PHYSICAL CHEMISTRY

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1961

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Abstract

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KINETICS OF THE HYDROLYSIS OF CAPROLACTAM IN AQUEOUS KOH SOLUTIONS

(Presented by Academician V. N. Kondrat' ev, 15 XII 1960)

It is known that solutions of alkalis in water, alcohols, and other organic solvents are effective catalysts. The extensive literature on the catalytic action of alkalis (NaOH and KOH) is, for the most part, qualitative in character. Quantitative works are devoted to studies in dilute and moderately concentrated alkali solutions. Because of the absence of quantitative data on the kinetics of chemical reactions in concentrated alkali solutions, it is as yet impossible to draw general conclusions concerning the mechanism of the catalytic activity of such media.

On the basis of experimental data on the kinetics of hydrolysis in dilute alkali solutions, a number of authors ($^{1-3}$) believe that the limiting stage is the interaction between the hydroxide ion and the reactant molecule B. In that case

$$W = K_{\text{eff}} \cdot C_{\text{B}} = K_{\text{ist}} \cdot a_{\text{OH}^-} \cdot C_{\text{B}} \frac{f_{\text{B}}}{f^*}; \qquad K_{\text{eff}} = K_{\text{ist}} \cdot a_{\text{OH}^-} \cdot \frac{f_{\text{B}}}{f^*}, \tag{1}$$

where a_{OH^-} is the activity of the hydroxide ion and f_{B}, f^* are the activity coefficients of the reactant and the activated complex.

At present there is direct experimental evidence that, for a whole series of processes, the catalytic action of acidic media consists in the conversion of the reactant into an ionized form, while the limiting stage is the stage of transformation of the ionized form. By analogy with catalysis in acidic media, it may be assumed that in alkaline media as well the reactant can undergo ionization, with the equilibrium between the ionized and nonionized forms being established rapidly. The data of Edward and Terry (^{2}), on the hydrolysis of diacetylamine and succinimide, and of Taft et al. (^{3}), on the hydrolysis of trifluoroacetanilide, may be regarded as evidence for this point of view. Let the ionization equilibrium constant of caprolactam B, expressed in terms of activities, be denoted by K_{p}.

$$\text{B} + \text{OH}^- \rightleftarrows \text{BOH}^-; \qquad K_{\text{p}} = \frac{a_{\text{B}} \cdot a_{\text{OH}^-}}{a_{\text{BOH}^-}}.$$

Under the condition that the degree of ionization is small, the following equation is valid for K_{eff}:

$$W = K_{\text{eff}} \cdot C_{\text{B}} = \frac{K_{\text{ist}}}{K_{\text{p}}} a_{\text{OH}^-} \cdot C_{\text{B}} \cdot \frac{f_{\text{B}}}{f^*}; \qquad K_{\text{eff}} = \frac{K_{\text{ist}}}{K_{\text{p}}} a_{\text{OH}^-} \cdot \frac{f_{\text{B}}}{f^*} \tag{2}$$

and, on the basis of formal kinetic regularities, it is impossible to distinguish between the two mechanisms mentioned.

In both cases the observed rate constant changes in direct proportion to the activity of hydroxide ions.

If the rate-limiting stage of amide hydrolysis also includes a molecule of water, then

$$\frac{K_{\text{eff}}}{a_{\text{H}_2\text{O}} \cdot a_{\text{OH}^-}} = K' \cdot \frac{f_{\text{B}}}{f^*},$$

where $K' = K_{\text{true}}$ according to mechanism (1) and $K' = \dfrac{K_{\text{true}}}{K_{\text{r}}}$ according to mechanism (2).

In the present work, the catalytic activity of aqueous KOH solutions was studied using the hydrolysis of caprolactam as an example. Kinetic measurements were carried out on an SFD-1 spectrophotometer. The use of a spectrophotometric method proved possible because, in the ultraviolet region of the spectrum, the absorption coefficients of caprolactam and of the product of its hydrolysis—aminocaproic acid—differ greatly. Chemically pure KOH was used for the experiments.

Because aqueous KOH solutions corrode glass, the alkali solutions were prepared immediately before the experiments. The experiments were carried out in the same manner as in the study of the dehydration reaction of ortho-benzoylbenzoic acid (^{4}).

The concentration of lactam in the experiments was 3-6 $\cdot 10^{-3}$ mol/l. In highly concentrated solutions (KOH above 46%), lactam is very difficult to dissolve (its solubility is apparently less than $1 \cdot 10^{-3}$ mol/l), and therefore attempts to study the process in such media had to be abandoned. In the investigated interval of KOH concentrations, caprolactam is completely hydrolyzed. As was to be expected, the process is monomolecular with respect to lactam. Figure 1 presents the kinetic curve and its logarithmic anamorphosis for the hydrolysis of caprolactam in 20.45% KOH at $T = 60°$. The monomolecular rate constant remains constant up to the complete conversion of caprolactam into aminocaproic acid.

Table 1

KOH, wt. %	Temp., °C	K_{eff}, min^{-1}	KOH, wt. %	Temp., °C	K_{eff}, min^{-1}
1.037	90	$0.570 \cdot 10^{-2}$	12.41	90	$0.676 \cdot 10^{-1}$
1.037	80	$0.315 \cdot 10^{-2}$	12.41	80	$0.405 \cdot 10^{-1}$
1.037	70	$0.170 \cdot 10^{-2}$	12.41	70	$0.191 \cdot 10^{-1}$
1.037	60	$0.075 \cdot 10^{-2}$	12.41	60	$0.108 \cdot 10^{-1}$
2.250	90	$0.993 \cdot 10^{-2}$	12.41	50	$0.506 \cdot 10^{-2}$
2.250	80	$0.464 \cdot 10^{-2}$	12.41	40	$0.199 \cdot 10^{-2}$
2.250	70	$0.310 \cdot 10^{-2}$	12.41	25	$0.474 \cdot 10^{-3}$
2.250	60	$0.132 \cdot 10^{-2}$	15.76	60	$0.147 \cdot 10^{-1}$
4.184	90	$0.207 \cdot 10^{-1}$	15.76	50	$0.690 \cdot 10^{-2}$
4.184	80	$0.120 \cdot 10^{-1}$	15.76	40	$0.314 \cdot 10^{-2}$
4.184	70	$0.610 \cdot 10^{-2}$	15.76	25	$0.745 \cdot 10^{-3}$
4.184	60	$0.320 \cdot 10^{-2}$	20.45	60	$0.244 \cdot 10^{-1}$
8.056	90	$0.403 \cdot 10^{-1}$	20.45	50	$0.112 \cdot 10^{-1}$
8.056	80	$0.221 \cdot 10^{-1}$	20.45	40	$0.479 \cdot 10^{-2}$
8.056	70	$0.112 \cdot 10^{-1}$	20.45	25	$0.123 \cdot 10^{-2}$
8.056	60	$0.503 \cdot 10^{-2}$	26.95	50	$0.214 \cdot 10^{-1}$
8.056	50	$0.230 \cdot 10^{-2}$	26.95	40	$0.980 \cdot 10^{-2}$
8.056	40	$0.109 \cdot 10^{-2}$	26.95	25	$0.227 \cdot 10^{-2}$
8.056	25	$0.295 \cdot 10^{-3}$	33.16	50	$0.384 \cdot 10^{-1}$
			33.16	40	$0.176 \cdot 10^{-1}$
			33.16	25	$0.410 \cdot 10^{-2}$
			37.25	50	$0.588 \cdot 10^{-1}$
			37.25	40	$0.350 \cdot 10^{-1}$
			37.25	25	$0.651 \cdot 10^{-2}$
			45.78	25	$0.159 \cdot 10^{-1}$

Table 2

KOH, wt. %	$\lg[K_{\text{eff}}]$ at 25°C	$\lg a_{\text{KOH}}$	$\lg a_{\text{OH}_\pm}$	$\lg a_{\text{H}_2\text{O}}$	$\lg \dfrac{K_{\text{eff}}}{a_{\text{OH}_\pm} \cdot a_{\text{H}_2\text{O}}}$	E_{eff}, kcal/mol
1.037	−4.42	−1.62	−0.81	−0.002	−3.61	16.9
2.250	−4.16	−1.04	−0.52	−0.005	−3.64	16.7
4.184	−3.85	−0.50	−0.25	−0.011	−3.59	16.7
8.056	−3.56	0.21	0.105	−0.025	−3.64	16.7
12.41	−3.27	0.76	0.38	−0.040	−3.61	16.5
15.76	−3.10	1.15	0.575	−0.054	−3.63	16.6
20.45	−2.91	1.70	0.85	−0.090	−3.67	16.7
26.95	−2.64	2.47	1.235	−0.134	−3.74	16.7
33.16	−2.39	3.22	1.61	−0.240	−3.76	16.3
37.25	−2.19	3.76	1.88	−0.320	−3.75	16.5
45.78	−1.80	4.96	2.48	−0.580	−3.70	–

Fig. 1. Kinetic curve (1) and its logarithmic anamorphosis (2) for the hydrolysis reaction of caprolactam in 20.45% KOH at 60°

Figure 1: Fig. 1. Kinetic curve (1) and its logarithmic anamorphosis (2) for the hydrolysis reaction of caprolactam in 20.45% KOH at 60°

Note. The values of a_{KOH} are taken from work (^{5}), and the values of $a_{\mathrm{H_2O}}$ from (^{6}).

In cases where the hydrolysis rate was low ($K_{\mathrm{eff}} \ll 2.5 \cdot 10^{-3}$ min^{-1}), the experiment at a given temperature was carried out only up to 40–70% conversion. The cuvette was then heated to 70–90°C, at which the reaction was completed.

Then the cuvette was cooled to the initial temperature and the value of the optical density of the solution, D_∞, was measured. Table 1 presents the rate constants for caprolactam hydrolysis at various temperatures in media with different KOH contents. These data fit the Arrhenius dependence well. Table 2 presents the rate constants K_{eff} at 25°. For the KOH concentration interval from 1.037 to 12.41%, the effective constants were calculated by extrapolation from high temperatures using the Arrhenius equation. The activation-energy values are practically independent of the KOH concentration and are equal to 16.6 ± 0.3 kcal/mol.

Fig. 1. Kinetic curve (1) and its logarithmic anamorphosis (2) for the hydrolysis reaction of caprolactam in 20.45% KOH at 60°.

As can be seen from Table 2, the rate constant for caprolactam hydrolysis, K_{eff}, in concentrated aqueous KOH solutions increases more sharply than the concentration of hydroxyl ions. For example, when the alkali concentration is increased from 1.037 to 45.78%, the rate constant at 25° increases by a factor of 417. This fact indicates that the catalytic activity of KOH is determined not only by the concentration of OH$^-$ ions, but also depends on the properties of the hydroxide ion in the given solution. Schwarzenbach (^{7}), by analogy with the acidity function for acid solutions, proposed characterizing alkaline media by an alkalinity function determined by an indicator method. However, his data cannot be used for quantitative characterization, since in his measurements the indicator and the solution under study were in different phases. In addition, Schwarzenbach did not show how the indicators he used ionize in alkaline media. The experimental data obtained in the present work on the hydrolysis of caprolactam with satisfactory

with sufficient accuracy fit the following equation

$$\frac{K_{\mathrm{eff}}}{a_{\mathrm{H_2O}} \cdot a_{\pm}} = \text{const}, \tag{3}$$

where $a_\pm$ is the mean ionic activity of aqueous KOH solutions. In view of the fact that equation (3) is obeyed over a wide range of alkali concentrations, there is reason to draw the following conclusions.

The rate-limiting stage of amide hydrolysis includes a water molecule. When the concentration of aqueous KOH solutions is changed, the activity of hydroxyl ions changes in the same way as the activity of potassium ions (when the KOH concentration changes, the activities of the OH^- and K^+ ions change by the same factor). This conclusion may also be justified by the fact that, according to the calculations of Bernal and Fowler, potassium and hydroxyl ions in solutions have one and the same radius ([8]).

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Received
8 XII 1960

REFERENCES

1. K. K. Ingold, *Mechanism of Reactions and Structure of Organic Compounds*, IL, 1960.
2. J. T. Edward, K. A. Terry, *J. Chem. Soc.*, 1957, 3527.
3. S. S. Biechler, R. W. Taft, *J. Am. Chem. Soc.*, **79**, 4927 (1957).
4. M. I. Vinnik, R. S. Ryabova, N. M. Chirkov, *ZhFKh*, **33**, 1993 (1959).
5. R. A. Robinson, R. M. Stokes, *Trans. Farad. Soc.*, **45**, 612 (1949).
6. E. Shibata, J. Kabayashi, S. Furukawa, *J. Chem. Soc. Japan*, **52**, 404 (1931).
7. D. Schwarzenbach, R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1944).
8. J. O. Bernal, R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

Note: Figure translations are in progress. See original paper for figures.