and 2720 cm.$^{-1}$ (unconjugated aldehyde) and 1005 cm.$^{-1}$ (methoxymethyl).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.31; H, 7.28.

Hexahydroacetophenone XXIII.—*t*-Butyl α-methyl-α,β-epoxycyclohexylideneacetate (22.6 g., 0.1 mole) was pyrolyzed[16] to give 6.13 g. (48.4%) of XXIII, b.p. 75–77° (23 mm.), n^{25}_{D} 1.4500–1.4502 (lit.[5] n^{25}_{D} 1.4462). It formed a 2,4-dinitrophenylhydrazone, m.p. 138.5–140° (lit.[17] m.p. 140°).

3,7-Dimethylocten-6-one-2 (XXIV).—*t*-Butyl α-methyl-β-methyl-β-(4-methyl-3-pentenyl)-glycidate (25.4 g., 0.1 mole) on pyrolysis yielded 11.32 g. (73.5%) of XXIV, b.p. 90–93 (18 mm.), n^{25}_{D} 1.4448 [lit. b.p. 88–90° (14 mm.),[18] n^{20}_{D} 1.4434[18]; b.p. 87° (13 mm.),[19] $n^{15.2}_{\mathrm{D}}$ 1.446[19]].

2,6-Dimethyl-3-methyleneheptanal-7 (XXII).—*t*-Butyl β-methyl-β-(3-methylene-4-methylamyl)-glycidate (35.87 g., 0.141 mole) was pyrolyzed to give 12.11 g. (55.7%) of XXII, b.p. 78–82° (14.5–15.0 mm.), n^{25}_{D} 1.4390–1.4408; infrared spectrum (CS_2): 885, 1640 and 3100 cm.$^{-1}$ ($>C{=}CH_2$); 1720, 2700 cm.$^{-1}$

$(-\underset{\displaystyle H}{\underset{|}{C}}{=}O)$.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.49; H, 11.53.

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[16] In a single experiment, which could not be reproduced, the pyrolysis of *t*-butyl α-methyl-α,β-epoxycyclohexylideneacetate gave as the major product 1-hydroxy-1-acetylcyclohexane. Reaction parameters which led to this abnormal reaction are being investigated.

[17] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Fourth Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 316.

[18] C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3973 (1959).

[19] J. Doeuvre, *Bull. soc. chim. France*, [4] **45**, 712 (1929).

[CONTRIBUTION FROM THE THOMPSON CHEMICAL LABORATORY, WILLIAMS COLLEGE, WILLIAMSTOWN, MASS.]

The Rearrangement of Pyridine N-Oxide with Acetic Anhydride: Kinetics and Mechanism

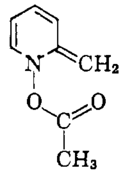
BY J. HODGE MARKGRAF,[1] HAMILTON B. BROWN, JR.,[2] SCOTT C. MOHR[2] AND RICHARD G. PETERSON

RECEIVED JULY 19, 1962

The thermal rearrangement of pyridine N-oxide with excess acetic anhydride to form 2-acetoxypyridine has been studied kinetically at a series of temperatures over the range 100–130°. A procedure was developed in which aqueous solutions of the hydrolyzed reaction mixture were analyzed spectrophotometrically; the accuracy of this method was within 1%. Four possible reaction courses were considered: intramolecular, intermolecular, ion pair and free radical. Kinetic expressions were derived for the first three processes. A series of runs over a tenfold change in concentration was conducted at each temperature. All runs, which were followed to at least 60% completion, exhibited pseudo-first-order kinetics. Additional runs with added salts were conducted. The intramolecular rearrangement of a free cation was excluded by the kinetic data. The free radical mechanism was excluded by the absence of gaseous decomposition products commensurate with such a process. No reliable distinction was possible between pathways involving free ions and ion pairs. Activation parameters were calculated.

Introduction

Katada[3] first reported that pyridine N-oxide in acetic anhydride rearranged thermally to yield 2-acetoxypyridine. Analogous reactions have been observed with other heterocyclic N-oxides. It has been in the picoline series,[4] however, that the mechanism of this type of rearrangement has received the most thorough inspection. Traynelis and Martello postulated the anhydrobase I[5,6] as the key intermediate in the rearrangement of 2-picoline N-oxide with acetic anhydride. The conversion of I to product, 2-pyridylmethyl acetate, was best explained by an intramolecular path, although no distinction was possible among concerted, ion pair or radical pair processes. More recently Oae, Kitao and Kitaoka[7] have studied the same rearrangement using acetic anhydride of which all three oxygens were equally enriched by oxygen-18. Their results, which definitely excluded intermolecular and free radical chain[8] processes, further substantiated an intramolecular pathway in which the two oxygen atoms of I became equilibrated by a radical pair process within the solvent cage.



I

The mechanism of the corresponding rearrangement of pyridine N-oxide has not received comparable attention. In this case there is no possibility for the generation of a species such as I. The preferred route to 2-acetoxypyridine, therefore, may well differ *a priori* from the route to 2-pyridylmethyl acetate. Hence intramolecular, intermolecular, ion pair and free radical chain pathways must be considered. The object of the work reported here was to distinguish by kinetic methods among the above possible processes.

Experimental[9]

Materials.—Pyridine N-oxide was prepared by the method of Ochiai.[10] The product was distilled *in vacuo* under nitrogen; b.p. 128–129° (7 mm.) (lit.[10] b.p. 138–140° at 15 mm.); picrate m.p. 182.5–182.8° (lit.[11] m.p. 179.5°). The white crystalline product was stored in the dark under nitrogen; neither discoloration nor hydration occurred over a period of months.

2-Pyridone was prepared by the method of Adams and Schrecker[12] from 2-aminopyridine. The product was recrystallized from benzene; m.p. 105–107° (lit.[13] m.p. 106°).

Acetic anhydride (J. T. Baker, analyzed reagent, assay 99.2%) was used without further purification. Butyric anhydride was redistilled through a short column; a middle fraction, b.p. 92.0–92.2° (15.5 mm.), was used.

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[1] To whom inquiries should be addressed.

[2] Based in part on the Honors Theses of H. B. Brown, Jr., (1961) and S. C. Mohr (1962).

[3] M. Katada, *J. Pharm. Soc. Japan*, **67**, 51 (1947); *C. A.*, **45**, 9536d (1951).

[4] (a) V. J. Traynelis and R. F. Martello, *J. Am. Chem. Soc.*, **80**, 6590 (1958), review much of the literature relative to such mechanisms and include references to related systems; (b) V. J. Traynelis and R. F. Martello, *ibid.*, **82**, 2744 (1960).

[5] I. J. Pachter, *ibid.*, **75**, 3026 (1953).

[6] A. R. Katritzky, *J. Chem. Soc.*, 191 (1957), isolated 1-benzoyloxy-1,2-dihydro-2-iminopyridine, a compound analogous to I, from the reaction of 2-aminopyridine N-oxide with benzoyl chloride.

[7] S. Oae, T. Kitao and Y. Kitaoka, *J. Am. Chem. Soc.*, **84**, 3359 (1962); for a preliminary report see S. Oae, T. Kitao and Y. Kitaoka, *Chem. Ind.* (London), 515 (1961).

[8] V. Boekelheide and D. L. Harrington, *ibid.*, 1423 (1955).

[9] Melting points and boiling points are uncorrected. Melting points were obtained on a modified Hershberg apparatus with total-immersion Anschütz thermometers. Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[10] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[11] J. Meisenheimer, *Ber.*, **59**, 1848 (1926).

[12] R. Adams and A. W. Schrecker, *J. Am. Chem. Soc.*, **71**, 1186 (1949).

[13] A. E. Chichibabin, *Ber.*, **56**, 1879 (1923).

Tetra-*n*-butylammonium acetate was prepared by the method of Thompson and Kraus[14]; the extreme hygroscopicity of the sample prevented a melting point determination. *Anal.* Calcd. for $C_{18}H_{39}NO_2$: N, 4.65. Calcd. for $C_{18}H_{39}NO_2\cdot{}^1/_2H_2O$: N, 4.51. Found: N, 4.46.

Apparatus.—The constant-temperature oil-bath (Precision Scientific Co. No. 66546) contained Dow Corning 550 Fluid. With efficient stirring and an insulated cover it was possible to regulate the bath temperature to less than ±0.1° over the range 100–130°. The thermometer was marked in tenths of a degree; its accuracy was certified by the Bureau of Standards.

Rate Measurement.—The following procedure was used in determining the kinetics of the rearrangement. All flasks and ampoules were swept with dry nitrogen. A solution was prepared containing a known weight of pyridine N-oxide in a known weight of acetic anhydride. Portions were transferred under nitrogen to 2-ml. glass ampoules; the weight of each aliquot was determined. The ampoules were sealed, preheated for 5 min. in an oil-bath at 100° and immersed simultaneously in the constant-temperature oil-bath. Ampoules were removed periodically, quenched in cold water and opened. The contents were transferred quantitatively to volumetric flasks, and water was added. Hydrolysis of both the acetic anhydride and the 2-acetoxypyridine[15] was complete within 5 min., after which appropriate dilutions were made. Deionized water was used in all dilutions. The absorbances of these solutions were determined with a Beckman model DU spectrophotometer.

It was found that aqueous solutions of pyridine N-oxide and 2-pyridone exhibited absorption maxima at 255 and 294 mμ, respectively. For both compounds standard solutions were prepared by weight, and Beer's law curves were determined for absorbance *versus* mole fraction of the compound over a tenfold change in concentration. Excellent linearity was obtained for each compound at both wave lengths; the intercept was the origin in all cases. The method of least squares was used to obtain the absorptivities. The mole fraction of pyridine N-oxide in the hydrolyzed reaction solutions was then calculated from the usual equation employing absorptivities and absorbances.[16] It was established that the presence of added sodium acetate or acetic acid affected neither the wave length of maximum absorption nor the absorbance of either compound. A control run of a complete rearrangement was carried out, including the preheat period and omitting only the constant temperature bath. At appropriate intervals ampoules were opened, the contents hydrolyzed and the absorbances of the solutions measured. The agreement between values for the mole fraction of pyridine N-oxide calculated from the weights of reagents and the mole fraction calculated from the absorbance measurements was within 1%.

The determination of the order of the reaction was made graphically. Various plots of a function of the pyridine N-oxide concentration *vs.* time indicated that the reaction was definitely pseudo-first order. All rearrangements were followed to a minimum of 60% reaction; nine or ten points were plotted in each run. Results of a typical kinetic run are given in Table I.

TABLE I

TYPICAL KINETIC RUN

Initial concentration: 0.0110 *M* pyridine N-oxide in acetic anhydride; temp. 100.05 ± 0.03°

Time, min.	Absorbance at 255 mμ	Absorbance at 294 mμ	n_{PNO} (calcd.)[a] × 10^7	n_{PNO} (obsd.)[b] × 10^7
360	0.240	0.015	3.961	3.634
722	.215	.025	3.911	3.235
1080	.210	.035	4.126	3.142
1452	.182	.041	3.893	2.705
1800	.172	.048	3.950	2.540
2160	.156	.053	3.961	2.287
2610	.142	.060	3.975	2.062
3060	.129	.066	3.989	1.853
3680	.112	.071	3.871	1.585
4325	.097	.077	3.864	1.346

[a] Initial mole fraction of pyridine N-oxide. [b] Mole fraction of pyridine N-oxide at time *t*.

Kinetic Runs with Added Salts.—The solubilities[17] of lithium acetate and sodium acetate in acetic anhydride were less than the desired concentration of 0.01 *M*.[18] Lithium perchlorate was not sufficiently soluble in the presence of pyridine N-oxide. Salts of adequate solubility were tetra-*n*-butylammonium acetate and sodium perchlorate.[17] The procedure was identical with that followed in ordinary kinetic runs. The added salt was ignored in the calculations for each ampoule, since its effect was negligible.

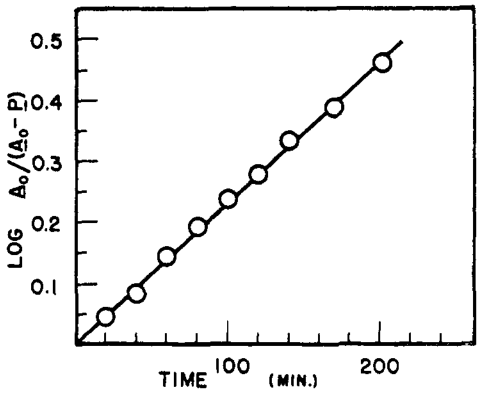

Fig. 1.—Pseudo-first-order rate of rearrangement of pyridine N-oxide (0.0307 *M*) in acetic anhydride at 130°; data from Table II.

Isolation of 2-Pyridone under Conditions of the Kinetic Experiments.—A solution of 0.2929 g. of pyridine N-oxide and 32.2224 g. of acetic anhydride (0.103 *M*) was maintained at 130.00 ± 0.1° for a period corresponding to 8 half-lives. The reaction solution was hydrolyzed, concentrated to dryness and the residue dried to give 0.2892 g. of solid material. The crude product was dissolved in chloroform, chromatographed on alumina and eluted with chloroform–95% ethanol (4:1 v./v.) to give white crystals, m.p. 105.4–106.4°. Infrared spectra[19] of the purified product and authentic 2-pyridone were identical.

Gas Collection.—A solution of 0.2653 g. of pyridine N-oxide and 32.1469 g. of acetic anhydride (0.0930 *M*) was purged for 5 min. with nitrogen, connected through long capillary tubing to a nitrogen-swept, mercury-filled gas buret with leveling bulb and maintained at 130.01 ± 0.03° for a period of 5 hours. The flask was permitted to equilibrate overnight to room temperature. After a correction was made for a change in barometric pressure, the net volume of gas evolved was 0.0 ml.

The gases in the system comprised of the gas buret, connecting tube and flask were collected in a sample tube which had been previously swept with nitrogen and evacuated. The mass spectrometric analyses[20] of the unknown sample and of acetic anhydride[21] indicated the absence of any methane or carbon dioxide produced by the reaction solution. Nitrogen, acetic anhydride, acetic acid and a trace of air were the only components in the reaction sample.

An aliquot was withdrawn from the reaction solution, hydrolyzed and diluted as described above. Spectrophotometric analysis indicated 79.5% reaction.

Conductance Measurements.[22]—Solutions were prepared by the same procedure employed for ordinary kinetic runs. The conductivity cell was composed of a pair of concentric cylindrical platinum electrodes mounted in glass; *ca.* 20 ml. of solution was required. The cell constant was determined in the normal manner. The conductivity bridge was model RC-1B, Industrial Instruments, Inc. The specific conductance (κ) was calculated by the usual expression involving the cell constant and the resistance. The results are given in Table IV.

Results

Kinetics.—The rates of the thermal rearrangement of pyridine N-oxide in acetic anhydride were measured at 130°, 120° and 100°. The extent of the reaction was followed by determining the decrease in absorption at 255 mμ due to pyridine N-oxide. A correction at 255 mμ was made for the contribution of 2-pyridone, the hydrolysis product from 2-acetoxypyridine. The rate constants, which were obtained by the method of least squares, are presented in Table II and Fig. 1.

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(14) W. E. Thompson and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1016 (1947).

(15) A. E. Chichibabin and P. G. Szokov, *Ber.*, **58**, 2650 (1925).

(16) E. I. Stearns, "Analytical Absorption Spectroscopy," M. G. Mellon, editor, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 374.

(17) V. Gutman and E. Nedbalek, *Monatsh.*, **89**, 130 (1958).

(18) The insolubility of sodium acetate in acid anhydrides tends to vitiate "cross-over" experiments.[4] In our hands 0.83 g. of sodium acetate was recovered quantitatively from 3.18 g. of butyric anhydride at 135° after 1.5 hr.

(19) Infrared spectra were taken as mineral oil mulls with a Perkin–Elmer Infracord model 137 spectrophotometer.

(20) Mass spectra were determined with a C.E.C. model 21-401 instrument at an ionization potential of 70 v. We are indebted to Mr. R. L. Ames and Mr. D. Clagett of Yale University for the analyses.

(21) H. Gutbier and H.-G. Plust, *Chem. Ber.*, **88**, 1777 (1955).

(22) We are indebted to Dr. Raymond C. Petersen of the Sprague Electric Co. for these determinations.

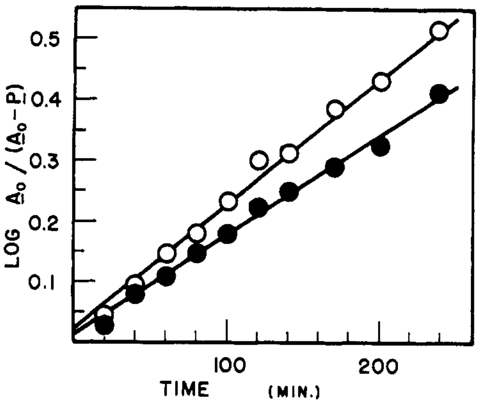


Fig. 2.—Pseudo-first-order rates of rearrangement of pyridine N-oxide in acetic anhydride at 130° as affected by added substances: ○, $NaClO_4$; ●, Bu_4NOAc; data from Table III.

In all cases a good pseudo-first-order plot was obtained; the intercept was the origin in every case. Plots of the data by a second-order equation failed to exhibit linearity.

Table II

Rates of Rearrangement of Pyridine N-Oxide in Acetic Anhydride

A_0,[a] M	Temp., °C.	$k \times 10^5$, sec.$^{-1}$
0.0106	130.05 ± 0.05	8.39
.0307	129.96 ± .06	8.90
.0487	129.97 ± .05	7.98
.0560	129.97 ± .07	7.84
.0573	130.03 ± .06	8.48
.1024	129.95 ± .05	8.40
	Av.	8.33
0.0119	120.03 ± 0.04	3.31
.0536	119.98 ± .03	3.41
.1013	120.01 ± .08	3.28
	Av.	3.33
0.0110	100.05 ± 0.03	0.411
.0617	99.99 ± .01	.406
.1007	100.01 ± .01	.406
	Av.	0.408

[a] Initial concentration of pyridine N-oxide.

The changes in rate caused by added salts were studied with respect to both common ion[23] and ionic strength effects. The results are given in Table III and Fig. 2. Satisfactory plots were obtained from the pseudo-first-order treatment; no change in the order of the reaction was observed.

Table III

Rates of Rearrangement of Pyridine N-Oxide in Acetic Anhydride

A_0,[a] M	Added substances Identity	Added substances M	Temp., °C.	$k \times 10^5$, sec.$^{-1}$
0.0414	Bu_4NOAc	0.0290	130.06 ± 0.03	6.31
0.0421	$NaClO_4$	0.0310	130.02 ± 0.03	8.19

[a] Initial concentration of pyridine N-oxide.

Gas Evolution.—The occurrence of free radical intermediates in the rearrangement of the picoline N-oxides has been demonstrated convincingly by Traynelis and Martello,[4] who not only identified and measured the evolved gases but also inhibited their generation by the addition of such free radical scavengers as *p*-benzoquinone and *m*-dinitrobenzene. The latter approach was not feasible in the present case because the absorption of such compounds in the ultraviolet region interfered with the analysis. An attempt was made to employ iodine as a suitable scavenger after it had been established that at the concentrations used (3.8 mole %) the analytical procedure remained valid.[24] The results, however, failed to exhibit a pseudo-first-order relationship and, in fact, were better accommodated by a second-order treatment.[26] Kinetic efforts were abandoned in favor of gas analysis. The total absence of any evolved gases was in contrast to *ca.* 2.5 ml. (at ambient conditions) calculated from the data of Traynelis and Martello[4a] for an equivalent amount of 2-picoline N-oxide.

Products.—The facility with which 2-acetoxypyridine is hydrolyzed to 2-pyridone precluded any convenient analytical scheme based on the initial product. Instead, the contents of each ampoule were hydrolyzed directly to a mixture of pyridine N-oxide, 2-pyridone and acetic acid. It was established that 2-pyridone was the principal product under the conditions of the kinetic runs.

Conductance.—The resistance (*R*) of a series of solutes in acetic anhydride were measured, and the specific conductances (κ) were calculated. The data are presented in Table IV.

Table IV

Conductances of Solutes in Acetic Anhydride (27°)

A_0,[a] M	Added substances Identity	Added substances M	R, ohms	κ, ohms^{-1} cm.$^{-1}$
0.0	None	0.0	57,000	2.7×10^{-7}
.01	None	.0	3,900	3.9×10^{-6}
.042	None	.0	2,380	6.4×10^{-6}
.10	None	.0	2,200	7.0×10^{-6}
.042	$NaClO_4$	.031	14.4	1.1×10^{-3}
.041	Bu_4NOAc	.029	20.1	7.6×10^{-4}
.0	None	.0	34,000	4.5×10^{-7}
.0	H_2O	.027	25,800	5.9×10^{-7}
.0	AcOH	.061	25,900	5.9×10^{-7}

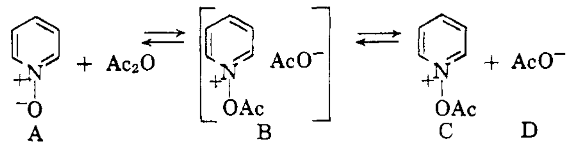
[a] Concentration of pyridine N-oxide.

Thermodynamic Activation Values.—From the kinetic data of Table II the activation parameters were calculated[27] from the theory of absolute reaction rate. The enthalpy of activation, $\Delta H^{\ddagger}$, obtained from the least squares slope of the line from a plot of log k/T *vs.* $1/T$ was 29.2 kcal./mole. The entropy of activation, $\Delta S^{\ddagger}$, was −5.5 e.u., calculated from the expression[28]

$$\Delta S^{\ddagger} = 2.303R[\log(k/T) - \log(k'/h) + \Delta H/2.303RT]$$

Discussion

The path of the reaction is perhaps best discussed in terms of the equilibria



(1)

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[23] We observed a similar depression of the rate with tetraethylammonium acetate, but its probable existence as the tetrahydrate raised problems in regard to changes in the solvent polarity. We do not feel that the possible hemihydrate of tetra-*n*-butylammonium acetate caused any such problems (*cf.* the conductance data).

[24] Such low concentrations of iodine failed to exhibit the enhanced absorption reported by Kubota[25] for a 1:1 complex of pyridine N-oxide and iodine.

[25] T. Kubota, *Nippon Kagaku Zasshi*, **78**, 196 (1957); *C. A.*, **53**, 2777e (1959).

[26] Product isolation was not carried out. It is likely that competitive reactions occurred; *cf.* E. Ochiai and T. Okamoto, *J. Pharm. Soc. Japan*, **67**, 86 (1947); *C. A.*, **45**, 9059h (1951).

[27] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 195.

[28] Where *k* is the pseudo-first-order rate constant at temperature *T*(°K.), *k'* is the Boltzmann constant, *h* is the Planck constant and *R* is the gas constant.

The formation of C has been generally accepted as the initial step in the rearrangement of heterocyclic N-oxides in acid anhydrides.[4,7,8] Recently Traynelis, *et al.*,[29] have obtained chemical evidence for the initial, reversible formation of 1-acetoxy-2-methylpyridinium cation in the rearrangement of 2-picoline N-oxide with acetic anhydride. The ion pair B is included because it must formally be involved at least as a transition state between A and C.

In the present case a subsequent, rate-determining intramolecular step leading from the free cation C to product P would involve

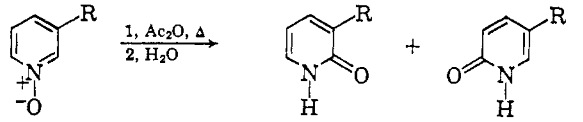
$$(A_0 - P)^{1/2} = A_0^{1/2} - (kt/2) \qquad (2)$$

as the rate expression.[30] A plot of $(A_0 - P)^{1/2}$ *vs.* time was non-linear and, therefore, the pseudo-first-order behavior of the reaction is inconsistent with the intramolecular rearrangement of the free cation.

On the other hand, a rate-determining step involving both ions C and D would lead to the observed first-order kinetics (Fig. 1), assuming that by-product acetic acid remains un-ionized in acetic anhydride.[31] With added acetate ion a decrease in rate was observed which is qualitatively consistent with the free cation C leading to product. Within the framework of eq. 1 such an interpretation is contradicted by the fact that the reduction in rate (24%) is far less than the approximate 100-fold decrease in rate estimated from conductance data. The effect of acetate ion must be accounted for by some other method—perhaps, for example, by the formation in acetic anhydride of a complex between acetate ion and pyridine N-oxide. Regardless of the exact reaction path, the ion pair B is necessarily the transition state in any reaction between ions C and D. It is important to realize, however, that the pathway within the ion pair may be intermolecular or concerted intramolecular.

The absence of any gas evolution commensurate with a free radical chain mechanism excludes any radical process except one so securely "caged" that it is indistinguishable from an ionic mechanism.[32]

The generation of a radical pair[4,7] from the N-acetoxypyridinium ion seems most unlikely because such a species, the pyridyl ion radical, would not have the delocalization operative in the picolyl radicals. The available evidence from a series of rearrangements of 3-substituted pyridine N-oxides supports an ionic process.



(3)

Equal amounts of the isomeric pyridones were obtained when R was methyl.[33] However, when R was a substituent exerting a $-I$ effect ($-COOH$,[33] $-COOCH_3$,[34] $-X$,[35] $-NO_2$[36]) the percentage of the 3-substituted 2-pyridone always predominated. The fact that the critical step in the rearrangement appears to be influenced by such an inductive effect suggests a nucleophilic attack. Although the thermodynamic activation parameters are not particularly arresting, the value of $\Delta S^{\ddagger}$ is indicative of a restricted transition state.

Acknowledgments.—The authors are indebted to Dr. Sidney D. Ross and Dr. Raymond C. Petersen for valuable discussions during this investigation. We also acknowledge with pleasure the support of this work by the National Science Foundation through grant NSF-G16776.

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(29) V. J. Traynelis, A. I. Gallagher and R. F. Martello, *J. Org. Chem.*, **26**, 4365 (1961).

(30) This relationship follows from $dP/dt = kC$, the equilibrium expression, the fact that $C = D$ and the low concentration of free ions as indicated by the conductance data—*i.e.*, $C << (A + B + P)$.

(31) (a) E. A. Evans, J. L. Huston and T. H. Norris, *J. Am. Chem. Soc.*, **74**, 4985 (1952); (b) T. B. Hoover and A. W. Hutchison, *ibid.*, **83**, 3400 (1961).

(32) The generation of free radical species is apparently temperature dependent. A referee reported that at higher temperatures the reaction of pyridine N-oxide with acetic anhydride afforded CO_2 and 2- and 4-picoline.

(33) B. M. Bain and J. E. Saxton, *J. Chem. Soc.*, 5216 (1961).

(34) V. Boekelheide and W. L. Lehn, *J. Org. Chem.*, **26**, 428 (1961).

(35) M. P. Cava and B. Weinstein, *ibid.*, **23**, 1616 (1958).

(36) E. C. Taylor and J. S. Driscoll, *ibid.*, **25**, 1716 (1960).

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

Kinetics of the Acid-catalyzed Transformation of Peroxyacetic Acid to Acetyl Peroxide in Acetic Acid

BY YOSHIRO OGATA, YOSHIAKI FURUYA, JUNJI MAEKAWA AND KENJI OKANO

RECEIVED OCTOBER 5, 1962

It was confirmed by paper chromatography that peroxyacetic acid in acetic acid was transformed reversibly to acetyl peroxide in the presence of sulfuric acid. The rate satisfied the first-order equation for reversible reactions. The plot of log *k vs.* H_0 gave a straight line with a slope of -1.04. A mechanism involving an attack of protonated acetic acid on peroxyacetic acid is postulated and discussed.

In the course of our kinetic investigation on the acid-catalyzed decomposition of peroxyacetic acid in acetic acid, it was found that the reaction slowed down and stopped when *ca.* one-half equivalent of the peroxyacetic acid was consumed. The rate could not be expressed by the simple first-order equation. Furthermore, it was of interest to note that the reaction mixture titrated iodometrically after standing overnight, liberated almost the same amount of iodine as that of reacted peroxyacetic acid. Thus, we assumed that the reaction was not a simple decomposition, but might be the transformation of peroxyacetic acid into acetyl peroxide.

$$CH_3COOOH + CH_3COOH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3COO_2COCH_3 + H_2O$$

The presence of acetyl peroxide was established by paper chromatography. The rate satisfied the first-order rate equation when the presence of an equilibrium between peroxyacetic acid and acetyl peroxide was taken into account.

Thus far acetyl peroxide has been prepared by the reaction of acetyl chloride or acetic anhydride with metallic peroxides or by the reaction of acetic anhydride