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.

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Solvent Deuterium Isotope Effects on Acid-Base Reactions

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

PENTTI SALOMAA

Department of Chemistry, University of Turku, Turku, Finland

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: $k_H = (1.33 \pm 0.02) \times 10^{-4} \ M^{-1} \ s^{-1}$, and $\varphi = 0.77 \pm 0.03_6$. The value 0.69 was used for l in the calculations.

Table 1. Rate coefficients k (M^{-1} s^{-1}) for the lyonium ion-catalyzed hydrolysis of *tert.*-butyl acetate in $H_2O - D_2O$ mixtures at 25°C. $n=$ atom fraction of deuterium.

n	$10^4 k$ (obs.)	$10^4 k$ (calc.)
0.000	1.33	1.33 ± 0.02
0.214	1.60	1.57 ± 0.02
0.432	1.84	1.87 ± 0.02
0.865	2.78	2.75 ± 0.04
0.983	3.04	3.10 ± 0.05
1.000	—	3.16 ± 0.05

$$k_D/k_H = 2.34 \pm 0.05$$

The values of Table 1 indicate no systematic deviations from eqn. (1) that could be detected by the present precision of the measurements. Some earlier values reported for k_H in light water at 25°C may be cited for comparison: 1.33×10^{-4},[3] 1.28×10^{-4},[4] and 1.36×10^{-4} M^{-1} s^{-1}.[5] The approximate value 2.0 for k_D/k_H referred to by Bunton and Shiner [6] is considerably lower than the present value, 2.34 ± 0.05.

The main interest here is in the value of k_D/k_H when calculated independently from the results obtained for the catalyzed $A_{AL}1$ hydrolysis and uncatalyzed $B_{AL}1$ hydrolysis in light water. The following relation was proposed for the fractionation factor of protons (deuterons) attached to oxygen atoms:[1]

$$\varphi_{OH} = 0.0092\, pK_{OH} - 0.147 \text{ (at 25°C)} \quad (2)$$

Here pK_{OH} is the negative logarithm of the acidity constant of the acidic proton in question in light water. If this proton is attached to a transition state, as in the present case, its acidity constant can be estimated from the rate coefficients of the uncatalyzed and hydronium ion-catalyzed hydrolysis reactions, as described by Kurz.[7] The rate coefficient of the uncatalyzed hydrolysis of *tert.*-butyl acetate at 25°C is 5.10×10^{-8} s^{-1},[2] which, along with the value given in Table 1 for the catalyzed reaction in light water, gives 3.4 for the pK of the transition state of the catalyzed reaction. This, in turn, when use is made of eqn. (2) and of the known value of l, predicts a value of 2.33 for k_D/k_H. This semiempirically calculated value is in excellent agreement with the experimental value, 2.34 ± 0.05. Put another way, one may consider the results of these calculations confirmatory evidence for the postulated reaction mechanisms.

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