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Acid-Catalyzed Hydrolysis of Sucrose

A *student study of a reaction mechanism*

By extending the experimental work in a kinetic study of a well-known elementary reaction, the hydrolysis of sucrose, the beginning student in chemistry can gather some insight into the mechanism of the reaction (Fig. 1). As usually carried out, the experiment stops short of this goal. It is often given as an example of a pseudo-first order reaction and the student merely determines a single value of the rate constant at a fixed concentration of catalyzing acid. If the experiment is carried out with various concentrations of acid the reaction can be demonstrated to be unimolecular. The experiment also illustrates a further property of acid solutions, namely, the proton donating power of acid solutions as measured by the Hammett acidity function (1–3).
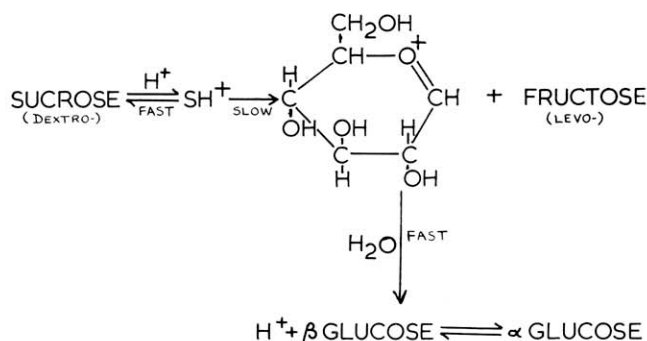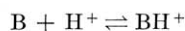

Figure 1.

For dilute solutions of acids the most useful measure of acidity is pH. In solutions of strong acids more concentrated than about 0.1 M, however, the acidity is more satisfactorily measured by the Hammett acidity function, H_0, or other acidity functions (3). H_0 is concerned with the protonation of a neutral base, B,

$$B + H^+ \rightleftharpoons BH^+$$

and is related to the extent of protonation by,

$$H_0 = pK_{BH^+} - \log_{10} \frac{[BH^+]}{[B]}$$

where pK_{BH^+} is the pK of the conjugate acid BH^+, and the [] brackets represent molar concentrations. The analogous function to concentration of acid is h_0, which is antilog $(-H_0)$. This function, h_0, increases far more rapidly than molarity of acid for concentrated solutions of strong acids. In other words, the proton donating power of concentrated solutions of strong acids is far greater than one would anticipate from their concentrations. In dilute solutions h_0 tends toward concentration, and H_0 tends toward pH.

There are two general mechanisms for acid-catalyzed hydrolyses. These are a *unimolecular* process,

$$S + H^+ \xrightleftharpoons{\text{(fast)}} SH^+$$

$$SH^+ \xrightarrow{\text{(slow)}} \text{products}$$
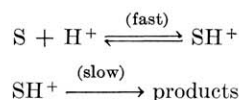
or a *bimolecular* process, where a molecule of water is involved in the rate-determining step,

$$S + H^+ \xrightleftharpoons{\text{(fast)}} SH^+$$

$$SH^+ + H_2O \xrightarrow{\text{(slow)}} \text{products}$$
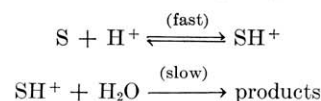
Although reactions which follow either mechanism can be made to follow pseudo-first order kinetics, the way in which the rate constant changes with increasing concentration of acid is completely different for the two mechanisms.

The rate of reaction for the unimolecular process is proportional to the proton donating power of the medium (4–6). The bimolecular process, on the other hand, has a rate which is proportional to concentration of acid or concentration of hydrogen ion, (4–6). This difference gives us a criterion of mechanism which is known as the Hammett-Zucker hypothesis (4). According to this hypothesis a graph of the rate constant, k, plotted against h_0 will be a straight line if the reaction is following a unimolecular mechanism. Further, a graph of $\log_{10} k$ against H_0 should also be linear and have a gradient of unity. Alternatively, if a graph of k against acid molarity or hydrogen ion concentration is linear then the reaction is following the bimolecular mechanism.

It is known that this criterion is by no means unique and should be used with a certain amount of caution (7, 8). Nevertheless, for a number of reactions it has been a very useful mechanistic tool. The present experiment makes use of this and enables students to use their kinetic measurements to greater purpose.

The Experiment

Although glucose is dextro-rotatory and fructose is levo-rotatory, the latter has a greater optical rotatory power, and the rate of the hydrolysis of the sucrose may be followed by measuring the decrease of optical rotation with time. When the reaction is complete the mixture of glucose and fructose is levo-rotatory (invert sugar). If on a polarimeter the rotations to the right (dextro-) are counted as positive, and rotations to the left (levo-) as negative, the rate constant is given by

$$k = \frac{2.303}{t} \log_{10} \left(\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \right)$$

where t is the time, α_0 is the angular rotation at time t

= 0, α_t is the rotation at time t, and α_∞ is the rotation at the end of the reaction.

The rate of the reaction is conveniently studied at 20°C with hydrochloric acid concentrations ranging from 0.25 to 3.0 M, and with a sucrose concentration of 10 g per 100 ml of *acidified* solution. The polarimetric measurements are started as soon as possible after mixing the reagents, and readings are taken at suitable intervals to cover the initial stages of the reaction. Particular attention should be paid to temperature control. Samples of each reaction mixture are preserved for about a week to measure the α_∞ values.
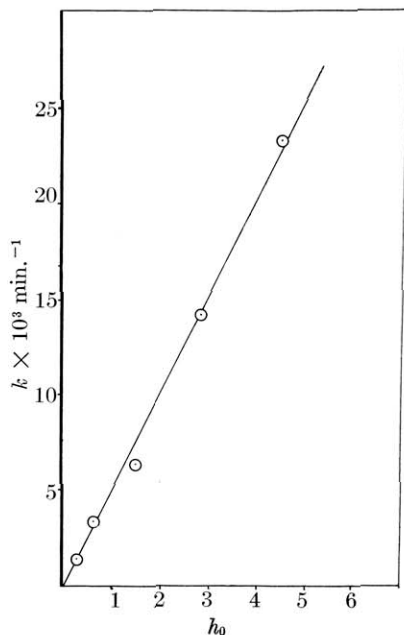
Figure 2. Dependence of k on h_0.

For each experiment graphs of t against $\log_{10}(\alpha_t - \alpha_\infty)$ are plotted, and from the gradients of the straight lines the values of the rate constants are calculated. By plotting the following graphs the student has to decide which of the two mechanisms the reaction has followed:

(1) k against antilog $(-H_0)$, i.e., h_0 (see Fig. 2).
(2) $\log k$ against H_0 (see Fig. 3)
(3) k against acid molarity (or $[H^+]$) (see Fig. 4).

Some values of H_0 for hydrochloric acid in the concentration range 0.1M to 3.5M are given in the table (5).

In Figures 2, 3, and 4 are plotted some results obtained by students (D. R. B. and R. A. R.) using a

Table 1. Some H_0 Values for HCl Solutions (5)

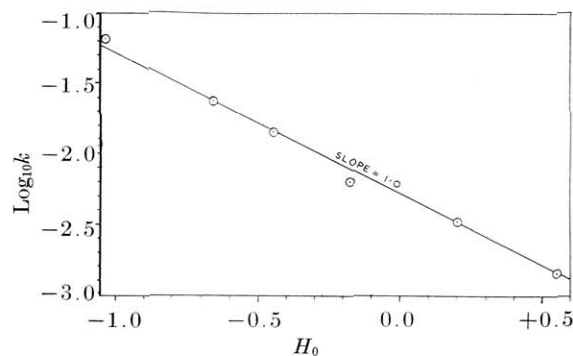| Molarity	H_0	Molarity	H_0	Molarity	H_0
0.1	0.98	0.75	−0.03	2.0	−0.67
0.25	0.55	1.00	−0.18	2.5	−0.87
0.50	0.20	1.5	−0.47	3.0	−1.05
				3.5	−1.23

Figure 3. Plot of log k against H_0.

Hilger polarimeter (model M412). The results clearly illustrate that the reaction has followed the unimolecular mechanism. In Figure 3 a line of unit slope has been drawn and the experimental results are in reasonable agreement with this, as originally found by Hammett and Paul (2).

The authors are grateful to Dr. R. A. Pritchard for helpful suggestions.

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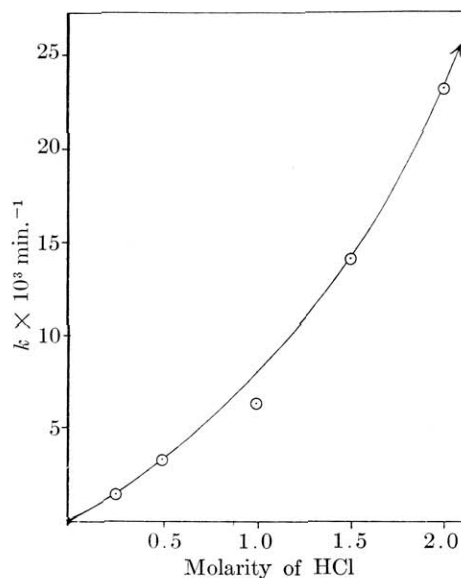
Figure 4. K as a function of acid molarity.