

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

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

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, how-

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

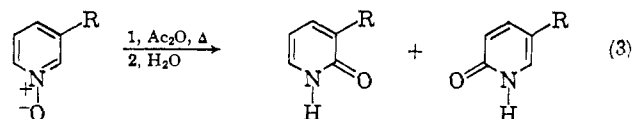
(30) This relationship follows from $dP/dt = kC$, the equilibrium expression, the fact that $C = D$ and the low concentration of free ions as indicated by the conductance data—*i.e.*, $C \ll (A + B + P)$.

(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).

ever, 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.



Equal amounts of the isomeric pyridones were obtained when R was methyl.³³ However, when R was a substituent exerting a $-I$ effect ($-\text{COOH}$,³³ $-\text{COOCH}_3$,³⁴ $-\text{X}$,³⁵ $-\text{NO}_2$ 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 ΔS^\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.

(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).

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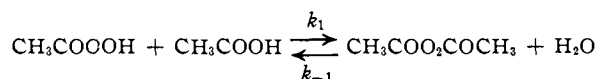
Kinetics of the Acid-catalyzed Transformation of Peroxyacetic Acid to Acetyl Peroxide in Acetic Acid

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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.



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

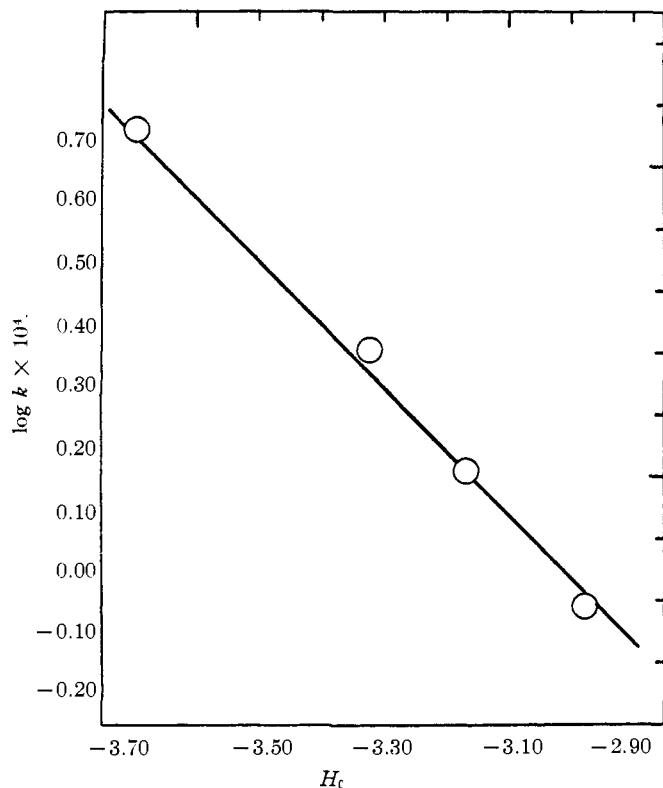


Fig. 1.—The plots of $\log k$ vs. H_0 for the transformation of peroxyacetic acid to acetyl peroxide at 40°.

with hydrogen peroxide,^{1,2} but nothing has been known about the conversion of peroxyacetic acid into acetyl peroxide by reaction with acetic acid; it is important to note that acetyl peroxide, a highly explosive compound, may be formed in the preparation³ of peroxycarboxylic acid under substantially anhydrous conditions. The present paper describes a kinetic study of this reaction by the iodometric estimation of peroxyacetic acid and acetyl peroxide.

Experimental

Materials.—Peroxyacetic acid was prepared by the reaction of acetic anhydride with aqueous hydrogen peroxide.⁴ Acetyl peroxide was prepared by the reaction of acetic anhydride with barium peroxide⁵ or sodium peroxide² in ether at 0°. After completion of the reaction, the ether was evaporated under vacuum. Acetic acid was then added for safe storage.

It is reported² that the obtained acetyl peroxide was 99% pure with 79% yield. The concentration of acetyl peroxide could be measured as stated in the above report² by iodometry after standing 15 hr. at 20°. No appreciable difference was observed between the measurement under air and nitrogen atmosphere.

A Typical Run for the Rate Measurements.—Five milliliters of a solution of ca. 0.1 M peroxyacetic acid in acetic acid was poured into a solution of 45 ml. of 4 N H₂SO₄ in acetic acid after both solutions had attained temperature equilibrium. Aliquots (each 5 ml.) were taken out at known intervals of time, being introduced to 100 ml. of an ice-cooled aqueous solution of ca. 0.1% potassium iodide. Iodine liberated by peroxyacetic acid was quickly titrated with 0.005 N sodium thiosulfate. The titrated solution was kept standing at 20° for about 15 hours to

(1) J. d'Ans and J. Mattner, *Chem.-Ztg.*, **74**, 435 (1950); J. U. Nef, *Ann.*, **298**, 274 (1897); E. G. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Princeton, N. J., 1961, p. 300.

(2) J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959).

(3) Cf. W. E. Parker, et al., *J. Am. Chem. Soc.*, **77**, 4037 (1955).

(4) T. W. Findley, D. Swern and J. T. Scanlan, *ibid.*, **67**, 413 (1945).

(5) B. C. Brodie, *Ann. Suppl.*, **3**, 209 (1864-1865); A. M. Clover and G. F. Richmond, *Am. Chem. J.*, **29**, 182 (1903).

allow any acetyl peroxide to be hydrolyzed to peroxyacetic acid. The amount of peroxyacetic acid thus produced was determined iodometrically as above.

The Paper Chromatography of Acetyl Peroxide.—The solution of the reaction product from peroxyacetic acid containing acetyl peroxide was developed with a mixture of diethyl ether and ethyl acetate (1:4) on Toyo Filter Paper No. 54 which had been preliminarily treated with a mixture of acetic acid (300 g.), acetic anhydride (80 g.) and zinc chloride (20 g.).⁶ Two pink spots were observed by spraying with a methanolic solution of 3% *p*-dimethylaminoaniline dihydrochloride. The values of R_f were found to be 0.83 and 0.75, which agreed with those for authentic samples of acetyl peroxide (0.82) and peroxyacetic acid (0.76), respectively. The initial reaction mixture gave two spots corresponding to peroxyacetic acid (R_f 0.75) and hydrogen peroxide (0.61), but no appreciable spot for acetyl peroxide.

Results and Discussion

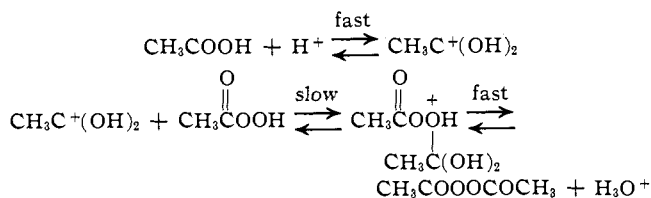
The kinetic data satisfy the first-order equation for reversible reactions, $\ln [Z/(Z-x)] = kt$, as shown in Table I, where Z is the concentration of consumed peroxyacetic acid at the equilibrium stage, x is the concentration of consumed peroxyacetic acid or acetyl peroxide at time t , and a is the initial concentration of peroxyacetic acid. The value $([AcO_2H] + [Ac_2O_2])$ is constant as is obvious from the table. The energy of activation was calculated to be 16.5 kcal./mole from the following average values of $k \times 10^4$ sec.⁻¹: 30°, 1.43; 40°, 3.11; and 50°, 7.73.

TABLE I

TYPICAL RATE DATA OF THE TRANSFORMATION OF PEROXYACETIC ACID TO ACETYL PEROXIDE IN ACETIC ACID
Nominal initial concn. of CH₃CO₂H, 10⁻² M; concn. of H₂SO₄, 3.6 N ($H_0 = 3.430$); temp., 40°

Time, min.	[CH ₃ CO ₂ H], ($a-x$), × 10 ² M	[(CH ₃ CO ₂) ₂ O], x , × 10 ² M	$Z-x$, × 10 ² M	k , × 10 ⁴ sec. ⁻¹
0	1.110	0.098	0.550	
15	0.965	.207	.405	3.20
30	.875	.280	.315	3.11
45	.795	.343	.235	3.15
60	.725	.400	.165	3.13
90	.663	.482	.103	3.10
120	.610	.505	.050	3.20
153	.585	.535	.025	3.16
				Av. 3.15

The plot of $\log k$ vs. H_0 gave a straight line with a slope of -1.04. Hence, it is reasonable to assume a mechanism involving protonated acetic acid such as



This mechanism is analogous to that of esterification. An attack of protonated peroxyacetic acid on acetic acid is less probable, since it would attack the carbonyl carbon atom instead of the carbonyl oxygen atom of acetic acid. An attack of acetyl carbonium ion is not likely because the formation of such a carbonium ion requires a more powerful electrophilic catalyst.

The rate constant of the reverse reaction, the hydrolysis of acetyl peroxide, was also measured in acetic acid containing a small amount of water. The pseudo-first-order constant was 3.17×10^{-4} sec.⁻¹ at 40° and with an acidity function of -3.430.

(6) J. Janoušek, *Faserforsch. u. Textiltech.*, **8**, 339 (1957).