Doklady of the Academy of Sciences of the USSR

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1962

SovietRxiv

Abstract

Full Text

Doklady of the Academy of Sciences of the USSR
1962. Vol. 143, No. 5

PHYSICAL CHEMISTRY

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KINETICS AND MECHANISM OF THE HYDROLYSIS OF BUTYROLACTAM IN AQUEOUS KOH SOLUTIONS

(Presented by Academician V. N. Kondrat͡ ev, October 16, 1961)

In many cases, on the basis of equations that relate the observed rate constant K_{ef} to some property of the medium (the activity of alkali, water, etc.), it is not always possible to draw unambiguous conclusions about the mechanism of the process, since entirely different mechanisms may be described by identical kinetic equations. Therefore, when studying the kinetics of a chemical process it is necessary to determine in what forms the reacting substance may exist in the given medium and which of these forms are reactive. The present work presents the results of a study of the mechanism of hydrolysis of butyrolactam in alkaline medium, in which, along with kinetic measurements, an attempt was made to determine experimentally the reactive particles.

In the hydrolysis of caprolactam (1) in KOH solutions from 1.04 to 45.8%, K_{ef} varies proportionally to the product of the mean ionic activity of the alkali $a_{\pm}$ and the activity of water $a_{\mathrm{H_2O}}$. These data made it possible to conclude that the catalytic action of KOH can be quantitatively characterized by the mean ionic activity $a_{\pm}$, while the rate-limiting stage of the process includes a molecule of water. The absence of changes in the infrared* and ultraviolet spectra of caprolactam upon going from aqueous to alkaline solutions shows that caprolactam is practically entirely in the unionized form. The infrared spectra were recorded only up to 20%, and the ultraviolet spectra up to 40% KOH, owing to the poor solubility of caprolactam in alkali. Thus, in the hydrolysis of caprolactam, on the basis of the above data, we were unable to establish whether the rate-limiting stage is the interaction between the hydroxyl ion and the reagent molecule, as proposed by Edward (2) and Taft (3), or whether the rate-limiting stage is the transformation of the ionized form.

Fig. 1. Change in the extinction coefficients of the bands of butyrolactam at 1395 (1), 1555 (2), 1650 (3), and 1740 cm^{-1} (4) as a function of alkali concentration.

Fig. 1

Figure 1: Fig. 1

Fig. 2. Change in extinction coefficients ($\lambda = 232\,\mathrm{m}\mu$) as a function of alkali concentration.

Figure 2: Fig. 2. Change in extinction coefficients ($\lambda = 232\,\mathrm{m}\mu$) as a function of alkali concentration.

In the case of butyrolactam, substantial changes are observed in the infrared and ultraviolet spectra when the strength of the alkali is varied (Figs. 1, 2). In H_2O, butyrolactam has an absorption band at 1665 cm^{-1}, which is assigned to stretching vibrations of the $C = O$ group. On going to alkaline solutions this band decreases and disappears completely in 49% KOH. In its place there appears a band at 1555 cm^{-1}, the intensity of which increases with increasing alkali strength. In solutions containing more than 30% KOH, two additional bands appear at 1740 and 1395 cm^{-1}. The kinetic measurements were carried out in the same manner as in the work on caprolactam (^{1}). In the present case, re-

* The infrared spectra were studied on an IKS-14 spectrophotometer in cells with germanium windows. Lactam solutions were studied in the form of "crushed drops." The concentration of lactam in alkali was 3-4 mol/l.

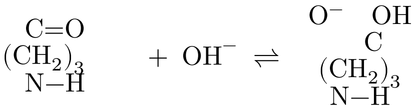
Table 1

KOH, wt. %	K_{eff}, 25°	E_{eff}, kcal/mol	KOH, wt. %	K_{eff}, 25°	E_{eff}, kcal/mol
1.037	−3.84	14.0			
2.250	−3.52	14.2	26.65	−2.42	15.6
4.184	−3.31	14.2	33.58	−2.26	16.4
8.056	−3.03	14.4	40.33	−2.17	17.2
12.41	−2.86	14.8	40.86	−2.15	—
15.76	−2.75	15.4	46.46	−2.22	17.2
20.45	−2.58	15.6	47.69	−2.27	17.2

the reaction is also irreversible, and the monomolecular constant remains constant up to complete conversion of the lactam into the amino acid. Table 1 presents the values of K_{eff} (25°) and the effective activation energies of the process. The values of K_{eff} in the concentration interval from 26.65 to 47.69% KOH were measured directly at 25°; the values of K_{eff} for more dilute solutions were calculated by extrapolation according to the Arrhenius equation from the rate constants at higher temperatures.

Fig. 2. Change in extinction coefficients ($\lambda = 232\,\mathrm{m}\mu$) as a function of alkali concentration

The change in the intensities of the bands at 1665 and 1555 cm^{-1} may be regarded as evidence for the existence of equilibrium forms of the lactam in alkaline solutions. If the band at 1665 cm^{-1} is assigned to the nonionized form of the lactam, then the band at 1555 cm^{-1} should be assigned to the ionized form, formed by addition of hydroxide to the carbonyl group:



$$\begin{matrix} \mathrm{C{=}O} \\ (\mathrm{CH_2})_3 \\ \mathrm{N{-}H} \end{matrix} + \mathrm{OH^-} \rightleftharpoons \begin{matrix} \mathrm{O^-}\quad \mathrm{OH} \\ \mathrm{C} \\ (\mathrm{CH_2})_3 \\ \mathrm{N{-}H} \end{matrix} \qquad \mathrm{(I)}$$

It is known (4) that in alkaline solutions of carboxylic and amino acids there is an absorption band in the region 1540-1560 cm^{-1}, which is assigned to vibrations of the $\mathrm{COO^-}$ group. Since K_{eff} increases with increasing degree of ionization, it may be assumed that the reactive species are the $\mathrm{BOH^-}$ ions. On the basis of data on the hydrolysis of caprolactam we must accept that the limiting stage involves a water molecule. If it is taken into account that under the conditions of butyrolactam hydrolysis the concentrations of the nonionized and ionized forms are comparable, then K_{eff}, $a_{\pm}$, and $a_{\mathrm{H_2O}}$ must be related by the equation*:

$$K_{\mathrm{eff}} = \frac{K_{\mathrm{true}} \cdot a_{\mathrm{H_2O}}}{1 + K_{\mathrm{p}}/a_{\mathrm{OH^-}}}, \qquad (1)$$

where K_{true} is the true rate constant of conversion of $\mathrm{BOH^-}$; $K_{\mathrm{p}} = \frac{a_{\mathrm{B}} \cdot a_{\mathrm{OH^-}}}{a_{\mathrm{BOH^-}}}$ is the equilibrium constant of process I. From a plot constructed in coordinates

$$\frac{a_{\mathrm{H_2O}}}{K_{\mathrm{eff}}} - \frac{1}{a_{\mathrm{OH^-}}},$$

the values $K_{\mathrm{true}} = 4 \cdot 10^{-3}\ \mathrm{min}^{-1}$ and $K_p = 4$ were calculated (Fig. 3). However, equation (1) can describe the experimental data only up to 15.76% KOH. At higher alkali concentrations, increased rate constants are observed in comparison with what would be expected according to equation (1). The kinetic and spectral data can be explained if it is assumed that in concentrated alkali solutions a new, doubly ionized form of the lactam appears:

$$[\text{lactam form}] + \mathrm{OH^-} \rightleftharpoons [\text{doubly ionized form}] + \mathrm{H_2O} \qquad \mathrm{(II)}$$

If it is assumed that the form $\mathrm{BO^{2-}}$ is also reactive and that the limiting stage is the interaction of this ion with a water molecule, then for K_{eff} the following equation will be valid:

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* In the present case and below it is assumed that the ratio of the activity coefficients $f_{\mathrm{BOH^-}}/f_{\neq}$ and $f_{\mathrm{B}}/f_{\mathrm{BOH}}$ does not depend on the alkali concentration.

Fig. 3

Figure 3: Fig. 3

$$K_{\text{eff}} = \frac{K_{\text{true}} \cdot K'_p \cdot \dfrac{(a_{\mathrm{H_2O}})^2}{a_{\mathrm{OH^-}}} + K'_{\text{true}} \cdot a_{\mathrm{H_2O}}}{1 + K'_p \cdot \dfrac{a_{\mathrm{H_2O}}}{a_{\mathrm{OH^-}}} + K_p \cdot K'_p \cdot \dfrac{a_{\mathrm{H_2O}}}{(a_{\mathrm{OH^-}})^2}}, \tag{2}$$

where K'_{true} is the true rate constant of the transformation of $\mathrm{BO^{2-}}$;

$$K'_p = \frac{a_{\mathrm{BOH^-}} \cdot a_{\mathrm{OH^-}}}{a_{\mathrm{BO^{2-}}} \cdot a_{\mathrm{H_2O}}}$$

is the equilibrium constant of process II.

For calculating K'_{true} and K'_p, equation (2) is conveniently represented in the form

$$y = -\frac{1}{K'_p} + \frac{K'_{\text{true}}}{K'_p} \cdot x,$$

where

$$x = \frac{a_{\mathrm{H_2O}}}{K_{\text{eff}}},$$

$$y = -K_p \cdot \frac{a_{\mathrm{H_2O}}}{a_{\mathrm{OH^-}}} \left(\frac{K_{\text{true}} \cdot a_{\mathrm{H_2O}}}{K_p \cdot K_{\text{eff}}} - \frac{1}{a_{\mathrm{OH^-}}} \right) + \frac{a_{\mathrm{H_2O}}}{a_{\mathrm{OH^-}}};$$

$K'_{\text{true}} = 2.62 \cdot 10^{-2}$ min^{-1}, $K'_p = 190$. (Fig. 4)

Apparently, the appearance of absorption bands at 1740 and 1395 cm^{-1} is associated with the formation, in appreciable concentrations, of the doubly ionized form. By analogy with carbonates (^{5}), these bands may be assigned to vibrations of the $\mathrm{COO^{2-}}$ group. The existence of three equilibrium forms of butyrolactam in alkaline solutions is confirmed by the following calculation. From the change in the extinction coefficient of the bands at 1665 cm^{-1}, the concentrations of the nonionized form (C_B) were calculated. Since up to 30% KOH the doubly ionized form is absent, in this range the concentration of the singly ionized form ($C_{\mathrm{BOH^-}}$) can be calculated from the change in

Fig. 3

Fig. 4

Fig. 4

Figure 4: Fig. 4

reaction scheme: lactam + OH^- hydroxylated anion + OH^- dianionic form + H_2O; hydration leads to cyclic hydrogen-bonded intermediates, which give reaction products

Figure 5: reaction scheme: lactam + OH^- hydroxylated anion + OH^- dianionic form + H_2O; hydration leads to cyclic hydrogen-bonded intermediates, which give reaction products

Table 2

KOH, wt. %	[B], %	[BOH^-], %	[B] + [BOH^-], %	KOH, wt. %	[B], %	[BOH^-], %	[B] + [BOH^-], %
H_2O	100	–	100	29.8	64	36	100
10.1	92	8	100	40.2	45	55	100
20.3	82	18	100	49.0	–	67	67

the extinction coefficient both of this same band and of the band at 1555 cm^{-1}. In turn, from the change in the extinction coefficient of the band at 1555 cm^{-1}, the concentration of BOH^- can be determined for solutions containing more than 30% KOH. As is seen from Table 2, precisely in the concentration range where the bands at 1740 and 1395 cm^{-1} appear, the balance with respect to the concentrations of B and BOH^- does not add up, which also serves as evidence for the presence of a third form.

For butyrolactam it is possible to calculate the true activation energy and the pre-exponential factor of the process of transformation of the once-ionized form. According to the calculations, in 26% KOH all the lactam is present in the form BOH^-, and E_{eff} represents the sum of the true activation energy and the heat ΔH_{H_2O}, characterizing the change in the activity of water with temperature in 26% KOH. Since $\Delta H_{H_2O} \sim 0$, $E_{\text{true}} = 15.6$ kcal/mol, and the pre-exponential factor $A_{\text{true}} = 4.5 \cdot 10^{-16}$ cm^3/molecule • sec.

On the basis of the data obtained, the following mechanism of lactam hydrolysis in alkali may be adopted:

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Received
12 X 1961

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