termine the equilibrium concentrations of the other three components. Duplicate measurements were made on each system. The maximum deviation from the average of duplicate values was 0.8%.

Results and Discussion

Values of $K^{100°}$ and σ are presented in Table I. The σ-values listed for di-*p*-substituted benzophenones were obtained by adding the σ-values of the two substituents.[10] A plot of log $K^{100°}$ *vs.* σ is shown in Fig. 2.

TABLE I

EQUILIBRIUM CONSTANTS FOR SUBSTITUTED BENZOPHENONES IN THE MEERWEIN–PONNDORF REACTION

	Compound	$K^{100°}$	σ
1	Benzophenone	0.3779	0.000
2	4-Bromobenzophenone	1.057	.232
3	4-Chlorobenzophenone	0.9980	.227
4	4,4′-Dichlorobenzophenone	1.501	.454
5	4-Methylbenzophenone	0.2555	− .170
6	4,4′-Dimethylbenzophenone	.1433	− .340
7	4-Methoxybenzophenone	.2071	− .268
8	4,4′-Dimethoxybenzophenone	.09731	− .536

Statistical treatment[11] of the data of Table I yields the following results: (1) equation of the regression line, $\log K^{100°} = -0.355 + 1.296\sigma$, where -0.355 is the value of $(\log K^{\circ})_{\text{calcd}}$ and 1.296 is the slope (ρ) of the regression line; (2) standard deviation from the regression line, 0.0605; (3) correlation coefficient, 0.992. The regression line is shown in Fig. 2.

From an examination of the Hammett equation,[7] $\log k - \log k^{\circ} = \rho\sigma$, it is obvious that ρ must be positive for reactions that are facilitated by substituents of positive σ-values, *i.e.*, for reactions which are favored by low electron densities at the reaction site. That the Meerwein–Ponndorf reaction is of this sort can be seen from an examination of the mechanism illustrated in Fig. 1. The equilibrium between (B) and (C) controls the over-all equilibrium constant of the reaction. As the positive charge on the indicated carbon atom in (B) is increased, the hydride ion transfer is facilitated and the forward reaction proceeds more readily. Electron-withdrawing substituents on R and R′ increase the positive charge on the central carbon atom and thus increase the over-all equilibrium constant of the reaction.

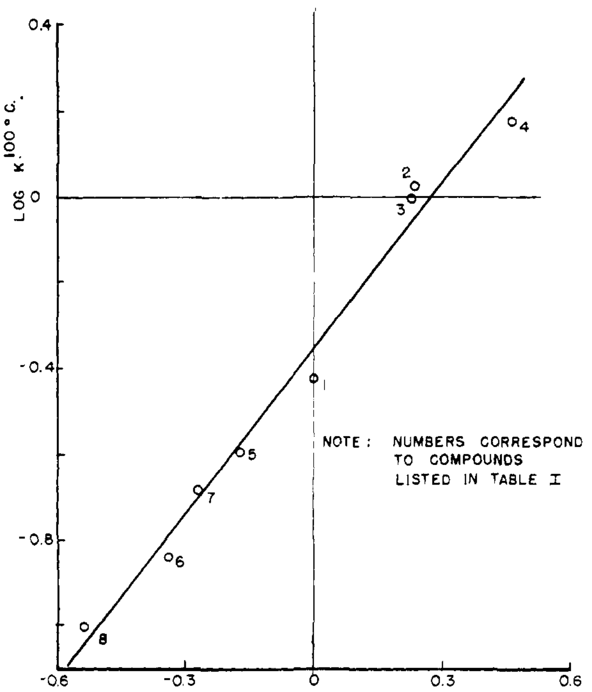

Fig. 2.—log $K^{100°}$ *versus* σ for Meerwein–Ponndorf reductions of substituted benzophenones.

The positive value for ρ obtained in this research is, therefore, in agreement with the mechanism proposed by Jackman and Mills.[4]

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[10] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[11] G. W. Snedecor, "Statistical Methods," 4th ed., The Collegiate Press, Inc., Ames, Iowa, 1946, Chaps. 6 and 7.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Kinetics of the Beckmann Rearrangement of Cyclohexanone Oxime

BY YOSHIRO OGATA, MASAYA OKANO AND KUNIO MATSUMOTO

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The rates of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in aqueous sulfuric or perchloric acid have been measured at 60 and 90° by employing the 2,4-dinitrophenylhydrazone method. The rate was found to be first order with respect to the stoichiometric concentration of the oxime. An approximately linear relationship between the logarithm of rate constant and the acidity function (H_0 or J_0) was observed. Based on the experimental data, some probable reaction mechanisms for this reaction are discussed.

Many studies on the probable mechanism of the Beckmann rearrangement have been carried out with oxime esters,[1] but there seems to be little kinetic evidence at least with free oximes in strong aqueous acids. Recently, Pearson and Ball[2] studied the kinetics of this reaction with acetophenone oxime in sulfuric acid, and Roček, *et al.*,[3] measured the rate of rearrangement of cyclohexanone oxime to ε-caprolactam in oleum, but neither gave a detailed discussion of the correlation between the rate and the acidity in terms of mechanism. The present kinetic studies provide information

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[1] *Cf.* B. Jones, *Chem. Revs.*, **35**, 335 (1944); G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 340; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 496.

[2] D. E. Pearson and F. Ball, *J. Org. Chem.*, **14**, 118 (1949).

[3] (a) O. Wichtele and J. Roček, *C. A.*, **46**, 10809 (1952); (b) G. Roček and Z. Bergl, *ibid.*, **48**, 3279 (1954).

on the probable mechanisms of the Beckmann rearrangement of cyclohexanone oxime in concentrated sulfuric or perchloric acid.

Experimental

Materials.—Toyo Rayon Co. cyclohexanone oxime was recrystallized from water, m.p. 89–90°. Cyclohexanone oxime-O-sulfonic acid was prepared by adding an equivalent of chlorosulfonic acid to cyclohexanone oxime in dry ether at 0° as given in the preparation of acetophenone oxime-O-sulfonic acid.[2] The product thus obtained in the form of very fine powder was extremely soluble in water and rapidly hydrolyzed.[4] Sulfuric and perchloric acids used were of the best grade.

General Procedure.—In a 200-cc. round-bottomed flask, *ca.* 2 g. of oxime was dissolved into a solution of 50 cc. of aqueous acid under cooling, and the flask was dipped in a thermostat regulated to the operating temperature. After the temperature equilibrium was established, 5-cc. aliquots were taken out at regular time intervals by a calibrated pipet and the amount of unreacted cyclohexanone oxime was determined by the following method.[5] The sample was poured into a *ca.* 100 cc. of aqueous solution containing an appropriate quantity of sodium hydroxide for neutralizing the acid present. After acidification of the solution with a few drops of dilute sulfuric acid, an appropriate amount (*ca.* 1.5–2 equivalents) of an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride (4.5 g. of hydrazine was dissolved in 1 l. of *ca.* 2 *N* hydrochloric acid) was added. Soon after the addition, the hydrazone precepitates. The solution was warmed after one hour and then cooled to *ca.* 20°; the precipitate was collected, dried at 80° for one hour and weighed. The initial concentration of oxime was determined from the initial aliquot. This analytical method proved to be satisfactory, since it gave a constant yield of 90 ± 1% in repeated blank tests. Furthermore, it was ascertained that the oxime-O-sulfonic acid also may be estimated in this way.

Experimental Results and Calculations.—Table Ia lists the rate with varying initial concentration and the effect of the concentration of acids. The first-order rate constants were calculated by means of the usual equation. From the literature[6,7] the values of the acidity function (H_0) and those of activity of water (a_{H_2O}) and acids ($a_{H_2SO_4}$ or a_{HClO_4}) in concentrated acids at 25° were quoted, except the J_0-values which were calculated by means of the equation[8] $J_0 = H_0 + \log a_{H_2O}$.

Table Ib shows the effect of neutral sulfates on the rate. The rates in the presence of other inorganic sulfates were not measured owing to their insolubility.

TABLE I

RATE CONSTANTS OF BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME

Init. concn. of oxime, M	Concn. of acid, %	log $a_{H_2SO_4}$ or log a_{HClO_4}	$-\log a_{H_2O}$	Acidity function $-H_0$	$-J_0$	$k \times 10^4$,[b] 1/sec.
(a) Effect of varying oxime and acid concn. on the first-order rate constant; H_2SO_4-catalyzed at 90.0 ± 0.5°						
0.261	48.4	2.67	0.41	3.00	3.41	0.194 ± 0.003
.285	53.0	3.28	.54	3.50	4.04	.276 ± .003
.248	57.7	3.95	.71	4.00	4.71	.413 ± .004
.299	62.0	4.64	.89	4.50	5.39	.60 ± .01
.292	66.0	5.30	1.09	5.00	6.09	.85 ± .01
.285[a]	66.0	5.30	1.09	5.00	6.09	.84 ± .01
.263	69.9	5.98	1.34	5.50	6.84	1.34 ± .02
.307	74.5	6.70	1.70	6.10	7.80	2.25 ± .02
.284	79.1	7.39	2.16	6.70	8.86	4.27 ± .03
.243[a]	79.1	7.39	2.16	6.70	8.86	4.31 ± .04
H_2SO_4-catalyzed at 60.0 ± 0.5°						
0.311	89.4	8.71	3.54	8.10	11.64	1.02 ± 0.01
.346	93.2	9.08	4.11	8.52	12.63	1.55 ± .02
.305	96.1	..	..	8.90	...	2.51 ± .03
.208	96.1	..	..	8.90	...	2.50 ± .02
.153	96.1	..	..	8.90	...	2.53 ± .04
.284	98.0	..	..	9.30	...	3.92 ± .04
.297	99.0	..	..	9.67	...	5.6 ± .1
.304	99.6	..	..	10.05	...	8.1 ± .1
$HClO_4$-catalyzed at 90.0 ± 0.5°						
0.276	47.4	4.45	0.41	3.00	3.41	0.142 ± 0.002
.258	50.7	5.09	.51	3.50	4.01	.183 ± .003
.244	53.9	5.73	.65	4.00	4.65	.228 ± .002
.282	57.0	6.54	.80	4.50	5.30	.317 ± .002
.297	59.9	7.31	.96	5.00	5.96	.424 ± .004

(b) The effect of neutral salts; catalytic acid, 76.8% sulfuric acid; temp. 90.0 ± 0.5°

Init. concn. of oxime, M	Salt added	Concn., M	$k \times 10^4$,[b] l./sec.
0.293	None		3.04 ± 0.03
.275	K_2SO_4	0.75	2.68 ± .04
.240	Na_2SO_4	.75	2.66 ± .04
.254	$(NH_4)_2SO_4$	.75	2.65 ± .03
.238	$(NH_4)_2SO_4$	1.50	2.29 ± .04
.259	$(NH_4)_2SO_4$	3.00	1.72 ± .03

[a] Cyclohexanone oxime-O-sulfonic acid was used instead of oxime. [b] Figures following ± mean probable errors.

Discussion of Results

The mechanism for the Beckmann rearrangement, postulated by Kuhara and by Chapman,[9] states that the ester of the oxime is an intermediate, its ionization being the rate-determining step. If it is assumed that the ionization and migration proceed simultaneously by way of a concerted mechanism,[2,10] the *trans* migration of this reaction[11] is explained.

Hammett[12] and Gold[8] in discussing the probable transition state from the relationship between the rate constant and the acidity function (H_0 or J_0, respectively), suggest that when the conjugate acid of the reactant takes part in the rate-determining step, a relation $\log k = -H_0 + \text{const.}$ should hold, while when its dehydrated form, $\log k = -J_0 + \text{const.}$, does. Their predictions of the unit slope relationship are not realized in our experiments as shown in Fig. 1, but there may be some significance in the approximately linear relation between log k and H_0 or J_0.

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(4) When an aqueous solution of barium chloride was added to that of oxime-O-sulfonic acid, the whole acid was precipitated immediately as barium sulfate instead of barium oxime-O-sulfonate.

(5) H. A. Iddles, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934); **11**, 102 (1939). This method, which is well known as a quantitative analysis of ketones, is also applicable to the ketoxime analysis. For the example, see ref. 2.

(6) The values of H_0: L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

(7) The values of a_{H_2O} and $a_{H_2SO_4}$ in sulfuric acid: N. C. Deno and R. W. Taft, Jr., *ibid.*, **76**, 244 (1954); E. Abel, *J. Phys. Chem.*, **50**, 260 (1946); those in perchloric acid: J. N. Pearce and A. F. Nelson, THIS JOURNAL, **55**, 3075 (1933); R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(8) V. Gold and W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

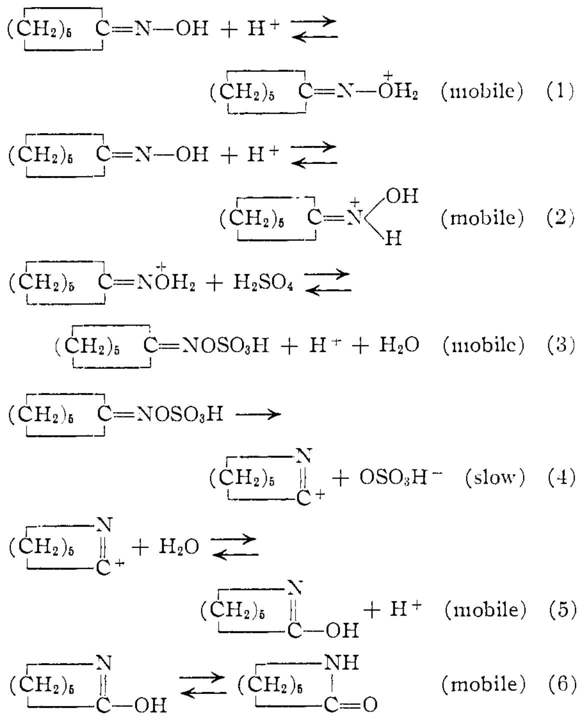
(9) M. Kuhara, "Beckmann Rearrangement," Kyoto Univ., Kyoto, Japan, 1926, p. 14; A. W. Chapman, *et al.*, *J. Chem. Soc.*, 1550 (1934); 448 (1936).

(10) B. Jones, *Nature*, **157**, 519 (1946).

(11) *Cf.* A. H. Blatt, *Chem. Revs.*, **12**, 215 (1933).

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1940, p. 273.

A mechanism similar to that postulated earlier involves the following steps. The other mechanisms will be discussed later.



$$(CH_2)_5C{=}N{-}OH + H^+ \rightleftarrows (CH_2)_5C{=}N{-}\overset{+}{O}H_2 \quad \text{(mobile)} \quad (1)$$

$$(CH_2)_5C{=}N{-}OH + H^+ \rightleftarrows (CH_2)_5C{=}\overset{+}{N}(OH)H \quad \text{(mobile)} \quad (2)$$

$$(CH_2)_5C{=}N\overset{+}{O}H_2 + H_2SO_4 \rightleftarrows (CH_2)_5C{=}NOSO_3H + H^+ + H_2O \quad \text{(mobile)} \quad (3)$$

$$(CH_2)_5C{=}NOSO_3H \longrightarrow (CH_2)_5[N{\equiv}C^+] + OSO_3H^- \quad \text{(slow)} \quad (4)$$

$$(CH_2)_5[N{\equiv}C^+] + H_2O \rightleftarrows (CH_2)_5[N{=}C{-}OH] + H^+ \quad \text{(mobile)} \quad (5)$$

$$(CH_2)_5[N{=}C{-}OH] \rightleftarrows (CH_2)_5[NH{-}C{=}O] \quad \text{(mobile)} \quad (6)$$

If step 4 with rate constant k_4 is rate-determining, the Brönsted rate equation may be given as

$$\frac{dx}{dt} = k_4[C_6H_{10}NOSO_3H]\frac{f_{RNOSO_3H}}{f_{AC}} = K_1K_3k_4[C_6H_{10}NOH]\frac{a_{H_2SO_4}}{a_{H_2O}} \times \frac{f_{RNOH}}{f_{AC}} \quad (7)$$

Here, K_1 and K_3 are the equilibrium constants of equation 1 and 3, respectively, f_{RNOH}, f_{RNOSO_3H} and f_{AC} the activity coefficients of oxime, oxime-O-sulfonic acid and activated complex, respectively (R represents C_6H_{10}). The stoichiometric concentration of oxime is expressed as

$$a - x = [C_6H_{10}NOH] + [C_6H_{10}N\overset{+}{O}H_2] + [C_6H_{10}\overset{+}{N}HOH] + [C_6H_{10}NOSO_3H] = [C_6H_{10}NOH]\left\{1 + K_1a_{H^+}\frac{f_{RNOH}}{f_{RN\overset{+}{O}H_2}} + K_2a_{H^+}\frac{f_{RNOH}}{f_{R\overset{+}{N}HOH}} + K_1K_3\frac{a_{H_2SO_4}}{a_{H_2O}} \times \frac{f_{RNOH}}{f_{RNOSO_3H}}\right\} \quad (8)$$

where f's are also the activity coefficients of the subscripted compounds, and K_2 is the equilibrium constant of equation 2. Although data are not available for all equilibrium constants, it would be reasonable to suppose that K_2 is much larger than K_1, since the organic nitrogen compound is generally more basic than the corresponding oxygen compound.[13] In addition, the facts that the basic strength of oximes[14] are comparable to that of aniline, and that cyclohexanone oxime, although insoluble in water, is readily soluble in dilute aqueous acid, support the supposition that the oxime in acids exists mainly in the form of its conjugate acid. Based on our experimental facts, the concentration of ester $C_6H_{10}NOSO_3H$ seems to be comparatively small. Thus the first two terms and the fourth term will be negligible compared with the third. Hence equation 8 is approximately replaceable by

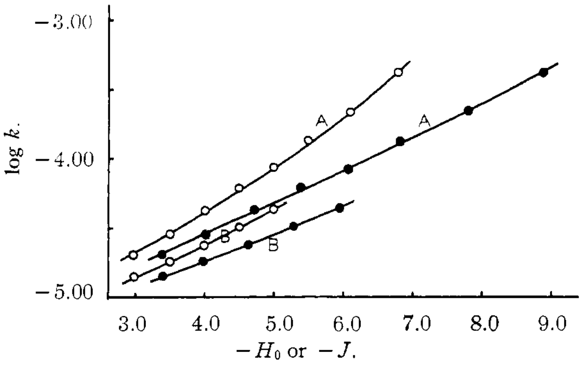


Fig. 1.—Relationship between log k and $-H_0$ (or $-J_0$): A, H_2SO_4-catalyzed; B, $HClO_4$-catalyzed; ○, log k *vs.* $-H_0$; ●, log k *vs.* $-J_0$.

$$a - x = [C_6H_{10}NOH]K_2a_{H^+} \times \frac{f_{RNOH}}{f_{R\overset{+}{N}HOH}} \quad (9)$$

and relationship 11 or 12 may be derived as

$$\frac{dx}{dt} = \frac{K_1K_3k_4}{K_2} \times \frac{a_{H_2SO_4}}{a_{H^+}a_{H_2O}} \times \frac{f_{R\overset{+}{N}HOH}}{f_{AC}}(a-x) \equiv k(a-x) \quad (10)$$

$$k = K\frac{a_{H_2SO_4}}{a_{H^+}a_{H_2O}} \times \frac{f_{R\overset{+}{N}HOH}}{f_{AC}} \left(K = \frac{K_1K_3k_4}{K_2}\right) \quad (11)$$

or

$$\log k = \log a_{H_2SO_4} - \log a_{H_2O} + H_0 + \text{const.} \quad (12)$$

Even if an accurate treatment is difficult because of the unavailability of data for activities and acidity functions at these reaction temperatures, relationship 12 seems fulfilled at least in the range of concentrations of sulfuric acid below 65%, as shown in Fig. 2b.[15]

Here, however, the line of unit slope at moderate acid concentration tends gradually to bend downward with increasing acid concentration. The deviation can be accounted for by the increasing contribution of the term $[C_6H_{10}NOSO_3H]$ in equation 8 with an increase of acid concentration; *i.e.*, if the term $[C_6H_{10}NOSO_3H]$ finally becomes much larger than the other terms, equation 12 should be changed to

$$\log k = \text{const.}$$

where the line is horizontal and log k is independent of the acidity, as Roček[3b] has found with the rearrangement in oleum.

The decrease of acidity produced by the presence of oxime or amide seems to be of considerably smaller contribution, since below *ca.* 95% sulfuric acid concentration the concentration of water is much larger than that of the reactant and product. The increase of dielectric constant with increasing

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(13) Reference 12, p. 24.

(14) *Cf.* O. L. Brady, *et al.*, *J. Chem. Soc.*, 1923 (1926); 950 (1929). K_B = *ca.* $10^{-10} - 10^{-12}$. Moreover we obtained cyclohexanone oxime hydrochloride by introducing gaseous hydrogen chloride into an ethereal solution of oxime. Although its strong hygroscopic property rendered the purification unsuccessful, its chlorine content showed *ca.* 85% of the theoretical.

(15) Since data for the a_{HClO_4} at 100° were unavailable, the line for perchloric acid could not be plotted in Fig. 2b.

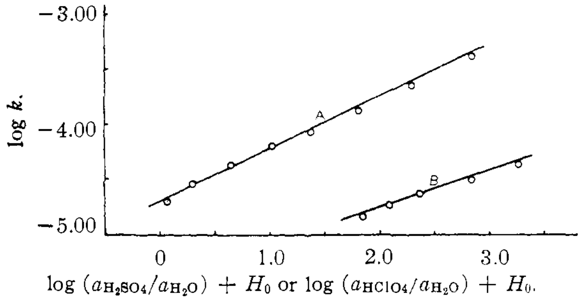


Fig. 2a.—Relationship between log k and log (a_{Acid}/a_{H_2O}) + H_0; the values of a_{Acid} at 25° were used: A, H_2SO_4-catalyzed, slope 0.48; B, $HClO_4$-catalyzed, slope 0.34.

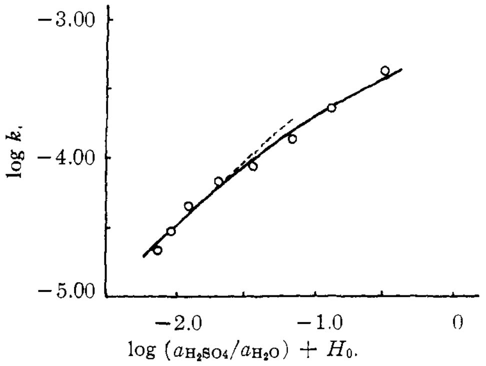


Fig. 2b.—Relationship between log k and log ($a_{H_2SO_4}/a_{H_2O}$) + H_0. The value of $a_{H_2SO_4}$ at 100° was used; H_2SO_4-catalyzed slope 0.92.

acid concentration does not seem to affect the lowering of the tangent, since the transition state for the reaction involves the separation of the opposite charges.

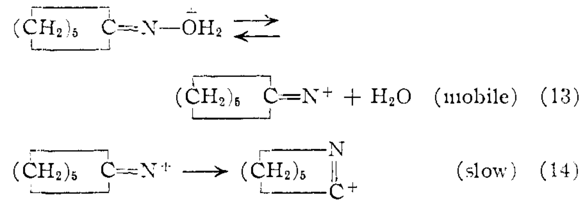
There is a difficulty in that the constant in equation 12 differs considerably between sulfuric and perchloric acids as shown in Fig. 2a, where the data at 25° are used. Whether this is due to the difference in the values of K_3 or not is obscure.

The possibility of mechanisms other than equations 1–6 will be discussed briefly. A rate-determining addition of proton to oxime 1 is not conceivable because of the high basicity of oxime. If step 3 were rate-determining, the following relation would be derived when the oxime concentration is as before expressed reasonably as [$C_6H_{10}NHOH^+$]

$$\frac{dx}{dt} = \frac{K_1k_3\, a_{H_2SO_4} f_{R\overset{+}{N}HOH}}{K_2 f_{AC}}(a - x)$$

Hence k would be proportional to the activity of the acid. In a similar manner, if step 5 determined the rate with step 4 in mobile equilibrium, k would not depend on the acidity. Also step 6 as rate-determining is improbable, because then k would decrease with an increase of acid concentration.

Lastly, as Bennett,[16] Hammett,[17] Pearson and co-workers[18] have pointed out, the possibility of the occurrence of the reaction by way of the dehydrated form of oxime-O-protonated compound, $C_6H_{10}\overset{+}{N}$ is also conceivable; *i.e.*, if step 4 is replaced by steps 13 and 14, a relationship 15 similar to 12 is obtained as follows.



$$\frac{dx}{dt} = K_1K_{13}k_{14}\,[C_6H_{10}NOH]\,\frac{a_{H^+}}{a_{H_2O}} \times \frac{f_{RNOH}}{f_{AC}}$$

$$k = \frac{K}{a_{H_2O}} \times \frac{f_{R\overset{+}{N}HOH}}{f_{AC}} \quad \left(K = \frac{K_1K_{13}k_{14}}{K_2} = \text{const.}\right)$$

or

$$\log k = -\log a_{H_2O} + \text{const.} \qquad (15)$$

This relationship 15 holds rather better than equation 12 for our experimental data, and the constant term in equation 15 differs little between sulfuric and perchloric acids (see Fig. 3). But a mechanism which involves a rate-determining attack of a naked nitrogen cation rapidly formed appears to encounter some difficulty in explaining the well-known *trans* migration in this rearrangement.[19]

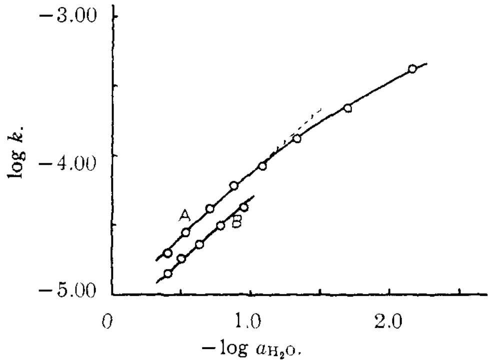


Fig. 3.—Relationship between log k and −log a_{H_2O}: A, H_2SO_4-catalyzed, slope 0.94; B, $HClO_4$-catalyzed, slope 0.92.

The presence of neutral inorganic sulfates tends to decrease the rate constant slightly. Perhaps this fact is due to a change in activity coefficient, but at present the solution is difficult.

Acknowledgments.—The authors wish to thank the referee and Professor R. Oda for their helpful suggestions, and Toyo Rayon Co. for their gift of the material.

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[16] *Cf.* A. W. Chapman, *J. Chem. Soc.*, 1226 (1935).

[17] Reference 12, p. 322.

[18] P. T. Scott, D. E. Pearson and L. J. Bircher, *J. Org. Chem.*, **19**, 1815 (1954); D. E. Pearson and W. E. Cole, *ibid.*, **20**, 489 (1955).

[19] The stereospecificity of this reaction may be explicable by the following assumption. When the pyramidal structure of nitrogen is broken at the dehydration step (eq. 13) the nitrogen cation is shifted immediately a little to the opposite side of the water molecule removed and held there under an unknown interaction with the nearer methylene group; then the rate-determining carbon–carbon bond fission occurs.