

# Generation of Free Radicals at Subzero Temperatures. IV.<sup>1</sup> On the Mechanism of Generation of Free Radicals from the Sodium Formaldehyde Sulfoxylate—Iron— Hydroperoxide System

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**ABSTRACT:** In order to elucidate the mechanism of generation of free radicals from the sodium formaldehyde sulfoxylate (I)—iron—hydroperoxide system, the reactions between (I) and  $\text{Fe}^{3+}$  and between (I) and  $\text{Fe}^{3+}$ -EDTA were studied in both acidic and alkaline media. The second-order rate constant ( $k_2$ ) for the former at pH 4 was  $76.0 M^{-1} \text{sec}^{-1}$ , and for the latter  $0.00294 M^{-1} \text{sec}^{-1}$  (pH 4) and  $0.447 M^{-1} \text{sec}^{-1}$  (pH 9) at  $18^\circ\text{C}$ . The reactions of  $\text{Na}_2\text{S}_2\text{O}_4$ — $\text{Fe}^{3+}$  and  $\text{Na}_2\text{S}_2\text{O}_4$ — $\text{Fe}^{3+}$ -EDTA were very rapid, and their rates were only roughly estimated. The mechanisms of generation of free radicals in the (I)— $\text{Fe}^{3+}$ —ROOH system and the  $\text{Na}_2\text{S}_2\text{O}_4$ — $\text{Fe}^{3+}$ —ROOH system were discussed on the basis of the data obtained.

**KEY WORDS** Free Radicals / Sodium Formaldehyde Sulfoxylate / Hydroperoxides / Sodium Dithionite / Initiation Mechanism /

A mixture of sodium formaldehyde sulfoxylate (I),  $\text{Fe}^{3+}$  and a hydroperoxide is an excellent system for initiation of free radical polymerization of vinyl monomers at low temperatures, such as the polymerization of vinyl chloride at  $-15^\circ\text{C}$ .<sup>2</sup> However, the kinetics and mechanism of the reaction in this system have not been studied in detail.

Kolthoff and Meehan compared this system with the sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ )—iron—hydroperoxide system.<sup>3</sup> They found that the reaction between sodium dithionite (II) and  $\text{Fe}^{3+}$ -EDTA is very fast (complete at  $0^\circ\text{C}$  in 10—20 sec at pH 9 in a solution initially  $0.001 M$  in each reactant), whereas the reaction between (I) and  $\text{Fe}^{3+}$ -EDTA is very slow under similar conditions (no measurable decrease in concentration within several hours). In spite of this large difference in the rates of reduction of  $\text{Fe}^{3+}$ , the rates of polymerization with these two systems were quite alike.

Kerber and his coworkers<sup>4,5</sup> studied the reaction between (I) and hydrogen peroxide and the reaction among (I), hydrogen peroxide, and  $\text{Fe}^{3+}$ . However, since they did not study the reaction between (I) and  $\text{Fe}^{3+}$ , the reaction among (I), ROOH, and  $\text{Fe}^{3+}$  could not thoroughly be understood.

Kerber and Gregory reported that when  $\text{Fe}^{3+}$ -EDTA instead of  $\text{Fe}^{3+}$  was mixed with (I) and hydrogen peroxide, polymerization was not initiated.<sup>5</sup> However, other workers reported that the system, (I)— $\text{H}_2\text{O}_2$ — $\text{Fe}^{3+}$ -EDTA, initiated polymerization.<sup>6-8</sup>

In order to elucidate the mechanism of the reaction among (I),  $\text{Fe}^{3+}$ , and ROOH, kinetic studies on the reactions between (I) and  $\text{Fe}^{3+}$ , between (I) and  $\text{Fe}^{3+}$ -EDTA, between (II) and  $\text{Fe}^{3+}$ , and between (II) and  $\text{Fe}^{3+}$ -EDTA have been carried out. The results will be described in this paper.

## EXPERIMENTAL

### Materials

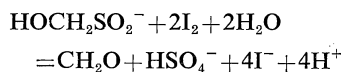
Iron (III) ammonium sulfate,  $\text{Fe}_2(\text{SO}_4)_3 \cdot$

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(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·24H<sub>2</sub>O, of reagent grade was recrystallized twice from water. EDTA·2Na (used for the experiments at pH 4), EDTA·4Na (used for the experiments at pH 9), and sodium formaldehyde sulfoxylate were used as received.

#### Determinations of the Concentrations of the Reactants

The concentration of sodium formaldehyde sulfoxylate (I) was determined by titration with a 0.1-N iodine solution.



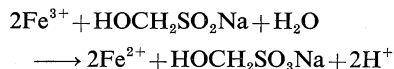
The concentration of Fe<sup>3+</sup> was determined from its absorption at 345 nm by using a Shimadzu spectrophotometer.

#### Kinetics

In a UV cell, an acetate-buffer solution and a Fe<sup>3+</sup>-stock solution were mixed, and nitrogen gas was bubbled through for 20 min. Then a deaerated solution of (I) was added, and the decrease of the Fe<sup>3+</sup> concentration was followed using its absorption at 345 nm.

### RESULTS AND DISCUSSION

In order to determine the stoichiometry between Fe<sup>3+</sup> and (I), an excess of Fe<sup>3+</sup> was allowed to react with (I), and the amounts of Fe<sup>3+</sup> remaining were determined. The results are shown in Table I. It is clear that 2 mol of Fe<sup>3+</sup> are consumed per mol of (I). This finding suggests the following equation.



Thus, the sulfoxylate sulfur (HO—S—OH) was

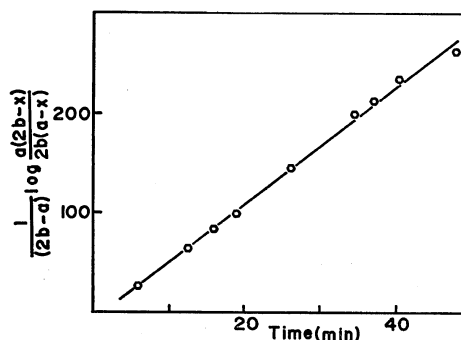
**Table I.** The reaction ratio between Fe<sup>3+</sup> and HOCH<sub>2</sub>SO<sub>2</sub>Na at pH 4

Run	Initial concentrations		Final concentration	[Fe <sup>3+</sup> ] <sub>used</sub> [I] <sub>used</sub>
	10 <sup>4</sup> × [I], M	10 <sup>4</sup> × [Fe <sup>3+</sup> ], M	10 <sup>4</sup> × [Fe <sup>3+</sup> ], M	
1	2.77	8.05	2.45	2.02
2	1.34	5.57	2.66	2.17
3	3.05	7.85	1.80	1.99
4	3.07	7.83	1.20	2.16
				Average 2.08

oxidized to the sulfite sulfur (HO—S—OH).

Then the rates of the reaction between (I) and Fe<sup>3+</sup> were determined. The reaction was found to be of second order and to fit the rate equation,  $dx/dt = -d[\text{Fe}^{3+}]/dt = k(a-x)(b-(1/2)x)$ , where  $x$  is the concentration of Fe<sup>2+</sup> at time  $t$ , and  $a$  and  $b$  are the initial concentrations of Fe<sup>3+</sup> and (I), respectively. An example of the rate plots is shown in Figure 1, and the rate constants obtained are summarized in Table II.

The reaction rate between (I) and Fe<sup>3+</sup>-EDTA at pH 9 was very much greater than what Kolthoff and Meehan reported, "at the same pH (pH 9), temperature (0°C), and concentration (0.001 M in each reactant), the reaction between Fe<sup>3+</sup>-EDTA and sodium formaldehyde sulfoxylate is very slow, no measurable decrease in concentration of Fe<sup>3+</sup>-EDTA occurring within several hours."<sup>3</sup> Calculation based on our data shows that the half-life of Fe<sup>3+</sup>-EDTA is 36.5 min at 18°C when the initial concentrations of (I) and



**Figure 1.** The rate of reaction between (I) and Fe<sup>3+</sup>-EDTA at pH 9, 18°C:  $a = [\text{Fe}^{3+}\text{-EDTA}]_0$ ,  $0.77 \times 10^{-3} M$ ;  $b = [\text{I}]_0$ ,  $1.11 \times 10^{-3} M$ .

**Table II.** The rate constants for the reaction between Fe<sup>3+</sup> and HOCH<sub>2</sub>SO<sub>2</sub>Na in acidic and alkaline media at 18°C

pH	Reactants	
	Fe <sup>3+</sup> and HOCH <sub>2</sub> SO <sub>2</sub> Na	Fe <sup>3+</sup> -EDTA and HOCH <sub>2</sub> SO <sub>2</sub> Na
4.0	76.0 M <sup>-1</sup> sec <sup>-1</sup>	0.00294 M <sup>-1</sup> sec <sup>-1</sup>
9.0	<sup>a</sup>	0.447 M <sup>-1</sup> sec <sup>-1</sup>

<sup>a</sup> Uncomplexed Fe<sup>3+</sup> precipitates in alkaline media.

**Table III.** The reaction between  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Fe}^{3+}$  or  $\text{Fe}^{3+}$ -EDTA at pH 4 and 18°C

Reactants	Time required for disappearance of the color of $\text{Fe}^{3+}$
$[\text{Fe}^{3+}], 2.6 \times 10^{-3} M$ $[\text{Na}_2\text{S}_2\text{O}_4], 6.3 \times 10^{-3} M$	18 sec
$[\text{Fe}^{3+}\text{-EDTA}], 2.6 \times 10^{-3} M$ $[\text{Na}_2\text{S}_2\text{O}_4], 6.3 \times 10^{-3} M$	35 sec

$\text{Fe}^{3+}$ -EDTA are 0.001 *M*. Thus, as a reducing agent (I) is less powerful than (II), but more powerful than hydrazine ( $k_2$  for  $\text{N}_2\text{H}_4\text{-Fe}^{3+}$ -EDTA was 0.089  $M^{-1}\text{sec}^{-1}$  at 0°C, pH 9).<sup>9</sup>

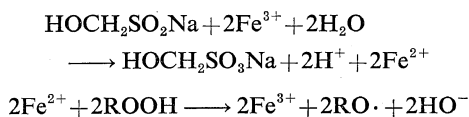
The reaction between  $\text{Fe}^{3+}$ -EDTA and (I) at pH 4 is very much slower than that between uncomplexed  $\text{Fe}^{3+}$  and (I). This fact must be kept in mind when  $\text{Fe}^{3+}$ -EDTA is used as a component of an initiating system.

In order to compare the reducing ability of (I) with that of  $\text{Na}_2\text{S}_2\text{O}_4$  (II), the rates of reduction of  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$ -EDTA with (II) were studied. Since the reaction was very fast, the approximate time of the disappearance of the color of  $\text{Fe}^{3+}$  was determined; the results being shown in Table III. Both  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$ -EDTA are reduced much faster by (II) than by (I). It is interesting that (II) can reduce both  $\text{Fe}^{3+}$ -EDTA and  $\text{Fe}^{3+}$  quite rapidly at pH 4, whereas (I) can reduce  $\text{Fe}^{3+}$  rapidly but  $\text{Fe}^{3+}$ -EDTA only very slowly at pH 4.

On the basis of the rate data reported here and those described in the literature, the initiating systems involving (I) and (II) can now be better understood.

(1)  $\text{Fe}^{3+}\text{-HOCH}_2\text{SO}_2\text{Na-ROOH}$  at pH 4

The rate constant for the bimolecular reaction between  $\text{Fe}^{3+}$  and (I) was 76.0  $M^{-1}\text{sec}^{-1}$  at 18°C. Since the reaction between  $\text{Fe}^{2+}$  and ROOH is very fast ( $k_2$  for the reaction between  $\text{Fe}^{2+}$ -EDTA and cumene hydroperoxide in aqueous solution at pH 3.72, 25°C is 1370  $M^{-1}\text{sec}^{-1}$  and that at pH 5.36, 0°C, is 240  $M^{-1}\text{sec}^{-1}$ ),<sup>10</sup> the reduction of  $\text{Fe}^{3+}$  with (I) is rate-determining in this system.



The rate of disappearance of ROOH is equal to one half of the rate of disappearance of (I).

$$-\frac{1}{2} \frac{d[\text{ROOH}]}{dt} = -\frac{d[\text{I}]}{dt} = k[\text{I}][\text{Fe}^{3+}]$$

As soon as  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ , the latter is quickly oxidized back to the former by the reaction with ROOH. Therefore, the concentration of  $\text{Fe}^{3+}$  can be regarded as constant. When  $[\text{Fe}^{3+}]$  is equal to  $10^{-6} M$ ,

$$-\frac{d[\text{I}]}{dt} = (7.6 \times 10^{-5})[\text{I}]$$

the half life is 152 min. These figures show that the (I)- $\text{Fe}^{3+}$ -ROOH system should initiate polymerization efficiently at pH 4. (See ref 11). In actual polymerization experiments, a somewhat higher concentration of  $\text{Fe}^{3+}$  must be used, since the medium is heterogeneous (ROOH is in the monomer phase and  $\text{Fe}^{3+}$  is in the aqueous phase).

When a mixture of vinyl chloride (100g), water (130g, pH 4), methanol (70g), sodium dodecylbenzenesulfonate (0.5g), (I) (0.014 *M*), hydrogen peroxide (0.029 *M*), and  $\text{Fe}^{3+}$ -EDTA ( $6 \times 10^{-6} M$ ) was stirred at -15°C for 4 hr, a 87-% yield of poly(vinyl chloride) was obtained.

(2)  $\text{Fe}^{3+}\text{-EDTA-HOCH}_2\text{SO}_2\text{Na-ROOH}$  at pH 4

The rate constant for the bimolecular reaction between  $\text{Fe}^{3+}$ -EDTA and (I) was 0.00294  $M^{-1}\text{sec}^{-1}$  at 18°C. When  $[\text{Fe}^{3+}\text{-EDTA}]_0$  is equal to  $10^{-6} M$ ,

$$-\frac{d[\text{I}]}{dt} = (2.94 \times 10^{-9})[\text{I}]$$

the half life is 65000 hr. This is not suitable for initiation of polymerization. If  $[\text{Fe}^{3+}\text{-EDTA}]_0$  is  $10^{-3} M$ , the half life is 65 hr. Kerber and Gregory reported that the  $\text{Fe}^{3+}\text{-EDTA-(I)-H}_2\text{O}_2$  system did not initiate polymerization whereas other workers reported the opposite.<sup>6-8</sup> One of the factors responsible for this discrepancy is probably the difference in the concentration of the  $\text{Fe}^{3+}\text{-EDTA}$  present in the initiating systems.

When a mixture of vinyl chloride (100g), water (130g, pH 4), methanol (70g), sodium dodecylbenzenesulfonate (0.5g), (I) (0.014 *M*), hydrogen peroxide (0.029 *M*), and  $\text{Fe}^{3+}$ -EDTA ( $6 \times 10^{-6} M$ ) was stirred at -15°C for 4 hr, no polymer was formed.

(3) Fe<sup>3+</sup>-EDTA—HOCH<sub>2</sub>SO<sub>2</sub>Na—ROOH at pH 9

Since uncomplexed Fe<sup>3+</sup> precipitate at pH 9, free Fe<sup>3+</sup> cannot be used at pH 9.

The rate constant for the bimolecular reaction between Fe<sup>3+</sup>-EDTA and (I) at pH 9 was 0.447 M<sup>-1</sup>sec<sup>-1</sup> at 18°C. When [Fe<sup>3+</sup>-EDTA]<sub>0</sub> is equal to 10<sup>-4</sup> M,

$$-\frac{d[I]}{dt} = (4.47 \times 10^{-5})[I]$$

the half life is 4.3 hr. This figure is suitable for polymerization.

When a mixture of styrene (25 g) and butadiene (75 g) was polymerized according to the conventional procedure of emulsion polymerization (in a glass bottle, 35 rpm)<sup>3</sup> in an emulsified system of water (180 g, pH 9), potassium myristate (5 g), (I) (3.1 × 10<sup>-5</sup> M), *p*-menthanehydroperoxide (3.0 × 10<sup>-4</sup> M) and Fe<sup>3+</sup>-EDTA (6 × 10<sup>-6</sup> M) at 5°C, the yields of polymer were 62% at 4 hr and 95% at 7 hr.

(4) Fe<sup>3+</sup>—Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>—ROOH and Fe<sup>3+</sup>-EDTA—Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>—ROOH at pH 4

Since (II) reduces Fe<sup>3+</sup>-EDTA and Fe<sup>3+</sup> very much faster than (I) does, free radicals can be produced rapidly at low temperatures.

When a mixture of styrene (25 g) and butadiene (75 g) was polymerized in an emulsified system of water (180 g, pH 4), potassium myristate (5 g), (II) (1.8 × 10<sup>-3</sup> M), *p*-menthanehydroperoxide (2.1 × 10<sup>-3</sup> M) and Fe<sup>3+</sup>-EDTA (0.001 M) at 0°C, the yields of polymer were 40% at 2 hr and 99% at 4 hr. However, the concentrations of

(II) and Fe<sup>3+</sup> should not be too great. Kolthoff and Meehan reported that dead-stop of the polymerization due to exhaustion of the initiators occurred when too much (II) was used.<sup>3</sup>

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11. If the free radicals produced are not wasted by reactions other than that with monomers, the rate of polymerization is determined by the rate of production of free radicals. If the polymerization is to be completed within a reasonable length of time (for instance, 2–20 hr), the desirable half-life of an initiator is approximately 1–10 hr.