Kinetics and Mechanism of Hydrolysis of Succinimide under Highly Alkaline Medium

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Received October 10, 1974

The kinetic study of hydrolysis of succinimide has been done in highly alkaline medium. The hydrolysis follows an irreversible first-order consecutive reaction path of the type A → B → C where k_1 and k_2 are the pseudo-first-order rate constants for reaction A → B and B → C, respectively. The variation of k_1 and k_2 with alkali concentration was found to be in agreement with equations $k_{1(\mathrm{obsd})} = B_1 + B_2[\mathrm{OH}^-]$ and $1/k_{2(\mathrm{obsd})} = C_1 + C_2/[\mathrm{OH}^-]$ where B_1, B_2, C_1, and C_2 are the arbitrary constants.

In the basic hydrolysis of succinimide and substituted imides, many interesting features have been observed by a number of investigators.[1-2] The effect of various groups and associated rings on the hydrolysis of imides was studied by Sircar.[3] Prabhudas[4] studied separately the first and second stage basic hydrolysis of succinimide in 0.07143, 0.05, and 0.04286 *M* sodium hydroxide solutions using usual one-step first- and second-order rate equations at temperatures ranging from 20 to 50°. He found that the first step was about 300 times faster than the second one for this reaction. He had simply given the stoichiometry of the basic hydrolysis of succinimide and had not discussed the mechanism. In the present study, the kinetics has been done in highly alkaline medium with the aim to establish the consecutive nature as well as the mechanism of two-stage hydrolysis of succinimide. The rate constants of the consecutive steps have been evaluated using the equation of Esson as discussed by Frost and Pearson.[5]

Experimental Section

Reagents. Succinimide was prepared by the method of Clarke and Behr.[6] The stock solution of carbonate-free sodium hydroxide was prepared and diluted to the required concentrations using double distilled water. All other reagents were of reagent grade.

Kinetic Measurements. A two-necked flask containing sodium hydroxide and sodium nitrate (used to maintain the ionic strength) was thermostated in an oil bath whose temperature was maintained within ±0.1°. Succinimide solution was then added and the evolved ammonia was flushed out by passing a continuous current of nitrogen gas and was absorbed in hydrochloric acid.[7,8] The evolved ammonia at different time intervals was estimated spectrophotometrically using Nessler's reagent.[9-13] The spectrophotometric measurements were made using a Bausch and Lomb Spectronic-20. The reaction vessel was fitted with a double-walled condenser to check any evaporation.

Results and Discussion

The basic hydrolysis of succinimide follows the reaction path

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{1}$$

where A, B, and C stand for succinimide, succinamic acid, and ammonia. For this reaction, the concentration of ammonia is related with time by the equation[5]

$$C = A_0\left[1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right] \tag{2}$$

where k_1 and k_2 are the pseudo-first-order rate constants and A_0 is the initial concentration of succinimide. By substituting a parameter, ρ, for k_2/k_1 in eq 2, we get

$$C = A_0\left[1 + \frac{1}{1 - \rho}(\rho e^{-k_1 t} - e^{-\rho k_1 t})\right] \tag{3}$$

Equation 3 has been solved for k_1 introducing various trial values of ρ using the Newton–Raphson method.[14] The best possible value of ρ was obtained by selecting one of those trial values for which the sum of the squares of the difference of observed and calculated values was found to be minimum. This fitting was done using a computer program developed for IBM-1130. The value of k_2 was determined from the exact value of ρ and k_1.

To study the effect of hydroxide ions, the kinetic measurements were made in sodium hydroxide solutions with concentrations ranging from 0.1 to 1.0 *M* at four different temperatures. The results are shown in Figures 1 and 2.

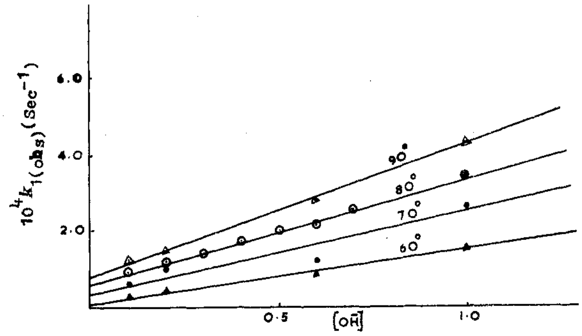

Figure 1. Effect of concentration of sodium hydroxide on pseudo-first-order rate constant for first step hydrolysis.

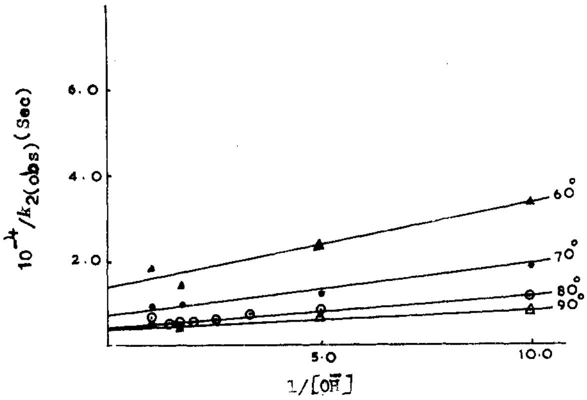

Figure 2. Effect of concentration of sodium hydroxide on pseudo-first-order rate constant for second step hydrolysis.

From these results it is clear that the variation of k_1 and k_2 with alkali concentration obeys the equations

$$k_{1(\mathrm{obsd})} = B_1 + B_2[\mathrm{OH}^-] \tag{4}$$

$$1/k_{2(\mathrm{obsd})} = C_1 + C_2/[\mathrm{OH}^-] \tag{5}$$

Table I
Linear Parameters Corresponding to $k_{1(\mathrm{obsd})}$ vs. $[OH^-]$[a]

Temp, °C	$10^5 B_1$, sec^{-1}	$10^4 B_2$, $M^{-1} sec^{-1}$
60	1.544 ± 0.743[b]	1.277 ± 0.125[b]
70	3.704 ± 3.11	2.032 ± 0.524
80	6.639 ± 0.527	2.568 ± 0.118
90	8.276 ± 0.839	3.366 ± 0.141

[a] Conditions: 0.004 *M* succinimide, 1.5 *M* ionic strength. [b] Error limits are standard deviations.

where B_1, B_2, C_1, and C_2 are arbitrary constants and have been evaluated using least-squares technique. The results are summarized in Tables I and II.

The mechanism consistent with the observed results to which we are led is as follows.

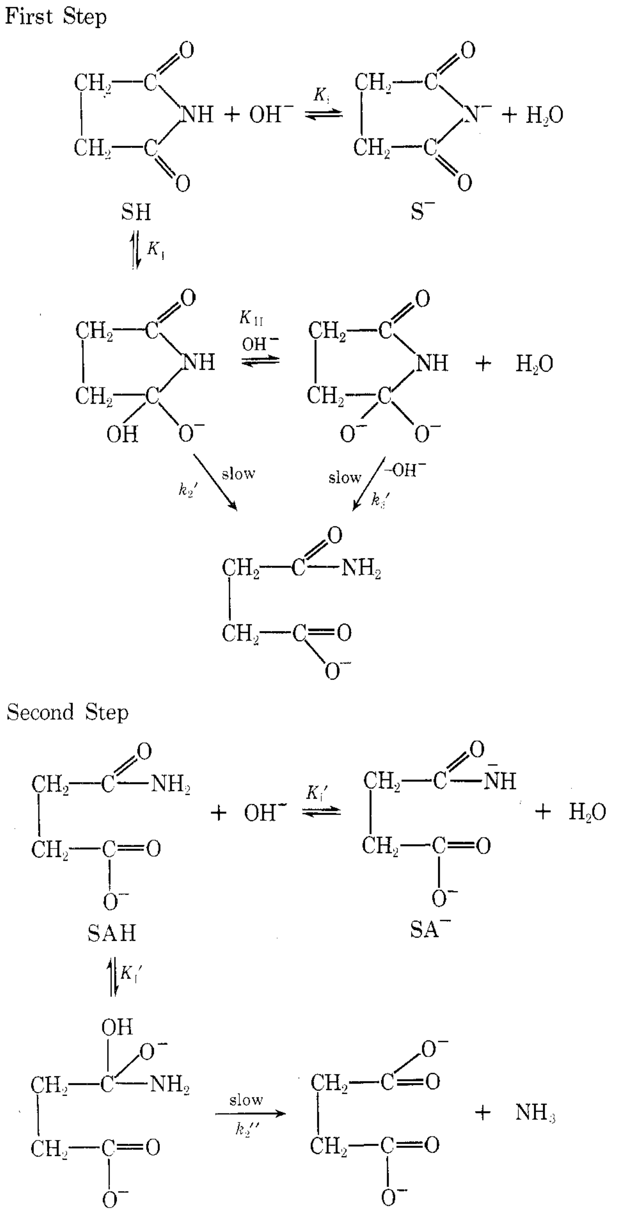

Table II
Linear Parameters Corresponding to $1/k_{2(\mathrm{obsd})}$ vs. $1/[OH^-]$[a]

Temp, °C	$10^{-3} C_1$, sec	$10^{-2} C_2$, *M* sec
60	13.72 ± 2.45[b]	18.99 ± 4.33[b]
70	7.937 ± 0.890	9.619 ± 1.568
80	4.622 ± 0.317	6.685 ± 0.683
90	4.713 ± 0.928	3.450 ± 1.636

[a] Conditions: 0.004 *M* succinimide, 1.5 *M* ionic strength. [b] Error limits are standard deviations.

The above mechanism is in close agreement with the results of various authors[12,15-23] on alkaline hydrolysis of monoamides, dihydropyrimidines, substituted anilides, and *N*-acylpyrroles. On the basis of this mechanism the following kinetic equations have been derived.

$$k_{1(\mathrm{obsd})} = \frac{K_I k_2'[OH^-]}{1 + K[OH^-]} + \frac{K_I K_{II} k_3'[OH^-]^2}{1 + K[OH^-]} \tag{6}$$

or

$$k_{1(\mathrm{obsd})} = \frac{K_I k_2'}{K} + \frac{K_I K_{II} k_3'}{K}[OH^-] \tag{7}$$

because $K[OH^-] \gg 1$ in this particular case; and

$$k_{2(\mathrm{obsd})} = \frac{K_I' k_2''[OH^-]}{1 + K'[OH^-]} \tag{8}$$

where k_2', k_2'', and k_3' are the rate constants corresponding to rate-determining steps for the decomposition of tetrahedral intermediates to products and $K = K_i/[H_2O]$, $K' = K_i'/[H_2O]$. Equations 7 and 8 confirm the dependence of rate constants on alkali concentration and are similar to eq 4 and 5.

Acknowledgment. The authors are thankful to Professor W. Rahman, Head, Department of Chemistry, A. M. U., Aligarh, for providing research facilities and also to C. S. I. R., India, for financial support to one of us (M.N.K.).

Registry No.—Succinimide, 123-56-8.

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