Kinetic Acidity Dependence in Concentrated Acids

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THE different ways in which rates of acid-catalyzed reactions depend on the acidity of concentrated solutions of strong mineral acids has long been regarded as a potential source of mechanistic information, and two major attempts at interpreting kinetic acidity dependence in terms of reaction mechanism have been made over the past quarter century.[1,2] Neither of these, however, has been wholly successful. Both treatments assume that the acidity dependence of a reaction proceeding by a given mechanism will bear a characteristic relationship to the acidity function, h_0, and that this relationship will not change beyond rather narrow limits. It seems to us that this assumption is not warranted, and that this may be the major shortcoming of these two treatments. We wish, therefore, to outline a new interpretation of kinetic acidity dependence which is free of this defect.

The mechanism of aromatic hydrogen exchange is now well established as simple protonation and deprotonation of the aromatic substrate:[3-5]

$$\mathrm{H'Ar} + \mathrm{H^+} \rightleftharpoons \mathrm{H'ArH^+} \rightleftharpoons \mathrm{HAr} + \mathrm{H'^+} \qquad (1)$$

This reaction occurs at similar velocities for 1,3,5-trihydroxybenzene as for 1,3,5-trimethoxybenzene, and there is no reason to believe that any fundamental difference exists in the aromatic hydrogen exchange of these two substrates. And yet, in moderately concentrated aqueous perchloric acid, the rate of exchange for trihydroxybenzene is proportional to $h_0^{0\cdot80}$ while that for trimethoxybenzene is proportional to $h_0^{1\cdot14}$;[6] the *w*-value[2] for the former is *ca.* +3 whereas that for the latter is *ca.* −2. But a similar difference appears in the equilibrium protonation of these two substances: at perchloric acid concentrations nearest to the acidities of the kinetic experiments, the protonation of trihydroxybenzene to give a carbon conjugate acid is controlled by $h_0^{1\cdot10}$; that of trimethoxybenzene, $h_0^{1\cdot95}$. This suggests that the difference in kinetic acidity dependences is a property of the substrates and should not be interpreted as a difference in mechanism. It implies also that the kinetic difference might be erased by a suitable comparison of kinetic and equilibrium acidity dependences.

Following usual practice,[7] the first-order rate constant for aromatic hydrogen exchange can be written in terms of a medium-independent rate constant, k^0, the activity of the hydrogen ion, $A_{\mathrm{H^+}} = C_{\mathrm{H^+}} f_{\mathrm{H^+}}$, and activity coefficients of the reactant, f_{HAr}, and transition state, $f^\ddagger$:

$$v/C_{\mathrm{HAr}} = k_1 = k^0 C_{\mathrm{H^+}} f_{\mathrm{H^+}} f_{\mathrm{HAr}}/f^\ddagger \qquad (2)$$

The transition state for aromatic hydrogen exchange has a structure which is intermediate between the structures of its two limiting forms: the initial state, HAr + H⁺, and the reaction intermediate, HArH⁺. The quantity $f^\ddagger$ can therefore be written in terms of the activity coefficients of these two limiting states as

$$f^\ddagger = (f_{\mathrm{HAr}} f_{\mathrm{H^+}})^{1-\alpha}\,(f_{\mathrm{HArH^+}})^{\alpha} \qquad (3)$$

Here, α is a parameter which measures the degree to which the transition state resembles the intermediate $\mathrm{HArH^+}$; it will have a numerical value between 0 and 1, and its value should be the same for closely similar substrates reacting by the same mechanism. Then

$$k_1 = k^0\, C_{\mathrm{H^+}}\, (f_{\mathrm{HAr}} f_{\mathrm{H^+}}/f_{\mathrm{HArH^+}})^{\alpha} \qquad (4)$$

The activity coefficient term of equation 4 can be expressed in terms of the indicator ratio, I, for equilibrium protonation ($I = C_{\mathrm{HArH^+}}/C_{\mathrm{HAr}}$), the stoicheiometric concentration of hydrogen ions, $C_{\mathrm{H^+}}$, and the acidity constant of $\mathrm{HArH^+}$, K

$$f_{\mathrm{HAr}} f_{\mathrm{H^+}}/f_{\mathrm{HArH^+}} = I\,K/C_{\mathrm{H^+}} \qquad (5)$$

This reduces equation 4 to measurable quantities and constants:

$$k_1/C_{\mathrm{H^+}} = k^0\, K^{\alpha}\, (I/C_{\mathrm{H^+}})^{\alpha} \qquad (6)$$

and α can be evaluated as the slope of a plot of $\log(k_1/C_{\mathrm{H^+}})$ against $\log(I/C_{\mathrm{H^+}})$. For trihydroxybenzene, $\alpha = 0\cdot48 \pm 0\cdot03$ and for trimethoxybenzene, $\alpha = 0\cdot44 \pm 0\cdot03$.

This analysis demonstrates that different kinetic acidity dependences can be consistent with a single reaction mechanism. It suggests that changes in reaction rate with acidity should not always be compared to a single acidity function, but that cognizance must be taken of the fact that different substrates can depend on the acidity of concentrated acids in different ways in their equilibrium protonation and therefore also in their rate of

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[1] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, pp. 273–277.

[2] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

[3] A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509; 1961, **84**, 3976.

[4] J. Colapietro and F. A. Long, *Chem. and Ind.*, 1960, 1056; F. A. Long and J. Schulze, *J. Amer. Chem. Soc.*, 1961, **83**, 3340; 1964, **86**, 331; B. C. Challis and F. A. Long, *J. Amer. Chem. Soc.*, 1963, **85**, 2524; R. J. Thomas and F. A. Long, *J. Amer. Chem. Soc.*, 1964, **86**, 4770.

[5] A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 1961, 81.

[6] It was previously reported (ref. 5) that the rate of aromatic hydrogen exchange for trimethoxybenzene depends on $h_0^{1\cdot07}$; this becomes $h_0^{1\cdot14}$ when new values of h_0 (K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1964, **42**, 1957 are used.

[7] J. N. Brönsted, *Z. phys. Chem.*, 1926, **119**, 19.

reaction. Since, in the general case, the manner in which the rate of a reaction changes with acidity will be a function of substrate structure as well as reaction mechanism, it would seem that kinetic acidity dependence cannot be a mechanistic criterion of wide applicability. Its use as a criterion of reaction mechanism might, however, be superseded by the function of providing detailed information about the structure of transition states in reactions of known mechanism.

The kind of analysis presented here is not limited to aromatic hydrogen exchange. It can be applied to other A-S_E2 reactions and can be extended to other mechanisms of acid catalysis as well.

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