

1. Edwards, J. O., Morrison, G. C., Ross, V. F. and Schultz, J. W. *J. Am. Chem. Soc.* **77** (1955) 266.
2. Bell, R. P. *The Proton in Chemistry*, Cornell University Press 1959, p. 13.
3. Gold, V. and Lowe, B. M. *J. Chem. Soc.* **A 1968** 1923.
4. Salomaa, P., Kankaanperä, A. and Lajunen, M. *Acta Chem. Scand.* **20** (1966) 1790.
5. Bell, R. P. Ref. 2, p. 179.

Solvent Deuterium Isotope Effects on Acid-Base Reactions

Part IV. Lyonium Ion-Catalyzed Hydrolysis of Tertiary Butyl Acetate in Isotopically Different Waters

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In the preceding part[1] of this study it was pointed out that the solvent deuterium isotope effect on an A-1 reaction should be calculable, provided that the rate coefficient for the uncatalyzed hydrolysis of the same compound in light water is also known. A further requirement is that the latter value has to refer to a mechanism of the S_N1 (or B-1) type. As an addition to the examples given previously, the present paper describes the experimental and semiempirically calculated results for *tert.*-butyl acetate. The uncatalyzed hydrolysis of this compound has been studied recently[2] and shown to take place by the $B_{AL}1$ mechanism.

The rate coefficients measured for the lyonium ion-catalyzed hydrolysis of *tert.*-butyl acetate in isotopically different waters are given in Table 1. As discussed earlier,[1] the standard free energies associated with transfer of the reactants and transition states from one solvent to another effectively cancel out in the present case, so that the rate coefficient k_n at an arbitrary deuterium atom fraction n should be given by the simple Gross equation

$$k_n = k_H \times \frac{1 - n + n\varphi}{(1 - n + nl)^3} \qquad (1)$$

Here k_H stands for the rate coefficient in light water, and the fractionation factors φ and l refer to the acidic hydrogen present in the transition state and those in the hydronium ion, respectively. Eqn. (1) was fitted to the experimental rate coefficients by the method of least squares, whereupon the following best values with their standard deviations were obtained for the parameters: $k_H = (1.33 \pm 0.02) \times 10^{-4} \, \text{M}^{-1} \, \text{s}^{-1}$, and $\varphi = 0.77 \pm 0.03_6$. The value 0.69 was used for l in the calculations.