9 do not reveal mechanisms. It seems likely that (9) involves hydrolysis of CN^- to give OH^- which then reacts with SO_2F_2 to form SO_3F^- and F^- ions. Equation 6 may involve the formation of $SO_2(CN)_2$ or some other intermediate with cyanide attached to sulfur.

Fluorosulfate Ion Not an Intermediate in Reactions 4-6. Solution S was prepared by shaking 20 ml of 0.1028 *N* NaOH with an excess of SO_2F_2. This gave a solution containing 0.0514 *M* F^- and 0.0514 *M* SO_3F^-. The fluoride specific ion electrode gave a reading for this solution corresponding to $[F^-] = 0.052$ *M* (a good check). The solution was found to be free from SO_4^{2-} ion.

Five milliliters of solution S was mixed with an equal volume of 0.08163 *M* NH_4OH and was then tested with the fluoride specific ion electrode after it had been seasoned in a similar solution. The emf remained constant while observed for a 13-min period and indicated $[F^-]$ to be 0.028 *M*. This is higher than 0.0259 (half of 0.0519) and can be in error, because of interference by hydroxide ion. It can be concluded, however, that not over 10% of the SO_3F^- ion reacted to give F^-. If the reaction of NH_3(aq) with SO_2F_2 involved SO_3F^- as an intermediate, it would be necessary for SO_3F^- to react rapidly with NH_3(aq), because ammonia quickly displaces both fluorine atoms from sulfuryl fluoride.

Five milliliters of solution S was mixed with 2.00 ml of 0.200 *M* phenol. The fluoride specific ion electrode indicated $[F^-]$ to be 0.038 *M*, in good agreement with 0.0368 *M* corresponding to no reaction of SO_3F^- with phenol. Two milliliters of 0.1028 *N* NaOH was then added to neutralize part of the phenol and give $C_6H_5O^-$. The fluoride sensitive electrode then indicated $[F^-]$ to be 0.029 *M*, in good agreement with 0.0286 *M*, corresponding to no reaction of SO_3F^- with either phenol or $C_6H_5O^-$ ion.

Five milliliters of solution S was mixed with 5 ml of 0.100 *M* NaCN. The fluoride specific ion electrode then indicated a constant value of $[F^-]$ of 0.028 *M*, a value close to that expected (0.0257 *M*) for no reaction. The solution was then titrated to the Bromothymol Blue end point with 0.1072 *N* HCl (volume used 4.50 ml) (theoretical volume for no reaction of SO_3F^- with CN^- is 4.66 ml). It can be concluded that not over 10% of the SO_3F^- reacted with CN^- and that fluorosulfate ion is not an intermediate in the rapid reaction of cyanide ion with aqueous SO_2F_2 to give SO_4^{2-} ion.

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Registry No. SO_2F_2, 2699-79-8; NH_3, 7664-41-7; C_6H_5OH, 108-95-2; NaCN, 143-33-9.

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Kinetics and Mechanism of the Reaction between Formate and Peroxodisulfate in Aqueous Solution

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A kinetic study is made of the reaction of formate with peroxodisulfate in aqueous solution. In the three ranges of concentrations of formate, the rate law approaches three different forms. The rate law for this reaction in a solution of pH 4.5 to 7 in the absence of oxygen, at concentrations of formate smaller than 0.01 *M*, is $-d[S_2O_8^{2-}]/dt = k_a[HCOO^-]^{1/2}[S_2O_8^{2-}]$ with an activation energy of 23 ± 1 kcal/mol. At concentrations of formate 0.01 to 0.2 *M*, the rate law is $-d[S_2O_8^{2-}]/dt = (k_b + k_c[HCOO^-]^{1/2})[S_2O_8^{2-}]$, and at the formate concentrations greater than 0.2 *M*, the rate is independent of the formate and described as $-d[S_2O_8^{2-}]/dt = k_d[S_2O_8^{2-}]^{3/2}$ with an activation energy of 21 ± 1 kcal/mol. The proposed mechanism is a chain reaction with $SO_4\cdot^-$, $OH\cdot$, and $CO_2\cdot^-$ radicals. Therefore, the reaction rate is greatly inhibited by the presence of radical scavengers like acrylonitrile and oxygen and also by iron(III). The effect of pH on the reaction rate is examined at the pH range 0.7 to 12.6. In the pH range from 4.5 to about 7, the reaction rate reaches a maximum constant value.

Introduction

Recently, the oxidation of oxalate and oxalic acid by peroxodisulfate[1] and by several other oxidants[2] has been studied. Both formate and oxalate molecules are subject to formation of the same radical $CO_2\cdot^-$ upon their oxidation. Therefore, the mechanism of the oxidation of the two molecules is anticipated to be analogous. However, the rate of oxidation of formate and oxalate is very different. Oxidation of oxalate by peroxodisulfate hardly occurs at room temperature without catalyst.[1] In contrast, oxidation of formate by the same oxidant under the same conditions occurs considerably faster. When peroxodisulfate, hereafter referred to as persulfate, reacts with formate under the conditions studied here, the stoichiometry of the reaction does not deviate appreciably from the reaction equation of $S_2O_8^{2-} + HCOO^- \rightarrow 2SO_4^{2-} + H^+ + CO_2$ to agree with the reports by the earlier researchers. However, there are a number of contradictory reports on the reaction between formate and persulfate, especially on the reaction order and the reaction mechanism. The reaction of persulfate with formate has been investigated by many researchers and reviewed by House[3] and by Wilmarth and Haim[4] in 1962. Kappanna[5] obtained markedly different results from those of an earlier study by Srivastava and Ghosh.[6] The latter found that the rate of reaction was independent of the formate concentration, but Kappanna concluded that the reaction was second order. Hart[7] has investigated the yield of CO_2 from the formate-persulfate reaction induced by the γ-ray and found that $G(CO_2)$ is a function of $[HCOOH]^{1/2}$, indicating the half-order in formate. Thus, in 1969 O'Flynn and House[8] reinvestigated the same reaction with a view to establishing (a) the reaction order and (b) pH dependence upon the rate,

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using a pH-stat method. They reported a kinetic equation $-d[S_2O_8^{2-}]/dt = k_{obsd}[S_2O_8^{2-}]$ to be independent of the formate concentration. However, the experiments of O'Flynn and House[8] were made only at the concentration range with (a) a formate of 0.05 *M* and persulfate concentrations 0.05, 0.0375, and 0.025 *M* and (b) a persulfate of 0.05 *M* and formate concentrations 0.05, 0.0375, and 0.025 *M*. It appears that this concentration range is too narrow to determine the reaction order of such a complex reaction. The present paper covers this difficult situation and affords the most probable mechanisms of reaction. The pH dependence on the formate-persulfate reaction is interesting. Previously, Hart[7] and O'Flynn and House[8] have found a marked dependence of pH on the reaction rate. Both groups have reported the similar phenomenon that there is a maximum in rate at a neutral pH range. Thus, the pH dependence on the rate is also examined at a wide range, pH 0.7 to 12.6, in the present study. The method of the earlier researchers[5,6,8] cited above is to titrate H^+ released from the formate-persulfate reaction with a standard alkali. This method has a disadvantage that the data at pH smaller than about 4 must take a large uncertainty level because the pH of the reaction mixture is greatly buffered by the formate-formic acid equilibrium ($pK_a = 3.8$).

Experimental Section

Chemicals. Reagent grade potassium formate and sodium sulfate were recrystallized twice from the redistilled water. Potassium peroxodisulfate and the redistilled water used are the same as described in the previous paper.[1]

Technique and Analysis. The procedure used for kinetics measurements and treatments of the reaction vessel is the same as described previously.[1] The concentration of persulfate reacted was determined polarographically at 0.2 V *vs.* sce at 25° in a solution 0.1 *M* in sulfuric acid and 0.01% polyacrylamide. Polyacrylamide was added as a maximum suppressor. To determine the concentration of formate, an excess of permanganate was added to a strong alkaline solution with formate in the presence of some nickel(II) nitrate as catalyst. After acidification with sulfuric acid, the residual permanganate was titrated back with ferrous ammonium sulfate solution. This method is essentially the same as the directions of Molotkova and Zolutkhin[9] cited in the literature.[10]

General Considerations. The presence of trace impurities in a chain radical reaction can be generally detected by the observation of a long induction period, after which the reaction increases markedly in rate. In some experiments, such an induction period was obviously detected; after the induction period was over, the rate of reaction usually returned to the expected rate, indicating the complete conversion of the impurities to kinetically inactive species. In some cases the induction period was considerably longer. The longest induction period in all the experiments was 2 hr, given in Figure 1 as an example of a detectable induction period. Unless stated otherwise, experiments were done in a solution of only formate and persulfate, for the purpose of avoiding impurities from other reagents. Numerical values of the reaction rate, $-d[S_2O_8^{2-}]/dt$, were evaluated from the initial slope of a plot of $[S_2O_8^{2-}]$ against time. This method has the possible disadvantage of emphasizing the data in the initial stage of the reaction. But this method is useful when the rate law is unknown and when the forms of rate law change according to the change in the concentration of reactants. In the present study, reactions were followed almost to completion. A plot of $[S_2O_8^{2-}]$ against time was almost straight during the initial stage of reaction, so the estimation of the initial rate of reaction was satisfactorily precise. Experiments detecting the induction period were discarded.

Results

The initial rate of the reaction between formate and persulfate was measured at the varied concentrations of formate and persulfate in a solution saturated with nitrogen gas in the dark at 40°.

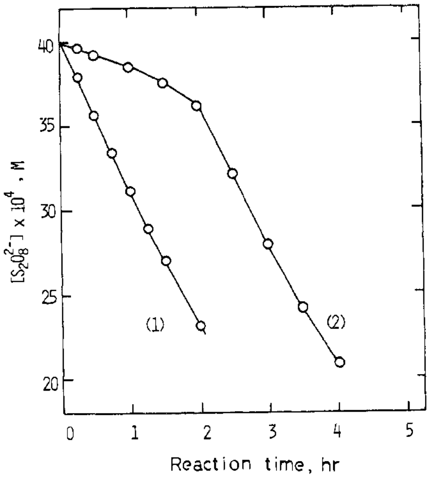

Figure 1. An example of induction period. Initial solution 4×10^{-3} *M* in potassium persulfate and 0.4 *M* in potassium formate. Solution saturated with nitrogen gas at 40°. (1) A normal case. (2) An induction period of about 2 hr.

Dependence of the Formate Concentration. In Table I the results obtained at the varied concentrations of formate are presented. The initial rate is half-order in formate at formate concentrations smaller than 0.01 *M* and is expressed as $k' + k''[HCOO^-]^{1/2}$ at the formate concentration range 0.01 to 0.2 *M*, where k' and k'' indicate constants. Finally, the rate becomes constant at formate concentrations greater than about 0.2 *M*. In Figures 2 and 3 a plot of $-[S_2O_8^{2-}]/dt$ against $[HCOO^-]^{1/2}$ at formate concentrations smaller than 0.01 *M* and at the formate range 0.01 to 0.2 *M* is given.

Dependence of the Persulfate Concentration. Dependence of persulfate on the initial rate, hereafter referred to as only the rate or $-d[S_2O_8^{2-}]/dt$ instead of the initial rate, was examined at three concentrations of formate, 0.002, 0.03, and 0.4 *M*. The results are given in Table II. At 0.002 and 0.03 *M* formate, the rate is proportional to the persulfate concentration. On the other hand, a plot of the rate against the persulfate concentration deviates obviously from a straight line when formate is 0.4 *M*. Thus, in order to know the reaction order with respect to persulfate at 0.4 *M* formate, the logarithm of $-[S_2O_8^{2-}]/dt$ was plotted against the logarithm of $[S_2O_8^{2-}]$. The plots were straight, with a slope of 1.5. This indicates that the rate is $^3/_2$ order in persulfate at 0.4 *M* formate.

Dependence of Temperature on the Reaction Rate. The rate of the reaction between formate and persulfate was measured at temperatures 35 to 55° at formate concentrations of 0.002 and 0.4 *M*. The logarithms of the overall rate constants k_a and k_d described by the two forms of rate law (refer to the Discussion) were plotted against $1/T$. From the Arrhenius plot of Figure 4, the activation energies E_a and E_d with respect to the corresponding reaction mechanisms were calculated as 23 ± 1 and 21 ± 1 kcal/mol, respectively. The experimental rate constant in the 35-55° range is thus given by the following expression

$$k_a = 3.23 \times 10^{12} \exp(-23{,}000/RT) \text{ sec}^{-1} M^{-1/2}$$

$$k_d = 2.09 \times 10^{11} \exp(-21{,}000/RT) \text{ sec}^{-1} M^{-1/2}$$

and the activation entropies $\Delta S_a^‡$ and $\Delta S_d^‡$ were estimated to be −1.4 ± 0.1 and −5.8 ± 0.1 eu at 40°, respectively.

Effect of Hydrogen Ion Concentration on Rate. The pH dependence on the rate of reaction was examined at formate

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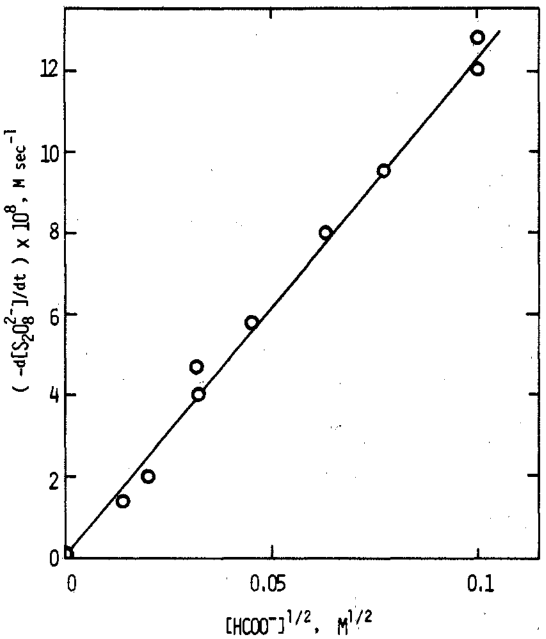

Figure 2. Reaction rate *vs.* square root of the formate concentration at concentrations smaller than 0.01 *M*. Conditions as in Table I.

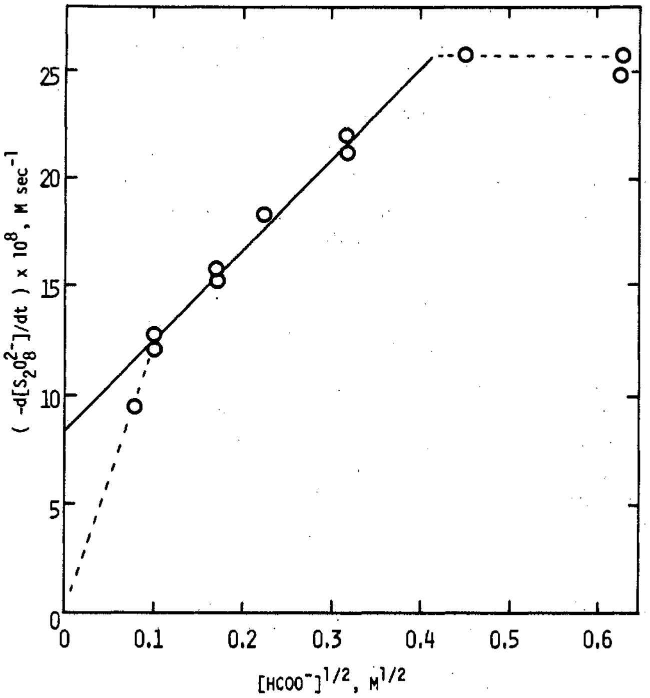

Figure 3. Reaction rate *vs.* square root of the formate concentration in the range 0.01–0.2 *M*. Conditions as in Table I.

Table I. Dependence of the Formate Concentration on Rate^a

[HCOO$^-$], *M*	($-$d[S$_2$O$_8^{2-}$]/d*t*) × 10^8, *M* sec^{-1}
0	0.1
0.0002	1.4
0.0004	2.0
0.001	4.0, 4.7
0.002	5.8
0.004	8.0
0.006	9.5
0.01	12.8, 12.0
0.03	15.8, 15.2
0.05	18.3
0.1	21.1, 22.0
0.2	25.6
0.4	25.7, 24.8
0.5	25.3
0.8	24.7

^{a} Solution 4 × 10^{-3} *M* in potassium peroxodisulfate and the varied concentrations of potassium formate; pH 5–6. Solution saturated with nitrogen gas in the dark at 40°.

Table II. Dependence of the Persulfate Concentration on Rate^a

[S$_2$O$_8^{2-}$]$_{\text{initial}}$ × 10^3, *M*	Formate concn, *M* 0.002	0.03	0.4
	($-$d[S$_2$O$_8^{2-}$]/d*t*) × 10^8, *M* sec^{-1}		
1.0	1.6, 2.0	3.4	2.5, 3.3
2.0	3.6	5.0, 5.8	8.0
3.0	3.9		15.8
3.2	5.3		
3.8			21.4
4.0	5.8	15.2, 15.8	27.0
5.0	7.6		33.3
6.0		23.0	47
6.5	10.0		
8.0	11.0	30.5	55, 83

^{a} Conditions as in Table I.

concentrations 0.01, 0.1 and 0.4 *M*. As seen in Table IV, the rate increases from pH 0.7 to a maximum at 4.5 and becomes constant at pH range 4.5–6. After pH 7, the rate decreases with increasing pH. As reported in Table I, the rate is independent of the formate concentration in the range 0.2–0.8 *M* formate. Nevertheless, characteristics of the pH dependence on rate are almost the same irrespectively with formate concentrations. For the purpose of comparison, a few data of the pH dependence on the rate of the hydrogen peroxide-persulfate reaction are also reported in Table IV. The characteristics are similar to those in the formate-persulfate reaction.

Effect of Concentration of Sulfate. In Table V the results obtained with the varied concentrations of sodium sulfate and various concentrations of sulfuric acid are reported. As can be seen in Table V, no appreciable effect of sulfate was observed at the sulfate concentration range 0.02–0.1 *M*.

Effect of Some Other Substances on the Reaction Rate. Several substances were added to the reaction mixture. As can be seen in Table VI, the reaction between formate and persulfate is completely inhibited by 1% acrylonitrile and is considerably inhibited by molecular oxygen, iron(III), and also cobalt(II). Only copper(II) is a powerful accelerator for this reaction.

Discussion

Before considering another possible reaction mechanism, the following reaction mechanism is presented to account for the results obtained.

$$S_2O_8^{2-} \rightarrow 2SO_4\cdot^- \quad \text{(very slow)} \tag{1}$$

$$HCOO^- + SO_4\cdot^- \rightarrow CO_2\cdot^- + H^+ + SO_4^{2-} \tag{2}$$

$$H_2O + SO_4\cdot^- \rightarrow OH\cdot + H^+ + SO_4^{2-} \tag{3}$$

$$HCOO^- + OH\cdot \rightarrow CO_2\cdot^- + H_2O \tag{4}$$

$$S_2O_8^{2-} + CO_2\cdot^- \rightarrow SO_4\cdot^- + SO_4^{2-} + CO_2 \tag{5}$$

Termination presumably occurs *via* eq 6, 7, and/or 8, according to the concentrations of reactants and the value of the ratio [HCOO$^-$]/[S$_2$O$_8^{2-}$]. When the formate concentration is relatively low, the contribution of reaction 2 may

$$CO_2\cdot^- + OH\cdot \rightarrow CO_2 + OH^- \tag{6}$$

$$CO_2\cdot^- + SO_4\cdot^- \rightarrow CO_2 + SO_4^{2-} \tag{7}$$

$$CO_2\cdot^- + CO_2\cdot^- \rightarrow C_2O_4^{2-} \tag{8}$$

Table III. Dependence of Temperature on Rate[a]

	Formate concn, M			
	0.002	0.4		
Temp, °C	$(-d[S_2O_8^{2-}]/dt) \times 10^7$, M sec^{-1}		Rate const, $M^{-1/2}$ sec^{-1} $k_a \times 10^4$	$k_d \times 10^3$
35	0.33	1.17	1.86	0.48
40	0.58	2.47	3.30	0.98
45	1.33	3.90	7.44	1.54
50	2.0	6.0	11.2	2.4
55	3.1	11.3	17.4	4.5

[a] Conditions as in Table I.

Table IV. pH Dependence on the Initial Rate of Reaction[a]

	Formate concn, M		
	0.01	0.1	0.4
pH	$(-d[S_2O_8^{2-}]/dt) \times 10^8$, M sec^{-1}		
0.7	1.9	6.7[c]	
0.9	2.2	5.6, 4.4[d]	4.4
1.7	3.1		
2.1	3.9	8.8,[b] 7.3[b,d]	
2.5		10.6	
2.95	6.1		
3.50		7.0[c]	18.2
3.90	8.9		
4.2	11.1	21.1	22.4
4.5			24.2
5–6	12.8, 14.0	21.1, 16.7,[d] 6.9[c]	24.8, 25.7
8.1(i)[e]	12.2, 14.0		
7–10(iv)[e]	10.0		
8.8–8.9(ii)[e]	8.9	7.1, 6.6,[d] 3.0[c]	8.6
10–11(iii)[e]	7.0		
11.1–11.4(iv)[e]	6.7	6.5, 2.0[c]	7.2
12.60(iv)[e]	6.1		

[a] Conditions as in Table I. [b] As in *a*, except formic acid instead of potassium formate. [c] As in *a*, except hydrogen peroxide instead of formate. [d] Solution saturated with oxygen instead of nitrogen. [e] The pH of the solution was varied by adding appropriate amounts of sulfuric acid in the case of pH smaller than 4.5 and a mixture of H_2SO_4 and $NaHCO_3$ (i), $NaHCO_3$ only (ii), Na_2CO_3 (iii), and NaOH (iv). In case of footnote *b* and pH 5–6, no addition is made.

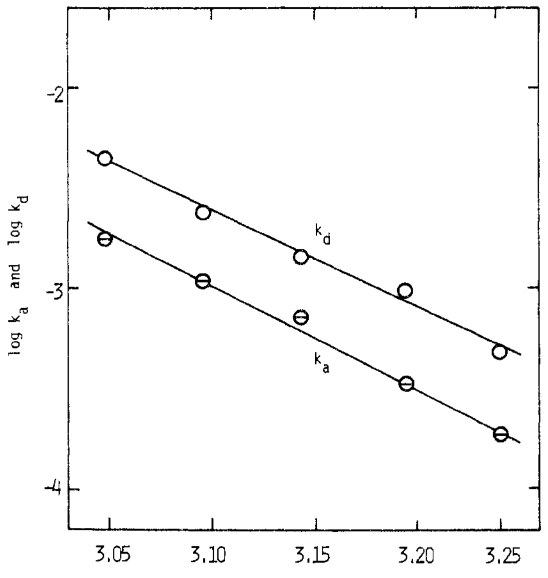

Figure 4. Arrhenius plot of rate constants k_a and k_d in Table III.

Table V. Effect of Concentration of Sulfate[a]

Na_2SO_4, M	H_2SO_4, M		$(-d[S_2O_8^{2-}]/dt) \times 10^8$, M sec^{-1}
0	0	pH 5–6	12.8
0.02	0		12.3
0.04	0		11.1
0.06	0		12.3
0.08	0		14.0
0.1	0	pH 5–6	12.8
0.08	0.02	pH 1.72	3.3
0	0.02	pH 1.70	3.1
0.04	0.06	pH 0.9	2.2
0	0.06	pH 0.9	2.2

[a] Conditions as in Table I, except 0.01 M in potassium formate and varied concentrations of sodium sulfate and/or sulfuric acid.

Table VI. Effect of Some Substances on the Reaction Rate[a]

	Reaction time, hr					
	0.5	1.0	1.5	2.0	3.0	8
Substances	$[S_2O_8^{2-}]_{reacted} \times 10^4$, M					
None	2.4	4.7	7.1	9.0	13.0	
None[b]	1.3	2.6	4.0	5.4	8.0	
1% acrylonitrile	0	0	0	0	0	*ca.* 0.2
4×10^{-5} M Cu(II)	27.8	34.2				
4×10^{-5} M Fe(III)	2.4	4.8	7.4	9.2	13.8	
1×10^{-4} M Fe(III)	1.2	3.2	5.6	7.4	12.0	
2×10^{-4} M Fe(III)[c]	0	1.8	3.6	5.0	10.6	
2×10^{-4} M Co(II)	0.8	1.6	2.8	3.4	7.4	

[a] Conditions as in Table I, except 0.01 M in potassium formate and the substances added. [b] As in *a*, except that the reaction mixture is saturated with oxygen gas. [c] At this concentration of iron(III), the reaction solution is slightly turbid.

be negligible and the most probable termination is reaction 6. Therefore, eq 9 is obtained under this condition

$$[CO_2\cdot^-]^2 + ([CO_2\cdot^-]k_1/k_5) = k_1/k_4[HCOO^-]/k_5k_6 \qquad (9)$$

by assuming the steady state concentrations for $SO_4\cdot^-$, $CO_2\cdot^-$, and OH· in the reactions 1, 3, 4, 5, and 6. Since the chain is long, the second term on the left in eq 9 should be negligibly small. The assumption that the second term on the left in eq 9 is negligible leads to eq 10. When

$$-d[S_2O_8^{2-}]/dt = \sqrt{k_1k_4k_5[HCOO^-]/k_6}[S_2O_8^{2-}] = k_a[HCOO^-]^{1/2}[S_2O_8^{2-}] \qquad (10)$$

the formate concentration is not so low, reactions 2 and 3 must occur competitively and simultaneously. If reaction 4 were rather fast, the largest contribution for termination should be reaction 7, and the assumption of the steady state concentrations for $CO_2\cdot^-$, $SO_4\cdot^-$, and OH· in reactions 1, 2, 3, 4, 5, and 7 affords eq 11, where, $k_b = (k_1k_3k_5[H_2O]/k_7)^{1/2}$,

$$-d[S_2O_8^{2-}]/dt = \sqrt{\frac{k_1k_3k_5[H_2O] + k_1k_2k_5[HCOO^-]}{k_7}}[S_2O_8^{2-}] = (k_b + k_c[HCOO^-]^{1/2})[S_2O_8^{2-}] \qquad (11)$$

$k_c = (k_1k_2k_5/k_7)^{1/2}$, and the value of $2k_bk_c[HCOO^-]^{1/2}$ is assumed to be negligibly small. When there is a sufficiently large value of the ratio $[HCOO^-]/[S_2O_8^{2-}]$, concentrations of OH· and $SO_4\cdot^-$ should be extremely low because the two radicals must react rapidly with $HCOO^-$ by reactions 2 and 4. Under such a condition, $CO_2\cdot^-$ is possibly excess and reaction 8 makes a maximum contribution to termination. Assumption of the steady state concentrations for OH·, $CO_2\cdot^-$, and $SO_4\cdot^-$ in reactions 1, 2, 3, 4, 5, and 8 leads to eq 12. It should be noted that reactions 3 and 4 presumably

$$-d[S_2O_8^{2-}]/dt = k_5\sqrt{k_1/k_8}[S_2O_8^{2-}]^{3/2} = k_d[S_2O_8^{2-}]^{3/2} \qquad (12)$$

hardly occur under the conditions where the formate concentration is large and that, however, eq 12 holds irrespectively whether reactions 3 and 4 are existent or not. These behaviors expressed by eq 10, 11, and 12 are clearly observed from the data in Tables I and II with Figures 2 and 3. From an Arrhenius plot of Figure 4 for k_a and k_d, the activation energies were determined to be $E_a = 23 \pm 1$ kcal/mol and $E_d = 21 \pm 1$ kcal/mol. The activation entropies were calculated at 40° to be $\Delta S_a^{\ddagger} = -1.4 \pm 0.1$ eu and $\Delta S_d^{\ddagger} = -5.8 \pm 0.1$ eu. The experimental rate constants are thus given by the expressions

$$k_a = 3.23 \times 10^{12} \exp(-23{,}000/RT) \text{ sec}^{-1} M^{-1/2}$$

$$k_d = 2.09 \times 10^{11} \exp(-21{,}000/RT) \text{ sec}^{-1} M^{-1/2}$$

From the relation between the experimental rate constants and the rate constants for the separate steps in the reaction mechanism, it follows that the activation energies determined from Figure 4 are functions of the activation energies for the separate steps, *i.e.*, $E_a = \frac{1}{2}(E_1 + E_4 + E_5 - E_6)$ and $E_d = E_5 + (E_1 - E_8)/2$. Using the values of E_a and E_d, using E_1 reported by Kolthoff and Miller,[11] and assuming that activation energies of termination reactions 6 and 8 are zero, the activation energies for reactions 4 and 5 are obtained to be 8 ± 4 and 4 ± 2 kcal/mol, respectively. The values of activation energies E_a and E_d obtained in this study are in agreement with 20.9 kcal/mol reported by Srivastava and Ghosh[6] but greatly differ from the result of O'Flynn and House[8] of 11.9 kcal/mol. It is here pointed out that the value of the activation energy of O'Flynn and House[12] does not seem to be reasonable from the following consideration. k_{obsd} in ref 8 corresponds to $k_{\text{obsd}} = (k_1k_3k_5/k_7)^{1/2}$, where k_n indicates the rate constants of reaction n in the present paper. Therefore, analysis of the activation energy E_{obsd}, assuming $E_1 = 33.5$ kcal by Kolthoff and Miller,[11] and $E_7 = 0$, leads to a result $E_3 + E_5 = -10$ kcal/mol. This large negative value of the activation energy for reactions 3 and 5 is entirely unreasonable. Here it is noted that k_{obsd} by O'Flynn and House[8] just corresponds to k_b on the right in eq 11 in this paper and that they have neglected reaction 2. If the values of $k_1 = 1.7 \times 10^{-7}$ sec^{-1} at 40°, calculated from data in ref 11, and of $2k_8 = 1 \times 10^9 M^{-1}$ sec^{-1}, reported by Getoff, *et al.*,[13] are used, the rate constants $k_5 = 5.3 \times 10^4 M^{-1}$ sec^{-1} and $k_4/k_6 = 1 \times 10^{-5}$ at 40° are evaluated from the analysis of k_a and k_d in Table III. Next, if the value of k_6 were assumed to be $1 \times 10^{10} M^{-1}$ sec^{-1} which corresponds to a limiting rate constant for the diffusion-controlled reaction of second order, the value of k_4 is $1 \times 10^5 M^{-1}$ sec^{-1}. Assuming that k_7 is also $1 \times 10^{10} M^{-1}$ sec^{-1}, the values of k_2 and $k_3[H_2O]$ are obtained to be $1 \times 10^3 M^{-1}$ sec^{-1} and 50 sec^{-1}, respectively, from the analysis of Figure 3 with eq 11. Here, it is significant to note that reactions 2 and 3 occur at the same rate at the formate concentration 0.05 *M* which is a concentration of an intermediate range of formate. It should be emphasized that most of the earlier researchers have not taken care of this matter and disregarded reaction 2 without any reasons. The other possible reactions are

$$SO_4\cdot^- + SO_4\cdot^- \rightarrow S_2O_8^{2-} \tag{13}$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2 \tag{14}$$

Occurrence of these two reactions is possible at the small values of the ratio $[HCOO^-]/[S_2O_8^{2-}]$ from the following consideration. When persulfate exists at a sufficiently large concentration, $CO_2\cdot^-$ should react rapidly with persulfate according to eq 5. Therefore, the $CO_2\cdot^-$ concentration must be extremely low. On the contrary, concentrations of $SO_4\cdot^-$ and $OH\cdot$ must be relatively larger, in particular, $OH\cdot$ radical should be a predominant species under such conditions that (a) formate concentration is very low and (b) the ratio $[HCOO^-]/[S_2O_8^{2-}]$ is very small. Termination under such a condition should be rather (13) and (14). If reaction 13 were assumed as a predominant termination, eq 15 is derived as a rate law. And if reaction 14 were assumed as a predominant termination, eq 16 is derived. However, the behaviors predicted by eq 15 and 16 were not observed in the present study. This is probably due to the fact that the ratio of $[HCOO^-]/[S_2O_8^{2-}]$ is not sufficiently small; *e.g.*, even the smallest ratio was 1/20. It is pointed out that the rate law of the formate-persulfate reaction is changeable according to the composition of the reaction solution and that this fact is probably an important reason for the many contradictory reports on the reaction order as well as the reaction mechanism.

$$-d[S_2O_8^{2-}]/dt = k_2(k_1/k_{13})^{1/2}[HCOO^-][S_2O_8^{2-}]^{1/2} \tag{15}$$

$$-d[S_2O_8^{2-}]/dt = \left\{\left(\frac{k_2k_4[HCOO^-]}{k_3[H_2O]} + k_4\right)\sqrt{\frac{k_1[S_2O_8^{2-}]}{k_{14}}} + \frac{k_1k_2[S_2O_8^{2-}]}{k_3[H_2O]}\right\}[HCOO^-] \tag{16}$$

The principal characteristics of the pH dependence on the formate-persulfate reaction rate are an increase in rate from pH 1 to a maximum at pH 5 to 7 and then a decrease with increasing pH up to 13. The characteristics are analogous with those observed by Hart[7] and by O'Flynn and House.[8] Halpern and Taylor[14] have found a similar dependence of pH in the oxidation of formate by several inorganic oxidants in aqueous perchloric acid solution and concluded that the pH dependence is due to differences in reactivity between formic acid, HCOOH, and formate ion, $HCOO^-$. As stated before, the reaction rate of the formate-persulfate reaction is independent of the formate concentration at larger than 0.2 *M*. Nevertheless, the pH dependence in 0.4 *M* formate was almost the same as that in the lower concentrations of 0.01 and 0.1 *M*. Therefore, the pH dependence is probably not caused by differences in reactivity between HCOOH and $HCOO^-$ but caused by differences in reactivity of many kinds of radicals which are formed according to pH change (refer to Appendix). When it is a highly acidic solution, $HCO_2\cdot$ and $HCO_2H\cdot^+$ would exist predominantly in the absence of oxygen and $HO_2\cdot$ and $H_2O_2\cdot^+$ in the presence of oxygen, from the pK_a values of the radical species. At pH larger than 4, $CO_2\cdot^-$ must be a predominant radical in the absence of oxygen and $O_2CO_2\cdot^-$ and $O_2\cdot^-$ in the presence of oxygen. When it is a strongly alkaline solution, $CO_3\cdot^-$ and $O\cdot^-$ may exist. If the pH dependence in the alkaline region were due to the oxidation reactions of CO_3^{2-} by $OH\cdot$ or $SO_4\cdot^-$ (refer to reactions 23, 24, and 25 in Appendix), the dependence should be affected by the kind of alkali. However, the pH dependence was independent of the kind of alkali, NaOH, $NaHCO_3$, and

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(11) I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, 73, 3055 (1951); the decomposition of persulfate is described by $-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_{1a}[H^+][S_2O_8^{2-}]$. The values of k_1 and k_{1a} respectively are 6.0×10^{-5} min^{-1} and $3.5 \times 10^{-3} M^{-1}$ min^{-1} at 50° at an ionic strength of 0.4. The activation energy for the k_1 path is 33.5 kcal and for the k_{1a} path 26.0 kcal.

(12) The activation energy reported in ref 8 was obtained at pH 8.0, in contrast with that in Table III, obtained at pH 5-6.

(13) N. Getoff, F. Schworer, V. M. Markovic, K. Sehested, and S. O. Nielsen, *J. Phys. Chem.*, 75, 749 (1971).

(14) J. Halpern and S. M. Taylor, *Discuss. Faraday Soc.*, 29, 174 (1960).

Na_2CO_3. Since $CO_2\cdot^-$ can convert to $O_2\cdot^-$ and $HO_2\cdot$ in the presence of oxygen, the oxidation of hydrogen peroxide (H_2O_2) was tested to compare with that of formate. In the peroxide-persulfate reaction, the reaction rates between pH 0.7 and 5 were almost constant, in contrast with the pH dependence in the formate-persulfate reaction. On the other hand, the reaction rate decreases greatly in an alkaline solution. This fact may indicate that $O_2\cdot^-$ is much less reactive than $HO_2\cdot$. In order to account for the characteristics of the pH dependence, the order in reactivity of radicals in the formate-persulfate reaction may be postulated to be as $HCO_2H\cdot^+ < HCO_2\cdot < CO_2\cdot^- > O_2CO_2\cdot^- > HO_2\cdot > O_2\cdot^-$. In case of a chain reaction involving several radicals, there are generally more factors to affect the rate of reaction. Since many reactions in the separate steps are competing against each other, the rate in each step and the lifetime of the radicals are also important factors to determine the overall reaction rate. The inhibiting effect of iron(III) is briefly accounted for by the following reactions.

$$\mathrm{Fe(III)} + CO_2\cdot^- \rightarrow \mathrm{Fe(II)} + CO_2 \qquad (17)$$

$$\mathrm{Fe(II)} + SO_4\cdot^- \rightarrow \mathrm{Fe(III)} + SO_4^{2-} \qquad (18)$$

Considering that the inhibiting effect of iron was not large, the above chain reaction does not seem to be fast under the conditions. Some iron ions may hydrolyze; in fact, the reaction mixture was slightly turbid at 2×10^{-4} *M* Fe(III) in Table VI. Under the same conditions, copper(II) was a very powerful catalyst. The copper catalysis will be accounted for by reactions 19 and 20.

$$\mathrm{Cu(II)} + CO_2\cdot^- \rightarrow \mathrm{Cu(I)} + CO_2 \quad \text{(fast)} \qquad (19)$$

$$S_2O_8^{2-} + \mathrm{Cu(I)} \rightarrow \mathrm{Cu(II)} + SO_4\cdot^- + SO_4^{2-} \quad \text{(fast)} \qquad (20)$$

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Appendix

The following reactions for the radical species are predicted according to the pH change. In the absence of oxygen

$$HCOOH\cdot^+ \rightleftarrows HCOO\cdot + H^+ \qquad (21)^{8}$$

$$HCOO\cdot \rightleftarrows CO_2\cdot^- + H^+ \quad pK_a = 3.9 \qquad (22)^{15}$$

$$CO_3^{2-} + OH\cdot \rightarrow CO_3\cdot^- + OH^- \quad k = 4.2 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1} \qquad (23)^{16}$$

$$CO_3^{2-} + SO_4\cdot^- \rightarrow CO_3\cdot^- + SO_4^{2-} \qquad (24)$$

$$HCO_3^- + OH\cdot \rightarrow CO_3\cdot^- + H_2O \quad k = 1.5 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1} \qquad (25)^{16}$$

$$HCO_3\cdot \rightleftarrows CO_3\cdot^- + H^+ \quad pK_a = 9.6 \qquad (26)^{17}$$

$$OH\cdot \rightleftarrows O\cdot^- + H^+ \quad pK_a = 10.9 \qquad (27)^{16,18,19}$$

In the presence of oxygen

$$CO_2\cdot^- + O_2 \rightleftarrows O_2CO_2\cdot^- \quad K = 4 \times 10^5\ M^{-1} \qquad (28)^{1}$$

$$CO_2\cdot^- + O_2 \rightarrow CO_2 + O_2\cdot^- \qquad (29)^{15}$$

$$CO_2\cdot^- + O_2 + H^+ \rightarrow HO_2\cdot + CO_2 \qquad (30)^{2,15,18,20}$$

$$HO_2\cdot + H^+ \rightleftarrows H_2O_2\cdot^+ \qquad (31)$$

$$HO_2\cdot \rightleftarrows H^+ + O_2\cdot^- \quad pK_a = 4.8 \qquad (32)^{20,21}$$

Registry No. $HCOO^-$, 71-47-6; $S_2O_8^{2-}$, 15092-81-6.

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Nuclear Magnetic Resonance Spectra of Platinum(II) Hydrides. AB_2X and AB_2MX Spin Systems

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^1H and ^{31}P nuclear magnetic resonance spectra are reported for the complex cations $[PtH(PEt_3)_3]^+$, *trans*-$[PtH(PEt_3)_2(PPh_3)]^+$, and $[PtH(PPh_3)_3]^+$. The hydridic hydrogen resonances of these cations show different center-band and ^{195}Pt side-band multiplet structures. An approximate analysis using the AB_2X and AB_2MX spin systems ($A = B = {}^{31}P$, $M = {}^{195}Pt$, and $X = {}^1H$) clearly shows the reasons for these differences and demonstrates that similar side- and center-band spectra occur only if $|\delta_{AB}| \gg {}^1/_2 |J_{AM} - J_{BM}|$. Similar results are expected for related spin systems of the $A_nB_m(M)X$ type. In certain circumstances (when $|\delta_{AB}| \simeq {}^1/_2 ||J_{AX} - J_{BX}| - |J_{AB}||$ in our particular cases) this type of analysis is not valid and it may be necessary to include the effects of remote magnetically active nuclei such as the protons in the tertiary phosphine ligands.

Introduction

Roundhill and coworkers[1] have recently described an example of a platinum complex, $[PtH(PPh_3)_3][(CF_3COO)_2H]$, in which the nuclear magnetic resonance (nmr) spectrum of the hydridic hydrogen shows different multiplet structures in the side bands (due to molecules containing ^{195}Pt, 33.8% abundant, $I = {}^1/_2$) and in the center band (due to molecules containing other platinum isotopes). These workers discussed their results using computer-simulated spectra for the AB_2X and AB_2MX spin systems but were unable to find a set of coupling parameters which would explain both side- and

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