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KINETICS OF THE ACID-CATALYSED FORMATION OF ALIPHATIC PERACIDS FROM HYDROGEN PEROXIDE AND ALIPHATIC ACIDS IN DIOXAN*

Y. OGATA and Y. SAWAKI
Dept. of Applied Chemistry, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya, Japan

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Abstract—The acid catalysed formation of peracids from substituted acetic acids and hydrogen peroxide has been studied kinetically in dioxan. The rates of peracid formation together with equilibrium constants increase with increasing concentration of sulphuric acid and are correlated with the acidity of the media. The substituent effect suggests that the reaction is controlled by steric rather than polar effects. A mechanism similar to acid-catalysed esterification is discussed.

THE reaction of acetic acid and hydrogen peroxide to form peracetic acid is acid-catalysed.[1] The rate of peracid formation and even the equilibrium constants have been found to increase with increasing concentration of catalytic mineral acid.[2,3] It was found that both rate and equilibrium constants show the proportionality to the Hammett's acidity function, h_0, of the media, i.e., aqueous acetic acid.[4]

The present paper is a kinetic study of peracid formation in dioxan treating the effects of acidity and substituents in acetic acids.

RESULTS

Rate law. The reaction of substituted acetic acids with hydrogen peroxide to form peracids in dioxan

$$RCO_2H + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RCO_3H + H_2O \qquad (1)$$

satisfies the same rate law as that found in acetic acid, i.e., $v = k[RCO_2H][H_2O_2]$.

Calculation of rate constants. Representing the initial concentration of acetic acid, hydrogen peroxide and water as a, b, and c respectively, the rate of peracid formation may be expressed as

$$dx/dt = k_1(a - x)(b - x) - k_{-1}(a + x)x$$

or

$$dx/dt = k_1(1 - 1/K_1)(\alpha - x)(\beta - x) \qquad (2)$$

Here, $K_1 = k_1/k_{-1}$ and

$$\alpha,\beta = \frac{1}{2(1 - 1/K_1)}\{(a + b + c/K_1) \pm \sqrt{(a + b + c/K_1)^2 - 4ab(1 - 1/K_1)}\}$$

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* Contribution No. 79.

[1] D. Swern, *Chem. Rev.* **45**, 1 (1949).

[2] K. Murai, G. Akazome and Y. Murakami, *Kogyo Kagaku Zasshi* **63**, 1233 (1960).

[3] T. Suzuki, I. Iwamoto and S. Suzuki, *Nippon Kagaku Zasshi* **83**, 1212 (1962).

[4] Y. Ogata and Y. Sawaki, *Bull. Chem. Soc. Japan* **38**, in press (1965).

The constancy of rate constant, k_1, thus calculated, is satisfactory as shown in Table 1. The slight fall of k_1 as the reaction proceeds may be attributed to the gradual decomposition of the original hydrogen peroxide on the peracid formed.

The effect of the initial concentration of acetic acid and water on the rate is almost independent of the initial concentration of acetic acid, while an increase of the initial concentration of water resulted in a substantial decrease in the rate; the latter fact is probably due to the decrease in acidity and is discussed later.

TABLE 1. A TYPICAL KINETIC RUN FOR THE FORMATION OF PERACETIC ACID IN DIOXAN AT 25°. INITIAL CONC., a = [CH_3CO_2H] = 1·051 M; b = [H_2O_2] = 0·2018 M; c = [H_2O] = 1·360 M; [H_2SO_4] = 0·20 M.

Time min	x = [CH_3CO_3H] M	$k_1 \times 10^6$ [a] $M^{-1}sec^{-1}$
140	0·0300	22·3
180	0·0367	22·9
240	0·0418	21·4
300	0·0482	21·5
390	0·0542	21·0
500	0·0586	20·7
1220	0·0706	— [b]

[a] α = 10·67; β = 0·0703.

[b] Calculated equilibrium constant: K_1 = 0·780.

TABLE 2. THE EFFECT OF CONCENTRATION OF ACETIC ACID AND WATER ON SECOND-ORDER RATE CONSTANTS FOR THE FORMATION OF PERACETIC ACID IN DIOXAN AT 25°[a]

[CH_3CO_2H] M	[H_2O] M	K_1	$k_1 \times 10^6$ $M^{-1}sec^{-1}$
2·097	0·9118	0·827	31·9
1·048	0·9118	0·843	32·5
0·5242	0·9118	0·802	34·2
0·2621	0·9118	0·830	35·4
0·5252	0·905	0·802	36·0
0·5252	1·215	0·835	28·4
0·5252	1·465	0·833	19·1

[a] Initial concentration: [H_2O_2] = 0·1108 M; [H_2SO_4] = 0·20 M.

Effect of acidity. The effect of acidity was studied in dioxan at various concentrations of sulphuric acid. The rate and the equilibrium constants increased with increasing concentration of the catalytic acid (Table 3). These phenomena were also observed with the reaction in acetic acid.[4] The plot of logarithm of k_1 vs. $-H_0$ is a straight line with a slope of 1·16, while the plot of log K_1 corresponds to a slope of 0·40 (Fig. 1).

Effects of temperature and substituents. The rates of peracid formation from substituted acetic acids were determined at various temperatures as shown in Table 4. The data gave the activation parameters listed. Energies and entropies of activation

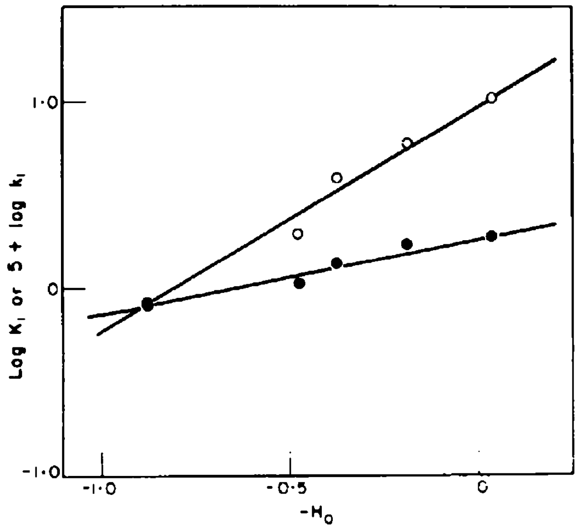

Fig. 1. Plots of log k_1 or log K_1 vs. $-H_0$ for the peracid formation from acetic acid and hydrogen peroxide in dioxan at 25°.

Table 3. Effect of acidity on the formation of peracetic acid in dioxan at 25°; Initial concentration: $[CH_3CO_2H]$ = 1·051 M; $[H_2O_2]$ = 0·2078 M; $[H_2O]$ = 2·360 M.

$[H_2SO_4]$ M	$-H_0$	K_1	$k_1 \times 10^6$ $M^{-1}sec^{-1}$
0·6	0·04	1·774	104·6
0·5	−0·18	1·672	57·8
0·4	−0·37	1·371	39·0
0·3	−0·47	1·049	19·1
0·2	−0·87	0·854	8·73

Table 4. Rate data for the peracid formation from substituted acetic acids in dioxan. Initial concentration: $[H_2SO_4]$ = 0·20 M; $[RCO_2H]$ = 0·9–1·5 M; $[H_2O_2]$ = 0·2018 M; $[H_2O]$ = 1·360 M

	K_1			k_1, $M^{-1}sec^{-1}$				
R	18°	25°	32°	18°	25°	32°	E_a kcal/mole	$-\Delta S\ddagger$ e.u.
CH_3	0·826	0·827	0·823	13·2	23·1	42·7	14·8	26·6
C_2H_5	0·823	0·818	0·813	12·3	22·0	42·2	15·5	24·3
n–C_3H_7	0·839	0·875	0·858	7·47	14·5	28·0	16·6	20·4
i–C_3H_7	0·777	0·786	0·788	6·93	13·1	24·4	15·2	25·3
i–C_4H_9	0·810	0·806	0·877	3·55	7·54	14·9	18·1	16·6
t–C_4H_9	0·573	0·630	0·566	2·36	5·61	10·2	18·3	16·6
$ClCH_2$	0·188	—	—	8·4	—	—	—	—
CH_3OCH_2	0·224	—	—	8·3	—	—	—	—

were 15 ~ 18 kcal mole^{-1} and -17 ~ -26 e.u., respectively; the values are similar to those of acid-catalysed esterification (15 ~ 20 kcal mole^{-1}, -15 ~ -30 e.u., respectively).

The plot of $\log k_1$ vs. Taft's steric substituent constant, E_s, is a straight line except with *t*-Bu (Fig. 2). The used E_s values are those for substituent R in the acyl component of ester RCOOR'.[5] Hence, the peracid formation was found to be affected almost exclusively by the steric factor.

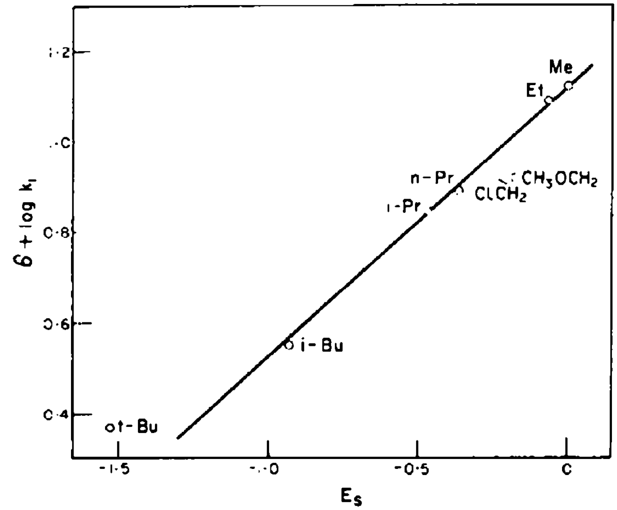

FIG. 2. Plots of $\log k_1$ vs. Taft's steric substituent constant, E_s, for the peracid formation from substituted acetic acids and hydrogen peroxide in dioxan at 18°.

DISCUSSION

Acidity dependence and reaction mechanism. The peracid formation satisfies the second-order kinetics, $v = k[\text{RCO}_3\text{H}][\text{H}_2\text{O}_2]$. The rate is accelerated by increasing concentration of sulphuric acid, the plot of $\log k_1$ vs. $-H_0$ is a straight line having a slope of 1·16. The rate of peracid formation without added mineral acid is approximately zero. These results together with the steric effect of substituents described below agree well with a mechanism similar to that of acid-catalysed esterification, which involves an intermediate protonated at the carbonyl oxygen of the carboxyl group.[6] See Eqns. 3, 4 and 5.

The rate-determining step may be step 4 or 5 on the basis of the rate law, but since the deprotonation 5 should be very fast as in the esterification, the most probable rate-determining step is 4.

As the equilibrium constant increased with increasing concentration of sulphuric acid, the plots of $\log K_1$ vs. $-H_0$ gave a line with a slope of 0·40. This fact may be explained by assuming the elimination of free water from the equilibrium system by the protonation, because water is a thousandfold stronger base than hydrogen peroxide.[7] The stoichiometric concentration of water is the sum of free and protonated

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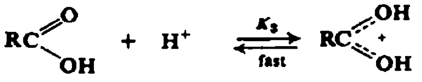
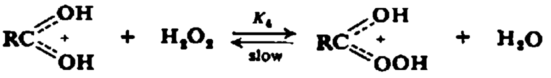
[5] R. W. Taft, Jr., edited by M. S. Newman, *Steric Effects in Organic Chemistry* p. 598. J. Wiley, New York (1956).

[6] R. Stewart and K. Yates, *J. Amer. Chem. Soc.* **82**, 4059 (1960).

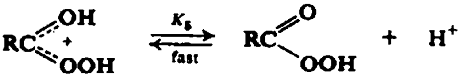
[7] M. G. Evans and N. Uri, *Trans. Faraday Soc.* **49**, 410 (1953).



$$RCOOH + H^+ \underset{fast}{\overset{K_3}{\rightleftharpoons}} RC(OH)_2^+$$ (3)



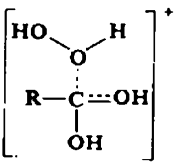
$$RC(OH)_2^+ + H_2O_2 \underset{slow}{\overset{K_4}{\rightleftharpoons}} RC(OH)(OOH)^+ + H_2O$$ (4)



$$RC(OH)(OOH)^+ \underset{fast}{\overset{K_5}{\rightleftharpoons}} RCOOOH + H^+$$ (5)

water, the latter being incapable of nucleophilic attack on carboxyl oxygen. The net concentration of free water, an effective nucleophile, decreases with increasing acidity much more sharply than hydrogen peroxide does, and hence, the apparent equilibrium constant should increase with increasing acidity of the medium.

Steric effect of substituents. The substituents in acetic acid exhibited a steric effect similar to that of the acid-catalysed esterification. The plots of log k_1 vs. E_s, or Taft's steric substituent constant, gave a straight line except with *t*-Bu. Hence, the steric susceptibility constant, δ, in Taft's equation, $\log (k/k_0) = \delta E_s$, is shown to be 0·57 at 18° (Fig. 2). This low susceptibility to steric retardation of rate by bulky substituents suggests a less hindrance between substituent and the incoming reagent, hydrogen peroxide, in peroxidation (activated complex I) than in esterification (II).



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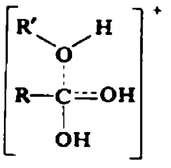

II

The steric strain in complex II caused mainly by the presence of two alkyl groups, R and R′, should be higher than that in complex I having one alkyl group and hydrogen peroxide which is less bulky and more nucleophilic than alcohols. A larger sensitivity to steric effect ($\delta = 2$) has been observed in acid-catalysed alcoholysis of esters.[8]

The equilibrium constants for chloro- and methoxyacetic acids were considerably smaller than those of unsubstituted fatty acids (Table 4). Since the rate of peracid formation for these two acids was in the range expected from the E_s value as shown in Fig. 2, these small values of K_1 may be attributed to the abnormally fast hydrolysis of the corresponding peracids. This fact may be understood by assuming that the acceleration of hydrolysis of these peracids is due to intramolecular hydrogen bonding between functional group X (Cl or OCH_3) and hydroperoxide group (III).

The chelated peracid (III) should be susceptible to the attack of water because of the easier acyl-oxygen fission by the electrostatic attraction between X—H bonding.

Energies and entropies of activation for substituted acetic acids also exhibited a

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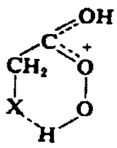
[7] Ref. 5, p. 644.

[8] L. L. Shaleger and F. A. Long, *Advances in Physical Organic Chemistry* p. 25. Academic Press, New York (1962).



III

close similarity to those of acid-catalysed esterification.[9] Since the range of temperature observed is limited (18°–32°), an exact evaluation of these activation parameters is difficult. However, the trend of ΔS† shows that the fall of freedom of complex I is independent of alkyl groups or is small with increasing alkyl chains.

EXPERIMENTAL

Materials. Commercial substituted acetic acids were heated with $KMnO_4$ for 6–10 hr, and then rectified over P_2O_5. Acetic acid, b.p. 118°; propionic acid, b.p. 140–141°; *n*-butyric acid, b.p. 163·0–163·5°; isobutyric acid, b.p. 153°; isovaleric acid, b.p. 175·0–175·5°; pivalic acid 163–164°; monochloroacetic acid, m.p. 63°; methoxyacetic acid, 105–106/25 mmHg. Dioxan was refluxed with Na for 10 hr and then rectified, b.p. 101–102°. H_2SO_4 and 30% H_2O_2 were used without further purification of commercial materials of guaranteed grade.

Rate measurement. The reaction was started by adding H_2O_2 solution of known concentration to a thermostated solution of aliphatic acid in dioxan containing an appropriate amount of H_2SO_4 and water. Conc. H_2SO_4 was previously mixed with water and then diluted with dioxan to prevent any possible attack of the acid on dioxan.

Aliquots (ca. 2 ml) were taken out at appropriate intervals and added into ice-cooled ca. 0·4 N H_2SO_4 (50 ml) containing 3 drops of 1% $MnSO_4$. Hydrogen peroxide was immediately titrated with $KMnO_4$ and the remaining peracid titrated iodometrically. Since the spontaneous decomposition of H_2O_2 and peracid was found to be negligible during these titrations, the content of peracid was calculated from both titres.

Equilibrium constants were determined according to the analysis after 30–170 hr, when ca. 20% of active O_2 had been decomposed.

Measurement of H_0. The determination of the Hammett's acidity function was done spectrophotometrically with the solutions corresponding to the reaction mixtures where water was added in place of H_2O_2. The indicator was *p*-nitroaniline having pK_{BH^+} of 0·99[10] and a maximum absorbance at 370–380 mμ. The results are listed in Table 3.

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[10] M. A. Paul and F. A. Long, *Chem. Revs.* 57, 1 (1957).