Constant Selectivity in Proton Transfer Reactions to Carbon Bases in Aqueous Sulphuric Acid; the Kinetic Acidity Function $H_C^\ddagger$

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Summary The acid-catalysed hydrogen exchange of 4-nitro-*NN*-dimethylaniline has been measured in aqueous sulphuric acid (25—100%), enabling the calculation of a kinetic acidity function $H_C^\ddagger$ which defines the selectivity of proton transfer reactions for a wide variety of carbon bases over a wide range of reactivity.

IN a previous paper[1] a close correspondence of α_A values (where α_A is a parameter which measures the degree to which the transition state resembles the Wheland intermediate[2]) was demonstrated for nuclear aromatic hydrogen exchange in D_2O–D_2SO_4 solution of compounds differing in reactivity over a range of 10^3. Extension of these measurements to the reaction of the 2,6-protons in 4-nitro-*NN*-dimethylaniline reveals its α_A values to be 0·624[3] ± 0·04 (r = 0·995) and $-\mathrm{dlog}k_{FB}/\mathrm{d}H_C$[4,5] to be 0·659 ± 0·008 (r = 0·996). The equivalent values for nuclear exchange in 4-methylbenzaldehyde are the same, within experimental error, as those for the amine even though the rate difference is 10^9. This constant selectivity, and, by implication, constant transition state structure, prompted us to investigate how selectivity was affected, if at all, by the structure and reactivity of other carbon bases.

TABLE 1. Representative rate constants for nuclear hydrogen exchange of 4-nitro-*NN*-dimethylaniline and the H_c scales.

% Acid	$7 + \log k_{obs}$	$7 + \log k_{FB}$[a]	$-H_c$[b]	$-H_c$[c]
23·15	1·643	3·94	1·78	1·50
44·98	1·441	6·09	4·73	4·76
60·59	1·033	7·73	7·35	7·24
77·78	0·699	10·40	11·03	11·29
82·54	0·496	11·07	—	12·30
98·55	0·427	12·85	—	15·00

[a] $\log k_{FB} = \log k_{obs} + H_0''' - 0·66$. [b] From ref. 5. [c] 'Corrected' and extended H_c values from graph of $\log k_{FB}$ vs. $-H_c$.[b]

Using the fact that the solubility of the amine enables the exchange rate to be measured in acidic solution in D_2O–D_2SO_4 (25—98%) not only allows the linear correlation with the H_C acidity scale to be followed over the lower acidity range but also allows it to be extended into the upper acidity region by linear extrapolation of the $\log k_{FB}$ *vs.* $-H_C$ correlation (for details see Table 1). By measurements on this single indicator, therefore, a kinetic acidity function $H_C^\ddagger$ can be derived (for details see Tables 1 and 2).

TABLE 2. The $H_c^\ddagger$ kinetic acidity function

% Acid	$-H_c$[a]	$-H_c^\ddagger$[b]	% Acid	H_c[a]	$-H_c^\ddagger$[b]
25	1·95	1·30	65	8·22	5·20
30	2·50	1·79	70	9·36	6·30
35	3·18	2·15	75	10·50	7·02
40	3·92	2·68	80	—	7·71
45	4·73	3·13	85	—	8·39
50	5·54	3·58	90	—	8·89
55	6·39	4·03	95	—	9·47
60	7·20	4·60	100	—	10·10

[a] From ref. 5. [b] Obtained by interpolation on the curve of ($\log k_{FB}$ − 2·95) *vs.* % acid, where 2·95 is the intercept on the $\log k_{FB}$ axis of the plot of $\log k_{FB}$ *vs.* $-H_C$.

For a thermodynamic acidity function, $H^0 = -\log(a_{H^+} f_B/f_{BH^+})$, where f_B/f_{BH^+} is effectively constant for a family of bases; for a kinetic acidity function $H^\ddagger = -\log(a_{H^+} f_B/f_{BH^\ddagger})$, where $f_B/f_{BH^\ddagger}$ is constant,[6] and a base may be said to follow such a scale, in this case $H_C^\ddagger$, if a plot of the

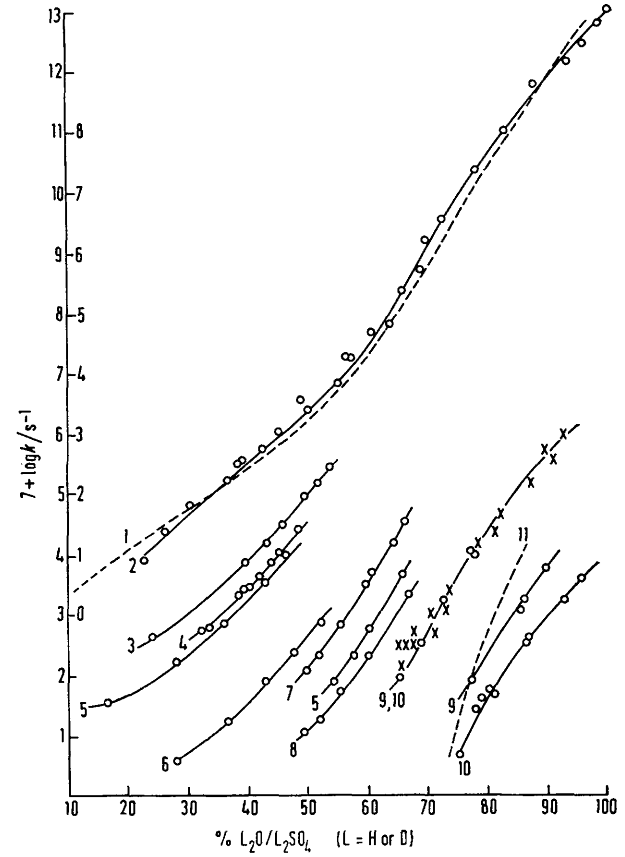

FIGURE. Selectivity of proton transfer to carbon bases in aqueous sulphuric acid.

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logarithmic rate constants for its protonation *vs.* the scale is linear with unit slope. From the results in Table 3, $H_C^\ddagger$ is seen to correlate kinetic carbon protonations both in aromatic rings and on unsaturated side chains; this scale therefore appears to describe the selectivity of $H^+(D^+)$ in aqueous sulphuric acid towards unsaturated carbon just as accurately as any thermodynamic acidity function describes the equilibrium protonation of appropriate bases.

Table 3. Summary of results for reactions in aqueous sulphuric acid involving rate-limiting proton transfer.[a]

Reaction	Temp. /°C	Acidity range/%	$-\mathrm{d}\log k/\mathrm{d}H_C^\ddagger$ [b]	No. of results
Aromatic nuclear exchange[c]	60	57—98	0·95±0·05	8
Stilbene isomerisation[d]	25	18—75	1·16[e]±0·14	12
	45	—	1·06±0·19	8
Styrene hydration[f]	25	10—70	1·08±0·13	6
Phenylbenzoylacetylene hydration[g]	25	27—79	0·87[h]±0·11	5
Cyclohexa-1,3-diene and cyclo-octa-1,3-diene hydration[i]	20—80	26—65	1·11±0·13	12
Phenylacetylene hydration[j]	25	25—60	1·03±0·05	4

[a] Reactivity variation introduced by change in acid concentration 10^9; by substrate variation, 10^9. [b] $-\mathrm{d}\log k/\mathrm{d}H_C^\ddagger = 1$ for exact adherence to scale. [c] This work and ref.1. Does not include value for benzene. [d] See 7 in the Figure. [e] Includes one value of 1·47 calculated from three readings only, over a 6% acidity range. [f] J.-C. Simandoux, B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. chim. France*, 1972, 4402. [g] D. S. Noyce and K. E. DeBruin, *J. Amer. Chem. Soc.*, 1968, **90**, 372. [h] Value may be low owing to correction made for O protonation using the H_0 acidity function; thus for $PhC{\equiv}C{\cdot}CO{\cdot}C_6H_4X$, $X = NO_2$, $-\mathrm{d}\log k/\mathrm{d}H_C^\ddagger = 0{\cdot}92$ where no correction is involved, but for X = Me, where extensive O protonation occurs at the acidities used for determination of rates of C protonation, $-\mathrm{d}\log k/\mathrm{d}H_C^\ddagger = 0{\cdot}79$. [i] J. L. Jensen, V. Uaprasert, and C. R. Fujii, *J. Org. Chem.*, 1976, **41**, 1675. [j] See 4 in the Figure.

This scale should also have a particularly wide applicability because not only steric effects[1] but also the influence of temperature[1] appear to be small.

The description of such a function is thus a direct consequence of the failure of reactivity variation to alter selectivity,[6] although the applicability of the scale to the widely different types of bases (aromatic, ethylenic, or acetylenic) could not have been predicted. This wide range of applicability is reminiscent of that observed in the constant selectivity of cation–anion reactions.[7] The overall generality of the situation is expressed by the Figure, where benzene is the only exception to adherence to the scale. Such a diagram appears to contradict the notions of Taylor[8] in so far as experimental selectivity parameters can be taken to reflect transition state structure. Among subsequent points which will concern us are (i) the 'anchoring' of the scale at acidities below 25% acid, (ii) exhaustive appraisal of relevant literature data by computer, (iii) investigation of the scale in aqueous perchloric acid, and (iv) the relevance or otherwise of the Marcus theory[9] to our results, in which a correlation between selectivity parameters for proton transfer reactions, such as α_A, and rate of reaction is predicted.

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[3] Calculated using equation 16 in ref. 1.

[4] log*k* (observed) values corrected to log*k* (free base) using a pK_a value of 0·66 and the H_0''' scale: E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671. See footnote to Table 1.

[5] H_C scale: M. T. Reagan, *J. Amer. Chem. Soc.*, 1969, **91**, 5506.

[6] See also: C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755, in particular pp. 760—761.

[7] C. D. Ritchie, *Accounts Chem. Res.*, 1972, **5**, 348.

[8] R. Taylor in 'Aromatic and Heteroaromatic Chemistry,' Senior Reporters C. W. Bird and G. W. H. Cheeseman, Specialist Periodical Reports, The Chemical Society, 1974, Vol. 2, p. 219.

[9] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; A. O. Cohen and R. A. Marcus, *ibid.*, p. 4249; G. W. Koeppl and A. J. Kresge, *J.C.S. Chem. Comm.*, 1973, 371.