The Kinetics of the Acid-catalyzed Transformation of Peroxybenzoic Acids to Acetyl Benzoyl Peroxides in Acetic Acid*

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It is well-known that peroxy acids are obtained by the hydrolysis of the corresponding peroxides.[1-3] However, the reverse reactions of peroxy acids to form peroxides have scarcely been studied at all. The present authors have reported previously on the acid-catalyzed reversible transformation of peroxyacetic acid to acetyl peroxide in acetic acid.[4]

It has been analogously supposed that peroxybenzoic acid in acetic acid may be reversibly transformed to acetyl benzoyl peroxide in the presence of sulfuric acid:

$$C_6H_5CO_3H + CH_3CO_2H \overset{H^+}{\rightleftarrows} C_6H_5COO_2COCH_3 + H_2O \qquad (1)$$

As expected, it was observed that the reaction led to acetyl benzoyl peroxide, which was identified by paper chromatography. The reaction rate followed the first-order kinetics if the reversibility of the reaction was taken into account. The present paper will describe the results of a kinetic study of this and related reactions by the iodometric determination of peroxybenzoic acid and acetyl benzoyl peroxide. Thus far, acetyl benzoyl peroxide has been

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[1] A. M. Clover and G. F. Richmond, *Am. Chem. J.*, **29**, 189 (1903).

[2] Parke Davis Co., German Pat. 156998.

[3] "Organic Syntheses," Coll. Vol. I, 431 (1941).

[4] Y. Ogata, Y. Furuya, J. Maekawa and K. Okano, *J. Am. Chem. Soc.*, **85**, 961 (1963).

prepared by the reaction of peroxybenzoic acid with acetic anhydride[5] or by the autoxidation of benzaldehyde in acetic anhydride.[6]

Experimental

Materials.—Peroxybenzoic acid, m. p. 41°C, was prepared by the hydrolysis of benzoyl peroxide.[3] Substituted peroxybenzoic acids were obtained by an analogous procedure from the corresponding benzoyl peroxides, prepared by the reaction of benzoyl chlorides with hydrogen peroxide.[7] Acetyl benzoyl peroxide was prepared by the autoxidation of a mixture of benzaldehyde and acetic anhydride,[6] m. p. 35.5°C. Acetyl peroxide was obtained by the reaction of acetic anhydride with barium peroxide in an ethereal solution at 0°C, the solvent being exchanged with acetic acid for safe storage.[8]

A Typical Run for the Rate Measurements.—Peroxybenzoic acid (ca. 0.138 g., 0.001 mol.) was introduced into an acetic acid solution (50 ml.) of 3.6 N sulfuric acid after the solution had been brought to a temperature equilibrium. Aliquots (5 ml. each) were taken out and worked up in a manner reported previously[4] in order to estimate peroxybenzoic acid and acetyl benzoyl peroxide. It was confirmed in a blank test that only 1% of acetyl benzoyl peroxide was hydrolyzed to peroxybenzoic acid under the same conditions after 2 min., although it was completely hydrolyzed after 15 hr. at 20°C.

Reaction Products Criterion.—A solution of the reaction products was developed with a mixture of acetic acid and water (2 : 3 in vol.) on acetylated Toyo Filter paper No. 54.[9] When sprayed with a methanolic solution of 3% *p*-dimethylaminoaniline dihydrochloride, the initial reaction mixture gave a single spot corresponding to peroxybenzoic acid (R_f : 0.66), while the mixture after 2 hr. gave two spots corresponding to peroxybenzoic acid (0.66) and acetyl benzoyl peroxide (0.45) and no appreciable spots for benzoyl peroxide (0.15), acetyl peroxide (0.92), peroxyacetic acid (0.97) or hydrogen peroxide (0.88). In the reverse reaction, the initial mixture of acetyl benzoyl peroxide in acetic acid gave a spot for acetyl benzoyl peroxide alone (0.45), while the mixture after 2 hr. gave two spots for acetyl benzoyl peroxide (0.45) and peroxybenzoic acid (0.66). Hence, the presence of equilibrium 1 is confirmed. Under these conditions, there was no appreciable interconversion between peroxybenzoic acid and acetyl benzoyl peroxide in the absence of sulfuric acid.

Results and Discussion

Since there is a large excess of acetic acid and water, the kinetics follow the pseudo first-order equation for reversible reactions, $\ln [z/(z-x)]=kt$, where z is the concentration of consumed peroxybenzoic acid at equilibrium, and x is the concentration of consumed peroxybenzoic acid at time t.

Assuming the pseudo first-order rate constants for forward and reverse reactions to be k_1 and k_{-1} respectively, the following rate and equilibrium equations are obtained[10]:

$$\ln [z/(z-x)]=(k_1+k_{-1})t=kt$$

$$z/(a-z)=k_1/k_{-1}$$

where a is the initial concentration of peroxybenzoic acid. Therefore, the forward rate constant, k_1, is expressed as:

TABLE I. TYPICAL RATE DATA OF THE TRANSFORMATION OF PEROXYBENZOIC ACID TO ACETYL BENZOYL PEROXIDE IN ACETIC ACID AT 45°C

Initial concn. of $C_6H_5CO_3H$, 2×10^{-2} M ; concn. of H_2SO_4, 3.6 N (H_0, −3.430) ; concn. of H_2O, 0.498 M ; concn. of $C_6H_5CO_3H$ in equilibrium, 0.524×10^{-2} M (observed value)

Time min.	$[C_6H_5CO_3H]$		$[CH_3CO\text{-}O_2\text{-}COC_6H_5]$ x'* $\times10^2$ M	$([C_6H_5CO_3H]+[CH_3CO\text{-}O_2\text{-}COC_6H_5])$ $(a-x)+x'$ $\times10^2$ M	$z-x$ $\times10^2$ M	k_1 $\times10^4$ sec^{-1}
	Remaining $a-x$ $\times10^2$ M	Consumed x $\times10^2$ M				
0	1.846		0.027	1.873	1.322	
10	1.675	0.171	0.203	1.878	1.151	1.62
20	1.529	0.317	0.339	1.868	1.005	1.61
40	1.272	0.574	0.592	1.864	0.748	1.67
70	1.016	0.830	0.835	1.851	0.492	1.65
110	0.804	1.042	1.035	1.839	0.280	1.65
170	0.636	1.210	1.193	1.829	0.112	1.70
230	0.569	1.277	1.253	1.822	0.045	1.69
						Av. 1.66

* x' is the concentration of formed acetyl benzoyl peroxide at time t.

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[5] A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900).

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[7] H. von Pechmann and L. Vanino, *Ber.*, **27**, 1510 (1894).

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

[9] J. Janoušek, *Faserforsch. u Textiltech.*, **8**, 339 (1957).

[10] L. P. Hammettt, "Physical Organic Chemistry," McGraw-Hill Book Co., New York (1940), p. 102.

TABLE II. THE CONSTANCY OF APPARENT EQUILIBRIUM CONSTANT WITH VARYING CONCENTRATION OF WATER IN THE REACTION MIXTURE WITH 3.6 N SULFURIC ACID AT 45°C

H_2O added vol. %	$[H_2O]$ M	$[CH_3CO_2H]$[a)] M	$\frac{z}{a-z}$ [b)]	Equilibrium constant[c)] $K\times10^2$
0	0.498	15.694	1.262	4.00
1	1.054	15.694	0.5504	3.70
3	2.160	15.172	0.3193	4.55
5	3.272	14.822	0.1468	3.24
10	6.040	13.952	0.0776	3.36

a) Concn. of acetic acid was calculated by means of the equation: [volume of CH_3CO_2H (ml.)] × [Sp. gr.]/[Mol. wt. of CH_3CO_2H] where sp. gr. is 1.049 at 20°C.

b) The value was calculated from the value of $[CH_3COO_2COC_6H_5]/[C_6H_5CO_3H]$ at equilibrium.

c) The constant was calculated by means of the following equation:

$$K=\frac{[CH_3COO_2COC_6H_5][H_2O]}{[C_6H_5CO_3H][CH_3CO_2H]}=\frac{z}{a-z}\cdot\frac{[H_2O]}{[CH_3CO_2H]}$$

where $[H_2O]$ is the sum of the concentrations of water in original acetic and sulfuric acids and the concentrations of added and formed water.

$$k_1=kz/a$$

As Table I shows, the value of k_1 holds constancy.

Moreover, the sum of the concentrations of peroxybenzoic acid and acetyl benzoyl peroxide ($[C_6H_5CO_3H]+[C_6H_5COO_2COCH_3]$) is very nearly constant during the reaction, as is shown in Table I; this means that the reaction is a transformation instead of a decomposition. The rate constant, k_1, holds constancy with varying initial concentrations of peroxybenzoic acid (0.615—1.846×10^{-2} M) with added benzoic acid (4×10^{-2} M).

As expected, equilibrium 1 moved to the left-hand side when the concentration of water was increased. The constancy of the calculated equilibrium constants in various concentrations of water is apparent from Table II.

The energy and entropy of activation were calculated to be 16.8 kcal. mol^{-1} and −25.7 e. u., respectively, from the following average values of $k_1\times10^4$ sec^{-1}: 40°C, 1.01; 45°C, 1.66; 50°C, 2.34; 55°C, 3.42.

The plot of $\log k_1$ vs. H_0 gave a straight line, with a slope of −0.96, as is shown in Fig. 1. Therefore, an activated complex with a proton may be suggested for the reaction.

The introduction of an electron-attracting group into the peroxybenzoic acid retarded the reaction, and the Hammett plot (Fig. 2) gave a negative ρ-value of −0.37. The introduction of an electron-releasing group, on the other hand, accelerated the reaction. The latter reaction, however, was accompanied by a side reaction, probably such as the cleavage

TABLE III. SUBSTITUENT EFFECT OF THE TRANSFORMATION OF SUBSTITUTED PEROXYBENZOIC ACIDS TO ACETYL BENZOYL PEROXIDES IN ACETIC ACID AT 45°C

Concn. of H_2SO_4, 3.6 N (H_0, −3.430)

Substituent	Forward first-order rate const. $k_1\times10^4$ sec^{-1}
p-OCH_3	(5.20)[a, b)]
p-CH_3	(1.96)[a)]
p-H	1.66
p-Cl	1.41
m-NO_2	0.92
p-NO_2	0.87

a) These data do not seem to express the true substituent effects because of possible side reactions.

b) The reaction for p-methoxyperoxybenzoic acid was done at 25°C.

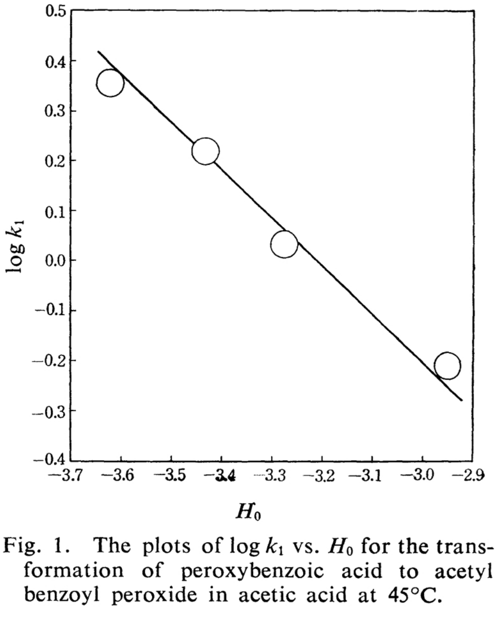


Fig. 1. The plots of $\log k_1$ vs. H_0 for the transformation of peroxybenzoic acid to acetyl benzoyl peroxide in acetic acid at 45°C.

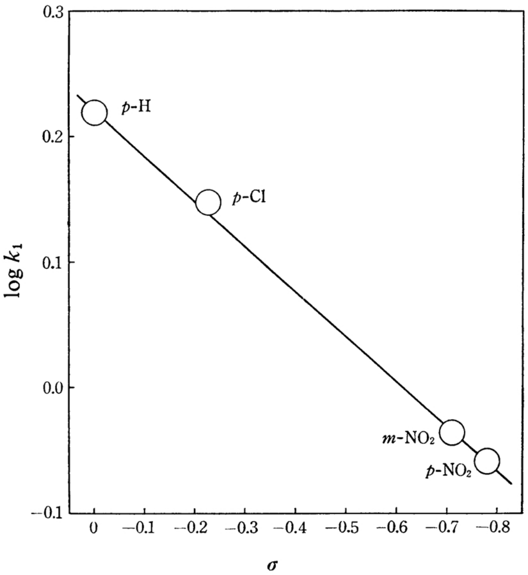
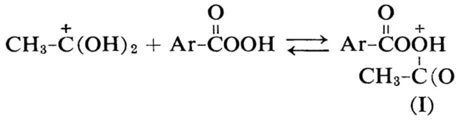


Fig. 2. Hammett plots for the transformation of substituted peroxybenzoic acid to the corresponding acetyl benzoyl peroxide in acetic acid at 45°C. (H_0, −3.430)

of the ether linkage of the methoxy group or the oxidation of the methyl group, since the active oxygen content of the system decreased during the reaction.

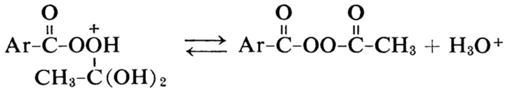
These facts suggest a mechanism analogous to that postulated for the acid-catalyzed transformation of peroxyacetic acid.[4)]

$$CH_3COOH + H^+ \xrightleftharpoons{\text{fast}} CH_3\text{-}\overset{+}{C}(OH)_2 \qquad (2)$$



$$CH_3\text{-}\overset{+}{C}(OH)_2 + Ar\text{-}\overset{O}{\overset{\|}{C}}OOH \rightleftharpoons \underset{\displaystyle CH_3\text{-}\overset{|}{C}(OH)_2}{Ar\text{-}\overset{O}{\overset{\|}{C}}O\overset{+}{O}H} \; \text{(I)}$$

(3)



$$\underset{\displaystyle CH_3\text{-}\overset{|}{C}(OH)_2}{Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\overset{+}{O}H} \rightleftharpoons Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}OO\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H_3O^+$$

(4)

The substituent effect with a negative ρ-value is consistent with a rate-determining attack of protonated acetic acid on peroxybenzoic acid (step 3). Moreover, complex I resembles the ortho acid monoester, which is the unstable intermediate in esterification; therefore, step 4 may be much faster than step 3.

The solvent effect was examined with formic, propionic, butyric, isobutyric or isovaleric acid as a solvent. The reactions in these solvents were all faster than that in acetic acid. However, side-reactions such as the oxidation of the solvent seem to occur quite often in these solvents.

Summary

It has been confirmed by paper chromatography that peroxybenzoic acid in acetic acid is transformed reversibly to acetyl benzoyl peroxide in the presence of a catalytic amount of sulfuric acid. The rate satisfies the first-order equation for reversible reactions. The plot of the logarithm of the forward rate constant vs. the acidity function has given a straight line with a slope of −0.96. The rate decreases upon the introduction of an electron-attracting group to the benzene ring of peroxybenzoic acid, the Hammett's ρ-value being −0.37. A mechanism analogous to that postulated previously with peroxyacetic acid, which involves a rate-determining attack of protonated acetic acid on peroxybenzoic acids, is consistent with these facts.

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