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The Relationship between H_R and H_0 in Moderately Concentrated Aqueous Perchloric and Hydrochloric Acids

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Summary H_R is a non-linear function of H_0 in 0·1 — 1·5 M aqueous perchloric and hydrochloric acids; this complicates data extrapolation through these regions but is of use in connection with mechanistic details of acid catalysis.

Different indicator acidity functions are in general linear functions of H_0 in concentrated aqueous acids, *i.e.* $H_x = a + mH_0$ with m covering the range 0·5 — 2·0.[1] In dilute solution, on the other hand, by definition $H_x = -\log C_{H^+} = H_0$, and m reduces to unity. In order to determine the relationship in the region intermediate between concentrated and dilute solution, we have carried out detailed measurements of H_R and H_0 in perchloric and hydrochloric acids. The results have an important bearing upon two commonly used methods of extrapolating data from concentrated to dilute solution, for the purpose *e.g.* of determining conventional pK_a's or hydronium ion catalytic coefficients, and are also of interest in connection with kinetic acidity dependence in concentrated acids.

2-Nitroaniline, 4-nitroaniline, and 3,5-dinitroaniline were used as indicators for measuring H_0, and 4,4′-dimethoxytriphenylcarbinol, 4,4′4″-trimethoxytriphenylcarbinol, and 4,4′-dimethoxy-4″-methyltriphenylcarbinol were employed for H_R. Twenty to forty determinations of the indicator ratio, I, of each base in each acid were made over the useful range of this quantity, $-1·5 < \log I < 1·5$;[2] these data were then reduced to values of H_0 and H_R by a wholly analytical (weighted least-squares) adaptation of the usual graphical method.[3]

The results for hydrochloric acid are shown in Figure 1: those for perchloric acid are quite similar. It may be seen that H_R and H_0 have the same value (equal to $-\log C_{H^+}$) up to $H_0 = H_R \simeq +1$ and that another linear relationship begins at $H_R \sim -1$, $H_0 \sim -0·5$ (in $HClO_4$: $H_R = -0·16 + 2·06\ H_0$, $r = 0·999$; in HCl: $H_R = 0·12 + 1·98\ H_0$, $r = 0·999$). In the region between these linear portions, however, H_R is a curved function of H_0.

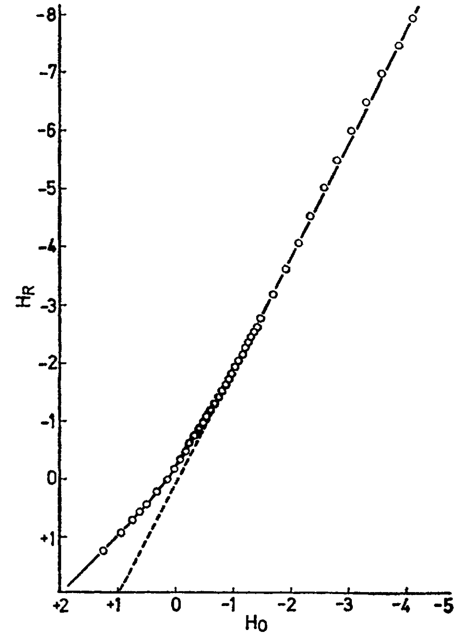

Figure 1. *Relationship between* H_R *and* H_0 *in aqueous hydrochloric acid at* 25°.

Because of this curvature, extrapolation of data from concentrated to dilute solution performed down H_0, on the assumption that the relationship $H_R = 2H_0$ is obeyed down to the point $H_R = H_0 = -\log C_{H^+} = 1{\cdot}00$, misses the mark by *ca.* one log unit. Extrapolations performed in the manner recommended by Bunnett and Olsen,[4] *i.e.* down $(H_0 + \log C_{H^+})$, are also incorrect because, above $C_{H^+} \sim 1{\cdot}5$ M, H_R is linear in H_0 and not $(H_0 + \log C_{H^+})$. By coincidence, however, extrapolations down H_0 are reasonably accurate if terminated at $H_0 = 0{\cdot}00$ under the commonly held (but mistaken) assumption that here $H_0 = -\log C_{H^+}$.

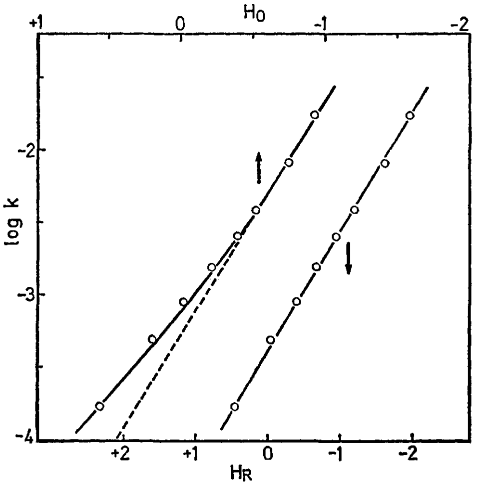

FIGURE 2. *Kinetic acidity dependence of* trans-*cyclo-octene hydration in perchloric acid at 25° compared with* H_0 (*top scale*) *and* H_R (*bottom scale*).

This curved relationship between H_R and H_0 opens up the possibility that similar effects may be found in kinetic phenomena. That is, in fact, the case in the hydration of *trans*-cyclo-octene: Figure 2 shows that log *k* for this reaction is linear in H_R but bears a curved relationship to H_0. The fact that this reaction has a very steep kinetic acidity dependence, $-\mathrm{d}\log k/\mathrm{d}\,H_R = 0{\cdot}8$, implies that the transition state of its rate-determining proton transfer step[5] resembles the carbonium ion product of this reaction step closely; the conjugate acids of H_R indicators are also carbonium ions.

These considerations suggest that the hydration of a more reactive olefin, which occurs through an earlier transition state, might not show a kinetic acidity dependence parallel to H_R. It is significant, therefore, that log *k* for the hydrolysis of phenyl vinyl ether, which occurs through rate-determining protonation of the double bond[6] is linear in H_0 but curved in H_R. Here $-\mathrm{d}\log k/\mathrm{d}\,H_0 = 1{\cdot}1$ and $-\mathrm{d}\log k/\mathrm{d}\,H_R$ would have been *ca.* 0·5 were not the relationship curved. It is generally agreed that the H_R and H_0 scales differ because of hydrogen bonding between water and the positively charged N–H bonds of the anilinium-ion conjugate acids of H_0 indicators; a comparable interaction cannot take place with the carbonium ions of the H_R system. It follows, then, that there must be an interaction with water in the transition state for phenyl vinyl ether hydrolysis which is absent from the transition state for the *trans*-cyclo-octene reaction. It is unlikely that this interaction occurs through the oxygen atom which is taking on positive charge in the vinyl ether transition state, for all of the H_R indicators used here also have analogous ether functional groups. It is rather more probable that the additional solvation takes place through the non-reacting O–H bonds of the hydronium ion proton donor, which still retain a significant fraction of their initial state positive charge in the relatively early vinyl ether transition state but not in the late olefin transition state.

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