Interpretation of the Kinetics of Acid-catalyzed Reactions in Water–Glycerol Mixtures

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IN Bunnett's analysis[1] of the kinetics of acid-catalyzed reactions in moderately concentrated aqueous mineral acid solutions, a parameter w $[= \mathrm{d}\log(k_\psi/h_0)/\mathrm{d}\log a_{H_2O}]$ has been defined and identified as an approximate measure of the hydration change occurring upon conversion of reactants into a transition state. The basic soundness of the hydration treatment depends upon whether the activity coefficients involved in the rate equation are cancelled by the Hammett acidity function; recent experience implies that, in general, exact cancellation is not to be expected.[2,3] It would therefore be highly desirable to seek other approaches to the direct evaluation of the "water balance" in acid-catalyzed reactions. We report that a method based on kinetics in water–glycerol mixtures appears to offer such an alternative.

The rates of acid-catalyzed hydrolysis of a ketal [2,2-dimethyl-1,3-dioxolan, (I)] and deoxymercuration of 1-iodo-2-methoxymercuriethane (II) and 2-iodomercuriethanol (III) increase with decreasing water content in solvents containing 0—50 wt. % glycerol ($\leqslant 10^{-2}$M in $HClO_4$). A modified Brønsted–Bjerrum rate equation for these reactions, each of which proceeds by an *A*-1 type mechanism, is given by Equation 1.[4] If the activity coefficient

$$\log k_\psi/c_{H^+} = w_g \log a_{H_2O} + \log k_0 f_S f_{H^+}/f_\ddagger \qquad (1)$$

term, $f_S f_{H^+}/f_\ddagger$, is relatively insensitive to changes in medium,[5] then the slopes of plots of $\log k_\psi/c_{H^+}$ against $\log a_{H_2O}$[6] yield w_g. It is evident from the Figure that such plots are sensibly linear and w_g-values were therefore calculated by a linear least-squares procedure.

Negative values of the hydration parameter, w_g, are to be expected for reactions utilizing the *A*-1 mechanism on the basis that the hydronium-ion reactant is more strongly hydrated than the transition state. This interpretation can be carried further if monomolecular hydration of positive OH protons[1,7,8] is taken to be the energetically most important factor in the overall solvation picture. According to this simplified viewpoint the hydronium ion exists as $OH_3(OH_2)_3^+$,[8] the transition states[9] from (I) and (II) as monohydrates and the transition state from (III) as a dihydrate. The net hydration numbers predicted by this simple treatment, -3 for (I) and (II) and -2 for (III), are seen to be in surprisingly close agreement with the w_g-values of the Table.

That glycerol is rather uniquely suited as a co-solvent for the present type of study is further indicated by a comparison of the kinetic behaviour of *A*-1 acetal/ketal hydrolysis in various water–co-solvent mixtures. In contrast to the rate enhancement with increasing glycerol content which we report, the rates of hydrolysis of various acetals and ketals are strongly retarded by the addition of dioxan,[10] ethanol,[11] acetone,[12] and dimethylformamide.[13] The reason for this difference may be related to the fact that aqueous glycerol solutions are very nearly ideal.[14]

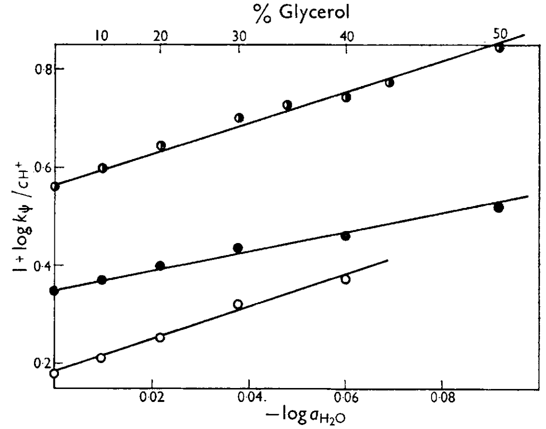

FIGURE *Variation of rate constants with water activity,* ○, *reaction of* 2,2-*dimethyl*-1,3-*dioxolan*; ⊙, 2-*iodomercuriethanol*; ◑, 1-*iodo*-2-*methoxymercuriethane. Ordinate for the last is actually* 2 + log k_ψ/c_{H^+}.

Many factors besides hydration influence solute behaviour in aqueous solvents.[14–16] Use of aqueous glycerol media in the study of kinetics of acid-catalyzed reactions promises to provide a general means of isolating the contribution of differential hydration from other effects. It should also be noted that the correspondence which apparently exists between Bunnett's w-values and the present w_g-values suggests that the latter might complement the former as empirical criteria of mechanism, particularly for acid-catalyzed reactions which are too fast to follow in the concentrated acid media required for Bunnett's treatment.

TABLE

Kinetic parameters for reaction in water–glycerol mixtures at 25° [a]

	No. points	k_2^0(M^{-1}sec.$^{-1}$)[b]	w_g	σ_w[c]	r[c]
2,2-Dimethyl-1,3-dioxolan(I):	29	0·151	−3·37	0·18	0·965
1-Iodo-2-methoxymercuriethane(II): ..	24	0·0363	−3·11	0·14	0·979
2-Iodomercuriethanol(III):	23	0·223	−1·89	0·11	0·968

[a] Reactions were followed spectrophotometrically. Pseudo-first-order rate constants were determined using infinity readings obtained after 10—20 half-lives or by the method of E. Swinbourne, *J. Chem. Soc.*, 1960, 2371. Second-order rate constants, $k_2 = k_\psi/c_{H^+}$, were independent of c_{H^+} in all solvent media.

[b] The second-order rate constant for reaction in pure water. These values are in fair-to-good agreement with those previously reported by P. Salomaa and A. Kankaanperä, *Acta Chem. Scand.*, 1961, **15**, 871, and L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *J. Org. Chem.*, 1962, **27**, 3421.

[c] σ_w is the standard deviation of the slope; r is the correlation coefficient: W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, 1951.

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[1] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **86**, 4956, 4968, 5973, 4978.

[2] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 233—242.

[3] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1966, **88**, 1177, and references cited therein.

[4] The symbols are those used in ref. 1.

[5] This assumption cannot of course be rigorously justified. Suffice it to say that under these conditions of low ionic strength (less than 0·01 M throughout) and only slightly changing dielectric constant (D varies from 78 in water to 64 in 50% glycerol) it is not unreasonable to suppose that log f_S and log $f_{H^+}/f_\ddagger$ are never appreciably different from zero.

[6] Water activities were computed from data given by G. Scatchard, W. Hamer, and S. Wood, *J. Amer. Chem. Soc.*, 1938, **60**, 3061.

[7] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 13—31.

[8] H. L. Clever, *J. Chem. Educ.*, 1963, **40**, 637; R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N.Y., 1959, pp. 80—84.

[9] The transition states of these *A*-1 reactions are assumed to resemble the conjugate acids of the respective substrates.

[10] J. Koskikallio and I. Tarvainen, *Acta Chem. Scand.*, 1962, **16**, 263.

[11] P. Salomaa, *Acta Chem. Scand.*, 1957, **11**, 461.

[12] R. K. Wolford, *J. Phys. Chem.*, 1963, **67**, 632.

[13] R. K. Wolford and R. G. Bates, *J. Phys. Chem.*, 1962, **66**, 1496.

[14] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd edn., Butterworths, London, 1959, ch. 9.

[15] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 1541.

[16] D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.