Brönsted Coefficients and Solvent Effects

By Brian G. Cox* and Alan Gibson

(*Department of Chemistry, University of Stirling, Stirling, Scotland*)

Summary It is shown that the use of solvent variation to alter the total free-energy change occurring during proton-transfer reactions does not lead to normal Brönsted β-values and the implications of this are discussed.

Brönsted β-coefficients relating rates and equilibrium constants for proton transfer reactions (equation 1) may in principle be obtained either from variations in the nature

$$SH + B^- \rightleftharpoons S^- + BH \qquad (1)$$

of B or S (*e.g.* by varying substituents), or from variation of the medium in which the reaction is carried out.[1] The latter method of obtaining β coefficients does not appear to have been tested directly but the equivalence of the two methods has been assumed in the interpretation of results obtained for proton abstraction by hydroxide ion in mixtures of dimethyl sulphoxide and water.[2] In these studies, values of $\Delta pK(pK_{SH} - pK_{BH})$ have been estimated using measured H– acidity functions.[3]

In the course of a study of the effects of changing solvent on the rates and kinetic hydrogen isotope effects of proton transfer reactions, we have measured rates and p*K*'s for a number of substrates SH and catalysts BH in several solvent systems. As an example of the results, kinetic and thermodynamic parameters for reactions between acetate ions and several substrates in water–dimethyl sulphoxide and water–trifluoroethanol mixtures are presented in the Table. They clearly show that there is no simple relationship between rates and equilibria, as do additional results for fluoride and monochloroacetate ions as catalysts and for reactions carried out in acetonitrile-water mixtures.

For a system to exhibit a normal Brönsted β $(0 \leqslant \beta \leqslant 1)$, it is necessary for the effects of a perturbation on the free energy of the system to vary monotonically with the extent of reaction. Because of the considerable difference in the effect of transferring anions of high charge density (capable of stabilization by H-bonding) and larger polarisable anions of low charge density from protic solvents (*i.e.* solvents containing relatively acidic protons) to dipolar aprotic solvents,[4] solvent variation would not in general be expected to lead to normal β values. Thus addition of dimethyl sulphoxide to water raises the activity of the acetate (RCO_2^-) and nitroalkane (RNO_2^-) anions by a similar amount relative to the larger and more polarisable transition state anion, leading to large rate increases but relatively small changes in ΔpK. Similarly the more acidic trifluoroethanol interacts more strongly with these anions than the transition-state anion.

Table

Rates and equilibria for acetate-catalysed proton transfer reactions from carbon acids in solvent mixtures at 25 °C.

x_{org}[a]	pK_{SH}	pK_{HOAc}	ΔpK[b]	$\log k_e/k_0$[c]
1. $Me_2SO–H_2O$ mixtures. (i) Me_2CHNO_2; $k_0(OAc^-) = 2{\cdot}70 \times 10^{-6}$ dm^3 mol^{-1} s^{-1}				
0·00	7·70	4·75	3·0	0·00
0·20	—	—	—	0·98
0·39	11·0	7·1	3·9	1·82
0·50	12·1	8·0	4·1	2·30
0·69	—	—	—	3·36
0·83	—	—	—	3·37
1·00	16·2[d]	12·0[e]	4·2	—
(ii) $MeCO{\cdot}CH(Me)CO_2Et$; $k_0(OAc^-) = 4{\cdot}30 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}				
0·00	12·4	4·75	7·7	0·00
0·20	12·3	6·0	6·3	0·99
0·28	—	—	—	1·28
0·39	12·7	7·1	5·6	1·75
(iii) $CH_3CH_2NO_2$; $k_0(OAc^-) = 3{\cdot}26 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}				
0·00	8·8	4·75	4·1	0·00
0·20	10·2	6·0	4·2	1·14
0·39	11·7	7·1	4·5	1·96
1·00	16·4[d]	12·0[e]	4·4	—
2. $CF_3CH_2OH–H_2O$ mixtures. $MeCH_2NO_2$; $k_0(OAc^-) = 3{\cdot}26 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}				
0·00	8·8	4·75	4·1	0·00
0·08	—	—	—	−0·05
0·20	10·2	5·8	4·4	−0·30
0·32	—	—	—	−0·41
0·50	11·5	7·1	4·4	−0·60

[a] Mole fraction of organic component. [b] $pK_{SH} - pK_{HOAc}$. [c] k_e are catalytic constants in solvent mixtures, measured as rates of iodination. [d] Ref. 6. [e] J. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, *J. Amer. Chem. Soc.*, 1968, **90**, 23; C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721. Average value.

These results also have implications for the interpretation of β values in water, as the extent to which pK's of acid involved in reactions are determined or modified by solvation will not in general be reflected in the transition states. For example, 1,1-dinitroethane reacts $10^{4 \cdot 8}$ times more rapidly with OH^- than does nitroethane,[5] despite a difference of only 3·44 pK units in the acidity, leading to a value of $\beta = 1{\cdot}4$. In dimethyl sulphoxide however, 1,1-dinitroethane is a stronger acid than nitroethane by 10 pK units.[6] This suggests that in water, the considerable rate difference reflects the much greater stabilization of the developing negative charge by the dinitro-group (as shown by the pK difference in dimethyl sulphoxide) but that the overall free energy difference between the reactions is reduced by considerably higher solvation of the mononitro-anion relative to the dinitro-anion. Such an effect might also explain the anomalous β values obtained for the ionization of substituted phenylnitroalkanes.[7]

It should be noted that the results in the Table refer to reaction between a neutral substrate and a negatively charged base. Both the kinetic and thermodynamic behaviour of systems of different charge type (*e.g.* $SH + B \rightleftharpoons S^- + BH^+$) are expected to differ from that observed here.

We thank Professor R. P. Bell for discussion.

(*Received*, *23rd May* **1974**; *Com.* **600**.)

---

[1] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 157, 241.

[2] R. P. Bell and B. G. Cox, *J. Chem. Soc.* (*B*), 1970, 194; 1971, 783; Z. Margolin and F. A. Long, *J. Amer. Chem. Soc.*, 1972, **94**, 5108; 1973, **95**, 2757; D. W. Earls, J. R. Jones, and T. G. Rumney, *J.C.S. Faraday I*, 1972, **68**, 925; L. Melander and Nils-Åke Bergman, in the press.

[3] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

[4] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1; B. G. Cox, *Ann. Reports* (*A*), 1973.

[5] R. P. Bell and R. L. Tranter, *Proc. Roy. Soc. A*, 1974, **337**, 517.

[6] V. M. Belikov, Yu. N. Belokoń, and N. G. Faleev, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, **2**, 272.

[7] F. G. Bordwell, W. J. Boyle, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.