The Kinetics of the Acid-Catalyzed Formation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide*

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It has been established that the formation and hydrolysis of peracetic acid is acid-catalyzed,[1] and also that the equilibrium constant for reaction 1 increases with an increase in the concentration of catalytic acid.[2,3]

$$CH_3CO_2H + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3CO_3H + H_2O \qquad (1)$$

In order to clarify these phenomena, the dependence of the rate and equilibrium constants on the concentration of mineral acid over a wider range has been studied, and the dependence has been correlated with Hammett's acidity function.

Experimental

Materials.—Commercal aetic acid was refluxed with potassium permanganate and rectified over phosphorus pentoxide; b. p. 117—118°C. Hydrogen peroxide (30%) and sulfuric acid were both of guaranteed grade. *p*-Nitro- and *o*-nitroanilines were recrystallized from water containing a small amount of methanol.

Kinetic Measurements. — A definite amount of aqueous acetic acid of a known concentration containing an appropriate amount of surfuric acid was thermostated and the reaction was started by adding 30% hydrogen peroxide. (Water had been added previously in order to prevent the evolution of the heat of neutralization when 30% hydrogen peroxide was added.)

Aliquots were taken out at appropriate intervals of time and analyzed for hydrogen peroxide and peracid by means of an unique method. The aliquot was poured into ca. 50 ml. of ice-cooled ca. 0.4 N sulfuric acid containing three drops of 1% aqueous manganese sulfate. The hydrogen peroxide was quickly titrated with potassium permanganate until a pink color appeared, and then the remaining peracid was titrated iodometrically after the addition of potassium iodide. The peracid content was calculated from the ratio of the titres of permanganate and thiosulfate consumed, since the decomposition of hydrogen peroxide and peracid was found to be negligible under these reaction conditions. This novel method, which does without the weighing of aliquots, gave an adequate accuracy in a blank test.

The Calculation of Rate Constants.—Since the decomposition of hydrogen peroxide and peracid under these conditions was unappreciable, the rate constants may be calculated as follows. By representing the initial concentrations of acetic acid, hydrogen peroxide and water as *a*, *b* and *c*, respectively, and the concentration of the peracid produced as *x*, the rate of the formation of peracetic acid may be expressed as:

$$v = k_1(a-x)(b-x) - k_{-1}(c+x)x$$

This equation is transformed to:

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

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

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

The rate constant k_1 thus calculated, has a good constancy, as is shown in Table I.

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* Contribution No. 78.

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

[2] S. Havel and J. A. Weigner, *Chem. Prumysl*, **10**, 293 (1960).

[3] T. Suzuki, I. Iwamoto and S. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 1212 (1962).

TABLE I. A TYPICAL RATE CONSTANT FOR THE FORMATION OF PERACETIC ACID IN 80 VOL.% ACETIC ACID AT 25°C

Initial concn.: $a=[CH_3CO_2H]=13.77$ M; $b=[H_2O_2]=1.014$ M; $c=[H_2O]=9.831$ M; $[H_2SO_4]=0.30$ M.

Time min.	$x=[CH_3CO_3H]$ M	$k_1\times10^6$ a) M^{-1} sec^{-1}
10	0.115	15.9
17	0.186	16.0
27	0.272	15.8
40	0.358	15.3
50	0.421	15.4
60	0.483	16.0
75	0.530	15.0
100	0.612	15.3
1800	0.800	—b)

a) $\alpha=26.04$; $\beta=0.777$
b) Calculated equilibrium constant (K_1) was 3.045.

The Measurement of H_0.—Hammett's acidity function of the reaction media (water was added in place of hydrogen peroxide) was measured using *o*- and *p*-nitroanilines as indicators. The absorption peaks were measured at 410 mμ for *o*-nitroaniline and at 370—380 mμ for *p*-nitroaniline; the shift of λ_{max} was observed upon varying the ratio of acetic acid to water. The H_0's were calculated from the equation; $H_0=pK_{BH^+}-\log(c_{BH^+}/c_B)$, where pK_{BH^+} is an indicator constant and c_{BH^+} is the concentration of the conjugate acid of the indicator and c_B is that of the neutral form of the same indicator. The values of pK_{BH^+} cited are −0.29 for *o*-nitroaniline and 0.99 for *p*-isomer.[4] These results are listed in Tables II and III.

Results and Discussion

The Rate Law.—The acid-catalyzed formation of peracetic acid follows Rate Eq. 2, while a typical run is shown in Table I. The rate law coincides with the data reported previously in the literature.[3,5] The rate of peracid formation in the absence of mineral acid was too slow to measure.

The Effect of the Acidity of the Media.—The rates and equilibrium constants for the formation of peracetic acid are shown in Table II, where it is obvious that they increase with an increase in the concentration of sulfuric acid. These facts have been reported as the proportionalities of rate and equilibrium constants to the concentration (<0.5 M) of mineral acid.[2-4] However, this is not true at higher concentrations of mineral acid (>0.5 M), and the polts of k_1 or K_1 vs. $[H_2SO_4]$ lie not on a straight line but on a curve (Fig. 1).

TABLE II. THE EFFECT OF ACIDITY ON THE RATE AND EQUILIBRIUM CONSTANTS FOR THE PERACID FORMATION IN 80 VOL.% ACETIC ACID AT 25°C a)

$[H_2SO_4]$ M	$-H_0$ b)	K_1	$k_1\times10^6$ M^{-1} sec^{-1}
3.0	2.43	12.81	1030
2.0	1.68	7.635	353
1.5	1.20	6.016	175
1.2	0.91	5.146	116
1.0	0.80	4.517	80.0
0.80	0.58	3.944	52.3
0.60	0.30	3.528	34.9
0.50	0.15	3.405	27.7
0.40	0.00	3.224	20.1
0.30	−0.15	3.045	15.1
0.20	−0.33	2.870	9.04
0.10	−0.63	2.708	4.25

a) Initial concn.: $[CH_3CO_2H]=11.5—13.9$ M; $[H_2O_2]=1.014$ M; $[H_2O]=9.831$ M
b) *o*-Nitroaniline was used as an indicator.

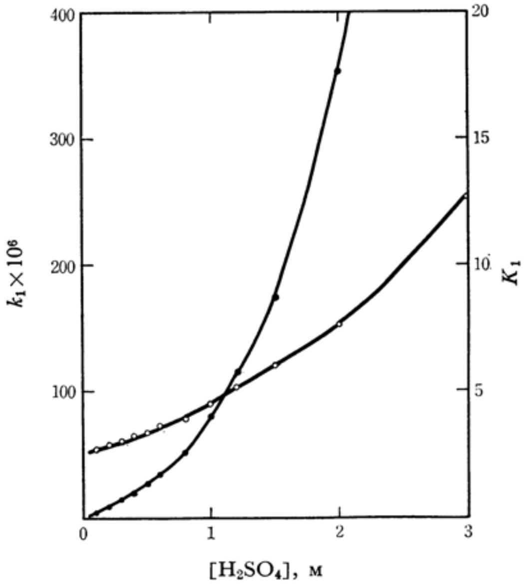

Fig. 1. Plots of k_1 and K_1 vs. $[H_2SO_4]$ in 80 vol.% acetic acid at 25°C.

—●— k_1 vs. $[H_2SO_4]$
—○— K_1 vs. $[H_2SO_4]$

This departure from linearity may be corrected for by plotting log k_1 or log K_1 against Hammett's acidity function; the plots then give a straight line with a solpe of 0.82 for log k_1 and 0.22 for log K_1 (Fig. 2).

The Effect of the Ratios of the Concentrations of Acetic Acid and Water.—The rate of peracid formation was found to increase with an increase in the ratio of concentrations of acetic acid and water at a constant concentration of sulfuric acid (Table III). The plots of log k_1 vs. $-H_0$ give a straight line with a slope of 1.10 or ca. unity, a considerably larger value than that in the

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[4] M. A. Paul and F. A. Long, *Chem. Revs.*, 57, 1 (1957).
[5] K. Murai, G. Akazome and Y. Murakami, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1233 (1960).

former slope (0.82). It should be noted that different indicators are used for the determination of the acidity function, and that this may cause a small difference in the observed acidity function.

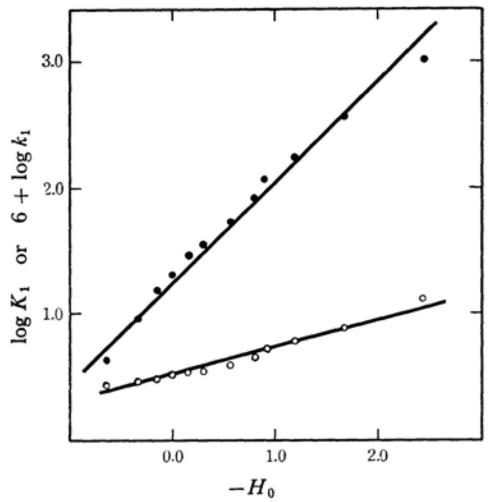

Fig. 2. Plots of $\log k_1$ and $\log K_1$ against the Hammett's acidity function in 80 vol.% acetic acid at 25°C.

—●— $\log k_1$ vs. $-H_0$
—○— $\log K_1$ vs. $-H_0$

TABLE III. EFFECT OF THE RATIO OF $[CH_3CO_2H]:[H_2O]$ at 25°C[a)]

Acetic acid Vol.%	$-H_0$[b)]	K_1	$k_1\times10^6$ $\text{M}^{-}\ \text{sec}^{-1}$
90	+0.065	3.551	28.6
80	−0.339	3.053	9.21
70	−0.607	2.909	7.01
60	−0.770	2.563	3.30
40	−0.871	2.080	1.76

a) Initial concn.: $[H_2SO_4]=0.20$ M; $H_2O_2=0.9350$ M.
b) *p*-Nitroaniline was used as an indicator.

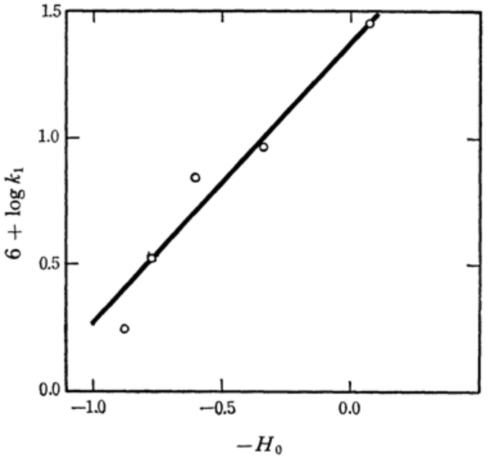

Fig. 3. Plots of $\log k_1$ vs. $-H_0$ in various ratio of $[CH_3CO_2H]:[H_2O]$ at 25°C.

Temperature Dependence.—The effect of the temperature on the rate was studied in 60 and 80 vol.% acetic acid; the results, together with the calculated activation parameters, are summarized in Table IV. The change in the energy and entropy of activation is unappreciable in going from 60% to 80% acetic acid.

TABLE IV. APPARENT ENERGIES AND ENTROPIES OF ACTIVATION FOR THE ACID-CATALYZED FORMATION OF PERACETIC ACID

Acetic acid vol.%	Temp. °C	K_1	$k_1\times10^6$ $\text{M}^{-1}\ \text{sec}^{-1}$	E_a kcal.·mol^{-1}	$\Delta S^{\ddagger}$ e. u.
80[a)]	18.0	2.948	5.04	15.0	−35.7
	25.0	2.907	9.54		
	18.0	2.828	16.5		
60[b)]	18.0	2.589	1.84	15.1	−33.2
	25.0	2.537	3.36		
	32.0	2.453	6.10		

a) Initial concn.: $[H_2SO_4]=0.20$ M; $[CH_3CO_2H]=12.36$ M; $[H_2O_2]=1.014$ M; $[H_2O]=9.831$ M.
b) Initial concn.: $[H_2SO_4]=0.20$ M; $[CH_3CO_2H]=8.611$ M; $[H_2O_2]=2.028$ M; $[H_2O]=19.66$ M.

The value for the entropy of activation (−33—−36 e.u.) implies a mechanism similar to that in the case of acid-catalyzed second-order esterification (−15—−30 e.u.).6) The value for the energy activation (15.1 kcal. mol^{-1}) also suggests a second-order mechanism resembling the ester hydrolysis. Both the energy and the entropy of activation are close to the activation parameters in an oxygen-exchange reaction between water and benzoic acid (16 kcal. mol^{-1} and −30 e.u. respectively).7)

The Reaction Mechanism.—The logarithm of the rate constant for peracid formation is proportional to $-H_0$. The energy and the entropy of activation are close to those in acid-catalyzed esterification. The substituent effect in acetic acid in dioxane was found to depend mostly on the steric factor, and to be little affected by the polar factor of the substituents.8) Tracer studies of the hydrolysis of peracid also reveal that the mechanism is analogous to the acyl-oxygen fission mechanism of ester hydrolysis.9) These facts suggest this probable mechanism for the peracid formation:

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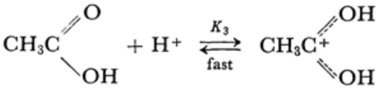
6) L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," Vol. I, Academic Press, New York (1963), p. 23.

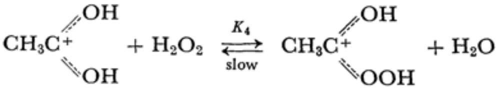
7) C. A. Bunton, D. H. James and J. B. Senior, *J. Chem. Soc.*, **1960**, 3364.

8) Y. Ogata and Y. Sawaki, *Tetrahedron*, in press.

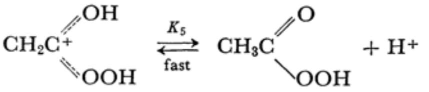
9) C. A. Bunton, T. A. Lewis and D. R. Liewellyn, *J. Chem. Soc.*, **1956**, 1226.



$$\mathrm{CH_3C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{H^+} \underset{\text{fast}}{\overset{K_3}{\rightleftarrows}} \mathrm{CH_3\overset{+}{C}}\begin{smallmatrix}\nearrow \mathrm{OH}\\ \searrow \mathrm{OH}\end{smallmatrix} \quad (3)$$



$$\mathrm{CH_3\overset{+}{C}}\begin{smallmatrix}\nearrow \mathrm{OH}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{H_2O_2} \underset{\text{slow}}{\overset{K_4}{\rightleftarrows}} \mathrm{CH_3\overset{+}{C}}\begin{smallmatrix}\nearrow \mathrm{OH}\\ \searrow \mathrm{OOH}\end{smallmatrix} + \mathrm{H_2O} \quad (4)$$



$$\mathrm{CH_2\overset{+}{C}}\begin{smallmatrix}\nearrow \mathrm{OH}\\ \searrow \mathrm{OOH}\end{smallmatrix} \underset{\text{fast}}{\overset{K_5}{\rightleftarrows}} \mathrm{CH_3C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OOH}\end{smallmatrix} + \mathrm{H^+} \quad (5)$$

The position of the protonation of the carboxyl group has been found to be mainly at carbonyl oxygen,[10] as has been described above. The rate-determining step is Eq. 4; hence, the rate of peracid formation should be proportional to the product of the concentrations of acetic acid and hydrogen peroxide, the logarithm of the rate constant being proportional to $-H_0$; this is indeed the case. The reaction of acetic acid with hydrogen peroxide in the absence of catalytic mineral acid was too slow to measure; hence, the reaction path through unprotonated acetic acid may be considered to be negligible.

Although the details of the mechanism are still unknown on the basis of the above results alone, a mechanism similar to those in the acid-catalyzed esterification may be assumed. Our data, together with those in the literature,[7,11] show a similarity of mechanisms in the esterification, the oxygen-exchange, and the peracid formation. Hence, a nucleophilic attack of hydrogen peroxide on protonated carboxylic acid is a probable course for the reaction.

The Effect of the Acidity on the Equilibrium Constants. — The equilibrium constant increased with an increase in the concentration of sulfuric acid. The plots of log K_1 vs. $-H_0$ gave a straight line, with a slope of 0.22 (Fig. 2). This fact may well be explained by assuming the elimination of free water from the reaction system by the protonation, since water is the strongest base among the components in Eq. 1.

$$K_1=\frac{[\mathrm{CH_3CO_3H}][\mathrm{H_2O}]}{[\mathrm{CH_3CO_2H}][\mathrm{H_2O_2}]}$$

It is known that water is a thousandfold stronger as a base than hydrogen peroxide;[12] hence, the protonation occurs only to water. The stoichiometric concentration of water is the sum of the free and the protonated water, the latter having little ability to make a uncleophilic attack on carboxyl carbon. The net concentration of free water, an effective nucleophile, decreases with an increase in the acidity much more rapidly than hydrogen peroxide does. Hence, the appearent equilibrium constant should increase with an increase in the acidity of the medium.

The protonation of acetic acid has been reported,[13] but no data is available on the protonation of peracetic acid. However, the extent of the protonation of acetic and peracetic acids should be much smaller than that of water and hydrogen peroxide, both of which are stronger as bases. Therfore, the protonation of these acids may be neglected in examining the effect of the acidity on the equilibrium constant, K_1.

Summary

The sulfuric acid-catalyzed reversible formation of peracetic acid from acetic acid and hydrogen peroxide in aqueous acetic acid has been studied kinetically. The rate of peracid formation is proportional to the product of the concentrations of acetic acid and of hydrogen peroxide, increasing with an increase in the concentration of sulfuric acid. The plot of the logarithm of the rate constant vs. $-H_0$ gives a straight line, with a slope of 0.82 and 1.10. The mechanism has been discussed in connection with the analogous acid-catalyzed esterification. The equilibrium constants for the present reaction also increase with an increase in the acidity, and the similar plot of log K_1 vs. $-H_0$ gives a straight line with a slope of 0.22. These facts are explicable by considering the protonation of water.

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

[11] I. Roberts and C. Urey, ibid., **61**, 2580 (1939).

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

[13] For quantitative estimation, see N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).