Kresge's modified treatment[54] using variable force constants predicts a sharper change of α than that of simple Marcus theory; this theory in general thus has no accord with our experimental observations.

Acknowledgments are made to the British Science Research Council for grants to C.C.G., S.R., and P.G.T. C.D.J. would like to thank the Department of Chemistry, University of North Carolina at Greensboro, for hospitality and financial support during part of the time this paper was being written.

References and Notes

(1) For a preliminary account of this work, see P. G. Taylor, C. D. Johnson, and S. Rose, *Chem. Commun.*, 101 (1977).
(2) Address correspondence to this author.
(3) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).
(4) C. D. Johnson and K. Schofield, *J. Am. Chem. Soc.*, **95**, 270 (1973).
(5) T. J. Gilbert and C. D. Johnson, *J. Am. Chem. Soc.*, **96**, 5846 (1974).
(6) For full details, see C. C. Greig, Ph.D. Thesis, University of East Anglia, 1970; P. G. Taylor, *ibid.*, 1976; S. Rose, M.Sci. Thesis, University of East Anglia, 1976.
(7) M. T. Reagan, *J. Am. Chem. Soc.*, **91**, 5506 (1969).
(8) U. Svanholm and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 962 (1972).
(9) E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **86**, 2671 (1964); N. C. Marziano, G. M. Cimino, and R. C. Passerini, *J. Chem. Soc., Perkin Trans. 2*, 1915 (1973); Dr. Nunciata Marziano, personal communication.
(10) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Am. Chem. Soc.*, **91**, 6654 (1969); see also J. Sierra, M. Ojeda, and P. A. H. Wyatt, *J. Chem. Soc. B*, 1570 (1970), for evidence that acidity measurements in deuterated acids show constant and very small variations from the same data for aqueous H_2SO_4.
(11) J. Banger, C. D. Johnson, A. R. Katritzky, and B. R. O'Neill, *J. Chem. Soc., Perkin Trans. 2*, 394 (1974).
(12) S. Olsson and M. S. Russell, *Ark. Kemi*, **31**, 439 (1970).
(13) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3619 (1955).
(14) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 3301 (1960).
(15) R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 4927 (1961).
(16) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1956).
(17) C. G. Stevens and S. J. Strickler, *J. Am. Chem. Soc.*, **95**, 3918 (1973).
(18) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609 (1955).
(19) D. P. N. Satchell, *J. Chem. Soc.*, 3911 (1956).
(20) This work.
(21) K. Schwetlick, K. Unverferth, and R. Mayer, *Z. Chem.*, **7**, 58 (1967).
(22) A. R. Butler and J. B. Hendry, *J. Chem. Soc. B*, 852 (1970): there is an error in this paper for the results reported for protodetritiation of 3-tritiothiophene at 1.9 °C. Dr. Butler has kindly supplied us with the correct results (entry 56, Table IV). They are as follows:

% H_2O-H_2SO_4	$10^4 k_{obsd}$, s^{-1}
60.35	0.036
66.10	0.30
68.80	1.01
71.50	3.38

(23) R. Danieli, A. Ricci, and J. H. Ridd., *J. Chem. Soc., Perkin Trans. 2*, 2107 (1972).
(24) G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, *J. Am. Chem. Soc.*, **99**, 3392 (1977).
(25) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, **90**, 1020 (1968).
(26) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, **90**, 1023 (1968).
(27) J.-P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 43 (1966).
(28) A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2*, 1065 (1973).
(29) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Am. Chem. Soc.*, **93**, 6181 (1971).
(30) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970); 783 (1971).
(31) A. J. Kresge, Y. Chiang, and S. A. Shapiro, *Can. J. Chem.*, **49**, 2777 (1971).
(32) K. Bowden and R. S. Cook, *J. Chem. Soc. B*, 1765 (1971).
(33) M. F. Semmelhack, R. J. DeFranco, Z. Mangolin, and J. Stock, *J. Am. Chem. Soc.*, **95**, 426 (1973).
(34) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, pp 410–413.
(35) R. P. Bell, "The Proton in Chemistry", 2nd ed., Cornell University Press, New York, 1973, Chapter 10.
(36) A. Pross, *Adv. Phys. Org. Chem.*, **14**, 83–96 (1977).
(37) A. J. Kresge, *Chem. Soc. Rev.*, **1**, 475 (1973).
(38) A. J. Kresge in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, Chapter 7.
(39) A. J. Kresge, R. A. More O'Ferrall, L. E. Hakka, and V. P. Vitullo, *Chem. Commun.*, 46 (1965).
(40) C. H. Rochester, "Acidity Functions", Academic Press, New York, 1970, p 126.
(41) K. Yates and R. A. McClelland, *Prog. Phys. Org. Chem.*, **11**, 387 (1974).
(42) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
(43) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 128.
(44) R. A. McClelland, T. A. Modro, M. F. Goldman, and K. Yates, *J. Am. Chem. Soc.*, **97**, 5223 (1975).
(45) C. D. Ritchie, *J. Am. Chem. Soc.*, **97**, 1170 (1975), and references therein.
(46) M. J. Cook, N. L. Dassanayake, C. D. Johnson, A. R. Katritzky, and T. W. Toone, *J. Am. Chem. Soc.*, **97**, 760 (1975).
(47) Reference 5, p 5852.
(48) W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 7233 (1977).
(49) A. J. Kresge, H. J. Chen. L. E. Hakka, and J. E. Kouba, *J. Am. Chem. Soc.*, **93**, 6174 (1971).
(50) R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **46**, 2469 (1968); **47**, 2263 (1969); **48**, 2538 (1970); K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 84 (1973); J. W. Pilkington and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1349 (1976).
(51) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976); V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10**, 252 (1977); Professor Tidwell, personal communication.
(52) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); A. O. Cohen and R. A. Marcus, *ibid.*, **72**, 4249 (1968).
(53) For a good detailed account of the influence of variation of $\Delta G_0^{\ddagger}$ and W^r values on the Brønsted plot curvature see D. J. Hupe and D. Wu, *J. Am. Chem. Soc.*, **99**, 7653 (1977).
(54) G. W. Koeppl and A. J. Kresge, *Chem. Commun.*, 371 (1973).

Kinetic Acidity Function $H_c^{\ddagger}$. 2. The Scale in Perchloric Acid

C. David Johnson,* Shaaron Rose, and Peter G. Taylor

Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, North Carolina 27412, and the School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, England

Received February 28, 1978

The acidity function $H_c^{\ddagger}$ defines the selectivity of proton transfer to carbon bases. Previously established for aqueous sulfuric acid media, it has now been extended to aqueous perchloric acid. The influence of substituents, temperature, ipso substitution, and base type on the scale are considered, and further general remarks on the reactivity–selectivity principle are made.

In the previous paper in this series we showed that selectivity of the hydrated proton toward aromatic, alkene, and alkyne bases in aqueous sulfuric acid was independent of reactivity. It was suggested that in consequence the rates could be correlated with a kinetic acidity function $H_c^{\ddagger}$ to a degree of accuracy similar to that involved in definition of extrathermodynamic acidity functions; $-\mathrm{d} \log k/\mathrm{d}H_c^{\ddagger}$ for reactions involving rate-limiting carbon protonation appeared generally to be about unity irrespective of base structure and reactivity for a total free energy change of about 68 kJ mol^{-1} (a rate change of 10^{12}). This result is now extended to aqueous perchloric acid. The available data are less profuse than for sulfuric acid, but are entirely adequate, covering a range of different bases, evaluated using a variety of kinetic techniques,

---

* University of East Anglia.

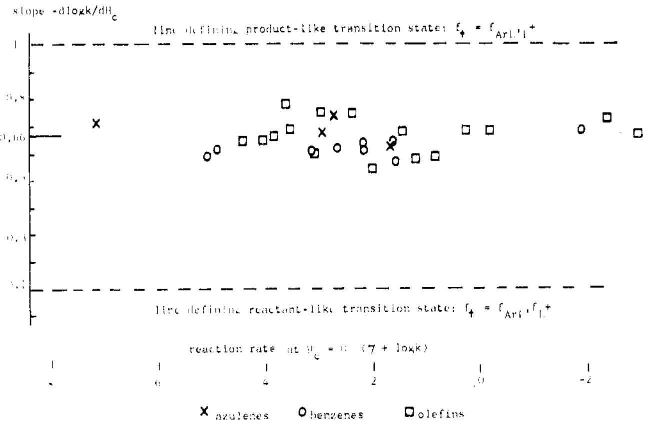


Figure 1. Constant selectivity displayed by H_3O^+ for aromatic, pseudo-aromatic, and olefinic substrates: ○, benzenes, ×, azulenes, □, olefins. Limiting slopes are defined and calculated in ref 17.

from a number of different laboratories. The only carbon bases for which results are not available are acetylenes; on the other hand, the results extend to pseudo-aromatic molecules, the azulenes, a class not previously discussed. The data, presented in Table I, bear out remarkably well the conclusions reached previously.[1]

The Kinetic Acidity Function $H_c^{\ddagger}$. The slopes of plots of log k vs. the extra-thermodynamic acidity function H_c[8] for compounds in Table I (excluding those measured at temperatures other than 25 °C, or bearing hydroxy or charged substituents, or whose rate profiles were defined by less than five rate determinations) were averaged, yielding a value of 0.661. This is well within experimental error of 0.648, the slope of $H_c^{\ddagger}$ against H_c in sulfuric acid, and confirms and extends the approximate linear interdependence of extra-thermodynamic acidity functions in aqueous mineral acids noted by Yates.[9] $H_c^{\ddagger}$ is therefore defined for perchloric acid by $0.661H_c$, and carbon bases may be said to obey the scale if their rates of protonation are such that $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ values are unity; i.e., plots of log k vs. percent $HClO_4$ are parallel. The reactivity range covered by the bases in Table I is 10^{10}; their close adherence to $H_c^{\ddagger}$ as measured by the excellent linearity of the plots of logarithmic rate constant against H_c together with the close parallelism as measured by $-\mathrm{d}\log k/\mathrm{d}H_c$ speaks convincingly for an apparently constant transition state structure, and selectivity invariant with reactivity (see Figure 1).

Substituent Effects. The constancy of $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ values necessarily demands acid independent ρ values for base series to which the Hammett equation applies. This can be tested using the rates for the five substituted styrenes K–O at 25 °C. We find $\rho = -3.71 \pm 0.17$ (correlation coefficient 0.9967), -3.81 ± 0.17 (0.9971), and -3.91 ± 0.16 (0.9973) at H_c values of 0, −5, and −10, respectively, using σ^+ values. The close correspondence of these values (which to a degree must be fortuitous, since enormously long extrapolations are involved for the reactive compounds at the high acidity, and the unreactive compounds at the low acidity) emphasises the interdependence of ρ values and $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ values. This may be expressed by a new variety of Cordes cross-relationship[10a,b]

$$\partial\sigma^+/\partial(-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}) = \partial H_c/\partial\rho = C \qquad (1)$$

C is formally about 50 from the figures given above, but in principle infinitely large, i.e., if the rate profiles are precisely parallel.

As in sulfuric acid media, the presence of hydroxy substituents lowers the slope parameter;[1,2,11] values of $-\mathrm{d}\log k/\mathrm{d}H_c$ for 1,3,5-trihydroxybenzene-*2-t* and 1,3-dihydroxy-2-methylbenzene-*4-t* are 0.441 ± 0.007 (0.9986, 1.40 °C) and 0.469 ± 0.024 (0.9950, 23.9 °C), respectively, the corresponding slopes against $H_c^{\ddagger}$ being 0.67 and 0.71.

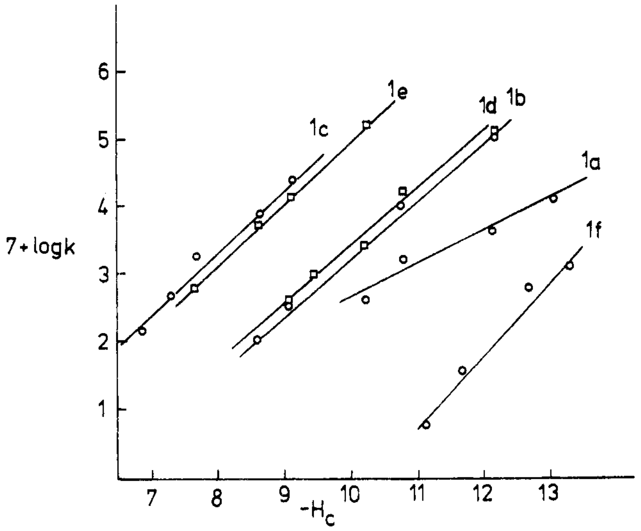
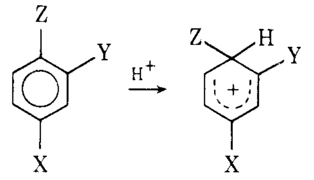


Figure 2. Rate profiles for ipso substitution in molecules reacting via the A1 mechanism (**1b–f**) and the A_SE2 mechanism (**1a**) in aqueous perchloric acid: **1a**, slope 0.47 ± 0.075 (0.9774), **1b** 0.840 ± 0.033 (0.9977), **1c**, 0.876 ± 0.061 (0.9905), **1d**, 0.825 ± 0.069 (0.9896), **1e**, 0.940 ± 0.020 (0.9996), **1f**, 1.139 ± 0.115 (0.9900); for this molecule, media is aqueous sulfuric acid.

Influence of Temperature. Results D, G, O, and U suggest that slope decrease created by temperature increase is low, probably lower than in sulfuric acid media. This is in keeping with observations on the H_A extra-thermodynamic scale in perchloric acid,[12] where temperature variation is also only slight. If this conclusion is correct, a corollary to it is that results, P, Q, and R show that $H_c^{\ddagger+}$ is the same as or parallel to $H_c^{\ddagger}$ in perchloric as in sulfuric acid.[13]

Ipso Substitution. *p*-Triphenylmethylphenol suffers ipso substitution[14] in perchloric acid to form an intermediate of form **1a**.[15] However, the value of $-\mathrm{d}\log k/\mathrm{d}H_c$ for this molecule is very close to those for other hydroxy-substituted molecules reacting via the A_SE2 mechanism (0.487 cf. 0.441 and 0.469; see above and Figure 2). This is in contrast to other aromatic molecules **1b–e** considered to react via the A1 mechanism,[15] whose rates show a much steeper dependency on H_c (see Figure 2), perhaps not unexpected for a mechanism involving a preequilibrium carbon protonation, and matched by a similar steep dependency for the A1 reaction **1f** of *tert*-butylbenzene in sulfuric acid[16] (see also Figure 2).



1a, X = OH; Y = H; Z = CPh_3
b, X = OH; Y = H; Z = *t*-Bu
c, X = H; Y = OH; Z = *t*-Bu
d, X = OCH_3; Y = H; Z = *t*-Bu
e, X = H; Y = OCH_3; Z = *t*-Bu
f, X = Y = H; Z = *t*-Bu

Conclusion. The Reactivity–Selectivity Principle Revisited

The results reported here point indisputably to the failure of the reactivity-selectivity principle once again. It is noteworthy that since our general report[17] on the breakdown of

Table I. Definition and Applicability of the $H_c^{\ddagger}$ Kinetic Acidity Function to Rate-Limiting Carbon Protonations in Aqueous Perchloric Acid

	compd, temp (°C)	registry no.	% acidity range covered (no. of points)	$-d \log k/dH_c$[a] (corr coeff)	$-d \log k/dH_c^{\ddagger}$[b,c]	7 + log k[d,e]	ref
	1. Aromatic and Pseudo-Aromatic Bases (Excluding Those with Hydroxy Substituents[f])						
A.[g]	1,3,5-trimethoxybenzene-*2-t*, 25.1	34649-94-0	8–24 (8)	0.620[h] ± 0.005 (0.9998)	0.94	4.80 ± 0.01	2
B.[g]	1,3,5-triethoxybenzene-*2-t* 25.1	34649-95-1	6–23 (8)	0.607[h] ± 0.036 (0.9894)	0.92	4.98 ± 0.04	2
C.[g]	1,3-dimethoxybenzene-*2-t*, 24.69	34649-96-2	19–46 (6)	0.571[h] ± 0.012 (0.9991)	0.86	1.50 ± 0.04	2
D.	1,3-dimethoxybenzene-*4-t*, 15.01	4713-58-0	10–40 (7)	0.634 ± 0.012 (0.9991)	0.96	1.53 ± 0.03	2
	24.69[g]		10–40 (6)	0.617[h] + 0.007 (0.9997)	0.93	2.07 ± 0.02	2
	35.03		10–37 (5)	0.615 ± 0.009 (0.9997)	0.93	2.59 ± 0.02	2
	45.01		10–31 (6)	0.614 ± 0.007 (0.9997)	0.93	3.05 ± 0.01	2
E.[g]	1,3-dimethoxy-2-methylbenzene-*4-t*, 25.10	34649-99-5	5–50 (11)	0.641[h] ± 0.014 (0.9978)	0.97	2.06 ± 0.05	2
F.[g]	methoxybenzene-*4-t*, 24.69	34650-00-5	44–61 (5)	0.682[h] ± 0.022 (0.9983)	1.03	−1.95 ± 0.16	2
G.	azulene, 7.3	275-51-4	14–33 (20)	0.705 ± 0.012 (0.9970)	1.08	7.16 ± 0.02	4
H.[g]	1-nitroazulene, 25	7206-56-6	11–41 (9)	0.628 ± 0.022 (0.9956)	0.95	1.60 ± 0.06	5
I.[g]	1-cyanoazulene, 25	53271-95-7	6–31 (8)	0.736 ± 0.022 (0.9972)	1.11	2.67 ± 0.04	5
J.[g]	1-formylazulene, 25	7206-61-3	6–19 (4)	0.680 ± 0.020 (0.9991)	1.02	2.89 ± 0.02	5
	2. Alkenes and an alkadiene[i]						
K.[g]	*p*-methoxystyrene, 25	637-69-4	12–30 (6)	0.712 ± 0.009 (0.9997)	1.08	2.77 ± 0.02	6
L.[g]	*p*-methylstyrene, 25	622-97-9	30–42 (6)	0.688 ± 0.015 (0.9990)	1.04	1.39 ± 0.06	6
M.[g]	styrene, 25	100-42-5	36–52 (6)	0.698 ± 0.006 (0.999)	1.06	0.22 ± 0.03	6
N.[g]	*p*-chlorostyrene, 25	1073-67-2	30–52 (5)	0.692 ± 0.016 (0.9992)	1.05	−0.23 ± 0.09	6
O.[j]	*p*-nitrostyrene, 25[g]	100-13-0	59–69 (6)	0.676 ± 0.041 (0.9927)	1.02	−3.01 ± 0.43	6
	50°C		50–61 (6)	0.743 ± 0.017 (0.9990)	1.12	−2.43 ± 0.13	6
P.	*m*-dimethylamino-α-aminostyrene, 80	68344-85-4	31–39 (3)	0.697 ± 0.016 (0.9997)	1.05	3.47 ± 0.02	6
Q.	*m*-aminostyrene, 80	15411-43-5	9–49 (7)	0.584 ± 0.015 (0.9984)	0.88	1.16 ± 0.05	6
R.	*m*-dimethylaminostyrene, 80	5339-11-7	9–51 (8)	0.596 ± 0.009 (0.9994)	0.90	0.79 ± 0.04	6
S.	2,3-dimethyl-2-butene, 25	563-79-1	10–23 (3)	0.797 ± 0.018 (0.9985)	1.21	3.56 ± 0.02	7
T.	2-phenylpropene, 25	98-83-9	10–33 (4)	0.768 ± 0.019 (0.9994)	1.16	2.95 ± 0.04	7
U.	1,3-cyclohexadiene, 40	592-57-4	10–33 (4)	0.760 ± 0.017 (0.9995)	1.15	2.32 ± 0.03	7
V.	*cis*-β-phenylvinyl methyl ether, 25	14371-19-8	9–22 (6)	0.644 ± 0.008 (0.9997)	0.97	4.48 ± 0.08	3
W.	*trans*-β-phenylvinyl methyl ether, 25	4110-75-2	14–30 (6)	0.641 ± 0.009 (0.9996)	0.97	3.92 ± 0.02	3
X.	*cis*-β-(*p*-nitrophenyl)vinyl methyl ether, 25	66821-15-6	16–30 (5)	0.653 ± 0.014 (0.9993)	0.99	3.70 ± 0.03	3
Y.	*trans*-β-(*p*-nitrophenyl)-vinyl methyl ether, 25	66821-16-7	27–40 (5)	0.578 ± 0.016 (0.9989)	0.87	3.18 ± 0.05	3
Z.	*cis*-β-cyanovinyl ethyl ether, 25	60036-64-8	43–50 (5)	0.536 ± 0.015 (0.9989)	0.81	1.96 ± 0.08	3
AA.	*trans*-β-cyanovinyl ethyl ether, 25	58243-08-6	47–55 (5)	0.605 ± 0.021 (0.9977)	0.92	0.82 ± 0.14	3

[a] Values of H_c taken from ref 8. [b] Should be unity for complete adherence to $H_c^{\ddagger}$ scale. [c] For definition of $H_c^{\ddagger}$ see text. [d] Intercept c in eq $(7 + \log k) = -mH_c + c$, where $m = d \log k/dH_c$. c is therefore obtained by extrapolation, a very lengthy one for unreactive compounds measured at high acidities. [e] Kresge[2] points out that H_c may be incorrectly "joined" to $-\log [H^+]$, but this produces no relative error in the values given in this column. [f] See text for discussion. [g] Data used for establishing $H_c^{\ddagger}$ in aqueous perchloric acid, see text. [h] Values are very close to those calculated in ref 2; small differences arise from variations in construction of the curved plot of H_c vs. percent $HClO_4$. [i] Involving reversible hydration; for calculation of the rate constants for the forward reaction (rate-limiting carbonium ion formation), see ref 6 and 7. [j] Data involved an extrapolation of the H_c, percent $HClO_4$ graph for the higher acidities.

this principle, several reports have appeared demonstrating its inadequacy in the area of free-radical chemistry,[18] where it was previously considered to be of particular validity, these reactive species epitomising the concept of the "unselective, rapid reagent",[19] and in reactions of esters with nucleophiles, where the total lack of any evidence for the operation of the reactivity–selectivity principle leads to a particularly simple picture.[20] The incorporation of all types of nucleophiles in this correlation is analogous to the validity of the H_c^+ function in describing the selectivity of the hydrated proton toward all types of carbon base.

The results impinge directly on two areas of major mechanistic interest: aromatic electrophilic substitution and proton transfer reactions. In so far as they represent an example of aromatic electrophilic substitution, the failure of the reactivity–selectivity principle is certainly not unprecedented. The principle breaks down unequivocally in diazo coupling[17,21] and bromination[22] reactions. A recent valuable paper on nitration[11b,23] also clearly reveals its inapplicability; selectivity as measured by the ratio of the logarithmic rate of nitration of the aromatic in aqueous sulfuric acid compared to the logarithmic rate for benzene may be influenced by factors such as minority species reaction or the influence of hydrogen-bonded substituents as discussed above for the hydroxy group, otherwise it is found to be close to unity over a wide free-energy range. Such results make it difficult to accept as proven or even likely the assertion that selectivity changes with reactivity in aromatic electrophilic substitution commensurate with "early" or "late" transition state variation.[24]

In so far as the results reported here and in the preceding paper[1] form an example of proton transfer reactions, however, the situation is less clear-cut; the overall picture is confused. The results described here cannot possibly be accommodated within the Marcus theory.[1] This lack of correlation with Marcus theory is supported by numerous recent reports of linear Brønsted plots for other examples of proton transfers,[19,25–27] often together with parallelism of plots within a family of such correlations (multiple structure–reactivity relationships);[19,26,27] these are to be contrasted with reports of pronounced curvature for such correlations, generally[28,29] but not always[30] ascribed to the operation of Marcus theory, or nonparallelism of a family of such plots[31,32] (i.e., nonzero Hammond or Cordes coefficients[10b]).

Since curvature may come about through a combination of straight line correlations for different acid or base catalyses with different slopes,[29] the investigation of Brønsted correlations using a standard set of bases in which reactivity is varied systematically would be of great value; such an investigation is stated to be in hand.[33]

We are also tempted to propose that the results reported in this paper and its predecessor fall into a particularly significant category; plots of log *k* for a particular hydrogen-exchange process vs. H_c^+ are examples of plots of one logarithmic rate series against another rather than against the corresponding logarithmic equilibrium process, thus constituting an example of Pfluger analysis.[19] This has been stressed[19] as of use in removing the influence of effects in the transition state not mirrored on either side of the equilibrium process, which might otherwise produce scatter or anomolous slopes.

A comprehensive view of the whole situation in proton transfer reactions is clearly required, and not just emphasis on one or two results to the exclusion of all others; equally clearly the explanation of why the Marcus theory, or the Polanyi–Bell–Leffler–Hammond–Thornton–Marcus[10b] (–Evans–Cordes–Jencks–Ogg?) theory, might appear visible in some cases often only covering short free-energy changes, and not in others closely analogous but covering much wider free-energy changes,[27,32,34] cannot be easily formulated.

Acknowledgments are made to the British Science Research Council for grants to P.G.T. and S.R. and to Dr. Joseph E. Dilts for help with the statistical analysis.

Appendix

In the reviews of this and the preceding paper, a number of criticisms were raised. At the request of the editor, we reply to the more forceful of these as an appendix. (The reviewer's comments are in italics.)

The exchange of 4-nitro-N,N-dimethylaniline may not proceed on the free base over the whole acidity range.

The minority species reaction is established by the change in the NMR pattern of the aromatic protons as reaction proceeds, which indicates that 2,6-substitution is occurring (see Experimental Section in part 1). The manner in which this pattern changes is invariant with acidity. If there was a changeover to conjugate acid reaction at high acidities, the 3,5 protons would suffer exchange. Further, the shape of the rate–acidity profile which shows decreasing rate with increasing acidity without any sharp breaks can only be logically interpreted as minority species reaction throughout.

Inaccuracies arise from the necessity to correct the amine rate data to free base reactivity using the H_0''' *acidity function, and this produces an artificial constancy of* $-d \log k/dH_c$.

(1) Remeasurement of several of the H_0''' indicators convinces us that Arnett's data for this scale are highly accurate. Replotting the log ionization constants for the individual indicators against the final scale gives accurate straight lines of slope close to unity, a realistic test that parallelism between adjacent indicators was adequate.

(2) It would be surprising if systematic curvature in the log $k_{fb} - H_c$ plot were exactly compensated by inaccuracies in the H_0''' scale.

(3) The data for the amine are indeed used as a foundation for assessment for the other exchange results; however, once a large number of such results have been shown to conform to the established pattern, the significance of this first set of results is only chronological.

Failure to detect curvature does not negate Marcus theory, because this predicts only a small change in α *for a reaction with a high intrinsic free energy . . . curvature is related to reactivity in a very simple way given by the Marcus equation.*

In part 1 it is indeed shown that Marcus theory may postulate only a small change in α values, if the preexchange term is set at zero. We show that even under these optimum conditions for least curvature, α would still change sufficiently to be detected within the rate range encompassed. But it is thus not true that curvature is related to Marcus theory in a simple way, because in fact a whole range of curvature can be accounted for depending on the relative values given to W^r and $\Delta G^{\ddagger}$, a fact clearly illustrated by a recent paper (ref 53 of part 1 and ref 30 of part 2). By this token, Marcus theory loses much predictive capacity, since its proponents have no means of assessing before the event the relative contributions of the two terms on the right-hand side of eq 18 in part 1.

Pfluger analysis does remove deviations from Brønsted plots, but it also removes curvature for which these papers purport to be searching.

Equation 19 of part 1 shows that Marcus theory does predict curvature for a log–log plot, since ΔG° will vary from one system to another; nevertheless, it is true that nonzero Hammond coefficients are best discerned (or shown to be absent) using log rate data against pK_a values for a set of "coherent" acids or bases in which acidity is changed by a set of consistent structural modifications. Cordes coefficients, on the other hand, can certainly be determined by log–log representations of the available data, and detection of these (or demonstration that they are zero) has been of equal concern to us.

The inference is drawn from zero Hammond or Cordes coefficients that transition state structure for a given reaction does not change as reaction rate is changed.

This inference is a facile one that indeed might be drawn from this work or any demonstration of the absence of a reactivity–selectivity effect. We believe however that in such cases all that can really be said is that experimental parameters commonly associated with transition state structure are invariant. As a reaction goes faster, how else could the decreasing energy of activation be made manifest than by some structural modification of the activated complex, involving effects either parallel (Hammond) or perpendicular to (anti-Hammond or Thornton) the reaction coordinate? The question at issue is our ability to define such effects experimentally.

Registry No.—Perchloric acid, 7601-90-3.

References and Notes

(1) C. C. Greig, C. D. Johnson, S. Rose, and P. G. Taylor, *J. Org. Chem.*, preceding paper.

(2) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Am. Chem. Soc.*, **93,** 6183 (1971); A. J. Kresge, Y. Chiang, and Y. Sato, *ibid.*, **89,** 4418 (1967).

(3) Y. Chiang, A. J. Kresge, and C. I. Young, *Can. J. Chem.*, **56,** 461 (1978).

(4) B. C. Challis and F. A. Long, *J. Am. Chem. Soc.*, **87,** 1196 (1965).

(5) J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86,** 331 (1964).

(6) W. M. Schubert and J. R. Keeffe, *J. Am. Chem. Soc.*, **94,** 559 (1972); W. M. Schubert and J. L. Jensen, **94,** 566 (1972).

(7) J. L. Jensen and D. J. Carre, *J. Org. Chem.*, **36,** 3180 (1971).

(8) M. T. Reagan, *J. Am. Chem. Soc.*, **91,** 5506 (1969).

(9) K. Yates and R. A. McClelland, *Prog. Phys. Org. Chem.*, **11,** 365 (1974).

(10) S. I. Miller, *J. Am. Chem. Soc.*, **81,** 101 (1959); E. H. Cordes and W. P. Jencks, *ibid.*, **84,** 4319 (1962); W. P. Jencks, *Prog. Phys. Org. Chem.*, **2,** 63 (1964); L. do Amaral, W. A. Sandstrom, and E. H. Cordes, *J. Am. Chem. Soc.*, **88,** 2225 (1966); G. E. Lienhard and W. P. Jencks, *ibid.*, **88,** 3982 (1966); W. P. Jencks, *Chem. Rev.*, **72,** 705 (1972); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 312; I. Roberts, C. D. Johnson, and P. G. Taylor, *Tetrahedron*, **33,** 2123 (1977); (b) D. A. Jencks and W. P. Jencks, *J. Am. Chem. Soc.*, **99,** 7948 (1977).

(11) (a) A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Koubba, *J. Am. Chem. Soc.*, **93,** 6174 (1971); R. A. McClelland, T. A. Modro, M. F. Goldman, and K. Yates, *ibid.*, **97,** 5223 (1975); P. B. D. de la Mare, A. Singh, T. G. Tillet, and M. Zeltner, *J. Chem. Soc. B*, 1122 (1971); for a discussion of the role of H bonding to carbonyl oxygen functions producing anomolous rate profile slopes in nitration see (b) R. B. Moodie, P. N. Thomas, and K. Schofield, *J. Chem. Soc., Perkin Trans. 2*, 1693 (1977).

(12) S. A. Attiga and C. H. Rochester, *J. Chem. Soc., Perkin Trans. 2*, 1411 (1975).

(13) Temperature variant experiments on molecules Q and R would be especially interesting. They can provide further evidence of the influence of temperature on $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger+}$ values. Also, by extrapolation via the Arrhenius plots, log k values at 25 °C may be ascertained. A fit on the σ^+ plot for styrene hydration demonstrates the coincidence of $H_c^{\ddagger}$ and $H_c^{\ddagger+}$.

(14) C. L. Perrin and G. A. Skinner, *J. Am. Chem. Soc.*, **93,** 3389 (1971); R. B. Moodie and K. Schofield, *Acc. Chem. Res.*, **9,** 287 (1976); K. Fujiwara, J. C. G. Giffney, and J. H. Ridd, *Chem. Commun.*, 301 (1977).

(15) T. A. Modro and K. Yates, *J. Am. Chem. Soc.*, **98,** 4247 (1976).

(16) H. Cerfontain, A. W. Kaandorp, and F. L. J. Sixma, *Recl. Trav. Chim. Pays-Bas*, **82,** 565 (1963).

(17) C. D. Johnson, *Chem. Rev.*, **75,** 755 (1975).

(18) M. Bellati, T. Caronna, A. Citterio, and F. Minisci, *J. Chem. Soc., Perkin Trans. 2*, 1835 (1976); A. Citterio, F. Minisci, O. Porta, and G. Sesana, *J. Am. Chem. Soc.*, **99,** 7960 (1977), and ref 3 therein; R. G. Kryger, J. P. Lorand, N. R. Stevens, and N. R. Herron, *ibid.*, **99,** 7589 (1977), and ref 31b therein.

(19) D. S. Kemp and M. L. Casey, *J. Am. Chem. Soc.*, **95,** 6670 (1973).

(20) C. D. Ritchie, *J. Am. Chem. Soc.*, **97,** 1170 (1975).

(21) V. Štěrba and K. Valter, *Collect. Czech. Chem. Commun.*, **37,** 1327 (1972); A. R. Butler, P. Pogorzelec, and P. T. Shepherd, *J. Chem. Soc., Perkin Trans. 2*, 1452 (1977); C. D. Johnson and K. Schofield, *J. Am. Chem. Soc.*, **95,** 270 (1973).

(22) H. M. Gilow and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1321 (1973).

(23) Note that eq ii in ref 11b shows how the experimental observation of constant selectivity directly implies the constancy of the final transition state structure term.

(24) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 163; G. A. Olah and H. C. Lin, *J. Am. Chem. Soc.*, **96,** 549 (1974); G. A. Olah, *Acc. Chem. Res.*, **4,** 240 (1971); M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, 1975, p 321; N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **100,** 1 (1978).

(25) G. Leary, I. J. Miller, W. Thomas, and A. D. Woolhouse, *J. Chem. Soc., Perkin Trans. 2*, 1737 (1977); M. B. Davy, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Am. Chem. Soc.*, **99,** 1196 (1977); J. M. Sayer and M. DePecol, *ibid.*, **99,** 2665 (1977); H. Al. Ravi and A. Williams, *ibid.*, **99,** 2671 (1977); K. Bowden, M. Hardy, and D. C. Parkin, *Can. J. Chem.*, **46,** 2928 (1968); C. D. Slater and Y. W. D. Chan, *J. Org. Chem.*, **43,** 2423 (1978).

(26) J. M. Sayer, M. Peskin, and W. P. Jencks, *J. Am. Chem. Soc.*, **95,** 4277 (1973).

(27) G. P. Tuszynski and R. G. Kallen, *J. Am. Chem. Soc.*, **97,** 2860 (1975).

(28) A. I. Hassid, M. M. Kreevoy, and T.-M. Laing, *Chem. Soc., Faraday Symp.*, **10,** 69 (1975); M. M. Kreevoy and S.-W. Oh, *J. Am. Chem. Soc.*, **95,** 4805 (1973).

(29) M. M. Kreevoy and D. E. Konasewich, *Adv. Chem. Phys.*, **21,** 243, (1972); W. K. Chwang, R. Eliason, and A. J. Kresge, *J. Am. Chem. Soc.*, **99,** 805 (1977); A. J. Kresge and W. K. Chwang, *ibid.*, **100,** 1249 (1978).

(30) D. J. Hupe and D. Wu, *J. Am. Chem. Soc.*, **99,** 7653 (1977); D. J. Hupe, D. Wu, and P. Shepperd, *ibid.*, **99,** 7659 (1977); R. P. Bell and S. Grainger, *J. Chem. Soc., Perkin Trans. 2*, 1606 (1976); in this latter paper the Brønsted relation for proton abstraction from 3-nitro-(+)-camphor is curved, while the relation for 3-deuterio-3-nitro-(+)-camphor is a straight line. This clearly points to proton tunelling as the cause of the curvature, since Marcus theory would demand both plots to be curved, the variation in isotope effect K_H/K_D coming about through the difference $(\lambda_D - \lambda_H)$ using standard Marcus formalism (see ref 1 and references therein).

(31) H. F. Gilbert and W. P. Jencks, *J. Am. Chem. Soc.*, **99,** 7931 (1977); R. H. Kayser and R. M. Pollack, *ibid.*, **99,** 3379 (1977); J. M. Sayer and W. P. Jencks, *ibid.*, **99, 464** (1977); P. R. Young and W. P. Jencks, *ibid.*, **100,** 1228 (1978).

(32) B. Capon and K. Nimmo, *J. Chem. Soc., Perkin Trans. 2*, 1113 (1975).

(33) A. J. Kresge and Y. C. Tang, *J. Org. Chem.*, **42,** 757 (1977).

(34) References 26 and 32 form a particularly striking example of this; the general acid catalysis of benzaldehyde aryl methyl acetal hydrolysis yields differing slopes of Brønsted plots over small free-energy variations, while the general acid catalysis of substituted *N,N'*-diphenylethylenediamine attack on formaldehyde and of dehydration of the subsequent carbinolamine intermediates are shown to give parallel linear Brønsted plots over large free-energy changes in both cases.