

Linear Free-energy Relationships concerning Rates and Equilibria in Moderately Concentrated Mineral Acids

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REACTIONS which occur in moderately concentrated sulphuric, hydrochloric, or perchloric acid solution usually manifest changes in rate or state or equilibrium, on change of acid concentration, which are much greater than can be attributed merely to the change in hydrogen-ion concentration.

We find that these phenomena can be treated profitably by means of linear free-energy relationships.

These relationships deal with equilibria between substrate S and protonated product SH⁺ or equi-charged product V, and with rate phenomena either involving or not involving proton accession in forming the transition state. For reactions involving proton acquisition between initial and final or transition state, the effect of changing the hydrogen-ion concentration is allowed for by relating equilibrium quotients, [SH⁺]/[S][H⁺], or second-order rate coefficients, k_2 . (The latter are $k_\psi/[H^+]$, where k_ψ is the pseudo-first-order rate coefficient.) The logarithms of these quantities, for reactions in a given mineral acid system, are in general linearly related to each other. For example (Figure 1), $\log([SH^+]/[S][H^+])$ for the equilibrium protonation of *N,N*,4-trimethyl-2,6-dinitroaniline in a series of sulphuric acid solutions¹ is linearly related to $\log k_2$ for the hydrolysis of ethyl acetate in the same solutions.²

In order to formulate these linear free-energy relationships in a standard fashion, one chooses as abscissa $\log k_2$ or $\log([SH^+]/[S][H^+])$ for some reference reaction for which good data are available for all the media of interest. These media are, for present purposes, at least 0.5–10M-sulphuric, -hydrochloric, and -perchloric acid solutions. We know of no real reaction for which sufficient data are available. However, the necessary data are available, and of good quality, for a hypothetical

reaction. This is the equilibrium protonation of a hypothetical aromatic primary amine (B) of $pK_{BH^+} = \text{zero}$. From the familiar equation,

$$H_0 = pK_{BH^+} + \log([B]/[BH^+]),$$

it follows that $\log([BH^+]/[B])$ is given by $-H_0$.

We may then write, for equilibria,

$$\begin{aligned} \log([SH^+]/[S]) - \log[H^+] = \\ (1 - \phi)(-H_0 - \log[H^+]) + \text{constant} \end{aligned}$$

where $(1 - \phi)$ is an arbitrary choice of a slope parameter. It is convenient, though not necessary, to add $(H_0 + \log[H^+])$ to each side of the equation.

$$\begin{aligned} \log([SH^+]/[S]) + H_0 = \\ \phi(H_0 + \log[H^+]) + \text{constant.} \end{aligned}$$

The constant is evaluated by considering approach

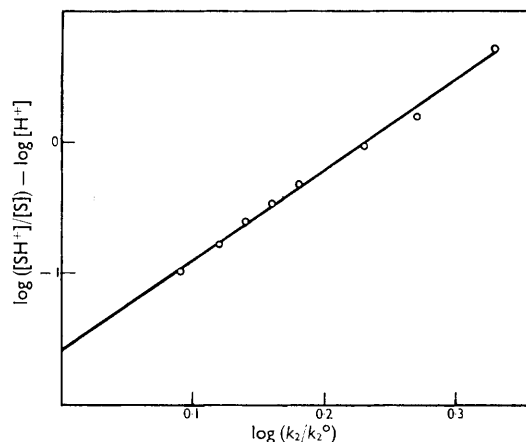


FIGURE 1. $\log([SH^+]/[S]) - \log[H^+]$ for equilibrium protonation of *N,N*,4-trimethyl-2,6-dinitroaniline¹ against $\log k_2$ (less $\log k_2$ at infinite dilution) for ethyl acetate hydrolysis,² both in sulphuric acid solutions.

¹ E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671.

² R. P. Bell, A. L. Dowding, and J. A. Noble, *J. Chem. Soc.*, 1955, 3106.

to infinite dilution in water; H_0 approaches $-\log[H^+]$, and the constant is pK_{SH^+} .

$$\log([SH^+]/[S]) + H_0 = \phi(H_0 + \log[H^+]) + pK_{SH^+}$$

This equation implies that pK_{SH^+} for any substrate can be evaluated from measurements of $[SH^+]/[S]$ on that substrate alone, as a function of acid concentration, with reference to the H_0 scale. The intercept in a plot of $\log([SH^+]/[S]) + H_0$ against $\log[H^+] + H_0$ is pK_{SH^+} . The slope, ϕ , expresses the medium-dependence of the equilibrium quotient.

pK_{SH^+} values have recently been estimated for a variety of substrates by the acidity function approach.^{1,3-5} If those estimates are correct and the linear free-energy relationship method is valid, the same pK_{SH^+} should be obtained either way. Using published data, we have estimated pK 's for 7 carboxyamides,³ 12 tertiary aromatic amines,¹ 13 triarylcarbinols⁴ (reactions forming carbonium ions) and 18 indoles⁵ by the linear free-energy relationship method, and compared them with published estimates of the same pK 's, obtained by the acidity function method. Agreement is good; the median pK discrepancy for these 50 substrates is 0.25 pK unit. (Substrates half-protonated at >70% sulphuric acid are omitted.)

In part, the discrepancies represent experimental error, and in part they are due to faults in construction of the acidity functions. The parameter

ϕ should be equal for all the bases used to construct an acidity function, but this condition is imperfectly satisfied by the bases actually used.

Typical ϕ values are +0.5 for carboxyamides, -0.4 for aromatic tertiary amines, -1.2 for triarylcarbinols, +0.2 for indoles unsubstituted in the pyrrole ring, -0.4 for 2- or 3-alkylindoles and -0.8 for 1-alkylindoles.

It is possible to estimate the pK of a substance without reference to any "acidity function", in the usual sense of the term. Thus pK_{SH^+} for *N,N*,4-trimethyl-2,6-dinitroaniline is -1.58 as the intercept in Figure 1; this compares with -1.57 by the standard linear free-energy relationship and -1.66 by the acidity function method.

For rate phenomena, plots of $\log k_\psi + H_0$ against $\log[H^+] + H_0$ are also linear. We have correlated 160 sets of kinetic data in this way; the median standard deviation of points from the linear regression lines was 0.03 log units, or 7%, which is the order of magnitude of experimental error. The slopes (ϕ) are useful to characterize the medium-dependence of rate coefficients; they lie mostly between -1 and +1. The intercepts represent $\log k_2$ at infinite dilution in water.

When a proton is not acquired in forming the final or transition state, one plots $\log([V]/[S])$ or $\log k_\psi$, respectively, against $\log[H^+] + H_0$. The slopes and intercepts have similar import.

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³ K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

⁴ N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

⁵ R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796.