[CONTRIBUTION FROM DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF ENGINEERING, NAGOYA UNIVERSITY, CHIKUSA-KU NAGOYA, JAPAN]

Kinetics of the Reaction of Cyclohexyl Aryl Ketones with Nitrous Acid in Sulfuric Acid

BY YOSHIRO OGATA, YOSHIAKI FURUYA, AND MASAHIRO ITO

The rates of the reaction of cyclohexyl p-tolyl (or phenyl) ketone with nitrous acid (0.0196–0.0385 M) in 84.0–94.9% sulfuric acid to form ε-caprolactam and p-toluic (or benzoic) acid have been measured by ultraviolet spectrophotometry. The rates were found to be first order with ketone; the rate constant k decreased with increasing concentration of sulfuric acid, and satisfied eq. 2 of the text. A probable mechanism which involves the rate-determining deprotonation from the protonated ketone forming enol, followed by a rapid nitrosation of enol and its Beckmann rearrangement, is discussed. The electron-releasing group, methyl, in the ketone tends to lower the rate. The apparent energy of activation for cyclohexyl p-tolyl ketone was 21.0 kcal./mole.

A novel and important procedure for the preparation of ε-caprolactam, a starting material for nylon 6, is the reaction of cyclohexyl aryl ketone or cyclohexanecarboxylic acid with nitrous acid in sulfuric acid or with nitrosylsulfuric acid; the process is called the SNIA process.[1] The reaction seems to go by way of cyclohexanone oxime and its Beckmann rearrangement. The authors have previously reported on the kinetics of the rearrangement,[2] but nothing has been known on the mechanism and kinetics of the main reaction of this SNIA process. The present paper describes our investigation on the kinetics of the reaction of cyclohexyl p-tolyl ketone (CTK) or cyclohexyl phenyl ketone (CPK) with nitrous acid in 84.0–94.9% sulfuric acid to form a mixture of ε-caprolactam and arylcarboxylic acid by means of ultraviolet spectrophotometry.

$$C_6H_{11}COAr + HNO_2 \longrightarrow C_6H_{10}NOH + ArCOOH$$
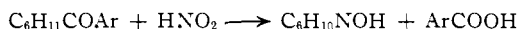
Experimental

Materials.—Cyclohexyl p-tolyl ketone (CTK, m.p. 66.0–67.0°), cyclohexyl phenyl ketone (CPK, m.p. 54.5–56.5°), and cyclohexyl p-methoxyphenyl ketone (m.p. 65.5–66.0°) were prepared by the ordinary methods starting from cyclohexanecarboxylic acid.[3,4] p-Toluic acid, obtained from Teijin Co., was recrystallized from water; m.p. 178–180°. Benzoic acid, m.p. 121–122°, was of guaranteed grade.

Reaction Products and their Analysis.—A mixture of CTK (2.0 g.) and sodium nitrite (1.4 g.) in 89% sulfuric acid was heated at 60° for 3.5 hr. The reaction mixture was treated according to the patent cited.[1] There was mixture of ε-caprolactam, m.p. and mixture m.p. 66.5–67.5° (0.85 g., 80%) and p-toluic acid, m.p. and mixture m.p. 179–180° (1.20 g., 90%).

The ultraviolet spectra of methanolic solutions (ca. 5 × 10⁻⁵ M) of CTK, toluic acid, ε-caprolactam, and sodium nitrite are shown in Fig. 1. The absorption maxima of CTK, CPK, p-toluic acid, and benzoic acid were 254, 242, 237, and 228 mμ, respectively, the absorption of caprolactam being negligible at these wave lengths. Mixtures of CTK, toluic acid, and sodium nitrite of known concentrations corresponding to 0, 20, 40, 60, 80, and 100% conversions were prepared and a plot of the difference of extinctions $(E_{237} - E_{254})$ vs. $(E_{230} - E_{254})$, both being a linear function of concentration of p-toluic acid (x), gave a straight line,[5] and the calculated conversion from the values of $(E_{237} - E_{254})$ at 0 and 100% conversion agreed well with the conversions calculated from the composition of the mixture within 1% error. The initial concentration of nitrous acid was measured by titration with aqueous permanganate.

A Typical Run for the Rate Measurements.—A 0.04 M solution of CTK in sulfuric acid and a 0.06 M solution of sodium nitrite in sulfuric acid were allowed to reach temperature equilibrium (60°) and 5 ml. of both solutions were mixed to start the reaction. Aliquots (each 0.5 ml.) were pipetted out at appropriate time intervals and each one was diluted with methanol to 5.0 × 10⁻⁵ M initial concentration of CTK for spectrophotometry. The conversion was calculated graphically from the observed values of $(E_{237} - E_{254})$.

(1) SNIA Viscosa, Italian Patent 603,606; 604,795 (1960).
(2) Y. Ogata, M. Okano, and K. Matsumoto, J. Am. Chem. Soc., **77**, 4643 (1955).
(3) H. R. Henze and A. F. Isbell, ibid., **76**, 4152 (1954).
(4) D. H. Hey and O. C. Musgrave, J. Chem. Soc., 3156 (1949).
(5) R. T. Vaughn and A. E. Stearn, Anal. Chem., **21**, 1361 (1949).

Results and Discussion

The rate was found to be first order with CTK or CPK with 84.0–94.9% sulfuric acid and 0.0196–0.0385 M nitrous acid. Rate data in 91.1% sulfuric acid at 60° are shown in Table I. The rate constant decreased with increasing acidity of the solution as is obvious in Table II.

TABLE I

THE FIRST-ORDER RATE CONSTANTS OF NITROSATION OF CYCLOHEXYL p-TOLYL KETONE IN 91.1% SULFURIC ACID AT 60°

Ketone, M	Sodium nitrite, M	$k \times 10^5$, sec.⁻¹
0.01	0.0196	4.15
.01	.0294	5.05
.02	.0294	4.60
.04	.0302	4.60
.05	.0289	4.20
.02	.0385	4.90

TABLE II

THE EFFECT OF ACIDITY ON NITROSATION OF CYCLOHEXYL p-TOLYL KETONE AT 60°

H₂SO₄, %	$k \times 10^5$, sec.⁻¹	$\frac{[SH^+]}{[S] + [SH^+]}$	[H₂O],ᵃ M	[HSO₄⁻],ᵃ M
84.0	35.8	0.602	2.30	13.4
85.5	20.8	.691	1.20	13.0
87.6	12.1	.798	0.63	11.7
89.6	5.64	.875	.33	10.3
91.1	4.15	.916	.19	8.8
94.9	1.53	.976	.03	5.1

ᵃ [HSO₄⁻] and [H₂O] calculated by assuming $K = 50$ at 25° for the equilibrium: $H_2O + H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^-$ [N. C. Deno and R. W. Taft, Jr., J. Am. Chem. Soc., **76** 244 (1954)].

Swain and Rosenberg[6] have reported that the racemization of optically active D-α-phenylisocaprophenone involves a rate-determining enolization of the conjugate acid of ketone and that the first-order rate constant fits the equation

$$k = \frac{[SH^+]}{[S] + [SH^+]} (3.46 \times 10^{-4}[H_2O] + 3.3 \times 10^{-6}[HSO_4^-])$$

(1)

Here [S] and [SH⁺] represent free and protonated ketones, respectively.

The ratio [SH⁺]/[S] in the present experiments was determined with 89.6% H₂SO₄ by spectrophotometry at 319 mμ to be 6.50, assuming $[SH^+] \cong [S] + [SH^+]$ in 99% sulfuric acid. The value of K_{SH^+} was 2.3 × 10⁷ from the equation $pK_{SH^+} = \log ([SH^+]/[S]) + H_0$, and the value of $[SH^+]/([S] + [SH^+])$ was calculated from the equation $[SH^+]/([S] + [SH^+]) = h_0/(K_{SH^+} + h_0)$. A plot of $[H_2O]/[HSO_4^-]$ vs. $k([SH^+] + [S])/([HSO_4^-][SH^+])$ gave a straight line (Fig. 2)

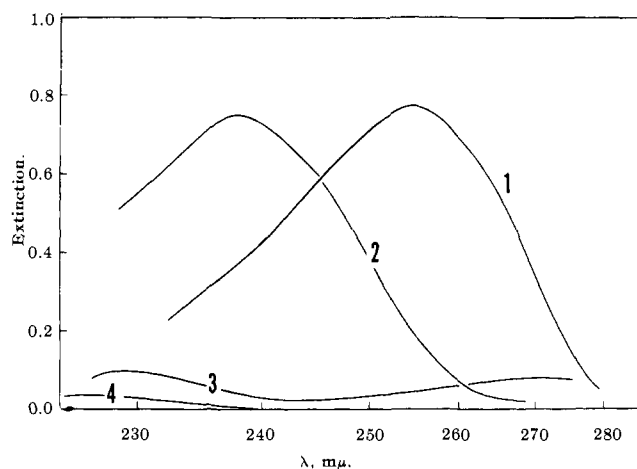(6) C. G. Swain and A. S. Rosenberg, J. Am. Chem. Soc., **83**, 2154 (1961).

Fig. 1.—Ultraviolet spectra of reactants and products in 5 × 10^{-5} M methanolic solution: 1, CTK; 2, p-toluic ac d; 3, sodium nitrite; 4, ϵ-caprolactam.
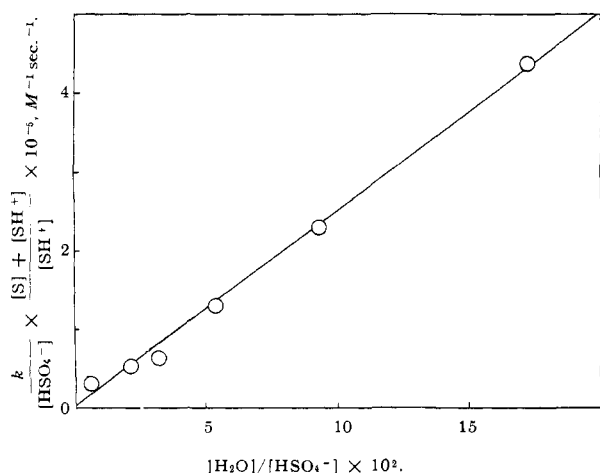

Fig. 2.—Plot on the effect of acidity for the nitrosation of cyclohexyl p-tolyl ketone in 84.0–94.9% sulfuric acid at 60°.

which led to an equation similar to eq. 1 for this reaction.

$$k = \frac{[SH^+]}{[S] + [SH^+]} (2.5 \times 10^{-4}[H_2O] + 1.0 \times 10^{-6}[HSO_4^-])$$

(2)

These facts suggest a mechanism having a rate-determining deprotonation[7] from protonated ketone carbon to yield enol, followed by a rapid nitrosation of

(7) Equation 2 shows that water acts as base 250 times as powerful as bisulfate ion.
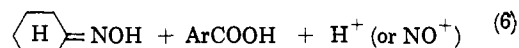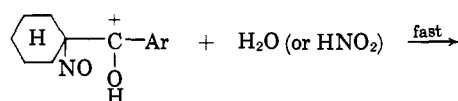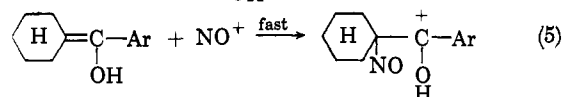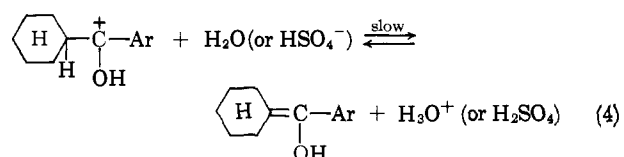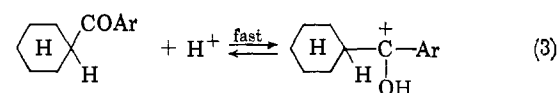
the enol and then the Beckmann rearrangement. Here, the nitrosating species may be nitrosoniu n ion, since nitrous acid is converted almost complete'y to nitrosonium ion in this concentrated sulfuric acid.[8,9]

The rate constant for step 7, which increased with the acidity of the solution in contrast to that for step 4, was reported to be 1.02 × 10^{-4} sec.$^{-1}$ at 60° in 89.4% sulfuric acid.[2]

This mechanism coincides with the fact that the introduction of an electron-releasing group (CH₃) to CPK retards the reaction as expected from the rate-determining deprotonation; $i.e.$, rate constants (k × 10^{-4} sec.$^{-1}$) in 87.6% sulfuric acid at 60° for CPK and CTK were 6.20 and 1.21, respectively. Cyclohexyl p-methoxyphenyl ketone did not give the expected products because of the side reaction.

First-order constants (k × 10^5 sec.$^{-1}$) for CTK in 89.6% sulfuric acid at 50, 60, 70, and 80° were found to be 2.95, 5.64, 16.8, and 39.2, respectively, which gave a straight line in a plot of log k $vs.$ $1/T$ and thence a value of 21.0 kcal./mole for the energy of activation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA, CALGARY, ALBERTA, CANADA]

Specific Solvation in Binary Solvent Mixtures. III. The Solvolysis of o-, m-, and p-Methyl and Nitrobenzyl Chlorides in Ethanol–Water Mixtures

BY J. B. HYNE AND R. WILLS

The effect of variation of position of ring substitution of methyl and nitro groups on the kinetic parameters of solvolysis of benzyl chloride in ethanol–water mixtures has been studied as a further test of the role of specific solvation in such kinetic systems. The observations are in accord with the model presented previously and indicate the steric effect of $ortho$ substituents in inhibiting solvation of the reaction center.

Introduction

The effect of variation of the p-substituent in benzyl chlorides on the activation parameters of solvolysis as the composition of the binary solvent system changes

was reported in the previous paper of this series.[1] These effects were shown to be in accord with the spe-

(1) J. B. Hyne, R. Wills, and R. E. Wonkka, $J. Am. Chem. Soc.$, **84**, 2914 (1962).