Catalysis by Undissociated Acids in Concentrated Aqueous Mineral Acid Solutions[1,2]

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Abstract: Specific rates of loss of tritium from 1,3-dimethoxybenzene-*4-t* to concentrated aqueous nitric, phosphoric, perchloric,[3] and sulfuric[3] acids show widely different behavior when correlated by the H_0 acidity function or as Bunnett–Olsen plots. When compared at equal extents of equilibrium protonation of azulene, however, rates in the monobasic acids become closely similar and considerably less than rates in each of the polybasic acids. This behavior is interpretated as general acid catalysis by the undissociated acid species HSO_4^- and H_3PO_4 present in the polybasic acids superimposed upon differences in medium effect on hydronium ion catalysis in all acids.

Catalysis of a chemical reaction by undissociated acids implies that proton transfer is taking place in its rate-determining step; general acid catalysis is therefore a valuable criterion of reaction mechanism. The diagnostic tests by which this form of catalysis may be detected can be applied in a straightforward manner to reactions occurring in dilute aqueous solution, for here salt effects on rate and equilibrium constants can be treated accurately. It is difficult, however, to evaluate the much greater medium effects produced by the massive amounts of solute present in concentrated acid solutions, and this mechanistic criterion has therefore received little application to the slower reactions which occur at conveniently measurable rates only in concentrated mineral acids.[4]

We have shown previously[3] that general acid catalysis of a typical rate-determining proton transfer reaction, aromatic hydrogen exchange, by the bisulfate ion present in moderately concentrated aqueous sulfuric acid may be detected easily when rates of reaction in sulfuric and perchloric acids are compared at the same extent of equilibrium aromatic protonation. This simple method of separating catalysis by the hydronium ion from that by undissociated acid species is based upon the assumption that the kinetically effective hydronium ion level of a concentrated acid solution is measured by the position of equilibrium between the kinetic substrate and its conjugate acid; *i.e.*, that medium effects operate on the kinetic and equilibrium processes involving hydronium ion in the same way.

If this hypothesis is correct, rates of aromatic hydrogen exchange, reduced to equal extents of equilibrium aromatic protonation, should be the same in perchloric acid as in some other completely dissociated acid, such as nitric; they should, however, be different in an incompletely ionized acid such as phosphoric. We have therefore extended our original measurements to solutions of nitric and phosphoric acids.

Results

In this, as in our previous study,[3] 1,3-dimethoxybenzene was used as the kinetic substrate. Rates of exchange of its aromatic hydrogens were determined by using tritium as a tracer: the rate of loss of radioactivity from 1,3-dimethoxybenzene-*4-t* was monitored as a function of time. The results of these experiments are summarized in Table I.

Table I. Rates of Loss of Tritium from 1,3-Dimethoxybenzene-*4-t* to Aqueous Acids at 25°

Wt % acid	$10^5 k_1$, sec^{-1}	Log ($C_{\mathrm{HArH}^+}/C_{\mathrm{HAr}}$)[a]
	HNO_3	
1.92	0.340	
4.80	1.09	−1.80
14.41	6.90	−0.50
33.62	70.7	1.22
38.42	109	1.64
	H_3PO_4	
14.11	1.41	−1.97
23.99	5.75	−1.18
28.22	9.90	−0.85
35.28	30.8	−0.29
42.33	93.5	0.32

[a] HAr = azulene.

In solutions where rates of hydrogen exchange can be determined in this way, only an immeasurably small amount of 1,3-dimethoxybenzene is converted into its conjugate acid.[5] This substrate, therefore, could not be used for the equilibrium determinations, and, as before,[3] azulene was used instead. Measurements were performed spectroscopically, taking advantage of the large change in uv absorption which accompanies the conversion of azulene into its conjugate acid.[6] These experiments are summarized in Table II.

Discussion

The presently obtained specific rates of loss of tritium from 1,3-dimethoxybenzene-*4-t* to nitric and phosphoric acid solutions, together with those measured previously for sulfuric and perchloric acids,[3] are presented in Figure 1 as plots of log k *vs.* H_0.[7] It can be seen that H_0 correlates these rates of the same reaction of a single substrate very poorly: at any given value of H_0, sizable differences in rate constant occur, and slopes,

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(1) Aromatic Protonation XI. Part X: A. J. Kresge, Y. Chiang, and S. A. Shapiro, *Can. J. Chem.*, **49**, 2777 (1971).

(2) This research was supported by grants from the U. S. Atomic Energy Commission (No. AT(11-1)-1025) and the Petroleum Research Fund of the American Chemical Society (No. 1180-A1,4).

(3) A. J. Kresge, L. E. Hakka, S. G. Mylonakis, and Y. Sato, *Disc. Faraday Soc.*, **39**, 75 (1965).

(4) For a notable exception, see W. M. Schubert and P. C. Myhre, *J. Amer. Chem. Soc.*, **80**, 1755 (1958).

(5) A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *ibid.*, **93**, 6174 (1971).

(6) F. A. Long and J. Schulze, *ibid.*, **86**, 322, 327 (1964).

(7) H_0 values were taken from R. H. Boyd, "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

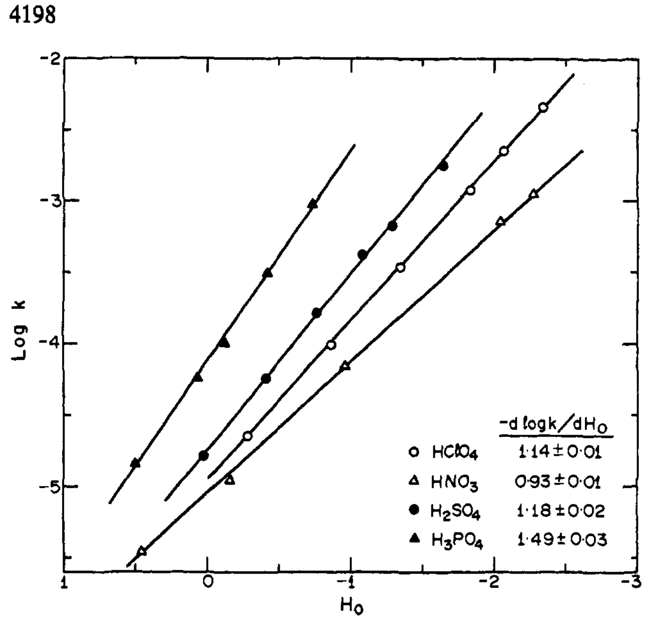

Figure 1. Rates of loss of tritium from 1,3-dimethoxybenzene-*4-t* compared with the H_0 acidity function.

$-d \log k/dH_0$, range from 0.9 to 1.5. Bunnett-Olsen plots,[8] which also use the H_0 function, show similar widely divergent behavior: $\phi = +0.12$ (HNO_3), -0.17 ($HClO_4$), -0.68 (H_2SO_4), and -0.64 (H_3PO_4).[9]

Table II. Extent of Equilibrium Protonation of Azulene in Aqueous Acids at 25°

Wt % acid	Log (C_{HArH^+}/ C_{HAr})^a	Wt % acid	Log(C_{HArH^+}/ C_{HAr})^a
	HNO_3		
7.01	−1.48	23.94	0.39
12.11	−0.75	27.12	0.65
16.15	−0.35	33.16	1.17
20.16	0.04		
	H_3PO_4		
20.85	−1.44	37.31	−0.13
23.88	−1.21	39.00	0.02
26.61	−0.97	40.58	0.17
29.11	−0.79	42.05	0.32
31.40	−0.60	43.42	0.46
33.54	−0.44	45.94	0.76
35.50	−0.29	48.16	1.08

Some of these differences could be the result of general acid catalysis by undissociated acid species. Medium effects, however, are not likely to remain constant in these various acids, and in fact differences in behavior not unlike those observed here have recently been convincingly explained in terms of differences in specific interaction between various acid anions and the reacting systems.[12] It is possible, therefore, that a good portion or perhaps all of the variation seen here is the result of medium effects on the reaction through hydronium ion alone. Clearly, effects of this kind must be removed before any decision concerning general acid catalysis can be reached.

It seems likely that differences in medium effect upon the hydronium ion catalyzed reaction would cancel if rates were compared on a basis which used a reference reaction very closely related to the kinetic process. The present system lends itself particularly well to such treatment, for aromatic hydrogen exchange is known[13-15] to occur by single-step protonation and deprotonation of the aromatic substrate (eq 1), through

$$HAr + H_3O^+ \rightleftharpoons \left[\overset{\delta+}{HAr}\text{---}H\text{---}\overset{\delta+}{OH_2}\right]^{\ddagger} \rightleftharpoons HArH^+ + H_2O \quad (1)$$

a reaction whose position of equilibrium can be measured by standard indicator methods.[5,6,13b] Such equilibrium measurements will provide an indicator acidity function which uses the very reaction to which the rate measurements refer, and, when rates are compared on this basis, the kinetic and reference processes will be as closely related as possible. This procedure eliminates initial state medium effects, for both kinetic and reference processes start out from the same initial state. The two terminal states, on the other hand, are of necessity different, but, insofar as the structural changes which accompany aromatic protonation occur in a regular and synchronous manner, medium effects on the transition state will be some fraction of medium effects on the final state. This fraction, moreover, will be reasonably constant over moderate changes in the nature or concentration of the solvent acid, for the position which the transition state occupies on the reaction coordinate for aromatic protonation is known[14b,16] to change only slowly with the reactivity of the system. Thus, medium effects on the hydronium ion catalyzed portion of the rate of aromatic hydrogen exchange can be expected to be some constant fraction of those on equilibrium aromatic protonation, and, when the equilibrium reaction is used as a reference for comparing rates of exchange in different acids, differences in medium effect will cancel out.

Figure 2 shows the present data treated in this way: values of log *k* for detritiation of 1,3-dimethoxybenzene-*4-t* measured in the four different acids are plotted against values of log C_{HArH^+}/C_{HAr} for azulene in the same media interpolated using the data of Table II. It can be seen that rates of reaction in the two essentially completely dissociated acids, perchloric and nitric,[17] are now nearly coincident. Together, they

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(8) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

(9) For H_2SO_4 solutions, C_{H^+} was taken to be equal to stoichiometric sulfuric acid concentrations, as recommended by Bunnett and Olsen;[8] for HNO_3 solutions, it was estimated using extents of dissociation based upon the nmr work of Redlich, Duerst, and Merbach;[10] and for H_3PO_4 solutions, it was calculated on the basis of $K_c = K_a/(f_\pm)^2$ with $pK_a = 2.148$[11a] and $\log f_\pm = -0.5\mu^{1/2}/(1 + \mu^{1/2}) + 0.1\mu$.[11b]

(10) O. Redlich, R. W. Duerst, and A. Merbach, *J. Chem. Phys.*, **49**, 2986 (1968).

(11) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959: (a) p 232; (b) p 520.

(12) C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 1258 (1968).

(13) (a) A. J. Kresge and Y. Chiang, *ibid.*, **81**, 5509 (1959); **83**, 2877 (1961); (b) *Proc. Chem. Soc.*, 81 (1961); (c) *J. Amer. Chem. Soc.*, **84**, 3976 (1962); **89**, 4411 (1967); (d) A. J. Kresge, Y. Chiang, and Y. Sato, *ibid.*, **89**, 4418 (1967); (e) A. J. Kresge, S. Slae, and D. W. Taylor, *ibid.*, **92**, 6309 (1970).

(14) (a) J. Colapietro and F. A. Long, *Chem. Ind. (London)*, 1056 (1960); F. A. Long and J. Schulze, *J. Amer. Chem. Soc.*, **83**, 3340 (1961); **86**, 331 (1964); R. J. Thomas and F. A. Long, *ibid.*, **86**, 4770 (1964); *J. Org. Chem.*, **29**, 3411 (1964); B. C. Challis and F. A. Long, *J. Amer. Chem. Soc.*, **85**, 2524 (1963); L. C. Gruen and F. A. Long, *ibid.*, **89**, 1287 (1967); (b) J. L. Longridge and F. A. Long, *ibid.*, **89**, 1292 (1967).

(15) R. D. Batts and V. Gold, *J. Chem. Soc.*, 4284 (1964).

(16) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).

(17) Recent nmr studies[10, 18] suggest that $HClO_4$ is completely ionized at all of the concentrations employed here and that HNO_3 is also completely ionized at the dilute end of the present concentration range but may be 30% associated in the most concentrated solution (38 wt %).

(18) J. W. Akitt, A. K. Covington, J. G. Freeman, and T. H. Lilley, *Trans. Faraday Soc.*, **65**, 2701 (1968).

define a line of slope = 0.6, showing that the kinetic process experiences 0.6 of the medium effect realized in the equilibrium reaction; this is in good agreement with a somewhat different analysis of medium effects on this reaction,[16] which also places the transition state 0.6 of the way along the reaction coordinate between reactants and products.

The fact that differences in medium effect upon the hydronium ion reaction in perchloric and nitric acid can be removed in this way suggests that the treatment can be extended to other acids. It follows, then, that the rate enhancements for sulfuric and phosphoric acids seen in Figure 2 are not the result of differences in specific interactions operating on the hydronium ion process. Both of these acid systems, on the other hand, contain appreciable quantities of undissociated acid species, and it would seem logical to ascribe the rate accelerations observed here to proton transfer from HSO_4^- and H_3PO_4. This assumption does in fact lead to approximate values of bimolecular rate constants for HSO_4^- (1.3×10^{-5} M^{-1} sec^{-1}) and H_3PO_4 (0.5×10^{-5} M^{-1} sec^{-1}) which are reasonable in that they are comparable in magnitude to $k_{H_3O^+}$ (0.8×10^{-5} M^{-1} sec^{-1}), as is usually the case for rate-determining proton transfer to carbon.[13e,19] These undissociated acid catalytic coefficients themselves show pronounced medium effects: both change to larger values with increasing sulfuric or phosphoric acid concentration; this, again, is as expected for ion-forming reactions such as these.

Thus, the differences in behavior in concentrated solutions of various acids observed here may be ascribed to significant catalysis by undissociated acid species in addition to medium effects on hydronium ion reactions. This confirms our previously advanced[3] hypothesis that general acid catalysis can occur to an appreciable extent in concentrated solutions of strong mineral acids. This work suggests also that such catalysis might be confirmed for other reactions provided that the comparison of rates is based upon a reference process which is sufficiently similar to the kinetic reaction.

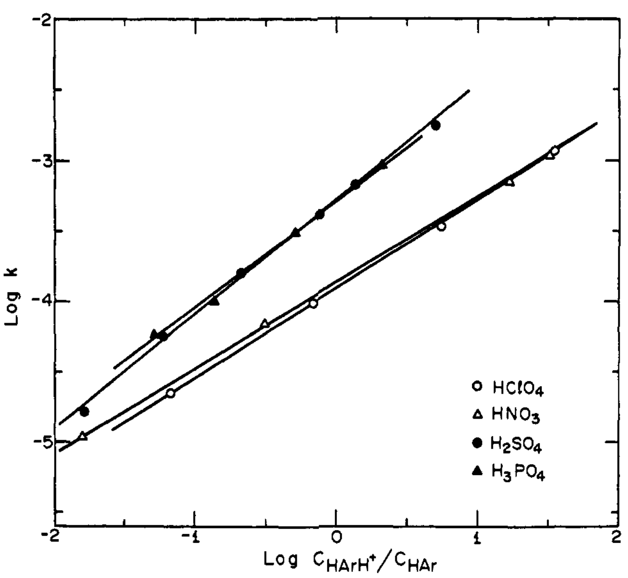

Figure 2. Rates of loss of tritium from 1,3-dimethoxybenzene-*4-t* compared with the extent of equilibrium protonation of azulene.

Experimental Section

The experimental methods used here have already been described.[3] Spectrophotometric measurements of the extent of azulene protonation in phosphoric acid solutions were performed as before by using the absorption maximum of the free base at 279 nm; nitric acid, however, absorbs strongly at this wavelength, and in this medium the absorption band of protonated azulene with λ_{max} 351 nm was therefore used instead.

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(19) J. M. Williams and M. M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 67 (1968); A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. MacDonald, and G. H. Schmid, *J. Amer. Chem. Soc.*, **93**, 4907 (1971); A. J. Kresge and Y. Chiang, unpublished work.