

efficiency. The metabolization of histamine corresponds to at least 110 $\mu\text{g}/\text{h/g}$ fresh liver.

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On the Applicability of the H_0 Acidity Function to the Case of Two Competing Mechanisms

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The H_0 acidity function has become the subject of a great number of studies on the mechanisms of acid catalysis^{1,2}, although cases have been also reported in which this function is of a limited applicability². Apart from the fundamental restrictions involved in assuming certain activity coefficient terms to remain constant in different media, there is the following particular case, in which the use of the acidity function may lead, at least partly, to fallacious conclusions.

Let us consider an acid-catalysed hydrolysis reaction in which the unimolecular and bimolecular mechanisms are in competition. The overall rate coefficient k , which can be measured experimentally, is then made up of the two individual rate coeffi-

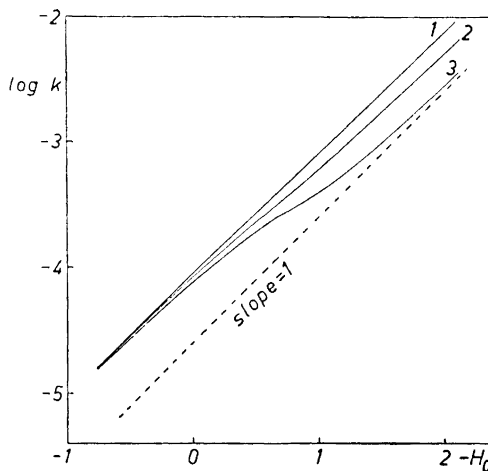


Fig. 1. A plot of $\log k$ against $-H_0$ for competing uni- and bimolecular reactions. Aqueous hydrochloric acid solutions, 25°C. In dilute acid the bimolecular reaction assumes 25% (curve 1), 50% (curve 2), and 75% (curve 3) of the overall reaction.

icients, k_1 and k_2 , which refer to the different mechanisms. If the Zucker-Hammett hypothesis is valid, k_2 should be proportional to the acid concentration, whereas $\log k_1$ should vary similarly as the value of $-H_0$ of the solution. Fig. 1 shows some examples calculated for the dependence of $\log k$ on $-H_0$ in such cases. The H_0 values of aqueous hydrochloric acid solutions used in the calculations are those revised by Paul and Long³.

The most striking feature is that the contribution of the bimolecular mechanism becomes largely masked by the unimolecular mechanism, when higher acidities are approached. Thus the curves are experimentally indistinguishable from a straight line of a slope of nearly unity, which would correspond to a purely unimolecular reaction, except that case where the bimolecular mechanism is the prominent in dilute acid; here the curve shows a clearly notable point of inflexion. Such a behaviour is thus highly characteristic of competing mechanisms which depend on the acidity of the solution in a different way.

An example of the masking of a mixed unimolecular and bimolecular reaction by

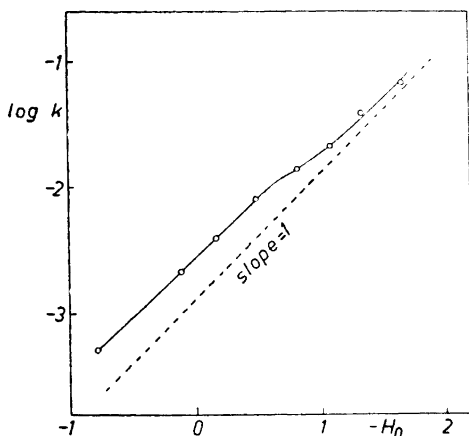


Fig. 2. A plot of $\log k$ against $-H_0$ for the hydrolysis of β -chloroethoxymethyl formate in aqueous hydrochloric acid solutions at 25°C.

the prominent unimolecular reaction is furnished by the hydrolysis of methoxymethyl formate, reported earlier⁴. On the other hand, a curve showing a point of inflexion was observed in the hydrolysis of β -chloroethoxymethyl formate (Fig. 2).

In cases like that of Fig. 2, an accurate determination of the rates of the individual reactions should require the use of more specialised kinetic methods. If, however, such methods are not available, the relative contributions may be roughly estimated, as described below. The most essential limitation in these calculations is that the value of k_2 is usually not strictly proportional to the acid concentration, and that the slope of the plot of $\log k_1$ against $-H_0$ may slightly differ from unity, and therefore the results should be regarded as very approximate.

It may be found that the position of the point of inflexion depends on the relative rates of the competing reactions. If R denotes the ratio of the rate of the unimolecular reaction to that of the bimolecular reaction in dilute hydrochloric acid, it can be calculated that the following numerical relation holds for the H_0 value of the point of inflexion:

$$R = 10^{H_0} \left(\frac{1 - 2.35 H_0 + 1.17 H_0^2}{-0.93 - 1.27 H_0 + 4.60 H_0^2} \right)$$

This equation was derived by representing the concentration of hydrochloric acid in 0.1–6.0 M solutions as a polynomial of H_0 of the second power, the coefficients of which were calculated by the method of least squares using weighed values of CHCl_3 (the weights were chosen as inversely proportional to the values of the acid concentration). The H_0 data given by Paul and Long³ were used.

The method of iteration may be also applied, taking into account that it is the unimolecular reaction that predominates at high acidities, and thus the value of k in these media gives the value of k_1 as a first approximation, from which the values of k_1 for dilute acids may be calculated with the use of the respective H_0 values. These give first approximations for the values of k_2 in dilute acid solutions ($k_2 = k - k_1$), from which, in turn, the values of k_2 for the higher acid concentrations may be calculated.

In the example shown in Fig. 2, the point of inflexion lies at a H_0 value of -0.67 ± 0.10 , from which it is estimated that in dilute acid the unimolecular reaction assumes $27 \pm 9\%$ of the overall reaction. Calculations by the iteration method gave a corresponding estimate of $39 \pm 7\%$. These percentages correspond to a value of $0.0022 \pm 0.0005 \text{ l mole}^{-1} \text{ s}^{-1}$ for the rate coefficient of the bimolecular reaction at 25°C, which is a very reasonable value, as the rate coefficients reported for the bimolecular $A_{AC}2$ hydrolysis of alkyl formates are of the same magnitude under similar conditions^{5,6}.

A full account of the experimental details and examples of other similar reactions will be published shortly.

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