140. V.A.Kargin, V.A.Kabanov, I.M.Papisov, and V.P.Zubov, Dokl.Akad.Nauk SSSR, 141, 389 (1961).
141. V.A.Kargin, V.A.Kabanov, and I.M.Papissov, J.Polymer Sci., C, No. 4, 767 (1963).
142. I.M.Papisov, V.A.Kabanov, and V.A.Kargin, Vysokomol. Soed., 7, 1779 (1965).
143. D.E.Ilyina, B.A.Krentsel, and G.E.Semenido, J.Polymer Sci., C, No. 4, 999 (1963).
144. H.C.Anderson, J.Polymer Sci., C, No. 6, 175 (1964).
145. A.I.Tsvetkov, D.A.Vital', and M.Yu.Tel'tovt, Izv.Akad. Nauk SSSR, Ser.Geol., 97 (1955).
146. E.K.Keler, see p.239 in Ref. 4.
147. E.V.Mashintsev, V.M.Neimark, and B.N.Egorov, Vestnik Akad.Nauk SSSR, No. 6, 64 (1963).
148. L.Erdey, F.Paulik, and J.Paulik, Acta Chim.Acad.Sci. Hung., 10, 61 (1956).
149. N.Grassie and H.W.Melville, Proc.Roy.Soc., 199A, 14 (1949).
150. G.J.Gordon, "The Stabilisation of Synthetic Polymers" (Translated into Russian), GKhI, Moscow, 1963, p.167.
151. B.Ya.Teitel'baum and L.G.Berg, Zhur.Anal.Khim., 8, 152 (1953).
152. L.G.Berg and K.P.Pribylov, Zavod.Lab., 28, 828 (1962).
153. H.G.Langer and R.S.Gohlke, Analyt.Chem., 35, 1301 (1963).
154. H.G.Langer, R.S.Gohlke, and D.H.Smith, Analyt.Chem., 37, 433 (1965).
155. V.A.Vol'nova, see p.121 in Ref. 4.
156. G.B.Ravich and G.G.Tsurinov, "Fazovaya Struktura Triglitseridov" (The Phase Structure of Triglycerides), Izd.Akad.Nauk SSSR, Moscow, 1952.
157. V.A.Kargin and T.I.Sogolova, Zhur.Fiz.Khim., 23, 530, 551 (1949).
158. T.I.Sogolova and G.L.Slonimskii, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 6, 389 (1961).
159. B.L.Tsetlin, V.N.Gavrilov, N.A.Velikovskaya, and V.V.Kochkin, Zavod.Lab., 22, 352 (1956).
160. B.Ya.Teitel'baum and M.P.Dianov, Vysokomol.Soed., 3, 594 (1961).
161. V.D.Gerasimov, G.A.Kuznetsov, and L.N.Fomenko, Zavod.Lab., 29, 996 (1963).
162. B.Ya.Teitel'baum, Vysokomol.Soed., 4, 655 (1962).
163. W.Wendlandt, "Thermal Methods of Analysis", Interscience, New York, 1964.

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U.D.C. 547.288.5

KINETICS AND MECHANISM OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES UNDER THE CATALYTIC ACTION OF SULPHURIC ACID AND OLEUM

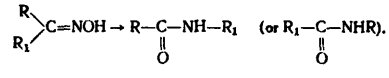
M. I. Vinnik and N. G. Zarakhani

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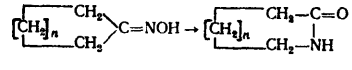
I. INTRODUCTION

In 1886 Beckmann[1] first carried out the conversion of oximes into acid amides. This reaction is called the Beckmann rearrangement. In the rearrangement of the ketoximes *N*-substituted amides of carboxylic acids are formed:



The Beckmann rearrangement was at first used only under laboratory conditions as a convenient and simple preparative method and as a method for establishing the structure of ketones. This reaction made it possible to synthesise a large number of amides, and also various amino-acids, which either were unknown or were obtained by complex processes of poor efficiency.

Recently the Beckmann rearrangement of a series of cyclic aliphatic ketoximes has attained great importance as an industrial method of obtaining lactams:



The rearrangement of cyclohexanone oxime into ϵ-caprolactam is of special importance. The industrial production of the lactam of ϵ-aminocapronic acid is one of the multi-tonnage processes of contemporary chemical industry. Wallach[2] obtained ϵ-caprolactam from cyclohexanone oxime under the catalytic action of sulphuric acid in 1900. ϵ-Caprolactam is the raw material for the production of one of the most important products of contemporary synthetic chemistry — caprolactam polyamide.

Lactams with a greater number of carbon atoms than ϵ-caprolactam also find application in industry, since they have been used as the basis of syntheses of polyamide resins with different physicochemical and mechanical properties.

The Beckmann rearrangement is an acid–base process and proceeds under the catalytic action of a large quantity of the reagents. The catalysts for this reaction are protic and aprotic acids. Concentrated sulphuric acid is usually employed, but phosphoric acid, phosphorus pentachloride, aryl sulphonyl chlorides, aluminium chloride, hydrogen bromide, and hydrogen fluoride are also used as catalysts. "Beckmann mixture" is an active catalyst for the rearrangement; it consists of a saturated solution of hydrogen chloride in glacial acetic acid, to which is then added ~ 20% acetic anhydride. This reagent is used under conditions when the oxime reacting is insoluble in other solvents.

Because of the great theoretical and practical interest of the Beckmann rearrangement, the literature devoted to an explanation of its mechanism is voluminous. There are

now over six hundred papers on the Beckmann rearrangement of various ketoximes and aldoximes. The most important information on this subject has been surveyed in detail in the review articles of Jones[3], Knunyants and Fabrichnyi[4], Donaruma and Heldt[5], and Zil'berman[6], and in Houben-Weyl[7].

Unfortunately, among the many publications devoted to the study of the mechanism of the Beckmann rearrangement, very few are of a quantitative nature. However, the ideas developed on the basis of synthetic data and also on the structure of the final and intermediate products of the rearrangement are undoubtedly of interest; such data are quite valuable for understanding the mechanism of the reaction.

The present review considers the kinetic data and mechanism of the Beckmann rearrangement of alicyclic ketoximes in aqueous solutions of sulphuric acid and in oleum. Sulphuric acid and solutions of sulphur trioxide in sulphuric acid are effective catalysts of this process; they are used in the industrial manufacture of ϵ-caprolactam. Parameters are known for these solutions which characterise the thermodynamic and catalytic properties used for establishing the mechanism of ionisation of the reagents and the mechanism of the limiting stage of the chemical process.

II. SOME PROPERTIES OF CONCENTRATED AQUEOUS SOLUTIONS OF SULPHURIC ACID

The Hammett acidity function H_0, the thermodynamic activity of the acid a_{HA}, and the thermodynamic activity of the water in the acid a_{H_2O} are quantitative characteristics of the catalytic activity of aqueous solutions of strong acids. It should be noted that in an investigation of the detailed mechanism of chemical reactions in acid media and particularly their early stages, a knowledge of the accurate values of H_0, a_{HA}, and a_{H_2O} of the solution in which the reaction is proceeding becomes particularly important. Fig.1 gives the values of H_0, $a_{H_2SO_4}$, and a_{H_2O} at 25° for concentrated aqueous solutions of sulphuric acid and dilute oleum. The values of $a_{H_2SO_4}$ were taken from Giauque and coworkers[8], the value of H_0 from Vinnik and coworkers[9], and the activity of water from Giauque and coworkers[8] and Vinnik and Ryabova[10].

The ionic and molecular compositions of aqueous solutions of sulphuric acid are also known[11,12]. Information about the equilibrium composition of the solution is needed to explain the mechanism of the physicochemical interaction of the reagent with the medium. The following species are in equilibrium in aqueous solutions of sulphuric acid: undissociated sulphuric acid H_2SO_4, the anions HSO_4^- and SO_4^{2-}, and also the ion pair $HSO_4^-.H_3O^+$ (or the hydrate of the acid $H_2SO_4.H_2O$). Fig. 2 shows the concentration of the ions HSO_4^- and SO_4^{2-}, the undissociated H_2SO_4 molecules, and the ion pairs $HSO_4^-.H_3O^+$ (or the species $H_2SO_4.H_2O$) as a function of the sulphuric acid concentration, after Zarakhani and Vinnik[12]. In dilute aqueous solutions of sulphuric acid, alicyclic oximes undergo hydrolysis. In aqueous solutions of the acid with >85–90% H_2SO_4, oximes are almost completely converted into lactams. As will be shown below, the rate constant of the Beckmann rearrangement increases with the concentration of the acid in the interval 85–100% H_2SO_4. In very dilute oleum the rate constant rises with increase in the concentration of sulphur trioxide in the solution. For these particular solutions the following

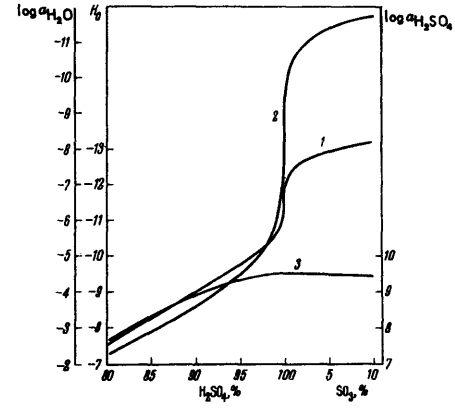


Fig. 1. Thermodynamic activity of water and acid and acidity function of concentrated aqueous solutions of sulphuric acid at 25°:
1) H_0; 2) $\log a_{H_2O}$; 3) $\log a_{H_2SO_4}$.

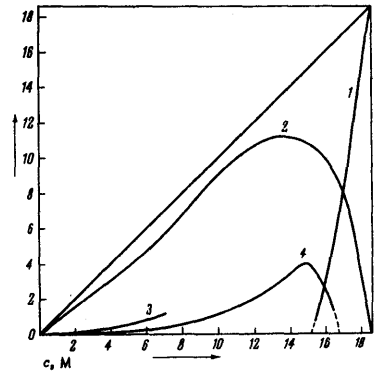


Fig. 2. Concentrations of ions and species in aqueous solutions of sulphuric acid:
1) H_2SO_4; 2) HSO_4^-; 3) SO_4^{2-}; 4) $HSO_4^-.H_3O^+$.

regularities are observed in the change of the parameters listed above. As the concentration of the acid is increased the acidity of the medium rises, the acidity function H_0 falls ($H_0 = -\log h_0$), the thermodynamic activity of the acid rises, and in the range 99–100% H_2SO_4 it is almost constant; the thermodynamic activity of water falls; the concentration of the HSO_4^- anions also decreases.

In oleum, as the concentration of sulphur trioxide is increased the concentration of the $H_3SO_4^+$ and $HS_2O_7^-$ ions rises but the concentration of the HSO_4^- anions falls[10]. The water activity a_{H_2O} also falls[10]. The activity of sulphuric acid $a_{H_2SO_4}$ in oleum falls — on account of the bonding by sulphur trioxide into pyrosulphuric acid and of ionisation, but apparently the decrease is slight.

III. SOME INFORMATION ABOUT THE MECHANISM OF IONISATION OF ALICYCLIC KETOXIMES IN AQUEOUS SOLUTIONS OF STRONG ACIDS

In acid solutions oximes are present in various forms coexisting in equilibrium. This has been shown by kinetic experiments on the hydrolysis of oximes in dilute aqueous

solutions of sulphuric and hydrochloric acids and also from information on the effect of additions of oxime on the acidity of concentrated solutions of sulphuric acid. As the concentration of the acid is increased, the effective rate constant of the hydrolysis of cyclohexanone oxime[13] and cyclopentanone oxime[14] at first rise, reach a maximal value, and then fall sharply. The maximal value of the rate constant of the hydrolysis is observed in extremely dilute solutions of the acid (see Fig. 3). For example, with cyclohexanone oxime the maximal rate constant is reached in 4.65×10^{-3}–6.52×10^{-3} M solutions of hydrochloric acid[15] and in 1.39×10^{-3}–5.2×10^{-3} M solutions of sulphuric acid[13]. The increase in the rate constant of the hydrolysis is connected with the appearance of reactivity in the protonated form of the oxime† $RNOH_2^+$:

$$RNOH + H^+ \rightleftarrows RNOH_2^+.$$

The decrease in the rate constant of the hydrolysis in such dilute solutions of acids can be explained only by change of the protonated form of the oxime into an unreactive form during the hydrolysis of the ion pair $RNOH_2^+.A^-$:

$$RNOH_2^+ + Cl^- \rightleftarrows RNOH_2^+ \cdot Cl^-,$$

$$RNOH_2^+ + HSO_4^- \rightleftarrows RNOH_2^+ \cdot HSO_4^-.$$

Hence from data on the dependence of the rate constant on acid concentration it follows that in aqueous solutions of strong acids alicyclic ketoximes are present in at least three forms: un-ionised RNOH, protonated $RNOH_2^+$, and ion pairs $RNOH_2^+.HSO_4^-$. The ion pair can also be named as a salt of the oxime‡. Calculations based on the data from hydrolysis show that alicyclic ketoximes are very strong bases. For example, cyclopentanone oxime and cyclohexanone oxime are already completely protonated in 0.05 *N* sulphuric acid[13,14] and hydrochloric acid[15] solutions. In more concentrated solutions the protonated form is completely converted into ion pairs. Cyclohexanone oxime in 2.5% H_2SO_4[13] and cyclopentanone oxime in 10% H_2SO_4[14] are found almost completely as the ion pairs $RNOH_2^+.HSO_4^-$. However, owing to the change in the activity coefficients of the ion pairs and protonated species in highly concentrated H_2SO_4 solutions, dissociation of the ion pairs occurs with formation of protonated species $RNOH_2^+$. For example, in 99% sulphuric acid the ion pairs of suberone oxime are completely dissociated and almost all the oxime in solution is present as the ions $RNOH_2^+$.

This conclusion is based on experiments on the influence of additions of oxime on the acidity of sulphuric acid solutions. In highly concentrated sulphuric acid small quantities of the dissolved substance change the acidity of the medium differently according to whether protonated species or ion pairs are formed. A change in the properties of the medium is reflected in the degree of ionisation of indicators used to measure the acidity function.

Water is known to be completely ionised in sulphuric acid solutions with >90% H_2SO_4:[16]

$$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-.$$

† Here and subsequently the following symbols are used: un-ionised form of oxime, RNOH; protonated form of oxime, $RNOH_2^+$; salt of oxime, $RNOH_2^+.A^-$; dehydrated salt, $RN^+.HSO_4^-$.

‡ The structure of the complex which consists of the protonated form of the oxime and the anion of the acid is unknown. It can be either an ion pair (a salt), or an ester of the oxime and sulphuric acid.

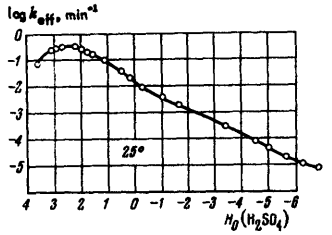


Fig. 3. Variation of the rate constant of the hydrolysis of cyclohexanone oxime with the acidity function H_0 of sulphuric acid.

TABLE 1. Effect of additions of suberone oxime on the ionisation of 2,4,6-trinitroaniline at 25°†.

H_2SO_4 concn., wt. %	Acid taken, g	Oxime added, g	$\log c_B/c_{BH^+}$ of indicator	H_0	H_0^*
99.145	6.684	—	−0.68	−10.64	—
	6.684	0.0868	−0.58	−10.54	−10.56
	6.684	0.281	−0.42	−10.38	−10.40
	6.684	0.413	−0.33	−10.29	−10.32
	6.684	0.544	−0.26	−10.22	−10.23

† H_0^* is the acidity function of a solution of 99.145% H_2SO_4 to which instead of the oxime an equal number of moles of water are added.

When the test substance changes the acidity function of the solution as does an equimolar amount of water, then it is present completely as the protonated form. When ion pairs are formed the change in the acidity function will be less than in the dissolution of the same number of moles of water. This criterion can be used to study the ionisation mechanism in 98–100% sulphuric acid where it is possible to use such small additions of the substance that concentrations can be used instead of activities in the expression for the equilibrium constant. Table 1 gives values of the acidity function for 99.145% acid with addition of suberone oxime. 2,4,6-Trinitroaniline was used as the indicator in measuring the acidity function. Relatively small additions of the oxime (up to 1 M) alter the acidity function of the medium by the same amount as equimolar additions of water. Consequently, oximes are present in these solutions as the protonated species $RNOH_2^+$.

IV. RATE CONSTANTS OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES

In connection with the analysis of kinetic data on the Beckmann rearrangement it is desirable to note which methods are used to determine the degree of conversion of oxime into lactam. In some published works the degree of conversion of oxime into lactam was determined from the quantity of unreacted oxime. Wichterle and Roček, in an investigation of the Beckmann rearrangement of cyclohexanone oxime in oleum[17–19], determined the concentration of oxime in the specimens by a colorimetric method[20], based on the formation of blue 1-chloro-1-nitrosocyclohexane:

$$C_6H_{10}NOH + Cl_2 = 2HCl + C_6H_{10}(Cl)NO.$$

Chlorinated urea was used as the chlorinating agent. Ogata and coworkers[21], who investigated the rearrangement of cyclohexanone oxime in sulphuric and perchloric

acids, determined the unreacted oxime in the form of the 2,4-dinitrophenylhydrazone. The analysis of oximes by their conversion into 2,4-dinitrophenylhydrazones was also done in the work by Pearson and coworkers[22]. Methods based on the isolation of the oxime or on converting it into a coloured compound are laborious and making an analysis with their use requires a relatively large quantity of oxime. These methods can be used for investigating the kinetics of relatively slow processes, since 2–3 min are needed for sampling. To obtain a kinetic curve, not less than ten points are needed and then the time for half-conversion should be ~ 10–20 min.

It is convenient to use a spectrophotometric method for the common determination of oxime and lactam in the reaction mixture. This method is based on differences in the molar absorptivities of the oxime and the lactam in solutions of sulphuric acid and oleum. At 222 nm the molar absorptivity of the oxime is considerably greater than that of the lactam. The spectrophotometric method allows the kinetics of the process to be studied at low oxime concentrations with hardly any effect on the properties of the medium (10^{-3}–10^{-4} M), and here there is no necessity to remove samples and the optical cuvette itself serves as the reaction vessel. Therefore the spectrophotometric method can be used to measure the rate of unimolecular processes which take place relatively rapidly, even those where the time for half-conversion is 30–40 s. Ultraviolet spectroscopy has been used[23-26]. Heldt[27] used a spectrophotometer for measurements in the infrared region of the spectrum to study the kinetics of the Beckmann rearrangement of the esters of oximes with *p*-toluenesulphonic acid. Thanks to this, he succeeded in determining the frequency of the absorption bands of intermediate products of the chemical process.

The Beckmann rearrangement of alicyclic ketoximes is an irreversible process. In experiments where the concentration of the oxime in the acid is low the process is first order relative to the oxime and the unimolecular constant remains unchanged right up to complete conversion of the oxime into the lactam. Tables 2–8 give the available published rate constants for the rearrangement of alicyclic ketoximes in sulphuric acid and in oleum.

The kinetics of the rearrangement of cyclohexanone oxime has been investigated in several works and these data are given in Tables 3–6. We have made experiments at low oxime concentrations[26].

Ogata and coworkers[21] studied the rearrangement of cyclohexanone oxime in relatively dilute aqueous solutions of sulphuric and perchloric acids. The sulphuric acid concentration was varied from 48.4 to 79.1% H_2SO_4 at 90° and from 89.4 to 99.6% at 60°. The perchloric acid concentration was varied within the range 47.4–59.9% $HClO_4$, at 90°. As regards the experiments in 48.4–79.1% H_2SO_4 solutions there is no doubt that under such conditions the oxime did not undergo complete hydrolysis. Since during the course of the experiments the unreacted oxime was determined the rate constants quoted[21] probably reflect the consumption of the oxime in the overall-process, including both hydrolysis and the Beckmann rearrangement. The rate constants obtained[21] for 89.4–99.6% acid cannot be doubted and are given in Table 5. Under identical conditions these constants are less than our values of the constants[26]. Pearson and coworkers[28] determined the rate constants of the Beckmann rearrangement of certain aliphatic and alicyclic ketoximes in 94.5% sulphuric acid. At the same temperature the rate constant for cyclopentanone oxime, cyclohexanone oxime,

TABLE 2. Rate constants of the Beckmann rearrangement of cyclopentanone oxime in sulphuric acid and in oleum (after Zarakhani and coworkers[25]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
91.74	70	$0.35\cdot10^{-2}$	99.85	40	$2.65\cdot10^{-2}$
	80	$0.91\cdot10^{-2}$		50	$7.71\cdot10^{-2}$
	90	$2.97\cdot10^{-2}$		60	$26.4\cdot10^{-2}$
	97	$5.64\cdot10^{-2}$		70	$78.2\cdot10^{-2}$
93.70	70	$0.48\cdot10^{-2}$		80	$21.4\cdot10^{-1}$
	80	$1.45\cdot10^{-2}$	99.91	25	$6.02\cdot10^{-3}$
	90	$3.90\cdot10^{-2}$	99.924	25	$1.00\cdot10^{-2}$
	97	$7.75\cdot10^{-2}$	99.933	25	$9.34\cdot10^{-3}$
95.42	70	$0.83\cdot10^{-2}$	99.94	25	$9.12\cdot10^{-3}$
	80	$2.48\cdot10^{-2}$	99.95	25	$1.29\cdot10^{-2}$
	80	$2.16\cdot10^{-2}$	99.986	25	$2.29\cdot10^{-2}$
	90.5	$5.94\cdot10^{-2}$	SO_3, wt. %		
	97	$12.5\cdot10^{-2}$			
97.18	70	$1.69\cdot10^{-2}$	0.1	25	$7.08\cdot10^{-2}$
	80	$4.40\cdot10^{-2}$	0.185	25	$8.51\cdot10^{-2}$
	90	$10.8\cdot10^{-2}$	0.22	25	0.10
	97.2	$22.4\cdot10^{-2}$	0.39	25	0.135
99.04	25	$2.95\cdot10^{-4}$	1.20	25	0.234
99.43	25	$5.62\cdot10^{-4}$	5.50	20	0.172
99.73	25	$1.05\cdot10^{-3}$		25	0.324
99.81	25	$2.24\cdot10^{-3}$		30	0.610
99.84	25	$3.09\cdot10^{-3}$	11.80	25	0.288
			17.20	25	0.309
			22.50	25	0.331
			27.00	25	0.308
				30	0.660
				40	1.920

TABLE 3. Rate constants of the Beckmann rearrangement of cyclohexanone oxime in sulphuric acid and in oleum (after Zarakhani and Vinnik[26]).

H_2SO_4, wt. %	T, °C	10^2k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	10^2k_{eff}, min^{-1}
	97	6.01	99.50	25	0.34
82.29	90	3.57	99.73	25	0.81
	80	1.41	99.74	60	26.0
	70	0.45		50	8.84
86.03	97	11.4		40	2.76
	97	11.3	99.81	25	1.17
	90	6.44	99.842	25	1.82
	80	2.29	99.85	25	1.35
	70	0.88	99.90	25	2.57
	60	0.28	99.91	25	3.02
			99.91	25	3.38
89.94	97	21.8	99.924	25	4.26
	90	10.8	99.933	25	4.79
	80	4.9	99.936	25	4.68
	70	1.67	99.945	25	5.75
	60	0.59	99.95	25	6.16
	50	0.20	99.95	25	6.6
92.73	97	32.0	99.97	25	7.75
	90	14.95	99.986	25	15.5
	80	6.62	100.00	25	17.4
	70	2.15			
	60	0.84	SO_3, wt. %		
	50	0.30			
94.71	90	26.3			
	80	10.6	0.1	25	33.1
	70	4.14	0.185	25	34.7
	60	1.56	0.22	25	42.6
	50	0.50	0.39	25	56.2
	40	0.15	0.42	25	56.2
97 37	90	54.0	1.2	25	91.1
	80	22.0	2.22	10	16 0
	70	9.37		15.2	61.0
	60	2.88		25	108.0
	50	1.00		30	190.0
	40	0.34	7.1	10.2	18.5
98.21	90	92.0		15	35.3
	80	38.7		20	61.0
	70	15.6		25	104.0
	60	5.83		30	190.0
			15.4	10	15.5
				15	32.2
				20	56.0
				25	116.0
				30	207.0

TABLE 4. Rate constants k_{eff} of the Beckmann rearrangement of cyclohexanone oxime in oleum (after Wichterle and Roček [19]).

SO_3, wt. %	T, °C	$10^2 k_{eff}$, min^{-1}
0	30	0.04
1	30	0.69
2	30	1.08
3	30	1.68
5	30	1.92
7.5	30	2.10
10	30	1.92
12.5	30	2.10
15	30	2.72
20	30	3.80
28	30	5.50

TABLE 5. Rate constants of the Beckmann rearrangement of cyclohexanone oxime in sulphuric acid solutions at 60° (after Ogata and coworkers [21]).

H_2SO_4, wt. %	Initial oxime concentration, M	$10^2 k_{eff}$, min^{-1}
89.4	0.311	0.61
93.2	0.346	0.93
96.1	0.305	1.51
96.1	0.208	1.50
96.1	0.153	1.54
98.0	0.284	2.35
99.0	0.297	3.36
99.6	0.304	4.86

TABLE 6. Rate constants of the rearrangement of some aliphatic and alicyclic ketoximes in 94.5% sulphuric acid (after Scott and coworkers [28]).

Ketone	T, °C	$10^3 k_{eff}$, min^{-1}	Ketone	T, °C	$10^3 k_{eff}$, min^{-1}
Acetone	90 66	1.17 ± 0.01	Di-isobutyl ketone	40.43	1.47 ± 0.00
	95.82	2.10 ± 0.03		50.59	5.34 ± 0.06
	98.43	2.81 ± 0.11		60.39	17.3 ± 0.1
	107.52	7.43 ± 0.02	Cyclopentanone	51.00	1.17 ± 0.01
Diethyl ketone	50.9	1.48 ± 0.01		60.92	4.09 ± 0.04
	60.31	4.49 ± 0.07		69.90	11.8 ± 0.1
	70.47	13.9 ± 0.3	Cyclohexanone	30.0	0.557 ± 0.003
Di-isopropyl ketone	21.86	2.36 ± 0.01		40.9	2.31 ± 0.04
	30.66	7.55 ± 0.04		50.9	7.85 ± 0.12
	40.9	26.9 ± 0.1	Cycloheptanone	40.82	0.51 ± 0.01
				51.03	1.92 ± 0.06
				60.62	6.20 ± 0.1

and cycloheptanone oxime (suberone oxime) differ somewhat from the data given in Tables 2, 3, and 7. It is impossible to find the precise reason for this discrepancy. It can be assumed that the decrease in the rate constants is connected with the fact that the experiments [28] were made at relatively large concentrations of the oximes (~ 0.1 M). These results are given in Table 6. The same table also gives the rate constants for the Beckmann rearrangement of certain aliphatic ketoximes in 94.5% sulphuric acid. Although in this article the discussion of the Beckmann rearrangement of aliphatic ketoximes is being especially avoided, these figures are nevertheless of interest for a comparison of the reactivity of various ketoximes.

Wichterle and Roček [17-19] investigated the Beckmann rearrangement of cyclohexanone oxime in oleum. This rearrangement is an exothermic process, the ΔH for this reaction in the gas phase being 22 kcal $mole^{-1}$. Since the

TABLE 7. Rate constants of the Beckmann rearrangement of suberone oxime in solutions of sulphuric acid and in oleum (after Vinnik and Zarakhani [24]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
83 1	96	$3.0 \cdot 10^{-2}$	87.89	96	$5.7 \cdot 10^{-2}$
	90	$1.57 \cdot 10^{-2}$		90.2	$3.55 \cdot 10^{-2}$
85.34	96	$4.65 \cdot 10^{-2}$		90	$3.35 \cdot 10^{-2}$
	90	$2.30 \cdot 10^{-2}$		80	$1.02 \cdot 10^{-2}$
	90	$2.22 \cdot 10^{-2}$		70	$3.31 \cdot 10^{-2}$
	80	$7.62 \cdot 10^{-3}$		60	$9.50 \cdot 10^{-2}$
	70	$2.26 \cdot 10^{-3}$	93.20	90	$8.63 \cdot 10^{-2}$
90.30	96	$9.20 \cdot 10^{-2}$		80	$3.10 \cdot 10^{-2}$
	90	$5.0 \cdot 10^{-2}$		70	$1.07 \cdot 10^{-2}$
	80	$1.71 \cdot 10^{-2}$		60	$3.22 \cdot 10^{-3}$
	70	$5.90 \cdot 10^{-3}$		50	$1.04 \cdot 10^{-3}$
	60	$1.91 \cdot 10^{-3}$	97.13	90	$21.1 \cdot 10^{-2}$
95.23	90	$13.7 \cdot 10^{-2}$		80	$8.85 \cdot 10^{-2}$
	80	$5.06 \cdot 10^{-2}$		70	$3.15 \cdot 10^{-2}$
	70	$1.71 \cdot 10^{-2}$		60	$9.20 \cdot 10^{-3}$
	60	$5.50 \cdot 10^{-3}$		50	$3.36 \cdot 10^{-3}$
	50	$1.75 \cdot 10^{-3}$	99.0	25	$4.08 \cdot 10^{-4}$
99.46	25	$6.6 \cdot 10^{-4}$	99.23	25	$4.68 \cdot 10^{-4}$
99.49	25	$7.1 \cdot 10^{-4}$	99.39	70	$17.9 \cdot 10^{-2}$
99.65	25	$1.17 \cdot 10^{-3}$		60	$6.4 \cdot 10^{-2}$
99.67	80	1.15		50	$1.96 \cdot 10^{-2}$
	70	$4.04 \cdot 10^{-1}$		40	$4.77 \cdot 10^{-3}$
	60	$1.33 \cdot 10^{-1}$		40	$4.67 \cdot 10^{-3}$
	50	$3.18 \cdot 10^{-2}$		25	$8.12 \cdot 10^{-4}$
	50	$2.92 \cdot 10^{-2}$	99.77	25	$1.95 \cdot 10^{-3}$
	40	$1.09 \cdot 10^{-2}$	99.77	25	$2.04 \cdot 10^{-3}$
	40	$1.07 \cdot 10^{-2}$	99.78	25	$2.13 \cdot 10^{-3}$
	25	$1.32 \cdot 10^{-3}$	99.85	25	$3.09 \cdot 10^{-3}$
			99.86	25	$4.57 \cdot 10^{-3}$
			99.886	25	$5.37 \cdot 10^{-3}$
SO_3, wt. %			99.910	25	$5.90 \cdot 10^{-3}$
			99.927	25	$1.07 \cdot 10^{-2}$
0.08	25	$6.32 \cdot 10^{-2}$	99.946	25	$1.17 \cdot 10^{-2}$
0.34	25	0.19	99.950	25	$1.51 \cdot 10^{-2}$
0.53	25	0.25	99.978	25	$2.76 \cdot 10^{-2}$
0.70	25	0.29	99.987	25	$3.39 \cdot 10^{-2}$
1.00	25	0.37	100	25	$5.0 \cdot 10^{-2}$
1.36	25	0.41			
5.00	25	0.48			
6.00	25	0.48			
7.5	25	0.49			
8.2	25	0.48			
8.45	25	0.49			
8.7	25	0.51			
10.3	25	0.49			

experiments were made with a relatively high concentration of oxime (~ 0.5 M), to avoid considerable overheating caprolactam was added to the reactor in addition to the oxime. Table 4 gives the rate constants for the rearrangement which they obtained.

In carrying out the reaction in oleum the rate constant is lowered by a high concentration of the oxime and also by additions of the lactam. The following facts may be quoted as an illustration. The rate constants of the Beckmann rearrangement of cyclohexanone oxime in oleum with 0.025-0.65 wt. % SO_3 at 25° have been determined [26] at ketoxime concentrations varying from 1.7×10^{-3} M to 32.4×10^{-3} M. Such concentrations of the oxime are almost without effect on the rate constant. These results are shown in Table 9. In the same table are given the rate constants for oleum with 1% SO_3, obtained by Wichterle and Roček [18].

In their experiments [18], the oxime concentration was ~ 0.5 M and together with this additions of caprolactam were made (14 g per 15 g oleum). This constant, even at 30°, is much less than the constant at 25° obtained with low oxime concentrations. This shows that additions of large amounts of oxime and lactam significantly lower the catalytic activity of oleum. As already mentioned above, low rate constants are also obtained in aqueous solutions of sulphuric acid in working with relatively large amounts of

TABLE 8. Rate constants of the Beckmann rearrangement of cyclododecanone oxime in sulphuric acid and in oleum (after Vinnik and Zarakhani[23]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
88.07	87.7	$6.2 \cdot 10^{-2}$	90.33	87.7	$9.10 \cdot 10^{-2}$
	78.6	$2.48 \cdot 10^{-2}$		78.6	$3.77 \cdot 10^{-2}$
	68.7	$8.41 \cdot 10^{-3}$		68.7	$1.31 \cdot 10^{-2}$
	58.9	$2.57 \cdot 10^{-3}$		58.9	$4.15 \cdot 10^{-3}$
	49.3	$7.85 \cdot 10^{-4}$		49.3	$1.21 \cdot 10^{-3}$
93.29	87.7	$1.58 \cdot 10^{-1}$	95.67	87.7	$2.52 \cdot 10^{-1}$
	87.7	$1.35 \cdot 10^{-1}$		78.6	$1.04 \cdot 10^{-1}$
	78.6	$6.9 \cdot 10^{-2}$		68.7	$3.89 \cdot 10^{-2}$
	68.7	$2.48 \cdot 10^{-2}$		58.9	$1.35 \cdot 10^{-2}$
	58.9	$7.75 \cdot 10^{-3}$		49.3	$3.43 \cdot 10^{-3}$
	49.3	$2.51 \cdot 10^{-3}$	99.85	25	$8.32 \cdot 10^{-3}$
97.67	78.6	$1.88 \cdot 10^{-1}$	99.856	25	$1.07 \cdot 10^{-2}$
	68.7	$7.05 \cdot 10^{-2}$	99.86	25	$1.23 \cdot 10^{-2}$
	58.9	$2.71 \cdot 10^{-2}$	99.886	25	$1.44 \cdot 10^{-2}$
	49.3	$8.67 \cdot 10^{-3}$	99.918	25	$2.24 \cdot 10^{-2}$
99.20	25	$1.02 \cdot 10^{-2}$	99.927	25	$2.89 \cdot 10^{-2}$
99.23	25	$1.26 \cdot 10^{-2}$	99.946	25	$3.46 \cdot 10^{-2}$
99.46	25	$1.91 \cdot 10^{-2}$	99.954	25	$4.47 \cdot 10^{-2}$
99.65	25	$3.1 \cdot 10^{-2}$	99.987	25	$7.95 \cdot 10^{-2}$
99.77	25	$5.25 \cdot 10^{-2}$	100.0	25	$1.26 \cdot 10^{-1}$
99.78	25	$5.89 \cdot 10^{-2}$			
99.79	25	$7.95 \cdot 10^{-2}$	SO_3, wt. %		
SO_3, wt. %			0.08	25	$1.91 \cdot 10^{-1}$
			0.34	25	$0.51 \cdot 10^{-1}$
1.38	24.9	1.16	0.53	25	0.69
	24.9	1.14	0.7	25	0.89
	20.0	0.64	1	25	0.98
	15	0.35	1.36	25	1.12
	10	0.18	3.86	25	1.57
11.4	25	1.51		25	1.57
	20	0.85		20	0.85
	15	0.45		15	0.44
	10	0.24		10	0.28
33	25	1.67			
	20	0.91			
	15	0.47			
	10	0.23			

TABLE 9. Effect of additions of the oxime and the lactam on the rate constant of the Beckmann rearrangement of cyclohexanone oxime in oleum.

T, °C	SO_3, wt. %	Cyclohexanone concn. $\times 10^3$, M	k_{eff}, min^{-1}	T, °C	SO_3, wt. %	Cyclohexanone concn. $\times 10^3$, M	k_{eff}, min^{-1}
25	0.65	1.01	0.810	25	0.40	2.06	0.546
		1.51	0.810			3.04	0.585
		2.82	0.770			4.73	0.540
		2.83	0.753			13.5	0.535
		3.69	0.695			19.7	0.558
		3.79	0.690	25	0.17	2.3	0.364
		7.51	0.604			7.35	0.334
		8.15	0.702			26.0	0.345
		12.7	0.615	25	0.025	1.73	0.215
		16.7	0.712			2.16	0.222
						30.3	0.184
						32.4	0.188
				30	1.0		$0.69 \cdot 10^{-2}$

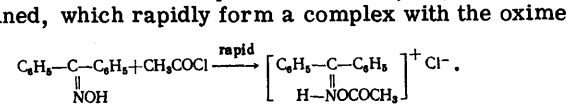
oxime (0.15–0.35 M). This should be taken into account in investigations where the rate constants are determined to provide information about the reactivity of substances of different chemical structure.

V. MECHANISM OF THE BECKMANN REARRANGEMENT OF OXIMES

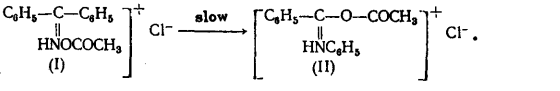
Until recently information on the mechanism of the Beckmann rearrangement of oximes was based on investigations of a preparative nature. Despite the fact that such investigations did not concern alicyclic ketoximes, it is helpful to analyse them, since it would be expected that in some of these conditions the rearrangement mechanism will not differ significantly for different ketoximes.

Sluiter[29] considered that not the oximes as such, but their esters, undergo the rearrangement. The exquisite preparative procedures of Kuhara[30] are based on this hypothesis.

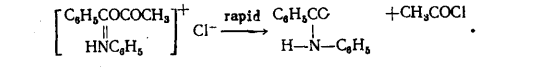
In studying the action of acid chlorides on the Beckmann rearrangement of benzophenone oxime, Kuhara observed that the ester of benzophenone and benzenesulphonic acid is rearranged at a very high rate. Under these conditions the chloroacetate exhibits much less reactivity and the acetate hardly undergoes any rearrangement. Benzophenone oximium acetate undergoes rearrangement on the addition of hydrogen chloride. Kuhara proposed the following mechanism. In the presence of HCl, acyl chlorides are obtained, which rapidly form a complex with the oxime:



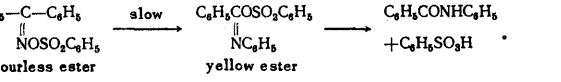
The isomerisation of this complex is the limiting stage:



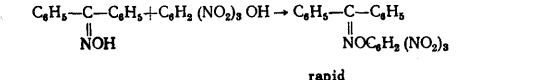
Complex (II) is an addition product of acetyl chloride and benzanilide. It decomposes rapidly with formation of benzanilide:

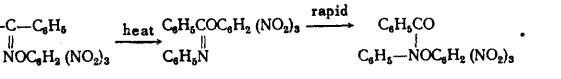


Kuhara showed that the benzenesulphonate which is formed in the reaction of benzenesulphonyl chloride with the sodium salt of benzophenone oxime is colourless. In time, this ester isomerises into another ester, which is yellow. In the presence of moisture (in moist air) the yellow ester is converted into benzanilide:

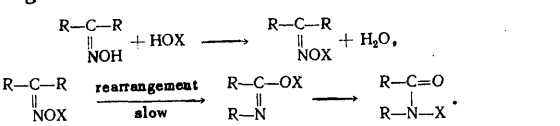


Chapman[31–34] obtained similar results for the Beckmann rearrangement of benzophenone oxime under the action of picric acid. The oxime and the acid form benzophenone oxime *O*-picryl ether which isomerises on heating into *N*-phenylbenzimidoyl *O*-picryl ether; the latter is rapidly converted into a salt of an anilide.





Chapman considers[31] that the formation of ethers can be explained by the catalytic action of many substances on the process of the Beckmann rearrangement of oximes. In the general example the mechanism can be represented by the following scheme:



According to Chapman, the chlorides and oxide chlorides of phosphorus and sulphur, aryl sulphonyl chlorides, and, probably, sulphuric acid also act in this way. On carrying out the rearrangement under the action of hydrogen chloride in dichloroethane solution, the kinetic curves for the process have an autocatalytic nature [31]. The action of hydrogen chloride cannot be explained by the mechanism given above. This is also shown by the results of Stieglitz and Peterson [35,36], who showed that *N*-chloro-compounds of the type R–C(=NCl)–R do not undergo the Beckmann rearrangement.

Pearson and Ball [37] consider that the mechanism for the Beckmann rearrangement proposed by Kuhara and Chapman explains the catalytic action of sulphuric acid in this process.

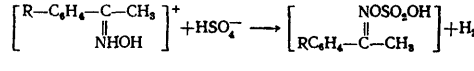
Firstly the oxime and acid form a salt-like complex. This stage is exothermic and in aqueous solutions of the acid it is reversible.

Stage I:



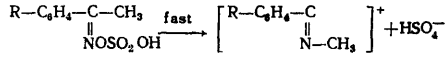
Then the salt-like complex loses water with the formation of the sulphate.

Stage II:



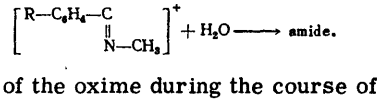
Unlike Chapman, Pearson and Ball assume that the dehydration stage, as a result of which sulphate is formed, is the slowest in the process. The sulphate is rapidly rearranged into a dehydrated ionised form of the amide (stage IIIa).

Stage IIIa:



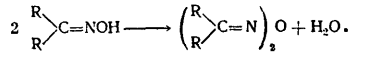
In aqueous solutions the ionised form of the amide rapidly adds on water (stage IIIb).

Stage IIIb:

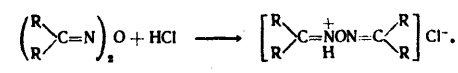


Dehydration of the oxime during the course of the Beckmann rearrangement has been demonstrated in experiments of Brodskii and Miklukhin [38,39]. They carried out the Beckmann rearrangement of benzophenone oxime in ethereal solution under the catalytic action of phosphorus pentachloride at 15°. After the process had ended, the reaction mixture was diluted with water containing an excess of ^{18}O. In the benzanilide obtained, the ^{18}O content was the same as in the water used for the saponification. In acid and neutral media benzanilide does not exchange this oxygen.

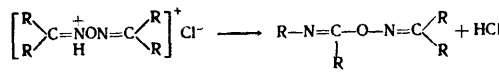
Stephen and Staskun [40] proposed another mechanism for the Beckmann rearrangement of ketoximes. In the opinion of these authors, the ketoximes form anhydrides:



Hydrogen chloride adds on to the molecule of the anhydride and forms a salt:

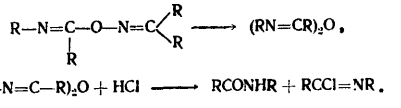


In the salt, according to the authors [40], the symmetry of the anhydride is destroyed, thanks to which it is rearranged into a ketoximimidate:



ketoximimidate

This rearranges into the imidoyl anhydride, which in the presence of HCl is converted into an amide:



This mechanism was proposed to explain the catalytic action of aprotic acids. According to this mechanism the reactive form is formed from the anhydride of the ketoxime. When the conditions are such that the fraction of the oxime present as anhydride is small, the process will be second order in relation to the oxime.

There are still no facts to confirm this conclusion. The authors of this scheme assume that the proton is attached to one of the nitrogen atoms. The possibility of attachment of the proton to the oxygen atom is not excluded.

We will analyse the kinetic demonstrations of the mechanism of the limiting stage of the Beckmann rearrangement of alicyclic ketoximes in sulphuric acid. As shown above, in aqueous solutions of sulphuric acid oximes are found in three forms: the un-ionised form RNOH, the protonated form $RNOH_2^+$, and the ion pairs $RNOH_2^+.HSO_4^-$. It is evident that no one of these forms in isolation is capable of reaction in the Beckmann rearrangement. The un-ionised form is not reactive since this process does not take place without a catalyst. The protonated form is also incapable of reaction in this process, since in solutions of the acid where almost all the oxime is present in this form the rate of the process rises on increasing the acidity of the medium. Under conditions where the rate constant of the Beckmann rearrangement rises the concentration of the ion pairs falls; in solutions with $>99\%$ H_2SO_4 the fraction of ion pairs calculated on the total oxime concentration can be neglected. Consequently, the ion pairs $RNOH_2^+.HSO_4^-$ are not reactive in this process.

In dilute oleum with increase in the SO_3 concentration in the solution the rate constant of the Beckmann rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime rises to a certain value and then remains constant on further increase of the oleum concentration (Fig. 4).

For unimolecular processes the value of the rate constant is often reached under conditions where all the reagent is present in a reactive form. This form can be either a complex of the reagent with the catalyst or an ionised form produced by interaction of the reagent with the solution containing the catalyst. The ratio of the observed rate constant to the limiting value of the rate constant expresses the ratio of the concentration of the reactive species to the total concentration of the reagent under the given conditions.

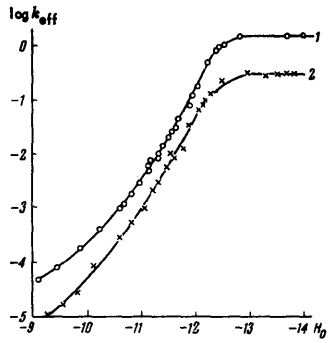


Fig. 4. Variation of log k_{eff} with H_0 in the Beckmann rearrangement of cyclopentanone oxime (2) and cyclododecanone oxime (1) in sulphuric acid and in oleum at 25°.

Judging from this criterion, in aqueous solutions of sulphuric acid right up to 100% H_2SO_4 the fraction of reactive species is low in comparison with the oxime concentration. This makes it possible to find the mechanism of formation of the reactive species from the dependence of the observed rate constants on the thermodynamic activities of the acid and water, and also the acidity of the acid solutions. In this it is understood that the kinetic experiments were made with the same low concentrations of oxime so that their effect on the values of the parameters mentioned could be neglected. The activity of the acid and water and the acidity functions for the range we are interested in are known for 25°. To be able to compare the values of k_{eff} with the quantities mentioned over wide ranges at 25° for relatively dilute solutions the rate constants were extrapolated from higher temperatures. Tables 10–13 give the values of k_{eff} at 25° for cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime

TABLE 10. Rate constants of the Beckmann rearrangement of cyclopentanone oxime at 25°*.

H_2SO_4, wt. %	log k_{eff}, min^{-1}	log a_{H_2O}	H_0	log $a_{H_2SO_4}$	log $k_{eff}a_{H_2O}$	$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}} k_{eff}$
91.74	—4.98	—3.92	—9.24	9.07	—8.90	
93.70	—4.76	—4.26	—9.54	9.20	—9.02	
95.42	—4.55	—4.55	—9.81	9.32	—9.10	
97.18	—4.05	—5.00	—10.10	9.41	—9.05	
99.04	—3.53	—5.85	—10.58	9.50	—9.38	—8.30
99.43	—3.25	—6.21	—10.79	9.51	—9.46	—8.18
99.73	—2.98	—6.82	—11.06	9.52	—9.80	—8.26
99.81	—2.65	—7.10	—11.19	9.52	—9.75	—8.08
99.842	—2.51	—7.26	—11.27	9.53	—9.77	—8.03
99.85	—2.45	—7.30	—11.28	9.53	—9.75	—8.10
99.91	—2.22	—7.70	—11.46	9.53	—9.92	—7.99
99.924	—2.00	—7.82	—11.53	9.53	—9.82	—7.82
99.933	—2.03	—7.90	—11.56	9.53	—9.93	—7.90
99.94	—2.04	—7.97	—11.60	9.53	—10.01	—7.94
99.95	—1.89	—8.12	—11.64	9.53	—10.01	—7.87
99.986	—1.44	—8.86	—11.85	9.53	—10.30	—7.98
SO_3, wt. %						
0.1	—1.15	—9.58	—12.05	9.53	—10.73	—8.21
0.185	—1.07	—9.77	—12.12	9.53	—10.84	—8.25
0.22	—1.00	—9.83	—12.15	9.53	—10.83	—8.20
0.39	—0.87	—10.10	—12.25	9.53	—10.97	—8.25
1.2	—0.63	—10.67	—12.47	9.52	—11.30	—8.35

* The activity of the acid $a_{H_2SO_4}$ is taken from Giauque and coworkers [8], the activity of water from Giauque and coworkers [8] and Vinnik and Ryabova [10], and H_0 from Ryabova and coworkers [9].

TABLE 11. Rate constants of the Beckmann rearrangement of cyclohexanone oxime at 25°.

H_2SO_4, wt. %	log k_{eff}	log a_{H_2O}	H_0	log $a_{H_2SO_4}$	log $k_{eff}a_{H_2O}$	$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}} k_{eff}$
82.29	—4.74	—2.55	—7.88	+7.99	—7.29	—7.40
86.03	—4.38	—3.07	—8.45	8.50	—7.45	—7.50
89.94	—4.05	—3.63	—9.02	8.92	—7.68	—7.58
92.73	—3.86	—4.09	—9.42	9.14	—7.95	—7.67
94.71	—3.59	—4.42	—9.69	9.27	—8.01	—7.59
97.37	—3.28	—5.06	—10.13	9.41	—8.34	—7.62
98.21	—2.96	—5.38	—10.32	9.46	—8.34	—7.48
99.50	—2.47	—6.31	—10.84	9.51	—8.78	—7.45
99.73	—2.09	—6.82	—11.05	9.52	—8.91	—7.38
99.74	—2.36	—6.85	—11.08	9.52	—9.21	—7.65
99.81	—1.93	—7.10	—11.19	9.52	—9.03	—7.36
99.842	—1.74	—7.26	—11.26	9.53	—9.00	—7.27
99.85	—1.87	—7.29	—11.28	9.53	—9.16	—7.41
99.90	—1.59	—7.61	—11.43	9.53	—9.20	—7.30
99.91	—1.52	—7.70	—11.46	9.53	—9.22	—7.29
99.91	—1.47	—7.70	—11.46	9.53	—9.17	—7.24
99.924	—1.37	—7.82	—11.51	9.53	—9.19	—7.21
99.933	—1.32	—7.90	—11.55	9.53	—9.22	—7.20
99.936	—1.33	—7.97	—11.57	9.53	—9.30	—7.26
99.945	—1.24	—8.00	—11.61	9.53	—9.24	—7.16
99.95	—1.21	—8.12	—11.64	9.53	—9.33	—7.22
99.95	—1.18	—8.12	—11.64	9.53	—9.30	—7.19
99.97	—1.11	—8.50	—11.74	9.53	—9.61	—7.40
99.986	—0.81	—8.88	—11.84	9.53	—9.69	—7.38
100	—0.76	—9.09	—11.94	9.53	—9.84	—7.43
SO_3, wt. %						
0.1	—0.48	—9.58	—12.06	9.53	—10.06	—7.51
0.185	—0.46	—9.77	—12.13	9.53	—10.23	—7.61
0.22	—0.37	—9.83	—12.16	9.53	—10.20	—7.55
0.39	—0.25	—10.10	—12.26	9.53	—10.35	—7.60
0.42	—0.25	—10.14	—12.27	9.53	—10.39	—7.63
1.2	—0.04	—	—	—	—	—
2.22	+0.03	—	—	—	—	—
7.1	+0.02	—	—	—	—	—
15.4	+0.06	—	—	—	—	—

TABLE 12. Rate constants of the Beckmann rearrangement of suberone oxime at 25°.

H_2SO_4, wt. %	log k_{eff}, min^{-1}	H_0	log $a_{H_2SO_4}$	log a_{H_2O}	log $k_{eff}a_{H_2O}$	$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}} k_{eff}$
85.34	—5.48	—8.34	8.42	—2.98	—8.46	—
87.89	—5.21	—8.73	8.72	—3.33	—8.54	
90.30	—4.76	—9.07	8.96	—3.69	—8.45	
93.20	—4.45	—9.48	9.17	—4.16	—8.61	
95.23	—4.23	—9.76	9.30	—4.52	—8.75	
97.13	—3.9	—10.08	9.41	—4.99	—8.89	
98.05	—3.7	—10.28	9.45	—5.31	—9.01	
99.23	—3.33	—10.68	9.50	—5.98	—9.31	—8.13
99.39	—3.09	—10.76	9.51	—6.16	—9.25	—8.00
99.46	—3.18	—10.81	9.51	—6.25	—9.43	—8.13
99.49	—3.15	—10.83	9.51	—6.30	—9.45	—8.13
99.65	—2.93	—10.96	9.52	—6.58	—9.51	—8.07
99.67	—2.88	—10.98	9.52	—6.65	—9.53	—8.07
99.77	—2.71	—11.11	9.52	—6.95	—9.66	—8.07
99.77	—2.69	—11.11	9.52	—6.95	—9.64	—8.05
99.78	—2.67	—11.13	9.52	—6.98	—9.65	—8.04
99.85	—2.51	—11.28	9.52	—7.30	—9.81	—8.05
99.86	—2.34	—11.31	9.53	—7.35	—9.69	—7.91
99.886	—2.27	—11.39	9.53	—7.50	—9.77	—7.91
99.910	—2.23	—11.47	9.53	—7.69	—9.92	—7.98
99.918	—2.08	—11.50	9.53	—7.78	—9.86	—7.89
99.927	—1.97	—11.53	9.53	—7.88	—9.85	—7.85
99.946	—1.93	—11.62	9.53	—8.08	—10.01	—7.92
99.960	—1.82	—11.70	9.53	—8.28	—10 10	—7.93
99.978	—1.56	—11.83	9.53	—8.67	—10.23	—7.87
99.987	—1.47	—11.89	9.53	—8.86	—10.33	—7.97
100	—1.30	—11.95	9.53	—9.09	—10 39	—7.97
SO_3, wt. %						
0.08	—1.2	—12.05	9.53	—9.38	—10.58	—8.06
0.34	—0.72	—12.23	9.53	—10.03	—10.75	—8.05
0 53	—0.60	—12 32	9.53	—10.26	—10.86	—8.07
0.7	—0.52	—12.37	9.52	—10.40	—10.92	—8.07
1	—0.42	—12.44	9.52	—10.50	—10.92	—8.00
1.36	—0 39	—12.51	9.52	—10.64	—11.03	—8.04

TABLE 13. Rate constants of the Beckmann rearrangement of cyclododecanone oxime at 25°.

H_2SO_4, wt. %	$\log k_{eff}$	H_0	$\log a_{H_2SO_4}$	$\log a_{H_2O}$	$\log k_{eff}a_{H_2O}$	$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}} k_{eff}$
90.36	−4.32	− 9.10	8.96	−3.69	−8.01	
93.34	−4.04	− 9.45	9.18	−4.19	−8.23	
95.70	−3.72	− 9.85	9.33	−4.62	−8.34	
97.70	−3.36	−10.20	9.44	−5.17	−8.53	
99.20	−2.99	−10.61	9.50	−5.95	−8.94	
99.23	−2.50	−10.68	9.50	−5.98	−8.88	
99.46	−2.72	−10.81	9.51	−6.25	−8.97	−7.67
99.65	−2.51	−10.96	9.52	−6.58	−9.09	−7.65
99.77	−2.28	−11.12	9.52	−6.95	−9.23	−7.69
99.78	−2.23	−11.14	9.52	−6.98	−9.21	−7.59
99.79	−2.1	−11.15	9.52	−7.02	−9.12	−7.49
99.85	−2.08	−11.28	9.52	−7.30	−9.38	−7.62
99.856	−1.97	−11.30	9.53	−7.33	−9.30	−7.53
99.86	−1.91	−11.31	9.53	−7.35	−9.26	−7.48
99.886	−1.84	−11 38	9.53	−7.50	−9.34	−7.49
99.918	−1.65	−11.50	9.53	−7.78	−9.43	−7.46
99.927	−1.54	−11.55	9.53	−7.88	−9.42	−7.40
99.946	−1.50	−11.63	9.53	−8.08	−9.58	−7.48
99.954	−1.35	−11.68	9.53	−8.20	−9.55	−7.40
99.987	−1.1	−11.87	9.53	−8.86	−9.96	−7.62
100.0	−0.9	−11.94	9.53	−9.09	−9.99	−7.58
SO_3, wt. %						
0.08	−0.72	−12.03	9.53	− 9.38	−10.10	−7.59
0.34	−0.29	−12.23	9.53	−10.03	−10.32	−7.62
0.53	−0.16	−12.31	9.53	−10.26	−10.42	−7.64
0.7	−0.05	−12.38	9.52	−10.40	−10.45	−7.59
1	−0.01	−12.43	9.52	−10.50	−10.51	−7.60
1.36	+0.05	−12.51	9.52	−10.64	−10.63	−7.64
3.86	+0.20					
11.4	+0.20					
33	+0.22					

from published sources[23-26]. In these tables values of H_0, a_{H_2O}, $a_{H_2SO_4}$, and values of $\log k_{eff}a_{H_2O}$ are given for corresponding concentrations of acid and oleum.

As these tables show, $\log k_{eff}a_{H_2O}$ remains constant in the range 91.74–97.18% H_2SO_4 for cyclopentanone oxime and in 85.34–90.3% acid for suberone oxime. Such a dependence can be obtained if two conditions are fulfilled: (a) the reactive form is produced in the dehydration of either $RNOH_2^+$ ions or the species $RNOH_2^+.HSO_4^-$; (b) almost all the oxime in the solution is present in a form which is dehydrated. On the basis of the above considerations the oxime can be present in such solutions as the ion pairs $RNOH_2^+.HSO_4^-$ and the protonated species $RNOH_2^+$. Dehydration of the ion pairs (salt) can be represented by Eqn. (1):

$$RNOH_2^+ \cdot HSO_4^- \rightleftarrows RN^+ \cdot HSO_4^- + H_2O. \quad (1)$$

Dehydration of the protonated species can be expressed by Eqn. (2):

$$RNOH_2^+ \rightleftarrows RN^+ + H_2O. \quad (2)$$

The ion pairs $RN^+.HSO_4^-$ can be considered as an association product of the dehydrated ions RN^+ with the HSO_4^- anions:

$$RN^+ + HSO_4^- \rightleftarrows RN^+HSO_4^-. \quad (3)$$

We will derive an equation for the variation of the observed rate constants k_{eff} on the quantities a_{H_2O}, $a_{H_2SO_4}$, and h_0 for instances when either the ions RN^+ or the ion pairs $RN^+.HSO_4^-$ are capable of reaction. We will use K_c to denote the thermodynamic constant of salt formation:

$$RNOH_2^+ + HSO_4^- \rightleftarrows RNOH_2^+ \cdot HSO_4^-,$$

$$K_c = \frac{a_{RNOH_2^+} \, a_{HSO_4^-}}{a_{(RNOH_2^+ \cdot HSO_4^-)}}, \quad (4)$$

where $a_{RNOH_2^+}$, $a_{(RNOH_2^+.HSO_4^-)}$, and $a_{HSO_4^-}$ are the activities of of the $RNOH_2^+$ cations, the $RNOH_2^+.HSO_4^-$ species, and the HSO_4^- anions. We will draw up the balance equation for the oxime under conditions when the concentration of the reactive species (this can be either the RN^+ ions or the $RNOH_2^+.HSO_4^-$ ion pairs) can be neglected. Such a condition is observed in the Beckmann rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime in sulphuric acid solutions up to 100% H_2SO_4.

$$C_0 = C_{RNOH} + C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-},$$

where C_0 is the total concentration of the oxime.

As already mentioned, alicyclic oximes have a high basicity. In solutions of acids where the Beckmann rearrangement occurs the relative concentrations of the un-ionised species of the oxime can be neglected:

$$C_{RNOH} \ll C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-},$$

$$C_0 = C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-}. \quad (5)$$

We will express $C_{RNOH_2^+}$ and $C_{RNOH_2^+.HSO_4^-}$ in terms of C_0 and the equilibrium constant K_c:

$$C_{RNOH_2^+} = \frac{C_0}{1 + \frac{a_{HSO_4^-}}{K_c} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+ \cdot HSO_4^-)}}}, \quad (6)$$

$$C_{RNOH_2^+ \cdot HSO_4^-} = \frac{C_0}{1 + \frac{K_c}{a_{HSO_4^-}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RNOH_2^+}}}. \quad (7)$$

The activity of the anions of the acid $a_{HSO_4^-}$ is conveniently expressed in terms of $a_{H_2SO_4}$ and h_0:

$$a_{H_2SO_4} = K_{2A} \cdot a_{H^+} \cdot a_{HSO_4^-},$$

where K_{2A} is the thermodynamic constant for the dissociation of the hydrogen sulphate ions:

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

At 25°,[41] $K_{2A} = 1.2 \times 10^{-2}$. Since in aqueous solutions of strong acids[42], $a_{H^+} = h_0$,

$$a_{H_2SO_4} = K_{2A} \cdot h_0 \cdot a_{HSO_4^-}; \quad a_{HSO_4^-} = \frac{a_{H_2SO_4}}{K_{2A} \cdot h_0}.$$

We will use K_2 and K_3 to denote the expressions in the activities of the equilibrium constants of the processes of dehydration (1) and (2):

$$K_2 = \frac{a_{(RNOH_2^+ \cdot HSO_4^-)}}{a_{RN^+ \cdot HSO_4^-} \cdot a_{H_2O}}; \quad K_3 = \frac{a_{RNOH_2^+}}{a_{RN^+} \cdot a_{H_2O}}.$$

We will express the concentrations of the $RN^+.HSO_4^-$ species and RN^+ ions in terms of C_0, the equilibrium constants, and the quantities a_{H_2O}, h_0, and $a_{H_2SO_4}$:

$$C_{RN^+} = \frac{\frac{f_{RNOH_2^+}}{C_0 K_3 \cdot f_{RN^+}} \cdot \frac{1}{a_{H_2O}}}{1 + \frac{a_{H_2SO_4}}{K_{2A} \cdot K_c \cdot h_0} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+ \cdot HSO_4^-)}}}, \quad (8)$$

$$C_{RN^+ \cdot HSO_4^-} = \frac{C_0 \cdot \frac{1}{K_2 \cdot a_{H_2O}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RN^+ \cdot HSO_4^-}}}{1 + \frac{K_{2A} \cdot K_c \cdot h_0}{a_{H_2SO_4}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RNOH_2^+}}}, \quad (9)$$

where $f_{RNOH_2^+}$, f_{RN^+}, $f_{RNOH_2^+.HSO_4^-}$, and $f_{RN^+.HSO_4^-}$ are the activity coefficients of the ions $RNOH_2^+$ RN^+, and the ion pairs $RNOH_2^+.HSO_4^-$ and $RN^+.HSO_4^-$ respectively.

It is assumed that the rate of the limiting stage is determined by the concentration of the dehydrated species. Therefore with change in the properties of the medium k_{eff} should change by the same equation as the concentration of the reactive species. We will analyse Eqns. (8) and (9). The analysis of these is most convenient with the example of suberone oxime, since it is reliably known that in 99% sulphuric acid it is present completely in the form of the protonated species $RNOH_2^+$. Consequently, for such solutions in Eqn. (8):

$$1 \gg \frac{a_{HSO_4^-}}{K_c} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+.HSO_4^-)}}$$

and

$$C_{RN^+} = \frac{C_0}{a_{H_2O}} \cdot \frac{f_{RNOH_2^+}}{K_3 \cdot f_{RN^+}}.$$

It is well known how the ratio of the activity coefficients $f_{RNOH_2^+}/f_{RN^+}$ changes with the sulphuric acid concentration. Since, in the present example we are considering the very narrow range from 99 to 100% H_2SO_4, where it is possible to neglect the relative concentration of the reactive species it can be assumed that $f_{RNOH_2^+}/f_{RN^+}$ is constant. Then

$$\frac{C_{RN^+}}{C_0} = \frac{\text{const}}{K_3 \cdot a_{H_2O}}.$$

If the dehydrated ion RN^+ is reactive, then in the range 99–100% H_2SO_4 for the effective rate constant the equation

$$k_{eff} a_{H_2O} = \text{const} \frac{k_{true}}{K_3}$$

should hold, where k_{true} is the true rate constant.

As Table 12 shows, the quantity $\log k_{eff} a_{H_2O}$ for suberone oxime is not constant in 99.23–100% H_2SO_4. In this range the quantity $\log k_{eff} a_{H_2O}$ falls by a factor of 12. This greatly exceeds the possible change in the ratio $f_{RNOH_2^+}/f_{RN^+}$ in this narrow range.

The quantity $\log k_{eff} a_{H_2O}$ is also not constant in such a narrow range for other oximes (see Tables 10, 11, and 13). Consequently, the limiting stage of the Beckmann rearrangement of alicyclic ketoximes is not the isomerisation of the dehydrated ions RN^+. Since in the sulphuric acid concentration range being considered suberone oxime is almost completely present as the ions $RNOH_2^+$, in Eqn. (9):

$$1 \ll K_{2A} \cdot K_c \cdot \frac{h_0}{a_{H_2SO_4}} \cdot \frac{f_{(RNOH_2^+.HSO_4^-)}}{f_{RNOH_2^+}}$$

$$C_{RN^+.HSO_4^-} = \frac{C_0 \cdot a_{H_2SO_4} \cdot f_{RNOH_2^+}}{a_{H_2O} \cdot h_0 \cdot K_{2A} \cdot K_2 K_c \cdot f_{RN^+.HSO_4^-}}, \quad (10)$$

and in the present instance it can be taken that in the narrow range 99–100% H_2SO_4 the ratio of activity coefficients $f_{RNOH_2^+}/f_{RN^+.HSO_4^-}$ will be almost constant, and

$$\frac{C_{RN^+.HSO_4^-}}{C_0} = \frac{\text{const}}{K_{2A} \cdot K_2 \cdot K_c} \cdot \frac{a_{H_2SO_4}}{a_{H_2O} \cdot h_0}.$$

In the range considered the concentration of the reactive species can be neglected. If the ion pairs $RN^+.HSO_4^-$ are reactive, then:

$$k_{eff} = k_{true} \frac{a_{H_2SO_4}}{a_{H_2O} \cdot h_0} \cdot \frac{\text{const}}{K_{2A} \cdot K_2 \cdot K_c}.$$

In this instance the product $k_{eff} a_{H_2O} h_0 / a_{H_2SO_4}$ will be constant.

On increasing the acid concentration from 99.23 to 100% H_2SO_4 the effective rate constant of the Beckmann rearrangement of suberone oxime rises by a factor of 108. As the results in Table 12 show, in this interval the quantity $k_{eff} a_{H_2O} h_0 / a_{H_2SO_4}$ is almost constant. The scatter which occurs $\left(\log \frac{k_{eff} a_{H_2O} h_0}{a_{H_2SO_4}} = -8 \pm 0.1\right)$ is evidently connected with the error in determining the effective rate constants, the activity of water, the acidity h_0, and also with possible small changes in the ratio $f_{RNOH_2^+}/f_{RN^+.HSO_4^-}$. This quantity is also almost constant in this range for other oximes (see Tables 10, 11, and 13). This suggests the conclusion that the dehydrated ion pairs in this process are reactive. To obtain the complete equation for the dependence of k_{eff} on a_{H_2O}, h_0, and $a_{H_2SO_4}$ it is necessary to add to the balance equation derived above the concentration of the reactive species $RN^+.HSO_4^-$:

$$C_0 = C_{RNOH_2^+} + C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-}.$$

If the $RNOH_2^+$ and $RNOH_2^+.HSO_4^-$ concentrations are expressed in terms of the concentration of the reactive species $RN^+.HSO_4^-$ and the equilibrium constants, we obtain:

$$C_{RN^+.HSO_4^-} = \frac{C_0}{1 + \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} \cdot K_{2A} \cdot K_2 \cdot K_c \cdot \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+}} + K_2 \cdot a_{H_2O} \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+.HSO_4^-}}}.$$

Precise analysis of this equation is difficult, since it is unknown how the activity coefficients in this equation change. There are grounds for assuming that with change in the sulphuric acid concentration over a wide interval (for example, from 85 to 100% acid) the activity coefficients of the ions and species mentioned change considerably. In the present instance the equation includes the ratios

$$\frac{f_{RN^+.HSO_4^-}}{f_{(RNOH_2^+.HSO_4^-)}} \text{ and } \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+}}.$$

There is reason to think that the ratio of the activity coefficients of two ion pairs will depend weakly on the acid concentration. As already mentioned above, in relatively dilute sulphuric acid solutions, where the Beckmann transformation occurs, the relation $\log k_{eff} a_{H_2O} = \text{const}$ is obeyed. Such a relation can be kept if the ion pairs $RN^+.HSO_4^-$ are reactive and the ratio $f_{RN^+.HSO_4^-}/f_{RNOH_2^+}$ is independent of the acid concentration. We assume that this ratio is constant also in more concentrated solutions of the acid.

We will represent $K_{2A} K_2 K_c f_{RN^+.HSO_4^-}/f_{RNOH_2^+}$ by $K_2' K_c'$ and $K_2 f_{RN^+.HSO_4^-}/f_{RNOH_2^+.HSO_4^-}$ by K_2'. Then:

$$C_{RN^+.HSO_4^-} = \frac{C_0}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}. \quad (11)$$

We will write the expression for W, the rate constant of the process:

$$W = k \frac{a^*}{f^*} = k \frac{a_{RN^+.HSO_4^-}}{f^*} = k \frac{C_{RN^+.HSO_4^-} \cdot f_{RN^+.HSO_4^-}}{f^*},$$

where a^* and f^* are the activity and activity coefficient of the activated complex. The activated state is formed from the ion pairs $RN^+.HSO_4^-$. The activated complex and the ion pairs $RO^+.HSO_4^-$ have the same composition; therefore we

will assume that the ratio $f_{RN^+.HSO_4^-}/f^*$ is independent of the composition of the reaction medium:

$$W = k_{true} \cdot C_{RN^+.HSO_4^-} = \frac{k_{true}\, C_0}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}$$

$$\frac{W}{C_0} = k_{eff} = \frac{k_{true}}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}, \qquad (12)$$

Eqn. (12) describes the variation of the effective rate constant k_{eff} of the Beckmann rearrangement of aliphatic ketoximes on the quantities a_{H_2O}, h_0, and $a_{H_2SO_4}$ of aqueous solutions of sulphuric acid and oleum. In solutions where $C_{RN^+.HSO_4^-} + C_{RNOH_2^+} \ll C_{RNOH_2^+.HSO_4^-}$ the following relation should hold:

$$k_{eff} \cdot a_{H_2O} = \frac{k_{true}}{K_2'}.$$

As already mentioned, such a dependence exists for suberone oxime and cyclopentanone oxime. It is not valid for cyclohexanone oxime and cyclododecanone oxime in the sulphuric acid concentration range studied.

As the constants quoted below show, even in 90% acid cyclohexanone oxime is found almost completely as the protonated species $RNOH_2^+$. In 90% acid for cyclododecanone oxime the concentrations of the $RNOH_2^+$ ions and $RNOH_2^+.HSO_4^-$ species are commensurate. Therefore, for these oximes the product $k_{eff}a_{H_2O}$ does not stay constant. For suberone oxime and cyclopentanone oxime, the salt formation constant K_c' can be determined from the kinetic data for solutions of the acid where the relative concentrations of the $RNOH_2^+.HSO_4^-$ species and $RNOH_2^+$ ions are commensurate. If

$$C_{RN^+HSO_4^-} \ll C_{RNOH_2^+.HSO_4^-} + C_{RNOH_2^+},$$

then

$$k_{eff} = \frac{k_{true}}{K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}. \qquad (13)$$

Eqn. (13) can be transformed:

$$\frac{1}{k_{eff} \cdot a_{H_2O}} = \frac{K_2' K_c'}{k_{true}} \cdot \frac{h_0}{a_{H_2SO_4}} + \frac{K_2'}{k_{true}}.$$

This equation describes the variation of k_{eff} with h_0, $a_{H_2SO_4}$, and a_{H_2O} and allows K_c' and K_2'/k_{true} to be calculated. Fig. 5 shows the variation of $1/k_{eff}a_{H_2O}$ with $h_0/a_{H_2SO_4}$ for suberone oxime.

The salt formation constant K_c' at 25° is 0.29 ± 0.02 for suberone oxime and 0.1 ± 0.02 for cyclopentanone oxime.

The ratio $k_{true}/K_2'K_c'$ is calculated from the variation of k_{eff} on a_{H_2O}, h_0, and $a_{H_2SO_4}$ for acid solutions where

$$C_{RNOH_2^+} \gg C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-},$$

If the limiting rate constants observed in oleum are true rate constants, then in dilute oleum there should be a transitional region where both the reactive form $RN^+.HSO_4^-$ and the ions $RNOH_2^+$ are present in commensurate concentrations.

In that region the effective rate constant should be given by the equation:

$$k_{eff} = \frac{k_{true}}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}}}. \qquad (14)$$

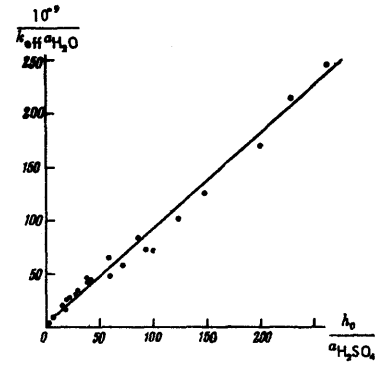


Fig. 5. Variation of $1/k_{eff}a_{H_2O}$ with $h_0/a_{H_2SO_4}$ for the Beckmann rearrangement of suberone oxime in sulphuric acid at 25°.

This equation can be used to calculate the value of k_{true} and $K_2'K_c'$. However, the true constants k_{true} calculated by Eqn. (14) are greater than the limiting values of the rate constants. For example, at 25° the limiting value of k_{eff} is 1.05 min^{-1} for cyclohexanone oxime, and the value of k_{true} calculated from Eqn. (14) is 1.35 ± 0.05 min^{-1}. For cyclopentanone oxime the limiting value of k_{eff} is 0.31 min^{-1} and the calculated value 0.6 ± 0.2 min^{-1}. Consequently, the limiting values of the rate constants in this instance do not correspond with the true values, that is, in solutions where k_{eff} no longer depends on the composition of the medium the reagents are not completely found in the reactive form. This is connected with the fact that in oleum containing 5–11% SO_3 the value of the constant $a_{H_2O}h_0/a_{H_2SO_4}$ (see Table 14) and therefore the degree of conversion of the oxime into the reactive form $RN^+.HSO_4^-$ does not change as the SO_3 concentration in the solution is varied.

Table 15 gives the values of the k_{true}, K_c', K_2', and $K_2'K_c'$ at 25° for four alicyclic ketoximes. K_2' and K_c' could not be calculated separately for cyclohexanone oxime. There are spectroscopic results which support the appearance of a new form of the oxime in the solutions of the acid where the

TABLE 14. Values of $\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}}$ for oleum at 25°.

SO_3, wt. %	5	6	7	8	9	10	11
$\log a_{H_2O}$	−11.40	−11.50	−11.58	−11.66	−11.73	−11.77	−11.82
H_0	−12.90	−12.98	−13.04	−13.1	−13.15	−13.21	−13.26
$\log a_{H_2SO_4}$	9.50	9.49	9.48	9.47	9.46	9.46	9.45
$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}}$	−8.0	−7.99	−8.02	−8.03	−8.04	−8.02	−8.01

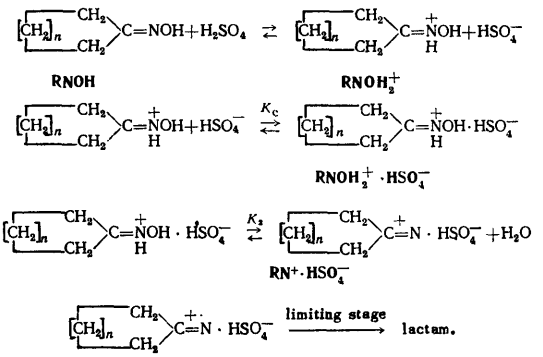
TABLE 15.

Oxime	k_{true}, min^{-1}	K_c'	$10^6K_2'$	$K_2'K_c'$	E_{true}, kcal $mole^{-1}$	log A_{true}	ΔH_{298}, kcal × × $mole^{-1}$
Cyclopentanone oxime	0.6±0.2	0.1±0.02	(2±1)·10^1	(2±1)·10^8	23.7±0.2	15.3±0.3	−7.0±2
Cyclohexanone oxime	1.35±0.05	—	—	(2.7±1)·10^7	21.5±0.2	13.6±0.17	—
Suberone oxime	0.96±0.04	0.29±0.02	(3.0±0.3)	(0.87±0.15)·10^8	23.5±0.2	15.4±0.2	−10±2
Cyclododecanone oxime	4.4±1.5	0.49±0.3	(5.7±1.9)	(1.9±0.9)·10^8	20.6±0.2	14.0±0.25	—

rate constant of the Beckmann rearrangement rises sharply. Fig. 6 shows the dependence of the molar absorptivity of cyclohexanone oxime at λ = 222 nm as a function of the concentration of sulphuric acid and oleum. As Fig. 6 shows, precisely in solutions where the H_2SO_4 concentration is over 99% and also in extremely dilute oleum the molar absorptivity of the oxime at λ = 222 nm rises sharply. This wavelength does not lie at the maximum absorption of the oxime; it is selected because the change in its absorption intensity was determined by the rate of the Beckmann rearrangement. Since this rise occurs in a rather narrow range of acid concentrations (from 99.9% H_2SO_4 to 0.1% SO_3) the possibility of explaining this by the displacement of the absorption maximum is excluded. Such effects are observed during the appearance of new forms of a substance which are distinguished from the other forms by the absorption coefficients at definite wavelengths.

In this way, on the basis of the results described, it follows that alicyclic ketoximes in concentrated sulphuric acid are present as four equilibrium forms: the un-ionised form, the protonated form, ion pairs, and dehydrated ion pairs. The form reactive in the Beckmann rearrangement is the dehydrated ion pair.

The mechanism can be represented as follows:



This mechanism does not differ in principle from that of Kuhara and Chapman proposed for the Beckmann rearrangement in non-aqueous solutions. According to Kuhara and Chapman the reactive form is the ester of the oxime and the acid. The results quoted do not agree with the mechanism proposed by Pearson and Ball[37]. According to them the ion pairs $RNOH_2^+.HSO_4^-$ should be reactive. As already mentioned above, the relative concentration of these falls in the sulphuric acid concentration region where there is a rise in k_{eff}. The limiting stage for the Beckmann rearrangement of alicyclic ketoximes can be either that of ion pair dissociation (rupture at the –N–O– bond) or that of rupture of the –C–C– bond of the ring in the $RN^+.HSO_4^-$ species. Since

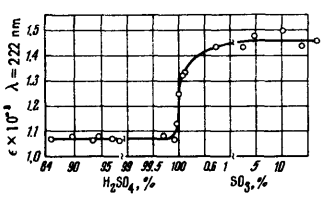
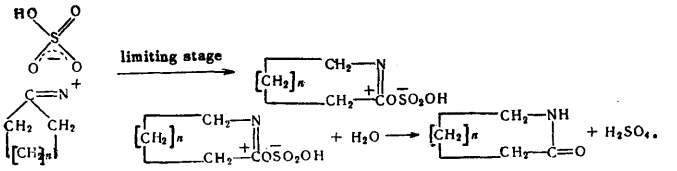


Fig. 6. Variation of the molar absorptivity (ϵ, litre mole^{-1} cm^{-1}) of cyclohexanone oxime at λ = 222 nm with the H_2SO_4 concentration.

the hydrated salt $RNOH_2^+.HSO_4^-$ is in equilibrium with the $RNOH_2^+$ cations, it can be suggested that the salt $RN^+.HSO_4^-$ is also in equilibrium with the products of its dissociation (RN^+ and HSO_4^-). In every instance ionisation, that is, rupture of the bond between nitrogen and oxygen, can proceed much more rapidly than rupture of a –C–C– bond and ring. It therefore seems likely that the limiting stage is the breaking of the –C–C– bond in the oxime. The breaking of a C–C bond and the formation of a C=N bond can proceed during the transfer of the positive charge from the nitrogen atom to the carbon atom. The HSO_4^- anion apparently assists the transfer of charge. In acids with a low water concentration and in oleum the dehydrated protonated form of the lactam is formed during the rearrangement. Hydration takes place during dilution of the reaction product with water.

Scheme of the limiting stage



In concentrated oleum, dehydrated ion pairs $RN^+.HS_2O_7^-$ can be formed:

$$2\,RNOH + 3\,H_2S_2O_7 \rightleftarrows 2\,RN^+ \cdot HS_2O_7^- + 2H_2SO_4.$$

As noted above, "Beckmann mixture" – consisting of a mixture of acetic acid and acetic anhydride, saturated with gaseous hydrogen chloride – is often used for preparations. Starting from the mechanism of the Beckmann rearrangement in sulphuric acid, the catalytic action of "Beckmann mixture" can be explained. For carrying out the process it is necessary to have an acid medium to bring about ionisation of the oxime. Since oximes are usually strong bases, the hydrochloric acid present in the "Beckmann mixture" is sufficient for this purpose. In the presence of an excess of acetic acid an ion pair (or salt of the oxime) can be formed. For the formation of the reactive form it is necessary that the salt consisting of the protonated form of the oxime and the anion of the acid be dehydrated. Judging from the available data the dehydration proceeds to an appreciable degree at very low activities of water. For example, in sulphuric acid the ion pairs of alicyclic ketoximes are dehydrated to a significant extent in the solutions where the water activity is less than 10^{-5}–10^{-6}. The presence of the anhydride in the mixture allows a low activity of water to be maintained in the solution. The water formed in the dehydration of the oxime in this medium is used up in the hydration of the anhydride and the activity of the water does not increase.

VI. TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES IN SULPHURIC ACID AND IN OLEUM

For the same concentration of sulphuric acid or oleum the rate constants of the Beckmann rearrangement k_{eff} at different temperatures fit the Arrhenius equation:

$$k_{eff} = Ae^{-E_{eff}/RT}.$$

TABLE 16. Activation energy E and preexponential factor A, s^{-1} of the Beckmann rearrangement of alicyclic ketoximes in sulphuric acid and in oleum.

H_2SO_4, wt. %	E, kcal mole^{-1}	log A
Cyclohexanone oxime		
82.29	25.0±1	11.8±0,7
86.03	24.0±1	11.4±0,7
89.94	23.7±1	11.5±0,7
92.73	23.4±0.5	11.5±0,4
94.71	22.9±0.5	11.4±0,4
98.21	22.2±0.5	11.5±0,4
99.74	21.5±0.2	11.6±0,2
SO_3, wt. %		
2.22	21.5±0,2	14,0±0,2
7.1	21.5±0,2	14,0±0,2
15.4	21.5±0,2	14,1±0,2
30—80*	24.8±0,4*	
Cyclopentanone oxime		
H_2SO_4, wt. %		
91.74	25,9±1	12,2±0.8
93.70	25,9±0,5	12,4±0,4
95.42	25,4±0,5	12,3±0,4
97.18	23,6±0,5	11,5±0,4
99.85	23,4±0,5	12,9±0,4
SO_3, wt. %		
5.5	23,7±0,2	15,1±0,15
27	23,7±0,2	15,1±0,15
Cyclododecanone oxime		
88,07	25,6±1	12,5±0,7
90,33	24,7±1	12,0±0,4
93,29	24,7±0,5	12,3±0,4
95,67	23,8±0,5	12,0±0,4
97,67	22,9±0,5	11,7±0,4
SO_3, wt. %		
1,38	21,1±0,2	13,7±0,15
3,86	20,6±0,2	13,5±0,15
11,4	20,6±0,2	13,5±0,15
33	20,6±0,2	13,5±0,15
Suberone oxime		
H_2SO_4, wt. %		
85,34	29,8±1	14,6±0,7
87,89	29,3±1	14,5±0,7
90,30	28,0±1	13,9±0,7
93,20	26,6±0,5	13,3±0,4
95,23	26,1±0,5	13,1±0,4
97,13	25,7±0,5	13,9±0,4
98,05	26,1±0,5	13,6±0,4
99,46	26,1±0,5	14,1±0,4
99,65	26,1±0,5	14,4±0,4
SO_3, wt. %		
7,5	23,5±0,2	15,10±0,15

* These quantities were obtained in work where the oxime concentration was ~ 0,5 M and in addition to the oxime a lactam was added (14 g lactam per 15 g oleum).

The activation energy which can be found from the Arrhenius equation depends on the concentration of sulphuric acid in solution. Table 16 gives the values of log A and E_{eff} for the rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime in solutions of sulphuric acid and in oleum from published data [23-26]. As the acid concentration is raised the activation energy falls. For example, with suberone oxime, E_{eff} = 29.3 kcal mole^{-1} in 87–89% acid and 23.5 kcal mole^{-1} in oleum with 7.5 wt. % SO_3. In solutions where almost all the oxime is in the reactive form the observed activation energy is constant. For example, in the rearrangement of cyclohexanone oxime the activation energy is constant in the range from 99.74% H_2SO_4 to 15.4% SO_3. To explain what the activation energy calculated by the Arrhenius equation represents it is necessary to analyse Eqn.(12) which expresses the dependence of k_{eff} on the quantities a_{H_2O}, $a_{H_2SO_4}$, and h_0. On taking into account the temperature dependence of the constant this equation must be written as:

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\cdot e^{\frac{-E_{true}}{RT}}}{1+\dfrac{B_2 e^{\frac{\Delta H_2}{RT}}\cdot B_c e^{\frac{\Delta H_c}{RT}}\cdot B_{H_2O} e^{\frac{-\Delta H_{H_2O}}{RT}}\cdot B_{h_0} e^{\frac{-\Delta H_{h_0}}{RT}}}{B_{H_2SO_4}\cdot e^{\frac{-\Delta H_{H_2SO_4}}{RT}}} + B_2\cdot B_{H_2O} e^{\frac{\Delta H_2-\Delta H_{H_2O}}{RT}}},$$

where E_{true} and A_{true} are the true activation energy and true preexponential factor, ΔH_2 and ΔH_c the standard changes in enthalpy of the dehydration and dissociation of the ion pair $RNOH_2^+.HSO_4^-$, and B_2 and B_c the entropy multipliers of the equilibrium constants K_2' and K_c'. ΔH_{H_2O}, ΔH_{h_0}, and $\Delta H_{H_2SO_4}$, and B_{H_2O}, B_{h_0}, and $B_{H_2SO_4}$ are the heats and entropy factors which characterise the change in the activity of water, the acidity, and the activity of sulphuric acid with temperature.

In solutions where

$$C_{RN^+.HSO_4^-} \gg C_{RNOH_2^+} + C_{RNOH_3^+.HSO_4^-},$$

$$A_{eff}\,e^{-E_{eff}/RT} = A_{true}\,e^{-E_{true}/RT},$$

and the activation energy and preexponential factor given by the Arrhenius equation will be the true values. In oleum, where the rate constant of the rearrangement does not change, ~ 70% of the total concentration of the alicyclic ketoximes studied are in the $RN^+.HSO_4^-$ form. Therefore, the activation energy and preexponential factor determinable under these circumstances are the true ones.

In relatively dilute solutions of acid§ almost all the oxime is present in the form of the ion pairs $RNOH_2^+.HSO_4^-$:

$$C_{RNOH_2^+.HSO_4^-} \gg C_{RNOH_2^+} + C_{RN+HSO_4^-}.$$

Here:

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\,e^{\frac{-E_{true}}{RT}}}{B_2 e^{\frac{\Delta H_2}{RT}}\,e^{\frac{-\Delta H_{H_2O}}{RT}}},$$

and

$$-E_{eff} = -E_{true} - \Delta H_2 + \Delta H_{H_2O}.$$

Such conditions are observed, for example, for suberone oxime in the range 85.3–90.3% H_2SO_4 and for cyclopentanone oxime in the range 91.74–96.2% H_2SO_4. It now becomes possible to determine ΔH_2 for the oximes mentioned. The values of E_{eff} and ΔH_{H_2O} for 90% sulphuric acid can be used for the calculations. Table 16 gives the values of E_{eff}; ΔH_{H_2O} = 5.0 kcal mole^{-1}. This quantity is calculated from the temperature dependence of the pressure of water vapour over solutions of the acid, which are taken from a handbook [43]. ΔH_2 is -7.0 ± 2 kcal mole^{-1} and -10 ± 2 kcal mole^{-1} for cyclopentanone oxime and suberone oxime respectively. In acid solutions where

$$C_{RNOH_2^+} \gg C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-}$$

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\,e^{\frac{-E_{true}}{RT}}\cdot B_{H_2SO_4}\,e^{\frac{-\Delta H_{H_2SO_4}}{RT}}}{B_2 e^{\frac{\Delta H_2}{RT}}\cdot B_c e^{\frac{\Delta H_c}{RT}}\cdot B_{H_2O} e^{\frac{-\Delta H_{H_2O}}{RT}}\cdot B_{h_0} e^{\frac{-\Delta H_{h_0}}{RT}}}$$

and

$$-E_{eff} = -E_{true} - \Delta H_2 - \Delta H_c + \Delta H_{H_2O} + \Delta H_{h_0} - \Delta H_{H_2SO_4}.$$

This condition is observed for solutions of the acid in the range 99.4–100% H_2SO_4. In connection with the fact that for such solutions the enthalpies ΔH_{H_2O}, ΔH_{h_0}, and $\Delta H_{H_2SO_4}$ are still unknown it seems impossible to calculate the value of ΔH_c. It should be noted that in the intermediate region where the $RNOH_2^+.HSO_4^-$ and $RNOH_2^+$ concentrations are commensurate, in the general example the rate constants at different temperatures should not obey the Arrhenius equation, since the expression for k_{eff} includes the sum of two quantities with exponential factors. However, for a narrow temperature interval the Arrhenius equation is satisfied. The effective activation energy cannot then be presented in the form of a sum of E_{true} and the change in the

§ Here by relatively dilute solutions of sulphuric acid we mean solutions in which the H_2SO_4 concentration is < 90 wt.%.

enthalpies of the equilibrium processes. This is also true where the concentrations of $RNOH_2^+$ and $RH^+.HSO_4^-$ are commensurate.

Table 15 gives the equilibrium constants K_2' and K_c', the product $K_2'K_c'$, E_{true}, and A_{true} for the four alicyclic ketoximes, and shows that E_{true} is less for ketoximes with an even number of carbon atoms than for those with an odd number of carbon atoms. This regularity is observed also for the activation energy of the Beckmann rearrangement of the oxime *p*-toluenesulphonates in chloroform[27]. From Heldt's results[27], the activation energies are 27 ± 1.3 and 23.4 ± 1.1 kcal mole^{-1} for cyclopentanone and cyclohexanone oximes and 24.4 ± 1.1 and 21.8 ± 1.2 kcal mole^{-1} for cycloheptanone and cyclo-octanone oximes respectively. For cyclohexanone oxime the preexponential factor is 4×10^{13} s^{-1}. This quantity is close to the normal preexponential factors for unimolecular reactions. For the remaining three oximes the intrinsic preexponential factors are greater than the normal values.

1. E. Beckmann, Ber., 19, 988 (1886); 27, 300 (1894).
2. O. Wallach, Annalen, 312, 171 (1900).
3. B. Jones, Chem. Rev., 35, 335 (1944).
4. I. L. Knunyants and B. P. Fabrichnyi, "Reaksii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Gos. Nauch. Tekh. Izd. Khim. Lit., Moscow, Vol. 3, 1954.
5. Guy Donaruma and W. Z. Heldt, Organic Reactions, Vol. XI, New York, 1960.
6. E. N. Zil'berman, Zhur. Khim. Prom., 277 (1955).
7. "Houben–Weyl. Die Methoden der organischen Chemie" (Translated into Russian), Goskhimizdat, 1949, Vol. 4, Book 1.
8. W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc., 82, 62 (1960).
9. R. S. Ryabova, I. M. Medvetskaya, and M. I. Vinnik, Zhur. Fiz. Khim., 40, 339 (1966) [Russ. J. Phys. Chem., 182 (1966)].
10. M. I. Vinnik and R. S. Ryabova, Zhur. Fiz. Khim., 38, 606 (1964) [Russ. J. Phys. Chem., 320 (1964)].
11. T. F. Young, Rec. Chem. Progr., 12, 81 (1951).
12. N. G. Zarakhani and M. I. Vinnik, Zhur. Fiz. Khim., 37, 503 (1963) [Russ. J. Phys. Chem., 260 (1963)].
13. M. I. Vinnik and N. G. Zarakhani, Zhur. Fiz. Khim., 34, 2671 (1960) [Russ. J. Phys. Chem., 1257 (1960)].
14. N. G. Zarakhani, V. V. Budylina, and M. I. Vinnik, Zhur. Fiz. Khim., 39, 1863 (1965) [Russ. J. Phys. Chem., 991 (1965)].
15. M. I. Vinnik, N. G. Zarakhani, I. M. Medvetskaya, and N. M. Chirkov, Dokl. Akad. Nauk SSSR, 126, 1300 (1959).
16. J. C. Brand, J. Chem. Soc., 1002 (1950).
17. O. Wichterle and J. Roček, Chem. Listy, Ročnik, 45, 257 (1951).
18. O. Wichterle and J. Roček, Chem. Listy, Ročnik, 45, 379 (1951).
19. O. Wichterle and J. Roček, Khimiya, 1, 384 (1951).
20. J. Roček and O. Wichterle, Chem. Listy, 45, 260 (1951).
21. I. Ogata, M. Okano, and K. Matzumoto, J. Amer. Chem. Soc., 77, 4673 (1955).
22. P. I. McNulty and D. E. Pearson, J. Amer. Chem. Soc., 81, 612 (1959).
23. M. I. Vinnik and N. G. Zarakhani, Dokl. Akad. Nauk SSSR, 152, 1147 (1963).
24. M. I. Vinnik and N. G. Zarakhani, Zhur. Fiz. Khim., 38, 907 (1964) [Russ. J. Phys. Chem., 491 (1964)].
25. N. G. Zarakhani, V. V. Budylina, and M. I. Vinnik, Zhur. Fiz. Khim., 39, 1561 (1965) [Russ. J. Phys. Chem., 831 (1965)].
26. N. G. Zarakhani and M. I. Vinnik, Zhur. Fiz. Khim., 40, 333 (1966) [Russ. J. Phys. Chem., 179 (1966)].
27. W. Z. Heldt, J. Org. Chem., 26, 1695 (1961).
28. P. T. Scott, D. E. Pearson, and L. I. Bircher, J. Org. Chem., 19, 1815 (1954).
29. C. H. Sluiter, Rec. Trav. chim., 24, 372 (1905).
30. M. Kuhara, A monograph edited by Shigern Komatsu, incorporating the complete work of Kuhara and entitled "Mitsuru Kuhara's work on the Beckmann Rearrangement" has been published by the Imperial University of Kyoto, Tokio, 1926.
31. A. W. Chapman, J. Chem. Soc., 1223 (1935).
32. A. W. Chapman and C. C. Howis, J. Chem. Soc., 806 (1933).
33. A. W. Chapman, J. Chem. Soc., 1550 (1934).
34. A. W. Chapman and F. A. Filder, J. Chem. Soc., 448 (1936).
35. I. Stieglitz and P. P. Peterson, Ber., 43, 782 (1910).
36. P. P. Peterson, Amer. Chem. J., 46, 325 (1911).
37. D. E. Pearson and F. Ball, J. Org. Chem., 14, 118 (1949).
38. A. I. Brodskii and G. P. Miklukhin, Dokl. Akad. Nauk SSSR, 32, 558 (1941).
39. A. I. Brodskii and G. P. Miklukhin, Zhur. Obshch. Khim., 12, 351 (1942).
40. H. Stephen and B. Staskun, J. Chem. Soc., 980 (1956).
41. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions" (Translated into Russian), Moscow, 1952.
42. N. B. Librovich and M. I. Vinnik, Dokl. Akad. Nauk SSSR, 166, 647 (1966).
43. "Spravochnik Khimika" (The Chemists' Handbook), Izd. "Khimiya", Moscow, 1964, Vol. III.

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