[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Mechanism of the γ-Ray-induced Chain Oxidation of Aqueous Ferrous Sulfate–Formic Acid–Oxygen Solutions

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A study has been made of the effect of ferrous sulfate, formic acid and oxygen concentration on the rate of the γ-ray-induced oxidation in the system ferrous sulfate–formic acid–oxygen. The oxidation of ferrous sulfate proceeds by a chain oxidation yielding up to 42 ferric ions per initiating radical. The results are discussed in terms of a mechanism involving free hydrogen atom and hydroxyl radical-induced initiation steps. These reactions are followed by five propagation steps. Hydrogen peroxide is an intermediate in one of the propagation steps, and termination occurs by reactions between some of the free radical species and the ferrous and ferric ions.

As a result of recent work[1–4] considerable progress has been made in our understanding of the mechanism of the γ-ray-induced oxidation of aerated ferrous sulfate solutions. The importance of this reaction stems from its general adoption as a standard for the chemical dosimetry of ionizing radiations. One of the principal drawbacks to a wider use of this reaction as a standard is its susceptibility to impurities. This was brought out when attempts were made by different laboratories to check values of R, the yield ratio $\mathrm{Fe}^{+++}_{(\mathrm{air})}/\mathrm{Fe}^{+++}_{(\mathrm{vac.})}$, obtained by γ-ray irradiation of dilute solutions of ferrous sulfate in the presence and absence of air.[5] Values of R varied roughly from two to four[1,4] although under certain conditions considerably higher values were obtained. General experience showed that the aerated yields were fairly constant whereas the yield in the evacuated solutions varied considerably.

Organic impurities were suspected as one of the causes of the large variation in results in view of the fact that Fricke and Brownscombe[6] had shown earlier that organic acids in very dilute solution had a pronounced effect on the reduction of X-ray-irradiated dichromate solutions. Dewhurst[7] studied the effect of a series of alcohols on the ferric ion yield in aerated solutions of ferrous sulfate. Pentanol was found to double the oxidation yield at a concentration of 10^{-4} M. It was found in preliminary experiments in this Laboratory that upon addition of formic acid to ferrous sulfate solution the yield of the γ-ray oxidation in the presence of air was enormously increased while the yield in air-free solutions was reduced. In this manner a very large ratio for R was experimentally demonstrated. This interesting behavior of the ferrous sulfate–formic acid system led to the present study of the mechanism of this reaction. During the course of these studies, it was found that in the initial stages of oxidation a chain reaction thirty to forty units in length sets in. Hydrogen peroxide was postulated as an intermediate in one of the propagation steps. Thermal experiments with the ferrous sulfate–formic acid–hydrogen peroxide–oxygen system confirmed this idea by giving $\mathrm{Fe}^{++}/\mathrm{H_2O_2}$ consumption ratios considerably higher than 2.0. Furthermore, these ratios increased as the proportion of hydrogen peroxide in this system was reduced. The primary advantage of γ-ray initiation in studying the kinetics of this reaction is that the reaction may be carried out at hydrogen peroxide concentrations at the steady state level of about 10^{-6} M. Under these conditions the kinetics of the reactions involving hydrogen peroxide are greatly simplified.

Experimental

Irradiations were carried out by the general procedure previously described.[8] The irradiation chamber is provided with 10, 30 and 80-curie $\mathrm{Co^{60}}$ sources, and these were used to study the effect of dosage rate. Triply distilled water, ferrous sulfate (reagent grade, Baker and Adamson), sulfuric acid (reagent grade, du Pont), formic acid (99–100%, Eastman Kodak Co.), and tank oxygen were used in the preparation of the solutions. The freshly prepared ferrous sulfate–formic acid solution was made from a 0.05 N ferrous sulfate stock solution by adding formic acid, sulfuric acid and triply distilled water to bring the concentration up to the desired normality. These solutions were used for several days, and then new solutions were made.

Both air-saturated and oxygen-saturated solutions were used. When filling cells with air-saturated solution, the solution was shaken with air for several minutes and then drawn by suction into cylindrical irradiation cells. The cells were 2 cm. in diameter and 5 cm. in length and were provided with $^5/_{20}$ capillary cones at one end. A ground glass $^5/_{20}$ standard taper cap was then placed on the capillary cone of the cell, and the thin glass tip at the other end of the cell sealed by melting the glass.

Oxygen-saturated solutions were prepared by two techniques. In one method the solution was evacuated as previously described[8] and then equilibrated with oxygen at the desired pressure. Then oxygen at a pressure slightly above atmospheric was applied in order to force the solution into the cells. A sealing technique similar to that described above was used to close the cells. As an additional precaution, however, the ground glass cap used was filled with the oxygen-saturated solution in order to prevent diffusion of oxygen out of the cell. A second simpler procedure generally adopted for oxygen-saturated solutions at atmospheric pressure consisted of the following: The air in a partially filled flask was replaced by oxygen, and the solution thoroughly shaken. After this process was repeated three times, the oxygen-saturated solution was carefully poured into a beaker in such a manner as to avoid excessive loss of dissolved oxygen. The irradiation cells were then quickly filled and sealed one after another in the way described for aerated solutions. Substantially identical results were obtained with these two procedures.

Ferric ion concentration was determined by measuring the optical density at 3020 Å. with a Beckman quartz spectrophotometer model DU. The equation $C = 449D$ was used to calculate the amount of ferric ion present when one-centimeter cells were used where C is the concentration in microequivalents per liter and D is the optical density. In the range of concentrations used, dilution of the ferrous sulfate solution was not necessary.

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(1) N. Miller, *J. Chem. Phys.*, **18**, 79 (1950).

(2) F. H. Krenz and H. A. Dewhurst, *ibid.*, **17**, 1337 (1949).

(3) T. Rigg, G. Stein, and J. Weiss, *Proc. Roy. Soc.* (*London*), **A211**, 375 (1952).

(4) E. J. Hart, THIS JOURNAL, **73**, 1891 (1951).

(5) H. A. Dewhurst, private communication.

(6) H. Fricke and E. R. Brownscombe, THIS JOURNAL, **55**, 2358 (1933).

(7) H. A. Dewhurst, *J. Chem. Phys.*, **19**, 1329 (1951).

(8) E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

Experimental Results

Dosage Curves.—Figure 1 is a characteristic dosage curve that is obtained using a solution consisting of 0.50 m*N* ferrous sulfate, 0.10 *M* formic acid and 1.2 m*M* oxygen in 0.8 *N* sulfuric acid irradiated at a dosage rate of 1.42 × 10^{18} e.v./l. min. The same general type of curve is obtained using β-rays from tritium disintegration or α-rays from Po^{210}. According to the mechanism to be discussed below, the data of Fig. 1 should yield a straight line when the reciprocal of the differential rate is plotted *versus* ferric ion concentration (see equations (14) and (16)). Such a curve appears in Fig. 2. The data of Fig. 2 are represented by the equation

$$1/r = 1.08 + 22.8(Fe^{+++})$$

where r is the differential rate of Fe^{+++} formation. The units used are millimole, liter and hour. According to this equation, the rate of oxidation at zero ferric sulfate is 0.926 mmole/l. hr. Under similar conditions of irradiation, the rate of oxidation of ferrous sulfate in the absence of formic acid is 0.0216 mmole/l. hr. Therefore the rate of oxidation of ferrous sulfate is increased 43-fold by the formic acid. Since oxidation of ferrous sulfate in the absence of formic acid is a non-chain process, with a high efficiency for utilizing the free radicals produced in the water by the γ-rays, it is apparent that the formic acid makes possible a chain reaction of 42 steps.

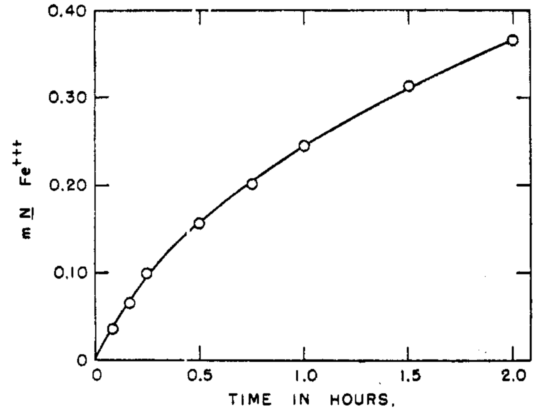

Fig. 1.—Oxidation of 0.5 × 10^{-3} *N* ferrous sulfate, 0.1 *M* formic acid, 1.2 × 10^{-3} *M* oxygen in 0.8 *N* sulfuric acid by Co^{60} γ-rays at a dosage rate of 1.42 × 10^{18} e.v./l. min.

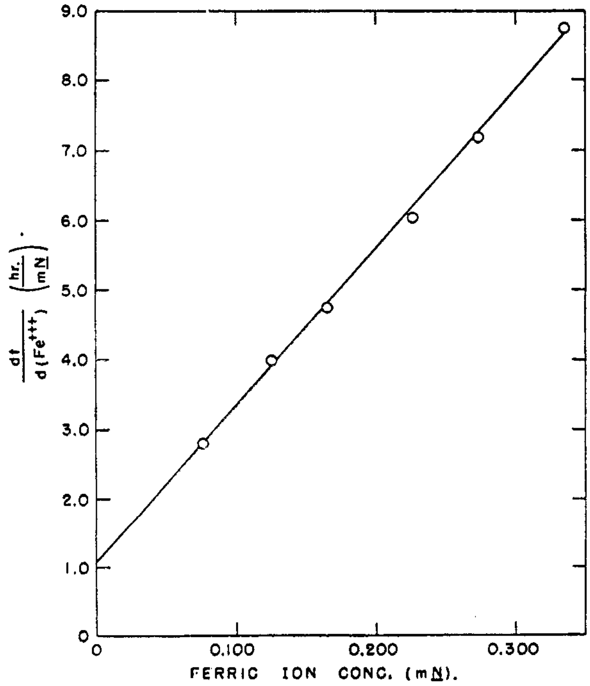

Fig. 2.—Effect of ferric ion concentration on the rate of oxidation of 0.5 m*N* ferrous sulfate, 0.1 *M* formic acid, 1.2 m*M* oxygen in 0.8 *N* sulfuric acid at a γ-ray dosage rate of 1.42 × 10^{18} e.v./l. min.

As is apparent from the above equation, the rate of oxidation is dependent on the original amount of ferric ion present. In Fig. 1 this amounted to 8.5 × 10^{-6} *N* Fe^{+++}. Correction for this amount of ferric ion has been made in plotting Fig. 2. In work below 5 × 10^{-6} *N* Fe^{+++}, short induction periods were sometimes found. Fractional distillation of the formic acid failed to remove the impurity to which this effect is attributed. In all cases, however, a preoxidation with hydrogen peroxide to about 4 or 5 micromolar Fe^{+++} eliminated this effect.

Oxygen Concentration.—Oxygen plays a far more prominent role in the oxidation of ferrous sulfate in the presence of formic acid than it does in its absence. In the oxidation of ferrous sulfate, the rate of oxidation is independent of oxygen concentration as long as measurable oxygen is present.[8] Upon addition of formic acid, it is found that within the limits of experimental error, the reciprocal of the initial rate varies linearly with the reciprocal of the oxygen concentration (Fig. 3). Oxygen is consumed at the rate of one oxygen molecule per two ferric ions produced so that quite appreciable amounts of oxygen are consumed during the course of the reaction.

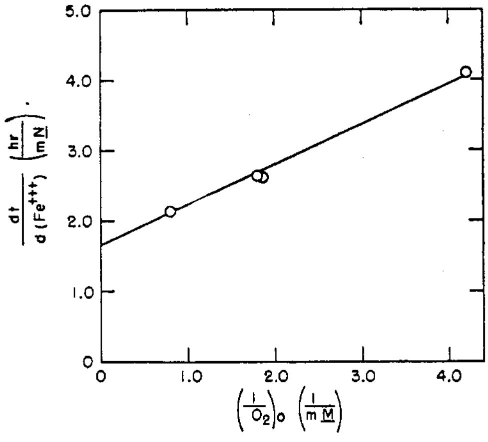

Fig. 3.—Effect of initial oxygen concentration on the rate of oxidation of 0.5 m*N* ferrous sulfate, 0.1 *M* formic acid in 0.8 *N* sulfuric acid at a γ-ray dosage rate of 1.42 × 10^{18} e.v./l. min.

Ferrous Sulfate Concentration.—The rate of oxidation of ferrous sulfate decreases with increasing concentration of ferrous sulfate. Data obtained using 0.1 *M* formic acid and 0.8 *N* sulfuric acid irradiated in air-saturated solutions at a dosage rate of 1.42 × 10^{18} e.v./l. min. are given in Table I.

TABLE I

EFFECT OF FERROUS SULFATE CONCENTRATION ON THE OXIDATION OF 0.1 *M* FORMIC ACID IN AIR-SATURATED 0.8 *N* SULFURIC ACID BY γ-RAYS AT A DOSAGE RATE OF 1.42 × 10^{18} E.V./L. MIN.

m*N* $FeSO_4$	mequiv. Fe^{+++}/l. hr.
0.1	0.312
0.5	.282
1.0	.258
5.0	.126
0.5 (Formic acid absent)	.0216

These data yield a straight line for the plot of reciprocal of rate *versus* ferrous sulfate concentration. (The Hochanadel[9] value of 15.5 Fe^{+++} produced/100 e.v. was used in cal-

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[9] C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

culating dosage from ferric ion yield.) At 0.1 mN ferrous sulfate, the yield is dependent on the time of standing after irradiation. Such an effect was not observed at the higher concentrations studied. The rates of oxidation were obtained by taking the slope of the dosage curve to the first experimental point. In view of the high curvature near the origin, the initial rates of the low concentration curves are actually higher than those given in Table I. At 5.0 mN ferrous sulfate, a linear dosage curve was found.

Formic Acid Concentration.—The effect of formic acid concentration was studied with 0.5 mN ferrous sulfate, 0.8 N sulfuric acid saturated with air, and using a dosage rate of 1.42 × 10^{18} e.v./l. min. According to the mechanism of oxidation deduced from the data, the reciprocal of the initial rate should be linear with the reciprocal of the initial formic acid concentration. The data are shown in Fig. 4. This curve is linear and predicts that there is still an increase in rate to be expected by employing still larger concentration of formic acid.

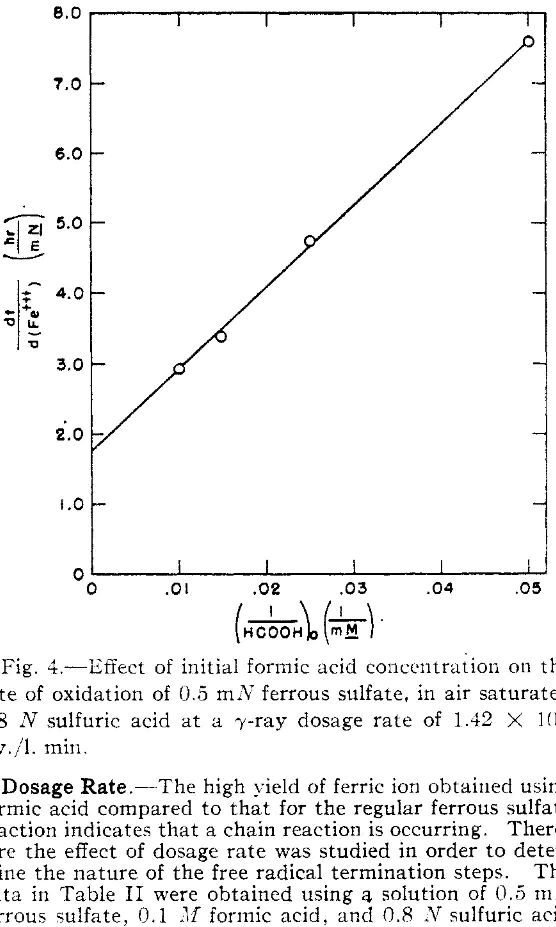

Fig. 4.—Effect of initial formic acid concentration on the rate of oxidation of 0.5 mN ferrous sulfate, in air saturated 0.8 N sulfuric acid at a γ-ray dosage rate of 1.42 × 10^{18} e.v./l. min.

Dosage Rate.—The high yield of ferric ion obtained using formic acid compared to that for the regular ferrous sulfate reaction indicates that a chain reaction is occurring. Therefore the effect of dosage rate was studied in order to determine the nature of the free radical termination steps. The data in Table II were obtained using a solution of 0.5 mN ferrous sulfate, 0.1 M formic acid, and 0.8 N sulfuric acid saturated with oxygen. This solution originally contained 30.1 × 10^{-6} N ferric ion. The rates were obtained by taking the slope between two points near the origin and without corrections for the initial ferric ion concentration. The rates of oxidation given in Table II are therefore somewhat lower than would be obtained from true initial slopes. However, the relative values with respect to variable dosage rates should be very closely the same whether taken at the origin or at a point slightly displaced from the origin. The results appear in Table II. These results show that the rate of oxidation is independent of dosage rate over a forty-fold range. Furthermore, this result demonstrates that termination of the chain reaction developed does not involve the interaction of two intermediate free radicals.

TABLE II

EFFECT OF γ-RAY DOSAGE RATE ON THE OXIDATION OF 0.5 mN FERROUS SULFATE–0.1 M FORMIC ACID IN OXYGEN-SATURATED 0.8 N SULFURIC ACID

Dosage rate (10^{20} e.v./l. hr.)	μ equiv. Fe^{+++}/l. hr.	Fe^{+++}/l. hr. (10^{20})	Fe^{+++}/100 e.v.
33.7	12240	73.7	218
11.15	4140	24.9	223
5.20	1890	11.4	219
1.97	755	4.55	231
0.875	336	2.02	231

Stoichiometry.—The stoichiometry of the γ-ray-induced reaction has been studied by measuring ferric ion formation, oxygen consumption, and carbon dioxide and hydrogen evolution. The results of an experiment carried out at a dosage rate of 5.6 × 10^{19} e.v./l. min. using 0.34 mM oxygen in a 0.55 mN ferrous sulfate–0.10 M formic acid solution appear in Fig. 5. Initially the following stoichiometric equation holds

$$2Fe^{++} + HCOOH + O_2 = 2Fe^{+++} + CO_2 + 2OH^-$$

As the oxygen concentration is decreased, carbon dioxide increases relative to oxygen reacted. This increase in carbon dioxide production is due to the radiation-induced decomposition of the formic acid present.

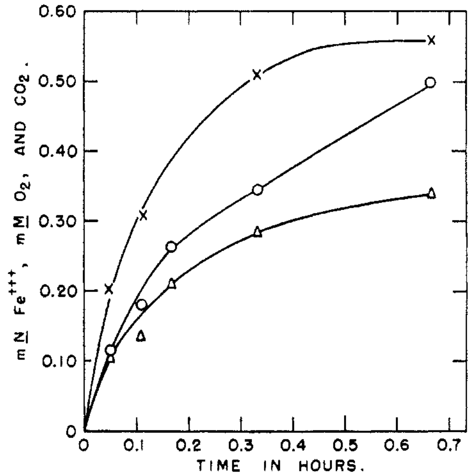

Fig. 5.—Relationship of reactants and products in a 0.55 mN ferrous sulfate, 0.1 M formic acid, 0.34 mM oxygen, 0.8 N sulfuric acid solution irradiated by γ-rays at a dosage rate of 5.6 × 10^{19} e.v./l. min.: O, CO_2 formed; Δ, O_2 used; X, Fe^{+++} formed.

Hydrogen Peroxide.—Kolthoff and Medalia[10] in a series of articles have shown that in the absence of oxygen, hydrogen peroxide reacts with ethanol in ferrous sulfate–hydrogen peroxide–ethanol solutions. Acetaldehyde was shown to be the principal organic compound formed. In the presence of oxygen the above reactants gave molar consumption ratios (Fe^{++}/H_2O_2) greater than two. This indicates that a chain-induced oxidation of ferrous ion by peroxy organic radicals occurs. In order to account for these results it was postulated but not proved that oxygen is absorbed, forming peroxy compounds capable of reacting with ferrous sulfate. Reactions were suggested, but a kinetic treatment of the data was not given.

Formic acid behaves similarly to ethanol as is shown in Table III, where a hydrogen peroxide-induced chain oxidation of ferrous sulfate is demonstrated. It is to be noted

TABLE III

CHAIN OXIDATION BY HYDROGEN PEROXIDE OF AIR-SATURATED 0.5 mN FERROUS SULFATE IN 0.8 N SULFURIC ACID

mM HCOOH	mM H_2O_2	mN Fe^{++} reacted	$\frac{(Fe^{++})\text{ reacted}}{(H_2O_2)\text{ taken}}$
100	0.0059	0.0963	16.3
100	.0124	.147	11.8
100	.0246	.201	8.2
0	.0059	.0118	2.0

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[10] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777, **3784**, 3789 (1949).

that the induced oxidation per unit of added H_2O_2 becomes greater at lower concentrations of hydrogen peroxide. It would appear that much higher ratios would be expected at the very low concentration present during the γ-ray irradiation of aerated ferrous sulfate–formic acid solutions. Under the experimental conditions of Fig. 1 a reaction chain of 42 steps is found. For chains of this length the products arise largely from the chain propagation steps, enabling one to obtain relatively simple kinetic expressions representing the data as will be shown in the subsequent section.

Mechanism

A mechanism in accord with the experimental results herein reported is given by the following series of reactions.

Eq. no.	Rate constant	
(1a)	k_a	$H_2O = H + OH$
(1b)	k_b	$H_2O = 1/2H_2 + 1/2H_2O_2$
(2)	k_2	$OH + HCOOH = H_2O + HCOO$
(3)	k_3	$HCOO + O_2 = HO_2 + CO_2$
(4)	k_4	$H + HCOOH = H_2 + HCOO$
(5)	k_5	$Fe^{++} + HO_2 = Fe^{+++} + HO_2^-$
(5a)	k_{5a}	$H^+ + HO_2^- = H_2O_2$
(6)	k_6	$Fe^{++} + H_2O_2 = Fe^{+++} + OH^- + OH$
(7)	k_7	$Fe^{+++} + HCOO = Fe^{++} + H^+ + CO_2$
(8)	k_8	$Fe^{++} + HCOO = Fe^{+++} + HCOO^-$
(9)	k_9	$Fe^{++} + OH = Fe^{+++} + OH^-$
(10)	k_{10}	$Fe^{+++} + HO_2 = Fe^{++} + H^+ + O_2$

The kinetics of the above mechanism are considerably simplified by considering the reaction as one initiated by processes 1a, 1b, 2 and 4, propagated by 2, 3, 5, 5a and 6, and terminated by 7, 8, 9 and 10. Since the rate of initiation equals the rate of termination, we have

$$2k_a + k_b/2 = k_7(Fe^{+++})(HCOO) + k_8(Fe^{++})(HCOO) + k_9(Fe^{++})(OH) + k_{10}(Fe^{+++})(HO_2) \quad (11)$$

Two ferrous ions are oxidized in the propagation cycle 2, 3, 5, 5a and 6. Therefore for long oxidation chains r, the rate of ferric ion production, may be represented closely by the series of equations

$$r = 2k_2(OH)(HCOOH) = 2k_3(HCOO)(O_2) = 2k_5(Fe^{++})(HO_2) = 2k_6(Fe^{++})(H_2O_2) \quad (12)$$

Combining (11) and (12) one obtains

$$\frac{1}{r} = \frac{1}{4k_a + k_b}\left[\frac{k_7(Fe^{+++})}{k_3(O_2)} + \frac{k_8(Fe^{++})}{k_3(O_2)} + \frac{k_9(Fe^{++})}{k_2(HCOOH)} + \frac{k_{10}(Fe^{+++})}{k_5(Fe^{++})}\right] \quad (13)$$

Equation (13) possesses the correct form to yield the observed relationships between rate of oxidation of ferrous ion and dosage rate, ferrous ion, formic acid and oxygen concentrations. Stoichiometrically we have

$$(Fe^{++}) = (Fe^{++})_0 - (Fe^{+++}) \quad (14)$$

Then (13) becomes (15), which is represented by the straight line in Fig. 2.

$$\frac{1}{r} = \frac{1}{4k_a + k_b}\left[\left(\frac{k_8}{k_3(O_2)} + \frac{k_9}{k_2(HCOOH)}\right) Fe_0{}^{++} + \left(\frac{k_7}{k_3(O_2)} - \frac{k_8}{k_3(O_2)} - \frac{k_9}{k_2(HCOOH)} + \frac{k_{10}}{k_5(Fe_0{}^{++} - Fe^{+++})}\right) Fe^{+++}\right] \quad (15)$$

Equation (15) is expected to hold only under conditions where comparatively long chains are obtained and the concentrations of formic acid and oxygen are not appreciably reduced. A further requirement is that the k_{10}/k_5 term be small compared to the k_7/k_3, k_8/k_3 and k_9/k_2 terms in (15). The present work was carried out at a pH of 0.5, and at this pH it is estimated from the work of Barb, Baxendale, George and Hargrave[11] that k_{10}/k_5 is 0.04. This term is small compared to the k_9/k_2 term calculated below under conditions up to one-half oxidation of the ferrous ion. As the reaction nears completion and $(Fe_0{}^{++} - Fe^{+++})$ approaches zero, then the k_{10}/k_5 term becomes large, and the simplifications assumed in the derivation of (13) no longer hold.

By considering the initial rate of oxidation, the dependence of the initial rate (r_0) on initial ferrous sulfate, oxygen and formic acid concentrations becomes

$$\frac{1}{r_0} = \frac{(Fe^{++})_0}{4k_a + k_b}\left(\frac{k_8}{k_3(O_2)} + \frac{k_9}{k_2(HCOOH)}\right) \quad (16)$$

The data of Tables I and II and Figs. 3 and 4 demonstrate that equation (17) is in accord with the experimental results.

The agreement between experiments and equations derived from the mechanism gives considerable support to the mechanism proposed. However, additional evidence for the individual steps can be cited in the literature or derived from work reported in this paper. Ample experimental evidence has been reported for the primary dissociation reactions (1a) and (1b) for γ-rays absorbed in dilute aqueous solutions. Recent work not only gives the relative rates of these reactions but also the absolute rate of production of free radicals and hydrogen peroxide by these reactions.[9,10] Similarly steps (5), (5a), (6) and (9) have been established for the γ-ray-induced oxidation of aerated ferrous sulfate solutions. The ferrous sulfate–hydrogen peroxide reaction proceeds through steps (5), (6), (9) and (10).[11] Step (2) has been used to explain the kinetics of the ozone–formic acid reaction[12] and steps (2) and (4) have been found necessary to explain the radiation-induced decomposition of formic acid in aqueous solution.[8,13] Since these reactions have been discussed elsewhere, special consideration need only be given reactions (3), (7) and (8).

Initially up to 80 ferrous ions are oxidized per original radical pair produced by the γ-rays. This long chain must therefore involve one or more efficient propagation steps. The propagation cycle must consume oxygen, form carbon dioxide, and produce a free radical that will oxidize ferrous ions. According to the stoichiometry established, two ferrous ions are formed per carbon dioxide produced per oxygen used. While it is possible to write other reactions between the formate radical and oxygen, reaction 3 is preferred since it involves the fewest number of free radical species and produces a radical known to oxidize ferrous ions.

Chain termination step 7 has been confirmed as a most efficient one by irradiation of oxygen-free, ferric sulfate–formic acid solutions. Ferrous sulfate is formed at a rate of two ions per initial dissociation of the water. This is predicted from the mechanism

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[11] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

[12] H. Taube, THIS JOURNAL, **63**, 2453 (1941).

[13] E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952).

$$\mathrm{OH} + \mathrm{HCOOH} = \mathrm{H_2O} + \mathrm{HCOO} \qquad (2)$$

$$\mathrm{H} + \mathrm{HCOOH} = \mathrm{H_2} + \mathrm{HCOO} \qquad (4)$$

$$2\mathrm{Fe}^{+++} + 2\mathrm{HCOO} = 2\mathrm{Fe}^{++} + 2\mathrm{H}^{+} + 2\mathrm{CO_2} \qquad (7)$$

The above work was carried out in 0.8 N sulfuric acid, and under these conditions ferric ion is not reduced in the absence of formic acid. The conclusion is that each of the formate radicals produced in reactions 2 and 4 is capable of reducing ferric ions. In view of this fact and the dependence of reciprocal of rate linearly on the ferric ion concentration, step 7 or an equivalent one must occur.

Evidence for step 8 as a termination one is obtained from a kinetic analysis of the data. Step 8 must be added to the other reactions 1–9 in order to obtain the correct relationship between initial rate of oxidation and initial oxygen pressure.

Ratios of rate constants k_8/k_3 and k_9/k_2 may be calculated independently from the straight lines in Figs. 3 and 4 by application of equation (17). The rate of initiation ($4k_a + k_b$) equals the rate of ferric ion formation in the absence of formic acid. This may be derived from eqs. 1a, 1b, 5, 5a, 6 and 9. (In the absence of formic acid the hydrogen atom from (1a) reacts with oxygen to form the hydroperoxy radical.) The empirical equations for Figs. 3 and 4 are equations 17 and 18, respectively

$$1/r_0 = 1.65 + 0.575/(\mathrm{O_2})_0 \quad \text{(oxygen curve)} \qquad (17)$$

$$1/r_0 = 1.75 + 117/(\mathrm{HCOOH})_0 \ \text{(formic acid curve)} \qquad (18)$$

Subscript 0 indicates initial conditions. Units are millimole, liter and hour. Under the experimental conditions employed $(\mathrm{Fe}^{++})_0 = 0.5$ mN and $4k_a + k_b = 0.0216$ mN Fe^{+++}/hr.; so equation (18) becomes

$$1/r_0 = 23\left(\frac{k_8}{k_3(\mathrm{O_2})_0} + \frac{k_9}{k_2(\mathrm{HCOOH})_0}\right) \qquad (19)$$

From equations (17), (18) and (19) one obtains the values shown below for the ratio of rate constants

	Fig. 3	Fig. 4	Average
k_8/k_3	0.025	0.09	0.06
k_9/k_2	7.2	5.1	6.2

Owing to the limited solubility of oxygen in the solution, the values obtained from Fig. 3 are probably less accurate than those obtained from Fig. 4.

The steady state concentration of hydrogen peroxide may be calculated for a characteristic run using equation (12). Barb, Baxendale, George and Hargrave[11] measured k_6 and report a value of 53 moles l.$^{-1}$ sec.$^{-1}$. At a dosage rate of 0.875×10^{20} e.v./l. hr. and a ferrous ion concentration of 0.5×10^{-3} M, r is found to equal 336×10^{-6} M Fe^{+++}/hr. Under these conditions the steady state concentration of hydrogen peroxide is found to be 1.76×10^{-6} M. Since the rate of oxidation decreases rapidly as ferric ion is formed, hydrogen peroxide concentration will be highest at the beginning of the irradiation. At this low concentration, hydrogen peroxide is not expected to react with the free radical species formed but must disappear primarily through reaction (6). The appreciable "after irradiation effect" found at ferrous sulfate concentrations of 10^{-4} molar may be explained by the attainment of steady state concentrations of 7×10^{-6} molar hydrogen peroxide.

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CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Studies in Low Concentration Chemistry. I. The Radiocolloidal Properties of Lanthanum-140[1]

BY GEO. K. SCHWEITZER AND W. MORRISON JACKSON

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A separation of carrier-free lanthanum-140 from barium-140 has been made, based upon the radiocolloidal properties of lanthanum-140 in basic solution. By use of separated lanthanum-140 in solution, the effects of pH and sodium nitrate concentration upon radiocolloidal formation were investigated. The per cent. of lanthanum that could be removed was found to increase, independent of coagulation time beyond 3.0 min., but dependent on sodium nitrate concentration, to a maximum of almost 100% as the pH is increased. After the attainment of the maximum, changes in pH and/or salt concentration had little effect upon the per cent. removal. Other electrolytes were added in varying amounts to lanthanum-140 solutions of constant pH. Per cent. removal decreased as the concentration of carbonate or citrate increased. Coagulation increased as the oxalate concentration increased up to 0.05 N and then decreased above this concentration.

Introduction

Certain carrier-free radionuclides in solution have been shown to behave more like colloids than like true solutes. These particles have been called radiocolloids. Unlike ordinary colloids, the solubility product apparently is not exceeded.[2]

Over fifteen elements have been shown to form radiocolloidal aggregates in solution. The study of the radiocolloidal behavior of lanthanum has been limited to dialysis experiments and the measurement of diffusion coefficients. Schubert and Conn[3] found that all of the lanthanum-140 in a fission product mixture was dialyzable in water, 0.01 M hydrochloric or 1.0 M nitric acid, while less dialyzed in 0.1 M phosphoric acid, 0.1 M hexafluosilicic acid or 0.1 M oxalic acid. The diffusion coefficient of lanthanum-140, corrected for viscosity effects, was found to be faster in nitric acid than in uranyl nitrate solutions.

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(2) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 142–148; M. Haissinsky, "Les Radiocolloids," Hermann et Cie, Paris, 1934; G. K. Schweitzer and M. Jackson, "Radiocolloids," U. S. Atomic Energy Commission Document ORO-48.

(3) J. Schubert and E. E. Conn, *Nucleonics*, **4**, No. 6, 2 (1949).