

# THE KINETIC STUDIES ON THE HYDROGEN PEROXIDE OXIDATION OF ORGANIC COMPOUNDS

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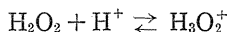
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## Preface

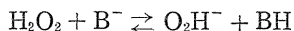
Pure or highly concentrated hydrogen peroxide often exhibits violent and radical reactions, but aqueous hydrogen peroxide is a mild oxidizing agent which usually reacts mildly and selectively with organic compounds via the ionic mechanism in most cases. In addition to these facts, aqueous hydrogen peroxide produce water and oxygen in the oxidation reaction; it is an useful oxidizing or bleaching agent for many kind of materials.

While aqueous hydrogen peroxide itself is a weak oxidant, the reactivity of hydrogen peroxide is greatly increased by the addition of acid, base or some metallic salts, *e.g.*,  $\text{Fe}^{2+}$ ,  $\text{OsO}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{SeO}_2$  etc. and these catalysts can be used for various hydrogen peroxide oxidations. For example, it can be used for the reactions: olefin $\rightarrow$ epoxide, hydroperoxide, paraffin $\rightarrow$ olefin, alcohol $\rightarrow$ hydroperoxide, ketone or aldehyde $\rightarrow$ ester or its hydrolysis products, carboxylic acid $\rightarrow$ peroxycarboxylic acid, phenol $\rightarrow$ quinone, primary amine $\rightarrow$ azoxy compound, secondary amine $\rightarrow$ hydroxylamine, tertiary amine $\rightarrow$ amine N-oxide, nitroso compound $\rightarrow$ nitro compound, sulfide $\rightarrow$ sulfoxide, sulfoxide $\rightarrow$ sulfone and so on.<sup>1)</sup>

The mechanism of these oxidations in an aqueous solution seems to be of ionic nature in most cases; *i.e.*, in the case of the acid-catalyzed reactions, the conjugate acid of hydrogen peroxide may be an active species.



Whereas the active species in the base-catalyzed reactions may be the conjugate base of hydrogen peroxide, as in the oxidation of aldehydes or nitriles and the nucleophilic substitutions with  $\text{O}_2\text{H}^-$ ,



some base-catalyzed oxidations may be an attack of  $\text{H}_2\text{O}_2$  on the conjugate base of an substrate, such as phenoxide or mercaptide ion which is more easily oxidized.

On the other hand, the metallic salts-catalyzed oxidation seems to go mostly by way of more active metallic peroxide intermediates (i) or intermediary hydroxyl radical (ii).

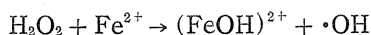
Examples of peroxide intermediates (i) are perosmic acid ( $\text{H}_2\text{OsO}_6$ ) from osmium tetroxide ( $\text{OsO}_4$ )<sup>2)</sup>, pervanadic acid ( $\text{HVO}_4$ ) from vanadium pentoxide ( $\text{V}_2\text{O}_5$ )<sup>3)</sup>, perselenious acid ( $\text{H}_2\text{SeO}_4$ ) from selenium dioxide ( $\text{SeO}_2$ )<sup>4)</sup>, and pertungstic

acid ( $\text{H}_2\text{WO}_5$ ) from tungstic acid ( $\text{H}_2\text{WO}_4$ )<sup>5</sup>). Our kinetic study previously reported on the selenium dioxide-catalyzed oxidation of dimethylaniline with hydrogen peroxide in 50–95% aqueous methanol yielding its N-oxide showed that the rate at constant acidity was expressed as:

$$v = k[\text{H}_2\text{O}_2][\text{SeO}_2][\text{Dimethylaniline}] + k'[\text{H}_2\text{O}_2][\text{SeO}_2]$$

The first term of this rate equation corresponds to a reaction between dimethylaniline and complex I produced rapidly from  $\text{SeO}_2$  and  $\text{H}_2\text{O}_2$ , while the second term corresponds mainly to a slow reaction between  $\text{SeO}_2$  and  $\text{H}_2\text{O}_2$  to yield complex II followed by a rapid reaction with dimethylaniline. The complexes I and II may be a kind of perselenious acid,  $\text{H}_2\text{SeO}_4$ .

An example of an intermediary hydroxyl radical (ii) is the Fenton's reagent which is an useful oxidant or an initiator for radical reactions.

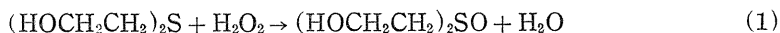


The following are a summary of our kinetic studies on the hydrogen peroxide oxidation catalyzed by molybdenum salt, phosphate-nitrile or sulfuric acid in aqueous or aquo-organic solvents, the substrate being thiodiglycol, olefins or carboxylic acids, respectively. These kinetic studies including the effects of acidity, substituent and temperature will disclose a probable mechanism for the reaction as described below.

## Chapter 1. Catalytic Hydrogen Peroxide Oxidation of Thiodiglycol in Aqueous Solutions

### 1-1. Introduction

In order to compare the catalytic activities of various inorganic compounds and to discover new catalysts in the aqueous hydrogen peroxide oxidation, the catalytic oxidation of thiodiglycol (TDG) was investigated.



The rate of the uncatalyzed hydrogen peroxide oxidation of TDG has been reported by Ross<sup>6</sup> to follow the second-order kinetics. We found that molybdate exhibited a stronger catalytic activity than well-known tungstates and selenous acid. The kinetics of sodium molybdate (SM)-catalyzed oxidation has also been investigated, since the mechanism for the catalysis of molybdates had not previously been clarified in detail.<sup>7</sup>

The present chapter describes the rate data and a probable mechanism of the SM-catalyzed hydrogen peroxide oxidation of TDG in aqueous solutions. In the course of this study, the rate of the oxidation of TDG by yellow sodium peroxymolybdate (YPM), together with the absorption spectra of the SM-hydrogen peroxide system, were measured.

### 1-2. Experimental

*Materials.*—TDG was purified by vacuum distillations; b.p. 131–134°C/3 mmHg. YPM was synthesized according to the Kobosev-Sokolov's procedure<sup>8</sup>. All the catalysts used were commercial reagents of G. R. grade.

*Typical Procedure for Kinetic Measurements.*—A buffered aqueous solution containing TDG, a catalyst, sodium acetate and acetic acid was thermostated at the reaction temperature; the reaction was started by adding a known amount of aqueous hydrogen peroxide. Aliquots were taken out at appropriate intervals of time, and their peroxide contents were determined iodometrically.

The SM-catalyzed oxidation was carried out in aqueous media at pH 0.5-6.2 and in aqueous sulfuric acid. No appreciable change in the rates was observed when the oxidation was started by mixing TDG with a prepared mixture of SM and hydrogen peroxide, or when the reaction was carried out in a brown flask.

The kinetics of oxidation by YPM was studied by means of the iodometry of active oxygen in a buffered reaction mixture of YPM and TDG.

*Ultraviolet Absorption Spectra.*—Absorption spectra (210-500  $m\mu$ ) were measured with a SM- $H_2O_2$  system in order to obtain some information on active species in the SM-catalyzed hydrogen peroxide oxidation. An absorption maximum was observed at the wavelength of 310  $m\mu$  with a solution at pH 4.7 or at 326  $m\mu$  with one at pH 0.8. No absorption maximum appeared in 210-500  $m\mu$  with an aqueous solution of hydrogen peroxide-TDG and with an aqueous solution of TDG-SM.

*Reaction Products Criterion.*—To examine the reaction products, a mixture of SM (0.002 mol.), hydrogen peroxide (0.12 mol.) and TDG (0.10 mol.) in 100 ml. of water was kept standing at 25°C for two hours. After the evaporation of the water under reduced pressure, the residue was dissolved in alcohol, the SM being filtered off. On recrystallization from alcohol crystals (11.3 g.) of thiodiglycol sulfoxide (82%) were obtained; m.p. 110.5-111.5°C (lit.<sup>9)</sup> m.p. 111°C).

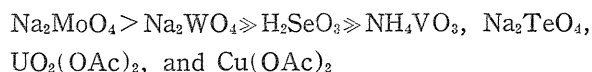
Upon the treatment of thiodiglycol sulfoxide ( $15 \times 10^{-3}$  M), the reaction product, with a mixture of SM ( $1 \times 10^{-4}$  M) and  $H_2O_2$  ( $8 \times 10^{-3}$  M) at 25°C and pH 4.7 or 0.8 for 4hr, no appreciable oxidation occurred.

### 1-3. Examination of the Catalyst Activity

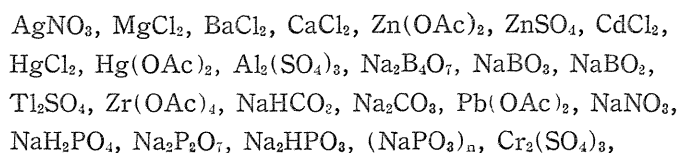
Sulfides, in general, can be oxidized to sulfoxides by hydrogen peroxide at room temperature.<sup>10)</sup> Ross<sup>9)</sup> has reported that the second-order rate constant for the uncatalyzed hydrogen peroxide oxidation of thiodiglycol (TDG) in aqueous solutions of pH 4-6 was  $2.17 \times 10^{-3} \text{ M}^{-1} \text{ sec.}^{-1}$  at 25°C.

Our examinations of the catalytic activities of various inorganic compounds at 25°C and pH 4.7 gave the following data:

Compounds with some activity:



Compounds with no activity:



Cr<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, KHSO<sub>4</sub>, Mn(OAc)<sub>2</sub>, KClO<sub>3</sub>,  
 KClO<sub>4</sub>, NaClO<sub>2</sub>, NaBrO<sub>3</sub>, KIO<sub>3</sub>, KIO<sub>4</sub>, CoSO<sub>4</sub>, Co(OAc)<sub>2</sub>,  
 Ni(OAc)<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub>

Compounds with side reaction :

CuCl<sub>2</sub>, CuSO<sub>4</sub>, Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, ZrOCl<sub>2</sub>, NaNO<sub>2</sub>, NaHSO<sub>3</sub>,  
 KSCN, K<sub>2</sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>,  
 NaBiO<sub>3</sub>, and Na<sub>2</sub>TeO<sub>3</sub>

It is evident in Table 1 that molybdate and tungstate are both active catalysts, while selenous acid is less active. However, the other four, NH<sub>4</sub>VO<sub>3</sub>, Na<sub>2</sub>TeO<sub>4</sub>, UO<sub>2</sub>(OAc)<sub>2</sub> and Cu(OAc)<sub>2</sub>, show only a small activity. It is of interest to note that the rate of SM-catalyzed oxidation is independent of the concentration of hydrogen peroxide, following the first-order kinetics. The comparison of the catalytic activities of sodium molybdate (SM) and tungstate seems less significant, since their kinetics are different. It is obvious, however, that the completion of oxidation with molybdate is faster than that with tungstate. The SM-catalyzed oxidation will be discussed in detail later.

Peroxytungstates have been suggested as active oxidation species in the tungstate-catalyzed epoxidation of olefins,<sup>11)</sup> and peroxyselenous acid, in the selenium dioxide-catalyzed oxidation of dimethylaniline<sup>12)</sup> and ketones.<sup>13)</sup>

No catalytic action of vanadic acid, a well-known catalyst,<sup>14)</sup> was observed under these conditions, although a faint activity was appreciable with ammonium vanadate. Faint catalytic activities were also observed with sodium tellurate, cuprous acetate and uranyl acetate. The uranyl acetate is known to catalyze the hydrogen peroxide oxidation of primary amines.<sup>15)</sup> Ferric and ferrous salts showed no appreciable activity.

TABLE 1. Catalyzed Hydrogen Peroxide Oxidation of TDG in Aqueous Solutions at 25°C and pH 4.7  
 Initial concn.: H<sub>2</sub>O<sub>2</sub>, 0.02570 M; TDG, 0.0390 M

Catalyst	[Cat.] M × 10 <sup>-4</sup>	Rate Constant <sup>a)</sup>		Catalyst coeff. <sup>a)</sup>	
		<i>k</i> <sub>2</sub> × 10 <sup>3</sup>	<i>k</i> <sub>1</sub> × 10 <sup>3</sup>	<i>k</i> <sub>2</sub> <sup>c</sup>	<i>k</i> <sub>1</sub> <sup>c</sup>
		M <sup>-1</sup> sec. <sup>-1</sup>	sec. <sup>-1</sup>	M <sup>-2</sup> sec. <sup>-1</sup>	M <sup>-1</sup> sec. <sup>-1</sup>
Na <sub>2</sub> MoO <sub>4</sub>	1	—	6.56	—	6.54
Na <sub>2</sub> WO <sub>4</sub>	1	69.2	—	670	—
H <sub>2</sub> SeO <sub>3</sub>	10	4.12	—	1.93	—
NH <sub>4</sub> VO <sub>3</sub>	10	2.54	—	0.35	—
Na <sub>2</sub> TeO <sub>4</sub>	10	2.42	—	0.23	—
UO <sub>2</sub> (OAc) <sub>2</sub>	10	2.39	—	0.20	—
Cu(OAc) <sub>2</sub>	10	2.37	—	0.18	—
None	0	2.17	—	—	—

$$\begin{aligned}
 \text{a) } v &= k_2[\text{H}_2\text{O}_2][\text{TDG}] \\
 &= (k_0 + k_2^c[\text{Catalyst}])(\text{H}_2\text{O}_2)[\text{TDG}] \\
 \text{or} \\
 v &= k_1[\text{TDG}] = k_1^c[\text{Catalyst}][\text{TDG}].
 \end{aligned}$$

## 1-4. Mechanism of SM-catalyzed Oxidation

*Rate Equations.*—The rate of SM-catalyzed oxidation is independent of the concentration of hydrogen peroxide and is first-order with respect to TDG if the concentration ratio of hydrogen peroxide *vs.* SM exceeds 2, as Table 2-A and Fig. 1 show. These pseudo-first order rates are proportional to the concentration of SM (Fig. 2). Thus, if  $2[\text{H}_2\text{O}_2] > [\text{SM}]$ , the rate equation is expressed as:

$$v = k_1[\text{TDG}] = k_1^c[\text{SM}][\text{TDG}] \quad (2)$$

TABLE 2. Rate Data on the Oxidation of TDG with SM-H<sub>2</sub>O<sub>2</sub> in the Range of  $2[\text{H}_2\text{O}_2] > [\text{SM}]$ 

Initial concn., M × 10 <sup>3</sup>			pH <sup>a)</sup> (Added compd.)	Temp. °C	k <sub>1</sub> × 10 <sup>4</sup> sec. <sup>-1</sup>
[SM]	[H <sub>2</sub> O <sub>2</sub> ]	[TDG]			
A) Effect of initial concns. of hydrogen peroxide and TDG					
0.050	5.070	2.670	4.7 (Ac)	25	2.57
0.050	5.098	5.340	4.7 (Ac)	25	2.76
0.050	5.012	8.010	4.7 (Ac)	25	2.75
0.050	12.50	8.010	4.7 (Ac)	25	2.67
0.050	25.02	10.68	4.7 (Ac)	25	2.82
2.0	5.63	9.03	4.7 (Ac)	0	18.3
2.0	8.53	9.03	4.7 (Ac)	0	18.8
2.0	8.47	4.51	4.7 (Ac)	0	18.2
0.025	9.705	9.027	0.8 (Su)	25	12.2
0.025	9.705	13.25	0.8 (Su)	25	12.2
0.025	6.470	13.54	0.8 (Su)	25	12.2
B) Effect of the acidity of the solutions <sup>b)</sup>					
0.025	11.12	12.17	-0.60 (Su)	25	11.9
0.025	11.12	12.17	-0.31 (Su)	25	11.8
0.025	11.12	12.17	+0.02 (Su)	25	12.2
0.025	11.12	12.17	+0.15 (Su)	25	12.5
none	52.99	42.43	-0.60 (Su)	25	75.8 <sup>c)</sup>
none	52.99	42.43	-0.31 (Su)	25	133 <sup>c)</sup>
none	52.99	42.43	-0.04 (Su)	25	236 <sup>c)</sup>
none	52.99	42.43	+0.15 (Su)	25	355 <sup>c)</sup>
C) Effect of temperature					
0.025	8.52	9.03	4.7 (Ac)	0	0.275
0.025	8.46	9.03	4.7 (Ac)	5	0.401
0.025	9.85	9.03	4.7 (Ac)	10	0.599
0.025	10.80	12.17	4.7 (Ac)	20	1.15
0.025	13.53	16.22	4.7 (Ac)	25	1.62
0.025	10.80	12.17	4.7 (Ac)	30	2.06
0.025	8.52	9.03	0.8 (Su)	0	2.97
0.025	8.46	9.03	0.8 (Su)	5	4.01
0.025	9.85	9.03	0.8 (Su)	10	5.66
0.025	10.80	12.17	0.8 (Su)	20	9.54
0.025	13.53	16.22	0.8 (Su)	25	11.9
0.025	10.80	12.17	0.8 (Su)	30	15.9
none	52.99	42.43	4.7 (Ac)	20	14.0 <sup>c)</sup>
none	52.99	42.43	4.7 (Ac)	25	21.1 <sup>c)</sup>
none	52.99	42.43	4.7 (Ac)	30	31.5 <sup>c)</sup>
none	52.99	42.43	4.7 (Ac)	35	45.9 <sup>c)</sup>

<sup>a)</sup> Added compound: Ac = AcOH-AcONa, Su = H<sub>2</sub>SO<sub>4</sub>.

<sup>b)</sup> Acidity function, -H<sub>0</sub>.

<sup>c)</sup> Second-order rate constant (M<sup>-1</sup>sec.<sup>-1</sup>),

$$v = k_2[\text{H}_2\text{O}_2][\text{TDG}].$$

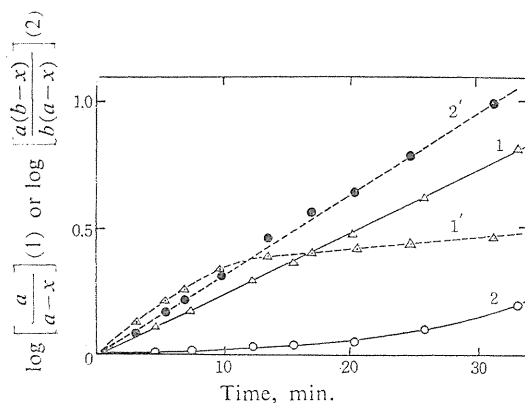


FIG. 1. Comparison of first-order (1) and second-order (2) rate equations at 0°C and pH 4.7.

	[TDG] <sub>init</sub> (a), M × 10 <sup>3</sup>	[H <sub>2</sub> O <sub>2</sub> ] <sub>init</sub> (b), M × 10 <sup>3</sup>	[SM] M × 10 <sup>3</sup>
1 (△), 2 (○) —	9.03	8.53	1
1' (△), 2' (●) - - - -	5.42	3.70	2

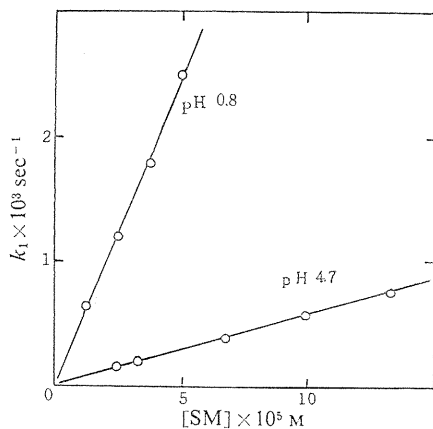


FIG. 2. Effect of concentration of SM on the rate in the range of  $2[\text{H}_2\text{O}_2] > [\text{SM}]$  at 25°C.

TABLE 3. Rate Data on the Oxidation of TDG with SM-H<sub>2</sub>O<sub>2</sub> in the Range of  $2[\text{H}_2\text{O}_2] < [\text{SM}]$ ; pH 4.7 (AcOH-AcONa) at 0°C

Initial concn., M × 10 <sup>3</sup>			$k_2^{(a)}$ M <sup>-1</sup> sec <sup>-1</sup>
[SM]	[H <sub>2</sub> O <sub>2</sub> ]	[TDG]	
2.0	0.924	1.806	0.856
2.0	1.924	1.806	0.862
2.0	2.879	1.806	0.749
2.0	2.879	2.709	0.706
2.0	2.879	4.514	0.786
2.0	3.611	1.924	0.860
2.0	3.695	5.417	0.711
4.0	2.879	4.514	0.856
6.0	2.879	4.514	0.783

<sup>a)</sup>  $v = k_2^{(a)} [\text{Active oxygen}] [\text{TDG}]$ .

([SM] is the initial concentration of Na<sub>2</sub>MoO<sub>4</sub>.) However, if  $[\text{H}_2\text{O}_2]/[\text{SM}]$  is less than 2, the rate is second-order (Table 3 and Fig. 1):

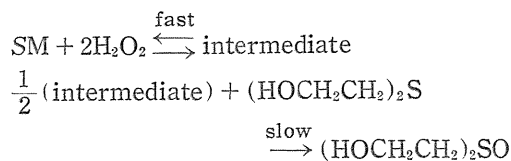
$$v = k_2' [\text{Active oxygen}] [\text{TDG}] \quad (3)$$

Here, [Active oxygen] expresses the concentration of active oxygen determined iodometrically. The value of  $k_2'$  holds constant while [SM] is varied, in so far as  $2[\text{H}_2\text{O}_2] < [\text{SM}]$ .

The pseudo-second order rate constant of the uncatalyzed oxidation is calculated from Table 2-C and Table 6 to be about  $2.0 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ , which is about 1/400 of the value of  $k_2'$ ,  $0.797 \text{ M}^{-1} \text{ sec}^{-1}$ . Hence,  $k_2'$  is not the rate constant

for hydrogen peroxide itself, but that for other active oxidizing species.

It is quite probable that one mole of SM is transformed quantitatively to a reactive intermediate by two moles of hydrogen peroxide:



Assuming that the formation of the intermediate is rapid and complete and that excess hydrogen peroxide has no effect on the rate, the rate should be independent of the concentration of hydrogen peroxide, when  $2[\text{H}_2\text{O}_2] > [\text{SM}]$ .

*Reactive Species in Solutions.*—The formation of the complex, YPM, was expected from the previous equations; this expectation was confirmed by the identification of YPM by means of ultraviolet spectrophotometry, together with the comparison of the data on oxidation by SM-H<sub>2</sub>O<sub>2</sub> with those on oxidation by YPM.

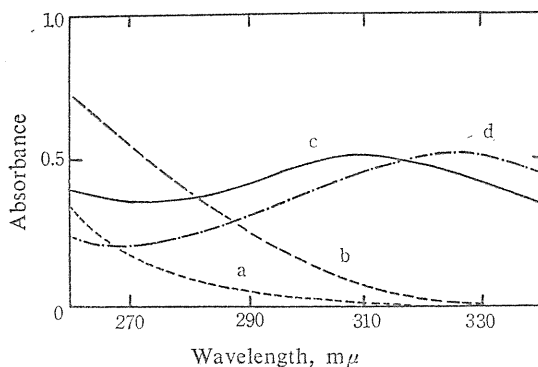


FIG. 3. Absorption spectra of SM-H<sub>2</sub>O<sub>2</sub> in aqueous solutions (a) SM at pH 4.7 (AcOH-AcONa), (b) SM at pH 0.8 (H<sub>2</sub>SO<sub>4</sub>), (c) SM-H<sub>2</sub>O<sub>2</sub> at pH 4.7 (AcOH-AcONa), (d) SM-H<sub>2</sub>O<sub>2</sub> at pH 0.8 (H<sub>2</sub>SO<sub>4</sub>).

TABLE 4. Relation of Absorbance with the Ratio  $[\text{H}_2\text{O}_2]/2[\text{SM}]$  ( $[\text{SM}] = 0.5 \times 10^{-3}$  M, pH = 4.7)

$[\text{H}_2\text{O}_2]$ $10^3$ M	$\frac{[\text{H}_2\text{O}_2]}{2[\text{SM}]}$ (A)	$E_{1\text{ cm}}$ (310 m $\mu$ )	$\frac{E_{1\text{ cm}}}{0.492}$ (B)	B/A
0.1635	0.164	0.072	0.147	0.900
0.3270	0.327	0.152	0.310	0.950
0.4905	0.491	0.226	0.460	0.938
0.6792	0.679	0.327	0.665	0.983
1.358	1.36	0.496	—	—
2.038	2.04	0.486	—	—
3.232	3.23	0.490	—	—
40	40	0.495	—	—

TABLE 5. Oxidation of TDG with YPM at 0°C and pH 4.7 (AcOH-AcONa)

Initial concentration, M × 10 <sup>3</sup>		$k_2''^a)$ M <sup>-1</sup> sec. <sup>-1</sup>
[Active oxygen]	[TDG]	
0.831	1.806	0.824
1.661	1.806	0.694
1.661	3.612	0.792

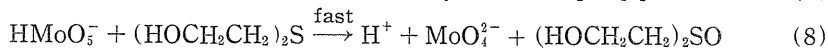
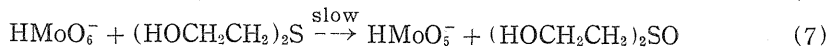
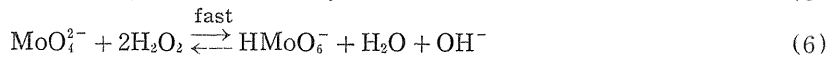
a)  $v = k_2''[\text{Active oxygen}][\text{TDG}]$ .

As shown in Fig. 3, an absorption maximum appeared at 310 m $\mu$  (pH 4.7) or at 326 m $\mu$  (pH 0.8) in the aqueous hydrogen peroxide-SM system, each maximum being identical with that of synthetic YPM at the corresponding pH. The absorbance of the aqueous hydrogen peroxide-SM system was determined at pH 4.7 with various concentrations of hydrogen peroxide while [SM] was kept constant (see Table 4). The absorbance at 310 m $\mu$  did not increase with an increasing amount of hydrogen peroxide in the range of  $2[\text{H}_2\text{O}_2] > [\text{SM}]$ . Therefore, two moles of hydrogen peroxide and one mole of SM react almost quantitatively to yield YPM. The shift of the absorption maximum up to 326 m $\mu$  (pH 0.8) suggests that YPM may exist in another form in the realm of higher acidity.

Table 5 shows the rate data on the oxidation of TDG by YPM, data which satisfy the second-order kinetics:

$$v = k_2''[\text{Active oxygen}][\text{TDG}] \quad (4)$$

Here, [Active oxygen] means the concentration of the active oxygen determined iodometrically. This pseudo-second-order rate constant,  $k_2''$ , is identical with  $k_2'$  in Eq. 3 within the range of experimental error. These facts suggest the following mechanism at pH 3-6:



Assuming that all the SM is converted to  $\text{HMoO}_6^-$  in this pH range and that  $a$  and  $b$  are the initial concentration of  $\text{HMoO}_6^-$  and TDG at time  $t$ , the rate is expressed as:

$$\begin{aligned} v &= k_2''[\text{HMoO}_6^-][\text{TDG}] \\ &= k_2''\left(a - \frac{x}{2}\right)(b - x) \end{aligned}$$

or

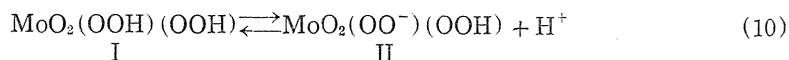
$$k_2''t = \frac{2}{b-2a} \ln \frac{2a(b-x)}{b(2a-x)} \quad (9)$$

Equation 9 is equal to Equations 3 and 4, and satisfies Equation 2, if  $[\text{HMoO}_6^-]$  is constant and equal to the initial concentration of SM.

SM reacts with two moles of hydrogen peroxide to form  $\text{Na}_2\text{MoO}_6$  (YPM) and with four moles of hydrogen peroxide to form red sodium peroxymolybdate



$\text{Na}_2\text{MoO}_8$ , an unstable peroxide decomposing to YPM at room temperature.<sup>9,16)</sup> It has been found that YPM exists in a neutral aqueous solution in the form of monoanion II.<sup>17)</sup>



Here the first ionization constant of I,  $K_1$ , is  $3 \times 10^{-3}$  and the second ionization constant,  $K_2$ , is  $7 \times 10^{-10}$ ; hence the dissociation of II is almost negligible in a neutral solution.<sup>17)</sup> When  $[\text{SM}]$  exceeds  $2 \times 10^{-3}$  M, SM exists in the form of polymolybdate,<sup>18)</sup> which reacts also with hydrogen peroxide to give II.<sup>19)</sup> These facts strongly suggest that the active species at pH 3-6 is  $\text{HMoO}_6^-$ .

*Effect of Acidity.*—The effect of the acidity of the solution on the SM-catalyzed oxidation rate is shown in Table 2-B and Fig. 4. The rate increases with increasing acidity of the solution; the plot of  $\log k$  vs. pH in the pH range of 2-3 fits a line of the unit slope (Fig. 4).

The rate constant at pH below 2 becomes independent of the acidity, as is obvious from the data obtained in dilute aqueous sulfuric acid (Table 2-B). However, the uncatalyzed oxidation is accelerated by acid at pH below 2, and this is probably the well-known acid catalysis in the hydrogen peroxide oxidation. The plot of  $\log k_2$  vs.  $-H_0$  gave a straight line with a slope of 0.90. The activation energies were calculated to be 11.2 kcal. mole<sup>-1</sup> at a pH above 3 and 9.21 kcal. mole<sup>-1</sup> at a pH below 2 (Table 6).

These facts imply two distinct active species, those at pH values below 2 and those above 3. Furthermore, the ultraviolet absorption spectrophotometry described above also endorses the presence of two active species at different pH's.

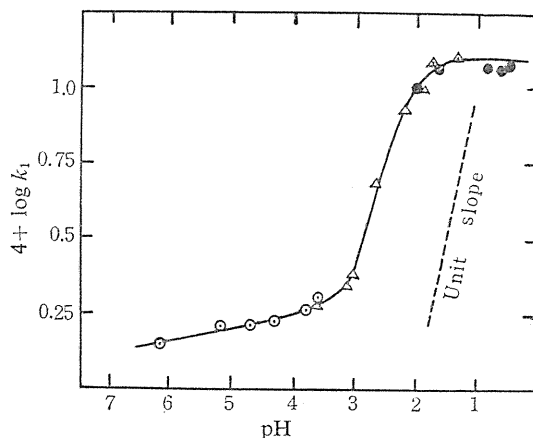


FIG. 4. Effect pH of reaction mixture on the first-order rate constant  $k_1$  at 25°C.

- ⊙ AcOH-AcONa
- △ HCl-KCl
- △ HCl
- H<sub>2</sub>SO<sub>4</sub>

TABLE 6. Energy of Activation and Entropy of Activation (calcd. from Table 2-C)

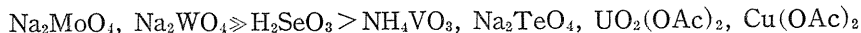
[SM] M × 10 <sup>-5</sup>	pH	<i>E<sub>a</sub></i> kcal. mol <sup>-1</sup>	<i>ΔS</i> <sup>‡</sup> (25°C) e.u.
none	4.7	14.25	-32.3
2.5	4.7	11.17	-38.4
2.5	0.8	9.21	-41.0

It is most probable that YPM at pH above 3 exist as  $\text{HMoO}_6^-$  (II), while at pH below 2 they exist as  $\text{H}_2\text{MoO}_6$  (I), which should be more active than  $\text{HMoO}_6^-$ . The ratio of  $[\text{H}_2\text{MoO}_6]$  to  $[\text{HMoO}_6^-]$  was calculated to be 100 : 3 at pH 1 and 1 : 30 at pH 4 by means of the first ionization constant of  $\text{H}_2\text{MoO}_6$  as determined by Csányi.<sup>17)</sup>

The shift of the absorption maximum from 310 to 326  $m\mu$  with a decreasing pH value is explicable by the transformation of  $\text{HMoO}_6^-$  to  $\text{H}_2\text{MoO}_6$ . Considering the ionization constants of  $\text{H}_2\text{MoO}_6$ ,  $\text{H}_2\text{MoO}_6$  should be about nine times as active as  $\text{HMoO}_6^-$  at 25°C.

### 1-5. Summary

The catalytic activities of some inorganic compounds for the hydrogen peroxide oxidation of thiodiglycol (TDG) have been examined in aqueous media at 25°C and at pH 4.7. It has been found that the order of catalytic activities was:



The rates of oxidation using all these catalysts, except sodium molybdate, may be expressed as:

$$v = k_2[\text{H}_2\text{O}_2][\text{TDG}]$$

The kinetics of this reaction has been studied in detail, especially, with the sodium molybdate (SM) catalyst by means of iodometry. The oxidation in the range  $2[\text{H}_2\text{O}_2] < [\text{SM}]$  follows the pseudo-second-order kinetics:

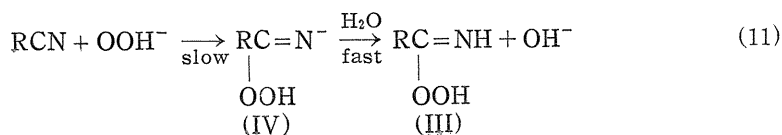
$$v = k'_2[\text{Active oxygen}][\text{TDG}]$$

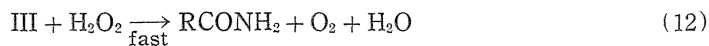
The values of  $k'_2$  were identical with the second-order rate constants obtained in the oxidation of thiodiglycol by yellow sodium peroxymolybdate. It is probable that dihydroperoxymolybdate,  $\text{HMoO}_6^-$ , produced rapidly from  $\text{Na}_2\text{MoO}_4$  and hydrogen peroxide, oxidizes thiodiglycol. The increase in the rate with a decreasing pH may be due to the transformation of  $\text{HMoO}_6^-$  to more active  $\text{H}_2\text{MoO}_6$ , since the  $\text{Na}_2\text{MoO}_4$ -hydrogen peroxide system gave two different ultraviolet absorption maxima corresponding to  $\text{HMoO}_6^-$  and  $\text{H}_2\text{MoO}_6$  at pH 4.7 and 0.8, respectively.

## Chapter 2. Alkali Phosphate-Catalyzed Oxidation by a Mixture of Nitrile and Hydrogen Peroxide

### 2-1. Introduction

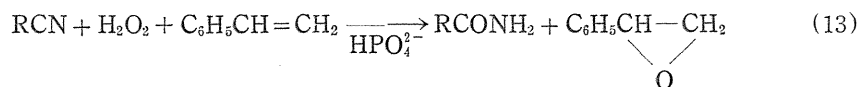
The reaction of benzonitrile with alkaline hydrogen peroxide has been found to proceed by way of peroxycarboimide acid (III):<sup>20) 21)</sup>





Peroxy-carboimidic acid can oxidize such other substrates as olefins,<sup>22)</sup> and it is a favorable oxidant which acts under milder and alkaline conditions and avoids the Baeyer-Villiger reaction,<sup>23)</sup> although the oxidation must be done under the controlled pH value (ca. 8).

An aqueous methanolic mixture of nitriles and hydrogen peroxide can oxidize styrene in the presence of alkaline phosphate, giving a high yield (above 95%) of epoxide according to the stoichiometric equation:



In this chapter are summarized the utility of alkali phosphate together with the kinetics of epoxidation of styrenes which treats the effect of basicity of the reaction media and of substituent effects in benzonitrile and styrene. A probable mechanism is postulated from these data. The reaction of nitriles with hydrogen peroxide in the presence of borate was also studied to compare with the case of phosphate.

## 2-2. Experimental

*Materials.*—Commercial benzonitrile, acetonitrile and styrene were purified by fractional distillations, b.p. 190°C, 83°C and 58°C (35 mmHg), respectively. Substituted benzonitriles were synthesized from the corresponding anilines:<sup>24)</sup> *p*-tolunitrile, b.p. 107–110°C (23 mmHg); *p*-anisnitrile was recrystallized from ethanol, m.p. 60°C; *p*-chloro- and *p*-nitrobenzonitrile were purified by recrystallization from ethanol, m.p. 93°C and 140°C, respectively. Substituted styrenes were prepared by the dehydration of phenylmethylcarbinols<sup>25)</sup> obtained from the corresponding acetophenones:<sup>26)</sup> *p*-chlorostyrene, b.p. 54–55°C (3 mmHg); *p*-methylstyrene, b.p. 43–44°C (5 mmHg); *m*-nitrostyrene, b.p. 100–103°C (5 mmHg). Cyclohexene was obtained from cyclohexanol,<sup>27)</sup> b.p. 82.5–83.5°C.

Hydrogen peroxide, phosphate and other inorganic reagents were all of guaranteed grade. Commercial methanol was used without further purification, since no appreciable difference in the rates was found between purified methanol and the commercial one.

*The Analytical Method.*—Hydrogen peroxide was analyzed iodometrically; 10 ml. of a reaction mixture was added to 30 ml. of ca. 0.1 N aqueous sulfuric acid containing 0.2–0.3 g. of potassium iodide, and the mixture was titrated with 0.1 N aqueous sodium thiosulfate immediately after the addition of three drops of a 1% sodium molybdate solution, thus avoiding the reaction of iodine with styrene. Neither nitriles nor styrenes interfered with the analysis.

The concentration of styrene oxide produced was determined by adding a 10 ml. aliquot to saturated aqueous sodium chloride (40 ml.) in a separatory funnel, extracting it with three 10 ml. portions of chloroform. The organic layer was washed three times with water and dried with anhydrous sodium sulfate. Then the oxirane oxygen content was determined by the pyridinium chloride-chloroform method.<sup>28)</sup> This method gave 90.0±1.0% of the recovery of styrene oxide and

was not interfered with the presence of nitriles and styrene. The estimation of styrene oxide was corrected by the above value.

*Examination of Effect of Phosphate Catalyst.*—An aqueous buffer solution (15 ml.; Table 7) was added to a 75 vol% methanolic solution (200 ml.) containing 0.1 M  $\text{H}_2\text{O}_2$  and if necessary, styrene or other compounds were also added. The mixture was kept at 40°C for 5 hr., then the concentration of peroxide determined iodometrically, and the content of epoxide estimated by the pyridinium chloride-chloroform method.<sup>28)</sup>

*A Typical Procedure for Rate Measurement.*—A 75% (v./v.) methanolic solution containing nitrile and styrene of a known concentration was buffered by the addition of potassium dihydrogen phosphate-sodium hydroxide and then thermostated in a brown flask. The epoxidation was started by adding a thermostated solution of hydrogen peroxide of the desired concentration. Aliquots were taken out at appropriate intervals, and the remaining hydrogen peroxide was estimated as has been described above. The oxirane content was also determined, if it was necessary. Most reactions were carried out to 40–50% conversion, and the constancy of rate constants was confirmed up to 80% conversion.

The decomposition of hydrogen peroxide itself was not appreciable, and its consumption in the presence of nitrile alone was so small that it was negligible in the calculation of the rate constants.

*Epoxidation of Cyclohexene with Benzonitrile-Hydrogen Peroxide.*—In a 300 ml. 3-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a thermometer, methanol (150 ml.), cyclohexene (16.4 g., 0.20 mole), benzonitrile (25.8 g., 0.25 mole), 30%  $\text{H}_2\text{O}_2$  (28.5 g., 0.25 mole), 0.1 M  $\text{Na}_2\text{HPO}_4$  aq. soln. (5 ml.) and finally 0.5 N NaOH aq. soln. (5 ml.) were added. The mixture was stirred at 40°C for 2 hr. while 0.5 N NaOH aq. soln. (4 × 5 ml.) was added gradually. Titration indicated the consumption of 0.191 mole of peroxide and the presence of 0.182 mole of epoxide (91% based on olefin). The mixture was diluted with water (50 ml.) and extracted with 3 × 50 ml. portions of chloroform. The combined extract, after washing and drying, was distilled to give 13.0 g. (65%) cyclohexene oxide, b.p. 57–58°C (55 mmHg);  $n_D^{25}$  1.4526 (lit.<sup>22)</sup> b.p. 54–55°C (50 mmHg);  $n_D^{20}$  1.4525).

*Epoxidation of Styrene by Benzonitrile-Hydrogen Peroxide.*—Styrene (20.8 g., 0.20 mole) was added in place of cyclohexene, and the reaction temp. (50°C) was raised up to 64°C for the first 20 min. After working up, the titration indicated the conversion of 0.193 mole of peroxide (97%) and the presence of 0.190 mole of epoxide (95%). No attempt was made to isolate the epoxy compound. Instead, the remaining  $\text{H}_2\text{O}_2$  (0.057 mole) was decomposed with  $\text{Na}_2\text{S}_2\text{O}_3$  and the mixture was concentrated in vacuo, extracted with hot chloroform, filtered and condensed by evaporation. Dilution of the condensed filtrate with excess pet. ether caused benzamide (m.p. 126–127°C, 22.4 g., 0.184 mole, 92% yield) to precipitate.

*Epoxidation of Cyclohexene by Acetonitrile-Hydrogen Peroxide.*—Acetonitrile (10.3 g., 0.25 mole) was used at 50°C and after 3 hrs.; titration indicated the conversion of 0.177 mole (89%) peroxide and the presence of 0.148 mole (74%) epoxide. Extraction and distillation gave 11.7 g. (60%) of cyclohexene oxide,

b.p. 58–59°C (58 mmHg);  $n_D^{25}$  1.4522.

*Epoxidation of Styrene by Acetonitrile-Hydrogen Peroxide.*—Epoxidation was started by the addition of 0.5 N NaOH aq. soln. (5 ml.) to a mixture of methanol (200 ml.), styrene (41.6 g., 0.04 mole), acetonitrile (20.6 g., 0.50 mole), 30% H<sub>2</sub>O<sub>2</sub> (57 g., 0.50 mole) and 0.1 M Na<sub>2</sub>HPO<sub>4</sub> aq. soln. (5 ml.). The mixture was stirred at 50°C for 3 hrs. during the gradual addition of 0.5 N NaOH aq. soln. (6 × 5 ml.). After the reaction, the consumed peroxide was estimated as 0.388 mole (97%) and the yield of epoxide as 0.326 mole (82%). Extraction and distillation gave styrene oxide, 36.2 g. (85% yield on the basis of consumed styrene), b.p. 86–87°C (27 mmHg);  $n_D^{20}$  1.5335 (lit.<sup>22</sup>) b.p. 98–99°C (35 mmHg);  $n_D^{20}$  1.5348, styrene (5 g.), b.p. 55–56°C (27 mmHg), being recovered.

*Oxidation of Dimethylaniline with Benzonitrile-Hydrogen Peroxide.*—A mixture of methanol (150 ml.), dimethylaniline (12.1 g., 0.10 mole), benzonitrile (11.4 g., 0.11 mole), 30% H<sub>2</sub>O<sub>2</sub> (12.5 g., 0.11 mole), 0.1 M Na<sub>2</sub>HPO<sub>4</sub> (5 ml.) and 1 N NaOH (5 ml.) was stirred at 30°C for 1 hr. with an addition of 1 N NaOH (5 ml.) in 30 min. Iodometry indicated 90% conversion of peroxide. The mixture was condensed in vacuo; water (50 ml.) was added and dimethylaniline extracted with ether. The aqueous layer was poured into a boiling aqueous solution of picric acid (23 g. in 450 ml. water) to precipitate 26.6 g. (73%) dimethylaniline oxide picrate, m.p. 138–139°C (lit.<sup>29</sup>) m.p. 137–138°C.

*Oxidation of Dimethylaniline by Acetonitrile-Hydrogen Peroxide.*—Acetonitrile was used in place of benzonitrile at 60°C according to the above procedure. The yield of N-oxide picrate was 28.5 g. (78%), m.p. and mixture m.p. 137–138°C.

*Oxidation of Aniline by Acetonitrile-Hydrogen Peroxide.*—A mixture of methanol (150 ml.), aniline (9.3 g., 0.10 mole), acetonitrile (20.5 g., 0.40 mole), 30% H<sub>2</sub>O<sub>2</sub> (46.5 g., 0.46 mole) and 0.1 M Na<sub>2</sub>HPO<sub>4</sub> (5 ml.) was stirred at 50°C for 4 hrs. with the gradual addition of 1 N NaOH (6 × 5 ml.). After 4 hrs., 0.45 mole of peroxide was consumed; the mixture was diluted with water and extracted with benzene. The extract, after washing with dil. HCl and then with water, dried and evaporated to dryness (8.6 g.). Recrystallization from a small amount of pet. ether gave 7.0 g. (71%) azoxybenzene, m.p. and mixture m.p. 35.3–35.5°C.

### 2-3. Utility of Phosphate Catalyst

The epoxidation of styrene with a mixture of nitrile and hydrogen peroxide was examined in a 75% methanolic solution with various buffers and is summarized in Table 7. The reaction of nitrile with alkaline hydrogen peroxide alone<sup>20, 21</sup>) is retarded almost completely by the addition of phosphate (run 3 and 4) and the yield of styrene oxide is almost quantitative on the basis of consumed peroxide (runs 1, 2 and 13), according to the stoichiometric equation (eq. 3). Acetonitrile is less reactive than benzonitrile (run 13).

On the other hand, the Radziszewski's reaction ( $\text{RCN} + 2 \text{H}_2\text{O}_2 \rightarrow \text{RCONH}_2 + \text{O}_2 + \text{H}_2\text{O}$ ), with a borate buffer, results in a low yield of styrene oxide (runs 15 and 16) and similarly when ammonia-ammonium chloride is used as buffer except that the consumption of peroxide was ca. 1/5 (runs 19 and 20).

The addition of sodium phosphate suppresses the Radziszewski's reaction in

TABLE 7. The Reaction of Benzonitrile with Hydrogen Peroxide with or without Styrene in 75% Methanol at 40°C for 5 hrs.; Initial concn.  $[\text{C}_6\text{H}_5\text{CN}] = [\text{H}_2\text{O}_2] = 0.1 \text{ M}$

Run no.	Buffer composition <sup>a)</sup>	Added compd. 0.0025 M	$[\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]$ $\text{M} \times 10^3$	Consumed $[\text{H}_2\text{O}_2]$ $\text{M} \times 10^3$	$\frac{[\text{C}_6\text{H}_5\text{CH}-\text{CH}_2]}{[\text{H}_2\text{O}_2]}$
					%
1	A	—	100	36.2	96.8
2	A	—	300	60.6	96.7
3	A	—	—	0.4	—
4	A	$\text{H}_2\text{O}^{\text{b)}$	—	3.4	—
5	A	$\text{H}_2\text{O}^{\text{c)}$	—	10.3	—
6	A	$\text{H}_2\text{O}^{\text{d)}$	—	16.3	—
7	A	$\text{Na}_2\text{CO}_3$	—	1.9	—
8	A	$\text{Na}_2\text{SO}_4$	—	1.9	—
9	A	$\text{Na}_2\text{SiO}_4$	—	1.1	—
10	A	$\text{Na}_2\text{B}_2\text{O}_7$	—	45.3	—
11	A	$\text{Na}_2\text{B}_2\text{O}_7$	100	44.2	51.0
12	A	$\text{H}_3\text{BO}_3$	—	7.3	—
13	A	$\text{CH}_3\text{CN}^{\text{e)}$	100	16.8	96.0
14	A	$\text{CH}_3\text{CN}^{\text{e)}$	—	1.8	—
15	B	—	200	44.7	33.0
16	B	—	100	46.2	21.2
17	B	—	—	48.0	—
18	B	$\text{Na}_2\text{HPO}_4$	—	47.9	—
19	C	—	100	8.5	38.0
20	C	—	—	8.2	—
21	C	$\text{Na}_2\text{HPO}_4$	—	1.6	—
22	C	$\text{H}_3\text{BO}_3$	—	24.7	—

a) Buffer A: A mixture of 0.2 M  $\text{KH}_2\text{PO}_4$ -0.2 N NaOH (4 : 5) (15 ml.) was added to the reaction mixture (200 ml.). The pH value observed in the absence of reactants was 11.35 and the addition of reactants decreased the value by ca. 0.5 pH unit, where the pH was held constant during the reaction.

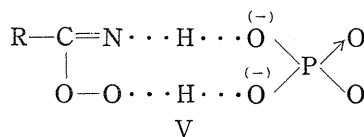
Buffer B: 0.41 M  $\text{H}_3\text{BO}_3$ -0.1 N NaOH (1 : 1) (15 ml.) was added to the reaction mixture (200 ml.). Observed pH value was 9.02.

Buffer C: 0.1 M  $\text{NH}_4\text{Cl}$ - $\text{NH}_4\text{OH}$  (1 : 2) was used, pH being 9.00.

b), c), and d) Reaction in 65%, 50% and 40% methanol, respectively.

e) Acetonitrile was used in place of benzonitrile.

an ammonia-ammonium chloride buffer (run 21), but not in run 18 (borate buffer). The addition of sodium borate or boric acid to the phosphate buffer also reduces the effect of the phosphate (runs 10, 11 and 12), while sodium carbonate, sulfate and silicate have no effect (runs 7, 8 and 9). The action of phosphate may be explained by assuming the formation of a stable complex (V) between  $\text{HPO}_4^{2-}$  and III, but an unstable complex between I and  $\text{H}_3\text{BO}_3$  (see Section 2-5).



However, when the water content in methanol is increased, the Radziszewski's reaction becomes apparent (runs 4, 5 and 6), suggesting a diminution in the

TABLE 8. Phosphate-Catalyzed Epoxidation and Oxidation with Nitrile and Hydrogen Peroxide

Oxidant <sup>a)</sup>	Substrate	Reaction		Yield (%) <sup>b)</sup>	
		Temp. (°C)	Time (hr.)	Titrated <sup>c)</sup>	Isolated
BN-H <sub>2</sub> O <sub>2</sub>	Cyclohexene	40	2	91	65
BN-H <sub>2</sub> O <sub>2</sub>	Styrene	50	2	95	— <sup>d)</sup>
BN-H <sub>2</sub> O <sub>2</sub>	<i>N,N</i> -Dimethylaniline	30	1	—	73 <sup>e)</sup>
AN-H <sub>2</sub> O <sub>2</sub>	Cyclohexene	50	3	74	60
AN-H <sub>2</sub> O <sub>2</sub>	Styrene	50	3	82	76
AN-H <sub>2</sub> O <sub>2</sub>	<i>N,N</i> -Dimethylaniline	60	1	—	78 <sup>e)</sup>
AN-H <sub>2</sub> O <sub>2</sub>	Aniline	50	4	—	71 <sup>f)</sup>

a) BN: Benzointrile; AN: Acetonitrile.

b) Yield based on the used substrate.

c) Yield calculated from the oxirane content by titrimetry.<sup>28)</sup>

d) No attempt was made to isolate styrene oxide, but benzamide (92%) was isolated.

e) Dimethylaniline oxide picrate.

f) Azoxybenzene.

interaction between phosphate and III. Therefore, methanol containing more than 35% water is not suitable for the epoxidation.

The results of the epoxidation of styrene and cyclohexene and the oxidation of aniline and dimethylaniline in the presence of alkali phosphate are summarized in Table 8.

The consumption of peroxide is over 90% and the epoxidation of styrene and cyclohexene using benzonitrile and hydrogen peroxide is complete in 2 hrs. The titration for oxirane oxygen also confirms a 90% yield of epoxide. In the case of acetonitrile, a longer reaction time is necessary and the yield of epoxide is lower.

The oxidation of dimethylaniline to its *N*-oxide is complete within 1 hr., the yield of picrate being 73-78%. Aniline may be oxidized to azoxybenzene in 71% yield.

#### 2-4. Kinetic Data of Epoxidation of Styrenes

*Rate Law.*—The rate of the epoxidation of styrene with nitrile and alkaline hydrogen peroxide catalyzed by phosphate in 75% methanol were determined by estimating the disappearance of hydrogen peroxide. The results of a typical kinetic run shown in Table 9 clearly indicate that the reaction is of third-order:

$$v = k_{11}[\text{RCN}][\text{H}_2\text{O}_2][\text{C}_6\text{H}_5\text{CH}=\text{CH}_2] \quad (14)$$

These third-order kinetics are satisfactory with various initial concentrations of reactants or phosphate (Table 10-A). The slight decrease in the rate with increasing concen-

TABLE 9. A Typical Third-Order Rate Constant for the Phosphate-Catalyzed Epoxidation in 75% Methanol at 40°C; Initial concn., [C<sub>6</sub>H<sub>5</sub>CN] = [H<sub>2</sub>O<sub>2</sub>] = 0.100 M; [C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>] = 0.200 M; Buffer, KH<sub>2</sub>PO<sub>4</sub>-NaOH (4 : 5), pH 11.35

Time min.	Conversion of H <sub>2</sub> O <sub>2</sub> , %	$k_{11} \times 10^3$ M <sup>-2</sup> sec <sup>-1</sup>
45	15.2	3.54
130	33.2	3.54
180	41.1	3.51
240	47.3	3.65
330	54.2	3.60
420	60.0	3.69
540	65.2	3.61

TABLE 10. Phosphate-Catalyzed Epoxidation of Styrene with a Mixture of Nitrile and Alkaline Hydrogen Peroxide in 75% (v./v.) Methanol Buffered with  $\text{KH}_2\text{PO}_4$ -NaOH at 40°C

A) Effect of the initial concentration of reactants. Buffer solution: 0.2 M $\text{KH}_2\text{PO}_4$ -0.2 N NaOH (4 : 5), pH=11.35					
[RCN] M	[ $\text{H}_2\text{O}_2$ ] M	[ $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ] M	Buffer soln. <sup>a)</sup> ml.	$k_{14} \times 10^3$ $\text{M}^{-2} \text{sec.}^{-1}$	
Benzonitrile					
0.100	0.100	0.100	15	4.01	
0.100	0.150	0.100	15	4.00	
0.200	0.100	0.100	15	4.13	
0.100	0.100	0.200	15	3.59	
0.100	0.100	0.300	15	3.25	
0.100	0.100	0.100	10	3.95	
0.100	0.100	0.100	20	4.15	
Acetonitrile					
0.100	0.100	0.100	15	1.21	
0.200	0.100	0.100	15	1.15	
0.300	0.150	0.150	15	0.94	
0.150	0.150	0.150	15	0.98	
B) Effect of pH. Initial concn.: [ $\text{C}_6\text{H}_5\text{CN}$ ]=[ $\text{H}_2\text{O}_2$ ]=[ $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ]=0.100 M, [Buffer soln.] = 15 ml. <sup>a)</sup>					
Buffer no.	0.2 M $\text{KH}_2\text{PO}_4$ : 0.2 N NaOH	pH (glass electrode)	at $t=5$ hrs.		$k_{14} \times 10^3$ $\text{M}^{-2} \text{sec.}^{-1}$
			Conversion, %	Consumption of $\text{H}_2\text{O}_2$ without styrene, %	
1	4 : 3	9.34	23.6	0.10	1.88
2	4 : 4	10.40	32.6	0.35	3.40
3	4 : 5	11.35	37.4	0.70	4.01
4	4 : 6	11.80	38.9	1.34	4.17
5	4 : 8	12.00	40.7	2.90	4.48
C) Effect of the solvent composition. Initial concn. is same as that in buffer 3 in B.					
Methanol	Solvent, vol.%		Added toluene, M	$k_{14} \times 10^3$ $\text{M}^{-2} \text{sec.}^{-1}$	
	Ethanol	Water			
75	0	25	0	4.01	
75	0	25	0.1	3.78	
75	0	25	0.2	3.61	
55	20	25	0	3.48	
85	0	15	0	2.65	
65	0	35	0	6.00	

a) Volume per 200 ml. of reaction solution.

tration of styrene may be attributed to the decrease in the polarity of the reaction mixture, as will be described below.

*Effect of pH.*—The effect of pH on the rate of epoxidation was examined by changing the composition of the phosphate buffer (Table 10-B). The rate of epoxidation increased only a little with the increasing pH except at pH values below 10, which is rather surprising if it is remembered that  $\log k$  linearly



increased with the pH value in the reaction of benzonitrile with hydrogen peroxide.<sup>20)</sup> Although a small amount of hydrogen peroxide was consumed in the absence of styrene, the yields of styrene oxide based on the peroxide consumed were essentially the same (93-96%) in each pH examined.

*Effect of the Polarity of Solvent.*—The rate of epoxidation was affected by the composition of the solvent (Table 10-C). The higher water content in the reaction mixture tended to increase the rate. Compare methanolic solvents with 15% and 35% water. Hence, the slight decrease of rate with increasing initial concentration of styrene may be attributed to the decrease in the polarity of the reaction mixture. The addition of toluene also resulted in the same decrease in the rate.

*Substituent Effect.*—Substituent effects are shown in Table 11-A and Fig. 5. The introduction of electron-attracting groups in benzonitrile increases the rate, the Hammett's  $\rho$ -value being 0.57, while substituents in styrene exhibit the reverse effect, giving a  $\rho$ -value of  $-0.51$ . These results suggest an electrophilic attack of the peroxy-carboimidic acid intermediate.

For the purpose of comparison, the reaction of substituted benzonitrile with alkaline hydrogen peroxide was also studied in the presence of borate (Table 11 B and Fig. 5); the resulting  $\rho$ -value of 1.14 in 75% methanol is somewhat smaller than that obtained in 50% acetone.<sup>30)</sup> This  $\rho$ -value is about two times greater than that in the phosphate-catalyzed epoxidation of styrene with a mixture of

TABLE 11. Substituent Effect in Benzonitriles and Styrenes in 75% Methanolic Buffers

Substituent		Temp., °C			$E_a$ kcal. mol. <sup>-1</sup>	$\Delta S^\ddagger$ (40°C) e.u.
Benzo- nitrile	Styrene	30.0	40.0	50.0		
A) Third-order rate constant ( $M^{-2} \text{sec.}^{-1}$ ) for the epoxidation in a phosphate buffer (pH=11.35) <sup>a)</sup>						
<i>p</i> -CH <sub>3</sub> O	H	2.49	3.78	5.72	8.1	-44
<i>p</i> -CH <sub>3</sub>	H	2.37	3.47	4.51	6.3	-46
H	H	3.24	4.01	4.97	4.1	-56
<i>p</i> -Cl	H	5.16	7.33	9.60	6.0	-49
<i>p</i> -NO <sub>2</sub>	H	—	11.3	—	—	—
H	<i>p</i> -CH <sub>3</sub>	4.10	5.28	6.84	5.0	-53
H	<i>p</i> -Cl	2.55	3.34	4.23	4.9	-54
H	<i>m</i> -NO <sub>2</sub>	1.26	1.83	2.60	7.5	-48
CH <sub>3</sub> CN <sup>b)</sup>	H	0.60	0.94	1.39	8.2	-46
B) Second-order rate constants ( $M^{-1} \text{sec.}^{-1}$ ) for the reaction of benzonitrile with hydrogen peroxide in a borate buffer (pH=9.02) <sup>c)</sup>						
<i>p</i> -CH <sub>3</sub> O	none	—	1.28	—	—	—
<i>p</i> -CH <sub>3</sub>	none	—	1.52	—	—	—
H	none	0.763	1.95	4.61	17.5	-19.8
<i>p</i> -Cl	none	—	5.45	—	—	—
<i>p</i> -NO <sub>2</sub>	none	—	14.2	—	—	—
CH <sub>3</sub> CN <sup>b)</sup>	none	—	—	0.264	—	—

<sup>a)</sup>  $v = k_{14}[\text{RCN}][\text{H}_2\text{O}_2][\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]$ ; initial concn.:  $[\text{RCN}] = [\text{H}_2\text{O}_2] = [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2] = 0.100 \text{ M}$ . <sup>b)</sup> Acetonitrile instead of benzonitrile. <sup>c)</sup>  $v = k[\text{RCN}][\text{H}_2\text{O}_2]$ ; initial concn.:  $[\text{RCN}] = [\text{H}_2\text{O}_2] = 0.100 \text{ M}$ .

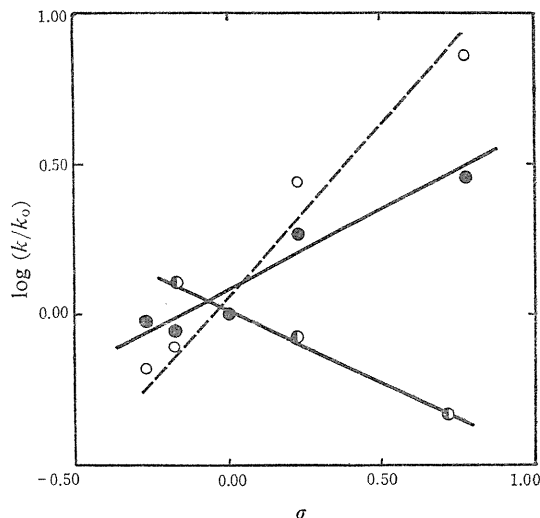


FIG. 5. Plots of logarithm of rate constants for the epoxidation of styrenes with benzonitriles and hydrogen peroxide in a phosphate buffer at 40 °C vs.  $\sigma$  (Hammett and Jaffe):

- Epoxidation of styrene with substituted benzonitriles
- ◐— Epoxidation of substituted styrenes with benzonitrile
- Reaction of substituted benzonitriles with hydrogen peroxide in a borate buffer

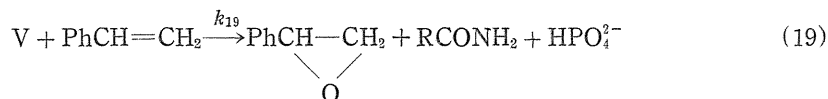
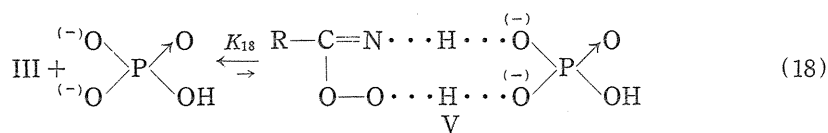
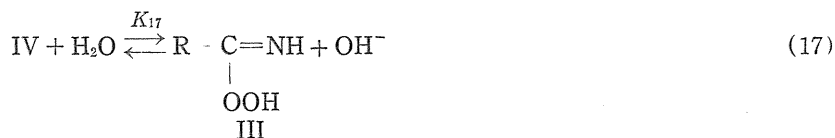
substituted benzonitriles and alkaline hydrogen peroxide. The energies and entropies of activation also substantially differ between these two reactions, 11-12 and 13.

#### 2-5. Discussion

The reaction of nitrile with alkaline hydrogen peroxide<sup>27)</sup> (the Radziszewski's reaction,  $\text{RCN} + 2\text{H}_2\text{O}_2 \rightarrow \text{RCONH}_2 + \text{O}_2 + \text{H}_2\text{O}$ ) is suppressed by the presence of phosphate, yielding styrene oxide almost quantitatively on addition of styrene. The kinetic results may be summarized as follows: (1) The phosphate-catalyzed epoxidation of styrene with nitrile and alkaline hydrogen peroxide follows third-order kinetics, being first-order in each reactant (nitrile, hydrogen peroxide and styrene). (2) The rate of epoxidation is essentially constant at various pH's, while the rate increases with the increasing polarity of the reaction mixture. (3) Electron-attracting substituents on the benzonitrile accelerate the rate of epoxidation to give a Hammett's  $\rho$ -value of 0.57, while the Radziszewski's reaction results in the  $\rho$ -value of 1.14. (4) Electron-releasing groups in the styrene accelerate the rate, exhibiting a negative  $\rho$ -value of  $-0.51$ . (5) The energy of activation is low and the entropy of activation is highly negative, while with the Radziszewski's reaction the former is higher and the later is less negative.

*Reaction Scheme.*—The kinetic data show that nitrile, hydrogen peroxide and styrene are involved in the transition state, while the phosphate catalysis suggests

that the oxidizing intermediate stabilized by phosphate dianion is effective for an electrophilic attack on olefin. These results agree with the following mechanism:



Assuming that the concentrations of III and IV are both very low and that equilibrium 18 is mobile and very favorable to the right side, the concentration of V may be expressed as:

$$\begin{aligned} [\text{V}] &\cong \frac{K_{17}[\text{IV}][\text{H}_2\text{O}]}{[\text{HO}^-]} \\ &\cong \frac{K_{16}K_{17}[\text{H}_2\text{O}][\text{RCN}]_s[\text{HO}_2^-]}{[\text{OH}^-]} \\ &\cong K_{15}K_{16}K_{17}[\text{RCN}]_s[\text{H}_2\text{O}_2]_s \end{aligned}$$

Here,  $k$  and  $K$  are the rate and equilibrium constants of the subscripted steps, respectively, and  $[\ ]_s$  represents its stoichiometric concentration. Hence, the rate equation is:

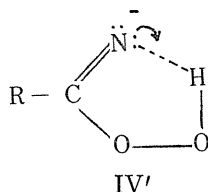
$$\begin{aligned} v &= k_{19}[\text{V}][\text{PhCH}=\text{CH}_2] \\ &= k_{19}K_{15}K_{16}K_{17}[\text{RCN}]_s[\text{H}_2\text{O}_2]_s[\text{PhCH}=\text{CH}_2]_s \end{aligned} \quad (20)$$

Rate equation 20 is consistent with the observed third-order kinetics and also with the independence of the rate on the hydroxide ion concentration (*i.e.*, pH).

The above mechanism assumes that IV is not so active as to epoxidize styrene and that III is rapidly stabilized by phosphate to prohibit the reaction with hydrogen peroxide.

*Active Epoxidizing Species.*—Phosphoric acid should exist exclusively in the form of dianion,  $\text{HPO}_4^{2-}$ , in these pH's in view of the dissociation constant. The

interaction of the dianion with the intermediate anion IV is less probable because of the electrostatic repulsion. While the intermediate III may easily form with the nucleophilic phosphate dianion, the intermediate V is so deactivated as to fail to oxidize hydrogen peroxide. The epoxidizing species is thought to be stabilized by the electron-releasing interaction of the phosphate dianion.



The intermediate anion, IV, presumably has a chelate structure IV', resembling that of peroxyacid,<sup>31) 32) 33)</sup> where the electrophilicity of the oxygen atom is increased by internal hydrogen bonding. However, the electrophilicity of peroxide oxygen should be greatly decreased with the anion IV' by the presence of a negative charge. Although the intramolecular activation of IV' by hydrogen bonding may actually exist, this effect would not surpass the electron-releasing power of the imide anion, since hydrogen bonding may contribute much less than does the inductive effect.

When boric acid was added to the phosphate buffer, the Radziszewski's reaction<sup>21)</sup> occurred in spite of the presence of an excess of phosphate and the rate increased with increasing amount of the added acid, although the pH's of the reaction mixture decreased.<sup>23)</sup> This promotion of the Radziszewski's reaction by boric acid is probably due to the ability of the acid to combine with the unshared electron pair of the nitrogen atom, decreasing the electron density on the peroxide oxygen atom.

*Substituent Effects.*—The substituent effects on both benzonitrile and styrene imply an electrophilic attack of V on the doubly-bound carbon atoms. The same effects have been observed with the peroxybenzoic acid epoxidation of olefins.<sup>34)</sup> The Hammett's  $\rho$ -value for the epoxidation with substituted benzonitrile is about one-half of that for the Radziszewski's reaction, indicating a lower sensitivity to the polar effect. This lower value of  $\rho$  can be well understood by considering the effect on equilibrium 17 reverse to that on equilibrium 16, thus leading to the decrease in total  $\rho$ -value.

The Hammett's plot for epoxidation with substituted benzonitriles in Fig. 5 shows a little departure from linearity especially for the *p*-methoxy group, while the plot for the Radziszewski's reaction is more satisfactory. The deviation of the former plot may be attributed to the overestimation of the resonance effect, since IV should be less resonance-stabilized than the benzoate anion; hence, the above deviation is conceivable.

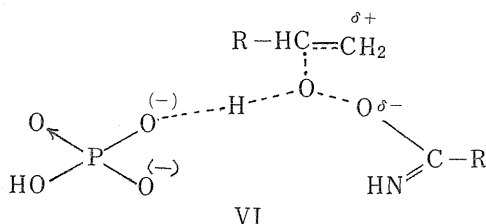
As for the epoxidation of substituted styrenes, the Hammett's plot is much more satisfactory, but it has a slight deviation as to *p*-substituents. According to the correction for  $\sigma$ -value using the  $\gamma$  parameter,<sup>35)</sup>

$$\sigma^+ = \sigma + \gamma \times \Delta\sigma_R$$

the value for  $\sigma$  (meta) is calculated to be  $-0.48$  from the rates for unsubstituted and *m*-nitrostyrene, and the  $r$ 's are  $0.62$  for *p*-methyl- and  $0.59$  for *p*-chlorostyrene. The  $r$ -value of  $0.61$  (average) is similar to  $0.48$  for the perbenzoic acid epoxidation of styrenes,<sup>26)</sup> suggesting a similar resonance effect in the transition state.

*The Approach of the Reagent to Substrate.*—The rate of epoxidation increased in solvents with higher dielectric constants, which seems to mean that an increase of polarity may increase the degree of dissociation of V, resulting in the regeneration of the stronger oxidant (III). This was confirmed by the fact that the reaction rate of benzonitrile with hydrogen peroxide alone increased with the increasing water content of solvent (see Table 7).

Considering the above discussion, the transition state may be expressed as VI:



As is to be expected, VI, a highly-crowded transition state, would require a highly negative entropy of activation, reflecting the hindered motion of each reactant. Thus, the present reaction is considered to be slowed down by the highly negative entropy of activation in spite of the low energy of activation. The less negative entropy of activation for the Radziszewski's reaction can be well explained by the less crowded transition state containing only two species, *e.g.*, nitrile and hydroperoxide ion.

## 2-6. Summary

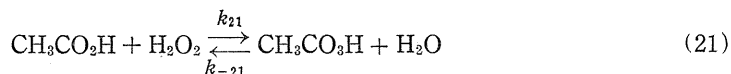
The reaction of nitrile with alkaline hydrogen peroxide is inhibited almost completely by the presence of phosphate; therefore, the epoxidation of styrene in this mixture gives nearly a quantitative yield of epoxide on the basis of consumed peroxide. This oxidizing agent was used to epoxidize styrene and cyclohexene in the yield of 74–95% and to oxidize dimethylaniline to its *N*-oxide (73–78%) and aniline to azoxybenzene (71%).

The phosphate-catalyzed epoxidation of styrenes with a mixture of nitriles and alkaline hydrogen peroxide have been studied kinetically in 75% methanol. The reactions satisfy third-order kinetics, being first-order in nitrile, hydrogen peroxide and styrene. The rate is essentially constant at various pH's, while it increases with the increasing polarity of the reaction medium. The energy of activation is low ( $6-8 \text{ kcal. mol.}^{-1}$ ), and the entropy of activation is highly negative ( $-50 \text{ e.u.}$ ). The effect of substituent in benzonitrile is to give a Hammett's  $\rho$ -value of  $0.57$ , while that in styrene resulted in a negative  $\rho$ -value of  $-0.51$ . It is probable that the peroxy-carboimidic acid (III), produced by mobile equilibria from nitrile and hydroperoxide ion, is stabilized by an intermolecular hydrogen bonding with the phosphate dianion, and that this species contributes mostly to the epoxidation of styrene in the following, rate-determining step.

### Chapter 3. Acid-Catalyzed Formation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide

#### 3-1. Introduction

It has been known that the formation and hydrolysis of peracetic acid is acid-catalyzed<sup>34)</sup> and also that the equilibrium constant for the reaction 21 increases with increasing concentration of catalytic acid.<sup>36) 37)</sup>



For the clarification of these phenomena the dependence of the rate and equilibrium constants on the concentration of mineral acid in a wider range was studied, correlating it with the Hammett's acidity function.

#### 2-3. Experimental

*Materials.*—Commercial acetic 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*-nitroaniline were recrystallized from water containing a small amount of methanol.

*Kinetic Measurement.*—A definite amount of aqueous acetic acid of known concentration containing an appropriate amount of sulfuric acid was thermostated and the reaction was started by adding 30% hydrogen peroxide. (Water was added previously to prevent the evolution of heat of neutralization when 30% hydrogen peroxide was added.)

Aliquots were taken out at appropriate intervals of time and analyzed for the contents of hydrogen peroxide and peracid by means of a 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. Hydrogen peroxide was quickly titrated with potassium permanganate until the pink color appears and then the remaining peracid was titrated iodometrically after the addition of potassium iodide. The content of peracid was calculated from the ratio of the titres of consumed permanganate and thiosulfate, since the decomposition of hydrogen peroxide and peracid was found to be negligible under these reaction conditions. This method without weighing of aliquots gave an adequate accuracy in blank test.

*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. Representing the initial concentrations of acetic acid, hydrogen peroxide and water as  $a$ ,  $b$  and  $c$ , respectively, and the concentration of produced peracid as  $x$ , the rate of formation of peracid is expressed as:

$$v = k_{21}(a - x)(b - x) - k_{-21}(c + x)x$$

The equation is transformed to:

$$v = k_{21}(1 - 1/K_{21})(\alpha - x)(\beta - x) \quad (22)$$

Here,  $K_{21} = k_{21}/k_{-21}$  and

$$\alpha, \beta = \frac{1}{2(1-1/K_{21})} \left\{ \left( a + b + \frac{c}{K_{21}} \right) \pm \sqrt{(a+b+c/K_{21})^2 - 4ab(1-1/K_{21})} \right\}$$

The rate constant,  $k_{21}$ , thus calculated hold good constancy as shown in Table 12.

*Measurement of  $H_0$ .*—The Hammett's acidity function of the media (water was added in place of hydrogen peroxide) was measured using *o*- and *p*-nitroanilines as an indicator. The absorption peaks were measured at 410  $m\mu$  for *o*-nitroaniline and at 370–380  $m\mu$  for *p*-nitroaniline, where the shift of  $\lambda_{max}$  was observed with varying the ratio of acetic acid to water.  $H_0$ 's were calculated from equation,  $H_0 = pK_{BH^+} - \log(c_{BH^+}/c_B)$ , where  $Kp_{BH^+}$  is an indicator constant and  $c_{BH^+}$  is the concentration of conjugate acid of an indicator and  $c_B$  is that of neutral form of the same indicator. The value of  $pK_{BH^+}$  cited is  $-0.29$  for *o*-nitroaniline and  $0.99$  for *p*-isomer.<sup>38)</sup> These results are listed in Table 13 and 14.

### 3-3. Results and Discussion

*Rate Law.*—The acid-catalyzed formation of peracetic acid follows the rate equation 2 and a typical run is shown in Table 12. The rate law coincides with the data reported previously in the literature.<sup>37) 39)</sup> The rate of peracid formation in the absence of mineral acid was too slow to measure.

*Effect of the Acidity of the Media.*—The rate and equilibrium constants for the formation of peracetic acid are shown in Table 13, where it is obvious that they increase with increasing concentration of sulfuric acid. These facts have been reported as the proportionalities of rate and equilibrium constants with the concentration ( $< 0.5$  M) of mineral acid.<sup>36) 37) 38)</sup> However, this is not true

TABLE 12. A Typical Rate Constant for the Formation of Peracetic Acid in 80 vol.% Acetic Acid at 25°C

Initial concns.:  $a = [\text{CH}_3\text{CO}_2\text{H}] = 13.77$  M;  
 $b = [\text{H}_2\text{O}_2] = 1.014$  M;  $c = [\text{H}_2\text{O}] = 9.831$  M;  
 $[\text{H}_2\text{SO}_4] = 0.30$  M

Time min.	$x = [\text{CH}_3\text{CO}_2\text{H}]$ M	$k_{21} \times 10^6$ <sup>a)</sup> M <sup>-1</sup> sec. <sup>-1</sup>
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	— <sup>b)</sup>

a)  $\alpha = 26.04$ ;  $\beta = 0.777$ .

b) Calculated equilibrium constant ( $K_{21}$ ) was 3.045.

TABLE 13. The Effect of Acidity on the Rate and Equilibrium Constants for the Peracid Formation in 80 vol.% Acetic Acid at 25°C<sup>a)</sup>

$[\text{H}_2\text{SO}_4]$ M	$-H_0$ <sup>b)</sup>	$K_{21}$	$k_{21} \times 10^6$ M <sup>-1</sup> sec. <sup>-1</sup>
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	3.523	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 concns.:  $[\text{CH}_3\text{CO}_2\text{H}] = 11.5 \sim 13.9$  M;  
 $[\text{H}_2\text{O}_2] = 1.014$  M;  $[\text{H}_2\text{O}] = 9.831$  M.

b) *o*-Nitroaniline was used as an indicator.

TABLE 14. Effect of the Ratio of  $[\text{CH}_3\text{CO}_2\text{H}] : [\text{H}_2\text{O}]$  at 25°C<sup>a)</sup>

Acetic acid Vol. %	$-H_0$ <sup>b)</sup>	$K_{21}$	$k_{21} \times 10^6$ M <sup>-1</sup> sec. <sup>-1</sup>
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 concns.:  $[\text{H}_2\text{SO}_4] = 0.20$  M;  $[\text{H}_2\text{O}_2] = 0.9350$  M.

b) *p*-Nitroaniline was used as an indicator.

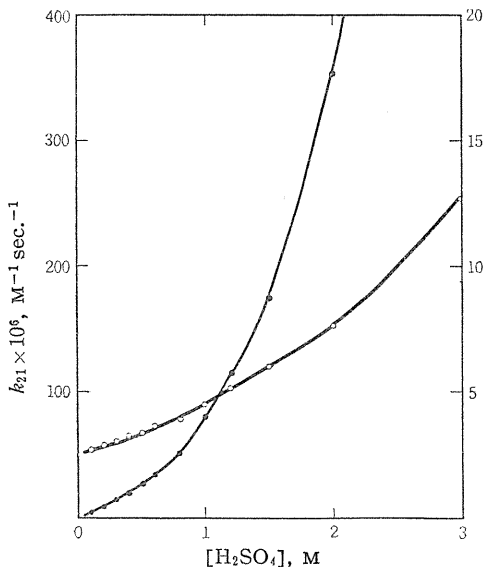


FIG. 6. Plots of  $k_{21}$  and  $K_{21}$  vs.  $[\text{H}_2\text{SO}_4]$  in 80 vol.% acetic acid at 25°C:  
 —●—  $k_{21}$  vs.  $[\text{H}_2\text{SO}_4]$ ;  
 —○—  $K_{21}$  vs.  $[\text{H}_2\text{SO}_4]$ .

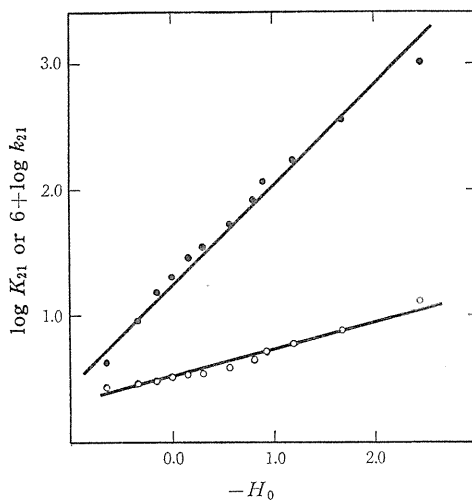


FIG. 7. Plots of  $\log k_{21}$  and  $\log K_{21}$  against the Hammett's acidity function in 80 vol.% acetic acid at 25°C.

—●—  $\log k_{21}$  vs.  $-H_0$   
 —○—  $\log K_{21}$  vs.  $-H_0$

at higher concentration of mineral acid ( $>0.5$  M), and the plots of  $k_{21}$  or  $K_{21}$  vs.  $[\text{H}_2\text{SO}_4]$  do not lie on a straight line but on a curve (Fig. 6).

This departure from linearity may be corrected by plotting  $\log k_{21}$  or  $\log K_{21}$  against the Hammett's acidity function; thus, the plots give a straight line with a slope of 0.82 for  $\log k_{21}$  and 0.22 for  $\log K_{21}$  (Fig. 7).

*Effect of the Ratios of Concentrations of Acetic Acid and Water.*—The rate of peracid formation was found to increase with increasing ratio of concentrations of acetic acid and water with constant concentration of sulfuric acid (Table 14). The plots of  $\log k_{21}$  vs.  $-H_0$  give a straight line with a slope of 1.10 or ca. unity, which is considerably larger value than that in the former slope (0.82). It should be noted that different indicators are used for the determination of acidity function.

*Temperature Dependence.*—The effect of temperature on the rate was studied in 60 and 80 vol.% acetic acid and the results together with the calculated activation parameters are summarized in Table 15. The change in energy and entropy of activation is unappreciable in going from 60% to 80% acetic acid.

The value for entropy of activation ( $-33\sim-36$  e.u.) implies the similar mechanism as the case of acid-catalyzed second-order esterification ( $-15\sim-30$  e.u.).<sup>40</sup> The value for energy of activation ( $15.1$  kcal. mole<sup>-1</sup>) suggests also a second-order mechanism resembling to the ester hydrolysis. Both energy and entropy of activation are close to the activation parameters in oxygen exchange reaction between water and benzoic acid ( $16$  kcal. mole<sup>-1</sup> and  $-30$  e.u., respectively).<sup>41</sup>



TABLE 15. Apparent Energies and Entropies of Activation for the Acid-Catalyzed Formation of Peracetic Acid

Acetic acid Vol. %	Temp. °C	$K_{21}$	$k_{21} \times 10^6$ $M^{-1} \text{sec.}^{-1}$	$E^a$ kcal. mole $^{-1}$	$\Delta S^*$ e.u.
80 <sup>a)</sup>	18.0	2.948	5.04	15.0	-35.7
	25.0	2.907	9.54		
	32.0	2.828	16.5		
60 <sup>b)</sup>	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.:  $[H_2SO_4] = 0.20 \text{ M}$ ;  $[CH_3CO_2H] = 12.36 \text{ M}$ ;  $[H_2O_2] = 1.014 \text{ M}$ ;  $[H_2O] = 9.831 \text{ M}$ .

b) Initial concns.:  $[H_2SO_4] = 0.20 \text{ M}$ ;  $[CH_3CO_2H] = 8.611 \text{ M}$ ;  $[H_2O_2] = 2.028 \text{ M}$ ;  $[H_2O] = 19.66 \text{ M}$ .

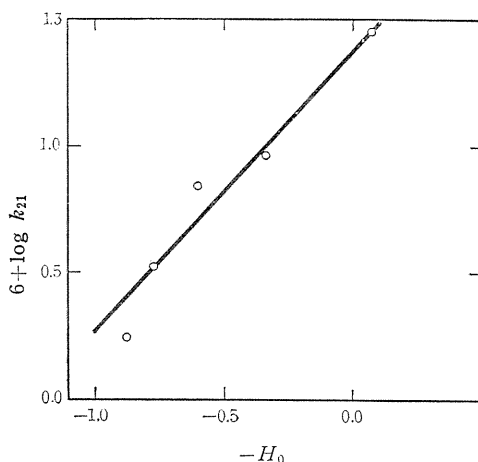
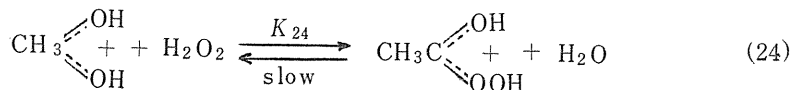
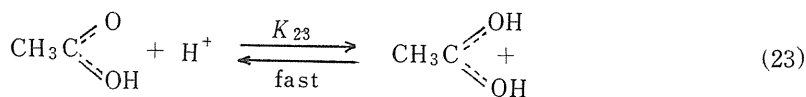
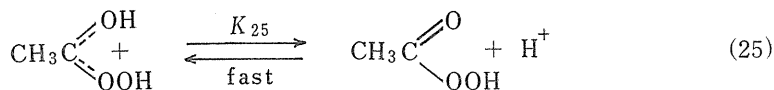


FIG. 8. Plots of  $\log k_{21}$  vs.  $-H_0$  in various ratio of  $[CH_3CO_2H] : [H_2O]$  at  $25^\circ C$ .

*The Reaction Mechanism.*—The logarithm of the rate constant for peracid formation is proportional to  $-H_0$ . Energy and 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 substituent.<sup>42)</sup> The tracer studies on the hydrolysis of peracid also reveals that the mechanism is analogous to the acyl-oxygen fission mechanism of ester hydrolysis.<sup>43)</sup> These facts suggest a probable mechanism for the peracid formation.





The position of protonation of the carboxyl group has been found to be mainly at carbonyl oxygen<sup>(4)</sup> as described above. The rate-determining step is Eq. 24, and hence the rate of peracid formation should be proportional to the product of the concentrations of acetic acid and hydrogen peroxide, the logarithm of rate constant being proportional to  $-H_0$ , which is 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 is negligible.

Although the detail of mechanism is still unknown from the above results alone, the similar mechanism like those in acid-catalyzed esterification may be assumed. The present data together with those in the literature<sup>(4), (5)</sup> show similarity in 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.

*Effect of Acidity on the Equilibrium Constants.*—The equilibrium constant increased with increasing concentration of sulfuric acid. The plots of  $\log K_{21}$  vs.  $-H_0$  gave a straight line with a slope of 0.22 (Fig. 8). 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. 21.

$$K_{21} = \frac{[\text{CH}_3\text{CO}_3\text{H}][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{H}_2\text{O}_2]}$$

It is known that water is a thousand-fold stronger base than hydrogen peroxide,<sup>(6)</sup> hence the protonation occurs only to water. The stoichiometric concentration of water is the sum of free and protonated water, the latter having little ability of nucleophilic attack on carboxyl carbon. The net concentration of free water, an effective nucleophile, decreases with increasing acidity much more rapidly than hydrogen peroxide does. Hence, the apparent equilibrium constant should increase with increasing acidity of the medium.

The protonation of acetic acid has been reported,<sup>(7)</sup> but no data is available on the protonation of peracetic acid. However, the extent of protonation of acetic acid and peracetic acid should be much smaller than that of water and hydrogen peroxide, both of which are stronger bases. Therefore, the protonation of these acids may be neglected in the effect of acidity on the equilibrium constant,  $K_{21}$ .

#### 3-4. 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 concentration of acetic acid and hydrogen peroxide, increasing with increasing concentration of sulfuric acid. The plots of logarithm of the rate constant vs.  $-H_0$  gives a straight line with a slope of ca. 1. The mechanism is discussed in connection

with the analogous acid-catalyzed esterification. The equilibrium constants for the present reaction also increase with increasing acidity and similar plots of  $\log K_{22}$  vs.  $-H_0$  gives a straight line with a slope of 0.22. These facts are explicable by considering the protonation of water.

#### Chapter 4. Acid-Catalyzed Formation of Aliphatic Peracid from Hydrogen Peroxide and Aliphatic Acid in Dioxane

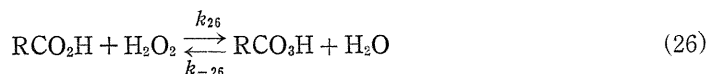
##### 4-1. Introduction

The reaction of acetic acid and hydrogen peroxide to form peracetic acid is acid-catalyzed.<sup>34)</sup> The rate of peracid formation and even the equilibrium constants have been found to increase with increasing concentration of catalytic mineral acid.<sup>37) 39)</sup> It was found that both rate and equilibrium constants shows the proportionality to the Hammett's acidity function,  $h_0$ , of the media, *i.e.*, aqueous acetic acid.<sup>48)</sup>

The present chapter deals with the kinetic study on the peracid formation in dioxane treating the effects of acidity and substituents of acetic acids.

##### 4-2. Results

*Rate Law.*—The reaction of substituted acetic acids with hydrogen peroxide to form peracids in dioxane



satisfied the same rate law as that found in acetic acid, *i.e.*,  $v = k[\text{RCO}_2\text{H}][\text{H}_2\text{O}_2]$ .

The rate constants were calculated as described in section 3-2. That is:

$$dx/dt = k_{26}(1 - 1/K_{26})(\alpha - x)(\beta - x) \quad (27)$$

Here,  $K_{26}$  and  $\alpha$ ,  $\beta$  is defined similarly.

The constancy of rate constant,  $k_{26}$ , thus calculated was almost satisfactory as shown in Table 16. The slight fall of  $k_{26}$  with proceeding of the reaction may be attributed to the gradual decomposition of formed peracid or original hydrogen peroxide.

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

*Effect of Acidity.*—The effect of acidity was studied in dioxane at

TABLE 16. A Typical Kinetic Run for the Formation of Peracetic Acid in Dioxane at 25°C  
Initial concn.,  $a = [\text{CH}_3\text{CO}_2\text{H}] = 1.051$  M;  
 $b = [\text{H}_2\text{O}_2] = 0.2018$  M;  $c = [\text{H}_2\text{O}] = 1.360$   
M;  $[\text{H}_2\text{SO}_4] = 0.20$  M.

Time min.	$x = [\text{CH}_3\text{CO}_3\text{H}]$ M	$k_{26} \times 10^6$ a) M <sup>-1</sup> sec. <sup>-1</sup>
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)  $\alpha = 10.67$ ;  $\beta = 0.0703$ .

b) Calculated equilibrium constant:  $K_{26} = 0.780$ .

TABLE 17. The Effect of Concentration of Acetic Acid and Water on Second-Order Rate Constants for the Formation of Peracetic Acid in Dioxane at 25°C<sup>a)</sup>

[CH <sub>3</sub> CO <sub>2</sub> H] M	[H <sub>2</sub> O] M	$K_{26}$	$k_{26} \times 10^6$ M <sup>-1</sup> sec. <sup>-1</sup>
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

<sup>a)</sup> Initial concentration: [H<sub>2</sub>O<sub>2</sub>]=0.1108 M;  
[H<sub>2</sub>SO<sub>4</sub>]=0.20 M.

TABLE 18. Effect of Acidity on the Formation of Peracetic Acid in Dioxane at 25°C  
Initial concentration: [CH<sub>3</sub>CO<sub>2</sub>H]=1.051 M;  
[H<sub>2</sub>O<sub>2</sub>]=0.2078 M; [H<sub>2</sub>O]=2.360 M.

[H <sub>2</sub> SO <sub>4</sub> ] M	$-H_0$	$K_{26}$	$k_{26} \times 10^6$ M <sup>-1</sup> sec. <sup>-1</sup>
0.60	+0.04	1.774	104.6
0.50	-0.18	1.672	57.8
0.40	-0.37	1.371	39.0
0.30	-0.147	1.049	19.1
0.20	-0.87	0.854	8.73

a straight line except with *t*-Bu (Fig. 2).

various concentrations of sulfuric acid. The rate and the equilibrium constants increased with increasing concentration of the catalytic acid (Table 18). These phenomena were also observed with the reaction in acetic acid.<sup>48)</sup> The plot of logarithm of  $k_{26}$  vs.  $-H_0$  gave a straight line with a slope of 1.16, while the plot of  $\log K_{26}$  corresponding to a slope of 0.40 (Fig. 9).

*Effect of Temperature and Substituents.*—The rates of peracid formation from substituted acetic acids were determined at various temperatures and shown in Table 19. The data gave activation parameters listed. Energies and entropies of activation were 15–18 kcal. mole<sup>-1</sup> and  $-17 \sim -26$  e.u., respectively; the values are similar to those of acid-catalyzed esterification (15–20 kcal. mole<sup>-1</sup>,  $-15 \sim -30$  e.u., respectively).

The plot of  $\log k_{26}$  vs. Taft's steric substituent constant,  $E_s$ , gave

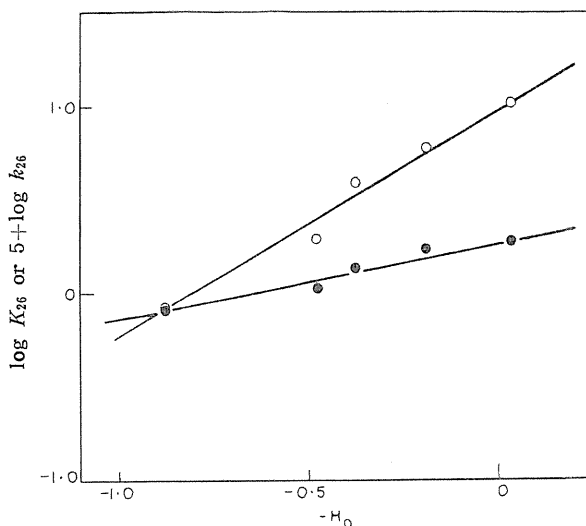


FIG. 9. Plots of  $\log k_{26}$  or  $\log K_{26}$  vs.  $-H_0$  for the peracid formation from acetic acid and hydrogen peroxide in dioxane at 25°C.

TABLE 19. Rate Data for the Peracids Formation from Substituted Acetic Acids in Dioxane

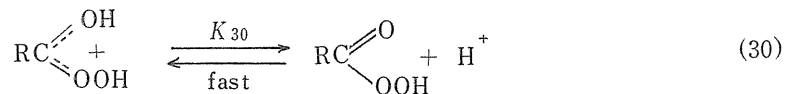
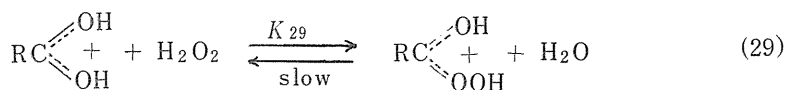
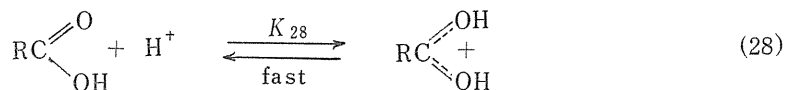
Initial concentration:  $[\text{H}_2\text{SO}_4]=0.20 \text{ M}$ ;  $[\text{RCO}_2\text{H}]=0.9\text{--}1.5 \text{ M}$ ;  
 $[\text{H}_2\text{O}_2]=0.2018 \text{ M}$ ;  $[\text{H}_2\text{O}]=1.360 \text{ M}$ .

R	$K_{26}$			$10^3 \times k_{26}, \text{M}^{-1}\text{sec.}^{-1}$			$E_a$ kcal. mole <sup>-1</sup>	$-\Delta S^\ddagger$ e.u.
	18°	25°	32°	18°	25°	32°		
CH <sub>3</sub>	0.826	0.827	0.823	13.2	23.1	42.7	14.8	26.6
C <sub>2</sub> H <sub>5</sub>	0.823	0.818	0.813	12.3	22.0	42.2	15.5	24.3
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	0.839	0.875	0.858	7.47	14.5	28.0	16.6	20.4
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	0.777	0.786	0.788	6.93	13.1	24.4	15.2	25.3
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	0.810	0.806	0.877	3.55	7.54	14.9	18.1	16.6
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	0.573	0.630	0.566	2.36	5.61	10.2	18.3	16.6
ClCH <sub>2</sub>	0.188	—	—	8.4	—	—	—	—
CH <sub>3</sub> OCH <sub>2</sub>	0.224	—	—	8.3	—	—	—	—

substituent R in acyl component of ester RCOOR'.<sup>43)</sup> Hence, the peracid formation was found to be affected almost exclusively by the steric factor.

#### 4-3. Discussion

*Acidity Dependence and Reaction Mechanism.*—The peracid formation satisfies the second-order kinetics,  $v = k[\text{RCO}_2\text{H}][\text{H}_2\text{O}_2]$ . The rate is accelerated by increasing concentration of sulfuric acid, the plot of  $\log k_{26}$  vs.  $-H_0$  gave a straight line having a slope of 1.16. The rate of peracid formation without added mineral acid was approximately zero. These results together with steric effect of substituents described below agree well with a mechanism similar to that of acid-catalyzed esterification, which involves an intermediate protonated at carbonyl oxygen of carboxyl group.<sup>44)</sup>

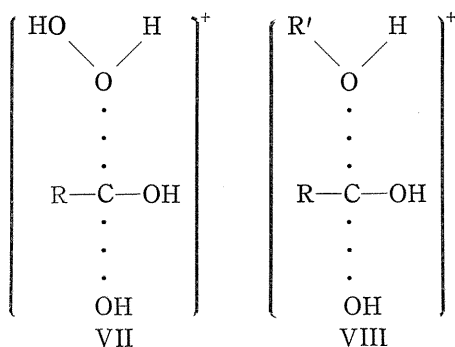


The rate-determining step may be step 29 or 30 on the basis of the rate law, but since the deprotonation 30 should be very fast as in the esterification, the most probable rate determining step is step 29.

The equilibrium constant increased with increasing concentration of sulfuric acid, the plots of  $\log K_{26}$  vs.  $-H_0$  gave a line with a slope of 0.40. This fact may be explicable by assuming the elimination of free water from the equilibrium system by the protonation, because water is the strongest base among the components (a thousandfold stronger base than hydrogen peroxide).<sup>45)</sup> The stoichiometric concentration of water is the sum of free and protonated water, the latter

having little ability of nucleophilic attack on carboxyl carbon. 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-catalyzed esterification. The plots of  $\log k_{26}$  vs.  $E_s$ , Taft's steric substituent constant, gave a straight line except with *t*-Bu. Hence, the steric susceptibility constant,  $\delta$ , in Taft's equation,  $\log(k/k_0) = \delta E_s$ , is shown to be 0.57 at 18°C (Fig. 10). This low susceptibility to steric retardation of rate by bulky substituents suggests a less hinderance between substituent and the incoming reagent, hydrogen peroxide, in peroxidation (activated complex VII) than in esterification (VIII).



The steric strain in complex VIII caused mainly by the presence of two alkyl groups, R and R', should be higher than that in complex VII having one alkyl

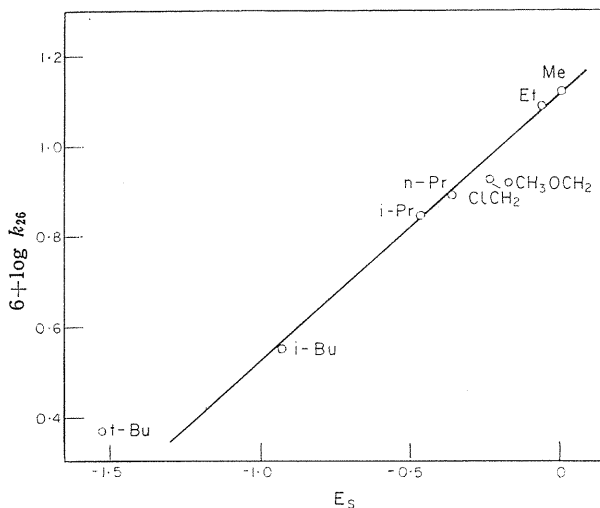
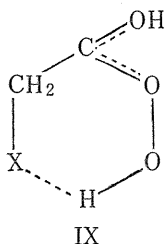


FIG. 10. Plots of  $\log k_{26}$  vs. Taft's steric substituent constant,  $E_s$ , for the peracid formation from substituted acetic acids and hydrogen peroxide in dioxane at 18°C.

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-catalyzed alcoholysis of esters.<sup>50)</sup>

As for equilibrium constants interesting facts were observed; *i.e.*, the equilibrium constants for chloro- and methoxyacetic acids were considerably smaller than those of unsubstituted fatty acids (Table 19). Since the rate of peracid formation for these two acids were in the range of those expected from  $E_s$  value as shown in Fig. 10, these small values of  $K_{26}$  may be attributed to the abnormally fast hydrolysis of the corresponding peracids. This fact may well be understood by assuming the acceleration of hydrolysis of these peracids by an intramolecular hydrogen bonding between functional group X (Cl or OCH<sub>3</sub>) and hydroperoxide group (IX).



The chelated peracid (IX) 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 close similarity to those of acid-catalyzed esterification.<sup>40)</sup> Since the range of temperature observed is limited (18°–32°C), an exact evaluation of these activation parameters is difficult. However, the trend of  $\Delta S^\ddagger$  shows that the fall of freedom of complex VII is independent of alkyl groups or is rather small with increasing alkyl chains.

#### 4-4. Experimental

**Materials.**—Commercial substituted acetic acids were heated with potassium permanganate for 6–10 hrs., and then rectified over phosphorus pentoxide. Acetic acid, b.p. 118°C; propionic acid, b.p. 140–141°C; *n*-butyric acid, b.p. 163.0–163.5°C; *i*-butyric acid, b.p. 153°C; *i*-valeric acid, b.p. 175.0–175.5°C; pivalic acid, b.p. 163–164°C; monochloroacetic acid, m.p. 63°C; methoxyacetic acid, b.p. 105–106/25 mmHg. Dioxane was refluxed with sodium metal for ten hrs. and then rectified, b.p. 101.3–102.0°C. H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> were used without further purification of commercial materials of guaranteed grade.

**Rate Measurement.**—The reaction was started by adding hydrogen peroxide solution of known concentration to a thermostated solution of aliphatic acid in dioxane containing an appropriate amount of H<sub>2</sub>SO<sub>4</sub> and water. Conc. H<sub>2</sub>SO<sub>4</sub> was previously mixed with water and then diluted with dioxane.

Aliquots (ca. 2 ml.) were taken out at appropriate intervals and added into ice-cooled ca. 0.4 *N* aq. H<sub>2</sub>SO<sub>4</sub> (50 ml.) containing three drops of 1% manganese sulfate. Hydrogen peroxide was immediately titrated with potassium permanganate and the remaining peracid was titrated iodometrically. Since the spontaneous

decomposition of hydrogen peroxide and peracid was found to be negligible during these titration, the content of peracid was calculated from both titres.

Equilibrium constants were determined according to the analysis after 30-170 hrs., when ca. 20% of active oxygen 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 mixture where water was added in place of hydrogen peroxide. The indicator was *p*-nitroaniline having  $pK_{BH^+}$  of 0.99<sup>38)</sup> and a maximum absorbance at 370 m $\mu$ . The results are listed in Table 18.

#### 4-5. Summary

The acid-catalyzed formation of peracids from substituted acetic acids and hydrogen peroxide have been studied kinetically in dioxane. The rates of peracid formation together with equilibrium constants increase with increasing concentration of sulfuric acid and correlated with the acidity of the media. The substituent effect suggested the reaction to be controlled by steric effect rather than polar one. A mechanism similar to acid-catalyzed esterification was discussed.

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