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Abstract

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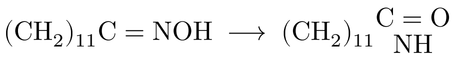
KINETICS AND MECHANISM OF THE BECKMANN REARRANGEMENT OF CYCLODODECANONE OXIME IN SULFURIC ACID MEDIUM

(Presented by Academician N. N. Semenov, 27 IV 1963)

The Beckmann rearrangement of oximes is one of the important methods of organic synthesis, and an extensive literature has been devoted to elucidating its mechanism. The rearrangement is an acid-base process. The mechanisms of rearrangement proposed by various authors have been discussed in detail in review articles ($^{1-4}$).

In the present work, the kinetics of the Beckmann rearrangement in sulfuric acid medium was studied in detail, and on the basis of kinetic data the mechanism of the elementary rate-limiting step was established. Cyclododecanone oxime was chosen as the object of study



$$(\mathrm{CH_2})_{11}\mathrm{C=NOH} \longrightarrow (\mathrm{CH_2})_{11}\begin{matrix}\mathrm{C=O}\\ \mathrm{NH}\end{matrix}$$

The rate of rearrangement of the oxime into lactam was investigated by a spectrophotometric method. The acid concentration was determined from the electrical conductivity (^{5}).

The process of conversion of cyclododecanone oxime into lactam is monomolecular with respect to the oxime and irreversible.

Table 1 gives the experimental values of K_{eff} for various temperatures and various concentrations of sulfuric acid.

Table 1

H_2SO_4, % by weight	T, °C	K_{eff}, min^{-1}	H_2SO_4, % by weight	T, °C	K_{eff}, min^{-1}	H_2SO_4, % by weight	T, °C	K_{eff}, min^{-1}	H_2SO_4, % by weight	T, °C	K_{eff}, min^{-1}
88.07	87.7	$6.2 \cdot 10^{-3}$	90.33	87.7	$9.10 \cdot 10^{-2}$	99.46	25	$1.91 \cdot 10^{-3}$	99.954	25	$4.47 \cdot 10^{-2}$
88.07	78.6	$2.48 \cdot 10^{-2}$	90.33	78.6	$3.77 \cdot 10^{-2}$	99.65	25	$3.1 \cdot 10^{-3}$	99.987	25	$7.95 \cdot 10^{-2}$
88.07	68.7	$8.41 \cdot 10^{-3}$	90.33	68.7	$1.31 \cdot 10^{-2}$	99.77	25	$5.25 \cdot 10^{-3}$	100.0	25	$1.26 \cdot 10^{-1}$
88.07	58.9	$2.57 \cdot 10^{-3}$	90.33	58.9	$4.15 \cdot 10^{-3}$	99.78	25	$5.89 \cdot 10^{-3}$	0.08% SO_3	25	$1.91 \cdot 10^{-1}$
88.07	49.3	$7.85 \cdot 10^{-4}$	90.33	49.3	$1.21 \cdot 10^{-3}$	99.79	25	$7.95 \cdot 10^{-3}$	0.34% SO_3	25	0.51
93.29	87.7	$1.58 \cdot 10^{-1}$	95.67	87.7	$2.52 \cdot 10^{-1}$	1.38% SO_3	24.9	1.16	0.53% SO_3	25	0.69
93.29	87.7	$1.55 \cdot 10^{-1}$	95.67	78.6	$1.04 \cdot 10^{-1}$	1.38% SO_3	24.9	1.14	0.7% SO_3	25	0.89
93.29	78.6	$6.9 \cdot 10^{-2}$	95.67	68.7	$3.89 \cdot 10^{-2}$	1.38% SO_3	20.0	0.64	1% SO_3	25	0.98
93.29	68.7	$2.48 \cdot 10^{-2}$	95.67	58.9	$1.35 \cdot 10^{-2}$	1.38% SO_3	15	0.35	1.36% SO_3	25	1.12
93.29	58.9	$7.75 \cdot 10^{-3}$	95.67	49.3	$3.43 \cdot 10^{-3}$	1.38% SO_3	10	0.18	3.86% SO_3	25	1.57
93.29	49.3	$2.51 \cdot 10^{-3}$	99.85	25	$8.32 \cdot 10^{-3}$	11.4% SO_3	25	1.51	3.86% SO_3	25	1.57
97.67	78.6	$1.88 \cdot 10^{-1}$	99.856	25	$1.07 \cdot 10^{-2}$	11.4% SO_3	20	0.85	3.86% SO_3	20	0.85
97.67	68.7	$7.05 \cdot 10^{-2}$	99.86	25	$1.23 \cdot 10^{-2}$	11.4% SO_3	15	0.45	3.86% SO_3	15	0.44
97.67	58.9	$2.71 \cdot 10^{-2}$	99.886	25	$1.44 \cdot 10^{-2}$	11.4% SO_3	10	0.24	3.86% SO_3	10	0.23
97.67	49.3	$8.67 \cdot 10^{-3}$	99.918	25	$2.24 \cdot 10^{-2}$	33% SO_3	25	1.67			
99.20	25	$1.02 \cdot 10^{-3}$	99.927	25	$2.89 \cdot 10^{-2}$	33% SO_3	20	0.91			
99.23	25	$1.26 \cdot 10^{-3}$	99.946	25	$3.16 \cdot 10^{-2}$	33% SO_3	15	0.47			
						33% SO_3	10	0.23			

Table 2 gives the effective constants K_{eff} for $T = 25°$ as a function of the strength of sulfuric acid. The values of K_{eff} in the interval 88.07%–97.67% H_2SO_4 were obtained by extrapolation according to the Arrhenius equation from data for higher temperatures.

Hammett (6) compared the rate constants of the rearrangement of acetophenone oxime with the acidity function and showed that in the range from 93.6% to 98.7% H_2SO_4 a linear dependence holds:

$$\log K + H_0 = \text{const.} \tag{1}$$

A similar relation for the case of the rearrangement of cyclododecanone oxime is obeyed for acid solutions containing from 90 to 99% H_2SO_4. As is seen from the data of Table 2, in stronger acids and in oleum this relation is not obeyed. In studying the hydrolysis of cyclohexanone oxime

Table 2

H_2SO_4, % by weight	lg K_{eff} $T =$ 25°	H_0	lg $a_{H_2SO_4}$	lg a_{H_2O}	lg $K_{eff} + H_0$	lg $K_{eff} \times a_{H_2O}$	lg $\frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4} K_{eff}}$.
90,36	−4,32	−8,6	8,96	−3,69	−12,92	−8,01	
93,34	−4,04	−9,01	9,18	−4,19	−13,05	−8,23	
95,70	−3,72	−9,36	9,33	−4,62	−13,08	−8,34	
97,70	−3,36	−9,71	9,44	−5,17	−13,07	−8,53	
99,20	−2,99	−10,17	9,50	−5,95	−13,16	−8,94	
99,23	−2,90	−10,19	9,50	−5,93	−13,09	−8,88	
99,46	−2,72	−10,32	9,51	−6,25	−13,04	−8,97	−8,16
99,65	−2,51	−10,47	9,52	−6,58	−12,98	−9,09	−8,14
99,77	−2,28	−10,64	9,52	−6,95	−12,92	−9,23	−8,11
99,78	−2,23	−10,66	9,52	−6,98	−12,89	−9,21	−8,07
99,79	−2,1	−10,67	9,52	−7,02	−12,87	−9,12	−7,97
99,85	−2,08	−10,79	9,52	−7,30	−12,87	−9,38	−8,11
99,856	−1,97	−10,80	9,53	−7,33	−12,77	−9,30	−8,03
99,86	−1,91	−10,82	9,53	−7,35	−12,73	−9,26	−7,97
99,886	−1,84	−10,88	9,53	−7,50	−12,72	−9,34	−7,99
99,918	−1,65	−11,0	9,53	−7,78	−12,65	−9,43	−7,96
99,927	−1,54	−11,04	9,53	−7,89	−12,58	−9,42	−7,91
99,946	−1,50	−11,13	9,53	−8,08	−12,65	−9,58	−7,98
99,954	−1,35	−11,18	9,53	−8,20	−12,53	−9,55	−7,90
99,987	−1,1	−11,40	9,53	−8,86	−12,50	−9,96	−8,09
100,0	−0,9	−11,46	9,53	−9,09	−12,36	−9,99	−8,06
0,08% SO_3	−0,72	−11,56	9,53	−9,38	−12,28	−10,10	−8,07
0,34% SO_3	−0,29	−11,74	9,53	−10,03	−12,03	−10,32	−8,11
0,53% SO_3	−0,16	−11,83	9,53	−10,26	−11,99	−10,42	−8,12

H_2SO_4, % by weight	lg K_{eff} $T =$ 25°	H_0	lg $a_{H_2SO_4}$	lg a_{H_2O}	lg $K_{eff} +$ H_0	lg $K_{eff} \times$ a_{H_2O}	lg $\frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4} K_{eff}}$.
0,7% SO_3	−0,05	−11,88	9,52	−10,49	−11,93	−10,45	−8,09
1% SO_3	−0,01	−11,95	9,52	−10,50	−11,96	−10,51	−8,08
1,36% SO_3	+0,05	−12,92	9,02	−10,64	−11,97	−10,63	−8,13
3,86% SO_3	+0,20						
11,4% SO_3	+0,20						
33% SO_3	+0,22						

Note. The values of $a_{H_2SO_4}$ and a_{H_2O} from 90,36% to 99% H_2SO_4 were taken from work (9).

(7) In aqueous solutions of hydrochloric and sulfuric acids, we came to the conclusion that in dilute acids (about $0,05\,N$) cyclohexanone oxime is completely ionized, while in concentrated acid solutions the ionized form associates with the acid anion into an ion pair:

$$\mathrm{RNOH_2^+ + HSO_4^- \rightleftarrows RNOH_2^+ \cdot HSO_4^-}. \qquad (2)$$

The Beckmann rearrangement of oximes proceeds at a measurable rate in sulfuric acid solutions containing more than 90% H_2SO_4. It is precisely in such solutions that, as the acid strength increases, the concentration of HSO_4^- anions (8) decreases, and therefore an increase in the degree of ionization of the ion pair according to equation (2) should be expected. The dependence of the rate constant on the acid strength cannot be quantitatively explained by a change in the concentration of the protonated form of the oxime $RNOH_2^+$. We therefore believe that the ions $RNOH_2^+$ are not reactive in the present process. The linear relationship between $\lg K_{eff}$ and H_0 could be explained by assuming that, as the strength of sulfuric acid increases, protonation of the ion pair (the oxime salt) occurs,

$$\mathrm{RNOH_2^+ \cdot HSO_4^- + H^+ \rightleftarrows RNOH_2^+ \cdot H_2SO_4},$$

and ions $RNOH_2^+ \cdot H_2SO_4$ are formed, which are the reactive species in the Beckmann rearrangement. In that case, one would expect that near 100% H_2SO_4, where the acidity of the medium is high, because of

Fig. 1

Figure 1: Fig. 1

Fig. 1

At a significant degree of protonation of the ion pair, K_{eff} will increase more slowly than follows from equation (1). In fact, as was already mentioned above, with increasing sulfuric acid concentration $\lg K_{\text{eff}} + H_0$ increases. This fact cannot be explained by a change in the activity coefficient of the ion pairs $\text{RNOH}_2^+ \cdot \text{HSO}_4^-$, and therefore we consider that such a mechanism does not occur. In the range of 99-100% H_2SO_4, the thermodynamic activity of water $a_{\text{H}_2\text{O}}$ changes more sharply than does the acidity of the medium (^{9}). Therefore it is reasonable to assume that the reactive oxime species are formed upon dehydration of either the ions RNOH_2^+ or the ion pairs $\text{RNOH}_2^+ \cdot \text{HSO}_4^-$ present in solution. The experimentally found dependence of K_{eff} on the acidity function, the activity of water, and the thermodynamic activity of sulfuric acid $a_{\text{H}_2\text{SO}_4}$ is quantitatively explained on the assumption that the rate of the limiting stage is determined by the concentration of the species $\text{RN}^+\text{HSO}_4^-$, formed upon dehydration of the ion pair $\text{RNOH}_2^+ \cdot \text{HSO}_4^-$:

$$\text{RNOH}_2^+ \cdot \text{HSO}_4^- \rightleftharpoons \text{RN}^+ \cdot \text{HSO}_4^- + \text{H}_2\text{O}. \tag{3}$$

Let us denote the equilibrium constant of reaction (2) by K_C, and that of reaction (3) by K_2

$$K_C = \frac{a_{\text{RNOH}_2^+} \cdot a_{\text{HSO}_4^-}}{a_{\text{RNOH}_2^+ \cdot \text{HSO}_4^-}}; \qquad K_2 = \frac{a_{\text{RNOH}_2^+ \cdot \text{HSO}_4^-}}{a_{\text{RN}^+ \cdot \text{HSO}_4^-} \cdot a_{\text{H}_2\text{O}}}.$$

Expressing the concentrations $C_{\text{RNOH}_2^+}$ and $C_{\text{RNOH}_2^+ \cdot \text{HSO}_4^-}$ through the equilibrium constants and $C_{\text{RN}^+ \cdot \text{HSO}_4^-}$, after substitution into the balance equation:

$$C_{\text{RNOH}_2^+} + C_{\text{RNOH}_2^+ \cdot \text{HSO}_4^-} + C_{\text{RN}^+ \cdot \text{HSO}_4^-} = C_0$$

we obtain an equation for the dependence of $C_{\text{RN}^+ \cdot \text{HSO}_4^-}$ on parameters characterizing the properties of the medium:

$$C_{\text{RN}^+ \cdot \text{HSO}_4^-} = \frac{C_0}{1 + K_C' \cdot K_2' \dfrac{a_{\text{H}_2\text{O}} \cdot h_0}{a_{\text{H}_2\text{SO}_4}} + K_2' a_{\text{H}_2\text{O}}}.$$

$$K_2' = K_2 \frac{f_{\text{RN}^+ \cdot \text{HSO}_4^-}}{f_{\text{RNOH}_2^+ \cdot \text{HSO}_4^-}}; \qquad K_C' \cdot K_2' = 4 K_2 K_C K_{2A} \cdot \frac{f_{\text{RN}^+ \cdot \text{HSO}_4^-}}{f_{\text{B}}} \cdot \frac{f_{\text{BH}^+}}{f_{\text{RNOH}_2^+}}.$$

K_{2A} is the thermodynamic dissociation constant of the acid anion:

$$\mathrm{HSO_4^-} \rightleftharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}}.$$

We assume that in concentrated sulfuric acid the ratios of activity coefficients

$$\frac{f_{\mathrm{RN^+\cdot HSO_4^-}}}{f_{\mathrm{RNOH_2^+\cdot HSO_4^-}}} \quad \text{and} \quad \frac{f_{\mathrm{RN^+\cdot HSO_4^-}}}{f_{\mathrm{B}}} \cdot \frac{f_{\mathrm{BH^+}}}{f_{\mathrm{RNOH_2^+}}}$$

are constant.

If the rate of the limiting stage is determined by the concentration of dehydrated species, then:

$$K_{\text{eff}} = \frac{K_{\text{true}}}{1 + K'_C \cdot K'_2 \dfrac{a_{\mathrm{H_2O}} \cdot h_0}{a_{\mathrm{H_2SO_4}}} + K'_2 \cdot a_{\mathrm{H_2O}}}. \tag{4}$$

If the relative concentration of the species $\mathrm{RN^+ \cdot HSO_4^-}$ is small, then:

$$\frac{1}{K_{\text{eff}} \cdot a_{\mathrm{H_2O}}} = \frac{K'_C K'_2}{K_{\text{true}}} \cdot \frac{h_0}{a_{\mathrm{H_2SO_4}}} + \frac{K'_2}{K_{\text{true}}}. \tag{5}$$

As is seen from Fig. 1, the experimental data fit this equation satisfactorily. From the slope and intercept of the straight line in the coordinates

$$\left(\frac{1}{K_{\text{eff}} a_{\mathrm{H_2O}}};\ \frac{h_0}{a_{\mathrm{H_2SO_4}}} \right)$$

the values

$$\frac{K'_2}{K_{\text{ist}}} = 1.25 \cdot 10^8$$

and $K'_C = 1$ were calculated. Judging from these values, already near 100% $\mathrm{H_2SO_4}$, owing to the decrease in the concentration of $\mathrm{HSO_4^-}$ anions, practically all the oxime is present in the form of $\mathrm{RNOH_2^+}$ ions, and

$$K'_C K'_2 \frac{a_{\mathrm{H_2O}} \cdot h_0}{a_{\mathrm{H_2SO_4}}} \gg K'_2 a_{\mathrm{H_2O}} + 1.$$

In this case the following dependence must hold:

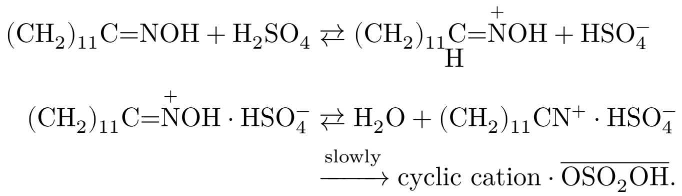
$$\lg K_{\text{eff}} \frac{a_{\mathrm{H_2O}} \cdot h_0}{a_{\mathrm{H_2SO_4}}} = \text{const.}$$

As follows from the data of Table 2, such a dependence is indeed observed for acid solutions containing more than 99.4% H_2SO_4, and in oleum. This dependence is also observed in solutions where K_{eff} does not depend on the concentration of SO_3. Consequently, in such solutions all the oxime is present in the form of $RNOH_2^+$ ions. The independence of the rate constant K_{eff} from the concentration of the catalyst in acid-catalyzed processes is usually regarded as the attainment of conditions under which all the reagent is present in the reactive form. In the case of the Beckmann rearrangement of cyclododecanone oxime, the constancy of K_{eff} is explained not by conversion of all the reagent into the reactive form, but by the constancy of the product

$$\frac{a_{\mathrm{H_2O}} \cdot h_0}{a_{\mathrm{H_2SO_4}}}$$

in oleum containing from 5 to 10% SO_3.

Below are given the equilibrium and rate-limiting stages of the Beckmann transformation of cyclododecanone oxime in an acid medium:



$$(\mathrm{CH_2})_{11}\mathrm{C{=}NOH} + \mathrm{H_2SO_4} \rightleftarrows (\mathrm{CH_2})_{11}\underset{\mathrm{H}}{\mathrm{C}}{=}\overset{+}{\mathrm{N}}\mathrm{OH} + \mathrm{HSO_4^-}$$

$$(\mathrm{CH_2})_{11}\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{OH} \cdot \mathrm{HSO_4^-} \rightleftarrows \mathrm{H_2O} + (\mathrm{CH_2})_{11}\mathrm{CN^+} \cdot \mathrm{HSO_4^-}$$
$$\xrightarrow{\text{slowly}} \text{cyclic cation} \cdot \overline{\mathrm{OSO_2OH}}.$$

Upon dilution of the acid with water, the rearrangement product is converted into the nonionized form of the lactam:

$$\text{cyclic cation} \cdot \overline{\mathrm{OSO_2OH}} + 2\mathrm{H_2O} \xrightarrow{\text{rapidly}} \text{lactam} + \mathrm{H_3O^+} + \mathrm{HSO_4^-}.$$

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