

# High-Intensity Radiolysis of Aqueous Ferrous Sulfate-Cupric

## Sulfate-Sulfuric Acid Solutions<sup>1</sup>

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The radiolysis of aqueous FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions has been studied at dose rates up to ~3 × 10<sup>27</sup> eV l.<sup>-1</sup> sec<sup>-1</sup> (~5 × 10<sup>10</sup> rads sec<sup>-1</sup>). G(Fe<sup>3+</sup>), which equals ~0.7 at low irradiation intensities, increased to ~4 with increasing dose rate, acidity, and the extent of oxygenation. This increase is significantly reduced for systems containing higher concentrations of Cu<sup>2+</sup>. Kinetic analysis of the results showed that the increase in G(Fe<sup>3+</sup>) values at the higher radiation intensities is due to the reactions H + H →<sup>k<sub>12</sub></sup> H<sub>2</sub>, H + HO<sub>2</sub> →<sup>k<sub>15</sub></sup> H<sub>2</sub>O<sub>2</sub>, and OH + HO<sub>2</sub> →<sup>k<sub>16</sub></sup> H<sub>2</sub>O<sub>3</sub>, and good agreement between calculated and experimental values is obtained using the following rate constant values (in l. mol<sup>-1</sup> sec<sup>-1</sup>): k<sub>12</sub> = 1.4 × 10<sup>10</sup>, k<sub>15</sub> = 2.0 × 10<sup>10</sup>, k<sub>16</sub> = 1.1 × 10<sup>10</sup>, and k<sub>14</sub> (for H + OH → H<sub>2</sub>O) = 2.0 × 10<sup>10</sup>. Our studies show also that (1) some of the hydrogen atoms are produced in primary radiolytic processes together with solvated electrons, (2) hydrogen sesquioxide, produced by the recombination of OH and HO<sub>2</sub> radicals, is capable of oxidizing four equivalents of Fe<sup>2+</sup> even in the presence of excess Cu<sup>2+</sup> ions and therefore the oxidation of Fe<sup>2+</sup> by H<sub>2</sub>O<sub>3</sub> does not proceed *via* processes which regenerates the HO<sub>2</sub> radical, and (3) radiation-produced hydrogen peroxide is partially decomposed during the pulse, particularly at the higher intensities.

### Introduction

The radiation chemistry of FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions has been examined by a number of investigators.<sup>2-5</sup> In most cases, these studies have been carried out either to elucidate the reactions which take place at relatively low radiation intensities or to evaluate the application of such systems as dosimeters.

In this paper, we report on a study of the radiolysis of the FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> system in the dose rate range up to ~3 × 10<sup>27</sup> eV l.<sup>-1</sup> sec<sup>-1</sup> (~5 × 10<sup>10</sup> rads sec<sup>-1</sup>). At such high radiation intensities, radical recombination reactions compete efficiently with radical-solute reactions,<sup>6-11</sup> and as a result, G(Fe<sup>3+</sup>) increases with increasing dose rate. Because of the rather low G value (~0.7) of this system at low dose rates, the relative increase in ferric yield is large, and is consequently convenient for studying the reaction kinetics in the high-intensity radiolysis of aqueous systems.

### Experimental Section

**Materials.** ACS reagent grade ferrous sulfate, cupric sulfate, and sulfuric acid were used without further purification. Singly distilled water was used for preparing the experimental samples since our previous experience showed no detectable difference between the response of samples prepared with the singly distilled water and samples prepared with water which had been triply distilled from a chromic-alkaline permanganate mixture using an all-quartz system.

**Irradiation.** Irradiation was carried out using a 10-MeV linear accelerator. The high-energy electron beam was focused through a collimator, a 3 × 6 mm hole in an aluminum block. The FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> samples were placed in a long tube (~500 mm long and 4 mm i.d.) which was moved lengthwise in front of the electron beam in a reciprocating manner at a rate so that no overlap of successive radiation pulses at the rate of 15 pulses/sec would occur. In addition, the average total dose for any given sample was also kept within the linear response region for FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> systems irradiated at low dose rates, and ranged between 3 × 10<sup>21</sup> and 1 × 10<sup>22</sup> eV l.<sup>-1</sup>.

**Dosimetry.** Radiation dosimetry was based principally on coulometric measurement of the collimated electron beam using a modified Keithley 610B elec-

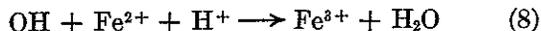
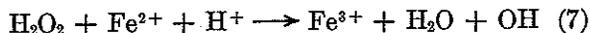
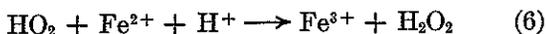
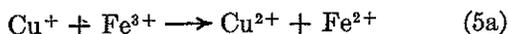
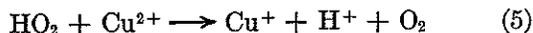
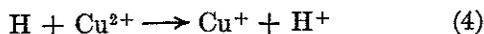
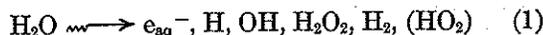
- (1) Partially reported as a postdeadline paper at the International Conference on Radiation Chemistry, Argonne, Illinois, August 14, 1968.
- (2) E. J. Hart and P. D. Walsh, *Radiat. Res.*, **1**, 342 (1954).
- (3) E. J. Hart, *ibid.*, **2**, 33 (1955).
- (4) E. Bjerbakke and K. Sehested, *Advances in Chemistry Series*, No. 81, American Chemical Society, Washington, D. C., 1968, p 579.
- (5) J. W. Halliday and R. D. Jarrett, ref 4, p 604.
- (6) A. Brasch and W. Huber, *Science*, **105**, 112 (1947).
- (7) F. Hutchinson, *Radiat. Res.*, **9**, 13 (1957).
- (8) J. Rotblat and H. C. Sutton, *Proc. Roy. Soc.*, **A255**, 490 (1960).
- (9) P. Ya. Glazunov and A. K. Pikayev, *Dokl. Akad. Nauk SSSR*, **130**, 1061 (1960).
- (10) A. R. Anderson and E. J. Hart, *J. Phys. Chem.*, **66**, 70 (1962).
- (11) J. K. Thomas and E. J. Hart, *ibid.*, **66**, 70 (1962); **68**, 2414 (1964).

trometer and the  $-dE/dx$  values of high energy electrons reported in the literature,<sup>12</sup> supplemented by comparative measurements of the response of standard Fricke dosimeters with the results reported by Thomas and Hart<sup>11</sup> and by Rotblat and Sutton.<sup>8</sup> The extent of ferric ion concentration was determined spectrophotometrically using a Cary Model 15 spectrophotometer at 25° and 302.5 nm ( $\epsilon$  2170).

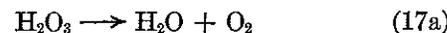
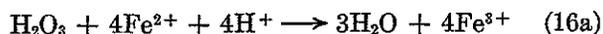
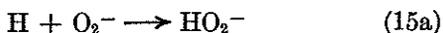
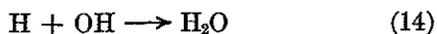
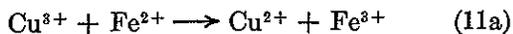
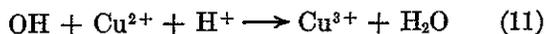
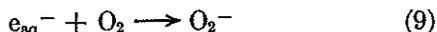
### Results and Discussion

A large number of experiments have been carried out to examine the behavior of aqueous  $\text{FeSO}_4\text{-CuSO}_4\text{-H}_2\text{SO}_4$  systems at different dose rates as a function of sample composition. The results show that although  $G(\text{Fe}^{3+})$  is usually higher at the higher dose rates, its magnitude is a function of the concentration of the cupric and hydrogen ions as well as the extent of oxygenation. These are summarized in Figures 1-3.

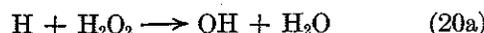
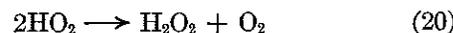
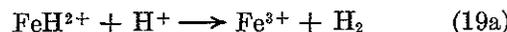
*Reaction Mechanisms.* Examination of our experimental data led to the conclusion that in addition to the reactions normally used in the description of the ferrous sulfate-cupric sulfate dosimeters, *i.e.*



it was necessary to include also the following reactions which influence either directly or indirectly the reaction kinetics at the high dose rates.



In an acidic medium,  $\text{O}_2^-$  is rapidly converted to  $\text{HO}_2$  according to (9a), and consequently, (15a) is not an important process under the conditions of our experiment. Several other processes, though well established in the radiolysis of aqueous systems, have also been neglected. These include



Specifically, although reaction 19 represents one of the key processes in the radiolysis of deaerated acidic ferrous sulfate solutions,<sup>13</sup> it is relatively unimportant under our experimental conditions because of the higher concentrations of the cupric ion. Similarly, reaction 20 is neglected because its rate constant is some four orders of magnitude lower than any other combination process listed in the preceding reaction mechanism. Reactions 20a and 20b are not explicitly included inasmuch as they are reflected in the empirical relationship between  $G(-\text{H}_2\text{O}_2)$  and  $[\text{H}_2\text{O}_2]$  in eq 28.

To a large extent, the probable values of the rate constants for these processes are known and have been summarized in the literature.<sup>14</sup>

*Analysis of the Reaction Kinetics.* Reactions 12, 15, and 16 represent the conversion of the reducing species H and  $\text{HO}_2$  into either inert  $\text{H}_2$  or the oxidizing species  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}_3$ , and are all favored by increasing radical concentration. Consequently,  $G(\text{Fe}^{3+})$  should increase with increasing dose rate as is indeed observed in our experiments.

Quantitatively, we have

$$G(\text{Fe}^{3+}) = G_{\text{obs}}(\text{Fe}^{3+}) - G_0(\text{Fe}^{3+}) =$$

$$\frac{100N_0}{IT} \int_0^\infty \{2k_{12}[\text{H}]^2 + 4k_{15}[\text{H}][\text{HO}_2] + 4k_{16}[\text{OH}][\text{HO}_2]\} dt - 2\Gamma(-\text{H}_2\text{O}_2) \quad (21)$$

where  $G_{\text{obs}}$  is the experimentally observed yield of ferric ions in the high intensity experiment,  $G_0$  is the yield when a similar sample is exposed to low intensity radiations such as the  $\gamma$  rays from a cobalt-60 source,  $N_0$  is Avogadro's number,  $I$  is the dose rate in eV/

(12) M. J. Berger and S. M. Seltzer, NASA SP-3012, 89 (1964).

(13) G. Czapski, J. Jortner, and G. Stein, *J. Phys. Chem.*, **65**, 960 (1961).

(14) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

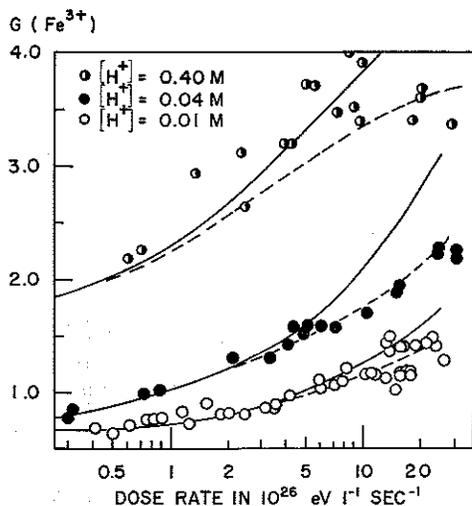


Figure 1. Effect of hydrogen ions on  $G(\text{Fe}^{3+})$ ;  $[\text{Cu}^{2+}] = 0.01 \text{ M}$ ,  $[\text{Fe}^{2+}] = 0.001 \text{ M}$ ,  $[\text{O}_2] = 0.00024 \text{ M}$ : —, calcd omitting  $\text{H}_2\text{O}_2$  decomposition; - - -, calcd including  $\text{H}_2\text{O}_2$  decomposition.

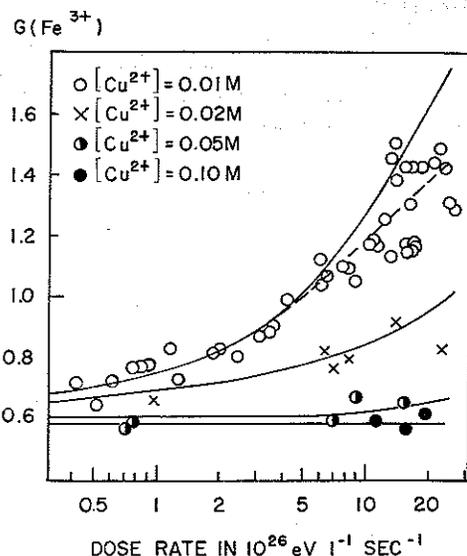


Figure 2. Effect of cupric ions on  $G(\text{Fe}^{3+})$ ;  $[\text{Fe}^{2+}] = 0.001 \text{ M}$ ,  $[\text{H}^+] = 0.01 \text{ M}$ ,  $[\text{O}_2] = 0.00024 \text{ M}$ : —, calcd omitting  $\text{H}_2\text{O}_2$  decomposition; - - -, calcd including  $\text{H}_2\text{O}_2$  decomposition.

l. sec,  $T$  is the pulse length in seconds, and  $\Gamma(-\text{H}_2\text{O}_2)$  is a measure of the extent of radiation-induced decomposition of the hydrogen peroxide molecules formed during the high-intensity radiolysis.

The terms in eq 21 are obtained by solving the simultaneous differential eq 22, 23, and 24 or 22a, 23a, and 24 together with eq 29 using reiterative numerical programs developed during the course of this research.

$$\frac{d[\text{H}]}{dt} = k_2[\text{e}_{\text{aq}}^-][\text{H}^+] + \frac{g_{\text{H}}^0 I}{100N_0} - \{k_3[\text{O}_2] + k_4[\text{Cu}^{2+}] + k_{14}[\text{OH}] + k_{15}[\text{HO}_2]\} [\text{H}] - 2k_{12}[\text{H}]^2 \quad (0 \leq t \leq T) \quad (22)$$

$$\frac{d[\text{H}]}{dt} = -\{k_3[\text{O}_2] + k_4[\text{Cu}^{2+}] + k_{14}[\text{OH}] + k_{15}[\text{HO}_2]\} [\text{H}] - 2k_{12}[\text{H}]^2 \quad (t > T) \quad (22a)$$

$$\frac{d[\text{OH}]}{dt} = \frac{g_{\text{OH}} I}{100N_0} - \{k_8[\text{Fe}^{2+}] + k_{11}[\text{Cu}^{2+}] + k_{14}[\text{H}] + (k_{16} + k_{17})[\text{HO}_2] + k_{18}[\text{SO}_4^{2-}]\} [\text{OH}] - 2k_{13}[\text{OH}]^2 \quad (0 \leq t \leq T) \quad (23)$$

$$\frac{d[\text{OH}]}{dt} = -\{k_8[\text{Fe}^{2+}] + k_{11}[\text{Cu}^{2+}] + k_{14}[\text{H}] + (k_{16} + k_{17})[\text{HO}_2] + k_{18}[\text{SO}_4^{2-}]\} [\text{OH}] - 2k_{13}[\text{OH}]^2 \quad (t > T) \quad (23a)$$

and

$$\frac{d[\text{HO}_2]}{dt} = \{k_9[\text{e}_{\text{aq}}^-] + k_5[\text{H}]\} [\text{O}_2] - \{k_6[\text{Cu}^{2+}] + k_{15}[\text{H}] + (k_{16} + k_{17})[\text{OH}]\} [\text{HO}_2] \quad (24)$$

in which  $g_{\text{H}}^0$  and  $g_{\text{OH}}$  designate respectively the primary 100-eV yield of the "residual" hydrogen atoms<sup>15</sup> and the hydroxyl radicals, and  $[\text{e}_{\text{aq}}^-]$ , the concentration of the solvated electrons, is given by

$$\frac{d[\text{e}_{\text{aq}}^-]}{dt} = \frac{g_e^0 I}{100N_0} - \{k_2[\text{H}^+] + k_9[\text{O}_2] + k_{10}[\text{Cu}^{2+}]\} [\text{e}_{\text{aq}}^-] \quad (25)$$

where  $g_e^0$  is the primary 100-eV yield of the electrons which have escaped from the spurs in the irradiated aqueous system. Under the conditions of our experiment, however, the steady-state concentration of the solvated electrons is reached in less than  $10^{-8}$  sec. Consequently, we have

$$[\text{e}_{\text{aq}}^-] = \frac{g_e^0 I}{100N_0 \{k_2[\text{H}^+] + k_9[\text{O}_2] + k_{10}[\text{Cu}^{2+}]\}} \quad (26)$$

The extent of radiation-induced decomposition of hydrogen peroxide,  $\Gamma(-\text{H}_2\text{O}_2)$  in eq 21 is calculated from eq 29 as follows. By disregarding the negligible contribution from eq 7 during the pulse, we have

$$\Gamma(-\text{H}_2\text{O}_2) = \int_0^T \left\{ k_{13}[\text{OH}]^2 + k_{15}[\text{H}][\text{HO}_2] + \frac{I}{100N_0} g_{\text{H}_2\text{O}_2}^0 \right\} dt - \int_0^T \left\{ k_{13}[\text{OH}]^2 + k_{15}[\text{H}][\text{HO}_2] + \frac{I}{100N_0} (g_{\text{H}_2\text{O}_2}^0 - G(-\text{H}_2\text{O}_2)) \right\} dt \quad (27)$$

Rigorous calculation of  $G(-\text{H}_2\text{O}_2)$  on the basis of the interaction of the various radiation-produced intermediates with  $\text{H}_2\text{O}_2$  and subsequent reactions cannot be

(15) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

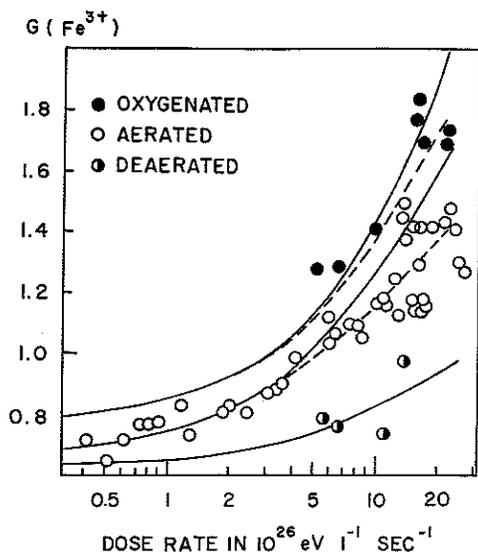


Figure 3. Effect of oxygen on  $G(\text{Fe}^{3+})$ :  $[\text{Cu}^{2+}] = 0.01 M$ ,  $[\text{Fe}^{2+}] = 0.001 M$ ,  $[\text{H}^+] = 0.01 M$ : —, calculated omitting  $\text{H}_2\text{O}_2$  decomposition; - - -, calcd including  $\text{H}_2\text{O}_2$  decomposition.

made at the present time, however, on account of the unavailability of established values of the rate constants for a number of possibly important processes such as the reactions between either  $\text{Cu}^{3+}$  or  $\text{Cu}^+$  ions and  $\text{H}_2\text{O}_2$  molecules. Consequently, the relationship

$$G(-\text{H}_2\text{O}_2) \sim 2 \times 10^2 [\text{H}_2\text{O}_2]^{1/2} \quad (28)$$

which describes quite well the experimental data of Balkwell and Oldham<sup>16</sup> on the radiolysis of hydrogen peroxide in aqueous solutions (for  $[\text{H}_2\text{O}_2] \lesssim 10^{-3} M$ ) was assumed to be also a reasonable approximation under the conditions of our experiment ( $[\text{H}_2\text{O}_2] \lesssim 10^{-4} M$ ), and eq 27 thus becomes

$$\Gamma(-\text{H}_2\text{O}_2) = \int_0^T \left\{ k_{13}[\text{OH}]^2 + k_{15}[\text{H}][\text{HO}_2] + \frac{I}{100N_0} g_{\text{H}_2\text{O}_2^0} \right\} dt - \int_0^T \left\{ k_{13}[\text{OH}]^2 + k_{15}[\text{H}][\text{HO}_2] + \frac{I}{100N_0} (g_{\text{H}_2\text{O}_2^0} - 2 \times 10^2 [\text{H}_2\text{O}_2]^{1/2}) \right\} dt \quad (29)$$

Because of the lack of good agreement among the literature values of some of the second-order radical reaction rate constants, a series of calculations was made using different rate constants. The results are illustrated in Figure 4, which shows that  $\Delta G(\text{Fe}^{3+})$  is not significantly affected by variations in  $k_{12}$  and  $k_{13}$ , but is noticeably affected by  $k_{14}$  and  $k_{16} + k_{17}$ . The best agreement between our calculated and experimental values are obtained using  $g_{\text{H}^+} = 0.6$ ,  $g_e = 3.1$ , and the rate constant values listed in Table I.

Discussions of some of the reactions and the effects of selected experimental parameters are now in order. These are given below.

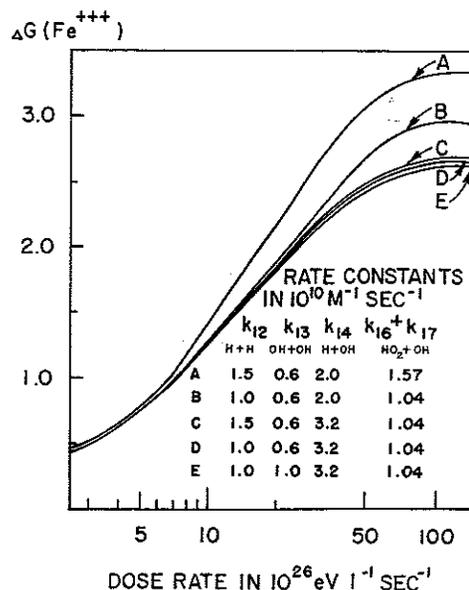


Figure 4. Effect of rate constants on calcd  $\Delta G$  values;  $[\text{Cu}^{2+}] = 0.01 M$ ,  $[\text{Fe}^{2+}] = 0.001 M$ ,  $[\text{H}^+] = 0.04 M$ ,  $[\text{O}_2] = 0.00024 M$ .

Table I: Pertinent Rate Constants in High-Intensity Irradiated  $\text{FeSO}_4$ - $\text{CuSO}_4$ - $\text{H}_2\text{SO}_4$  Solutions<sup>a</sup>

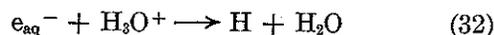
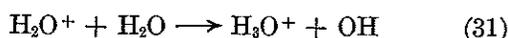
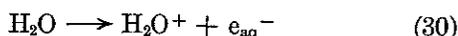
Rate constant	Reaction	Value (in $l. \text{mol}^{-1} \text{sec}^{-1}$ )
$k_2$	$e^- + \text{H}^+$	$2.0 \times 10^{10}$
$k_3$	$\text{H} + \text{O}_2$	$1.9 \times 10^{10}$
$k_4$	$\text{H} + \text{Cu}^{2+}$	$1.5 \times 10^8$
$k_5$	$\text{HO}_2 + \text{Cu}^{2+}$	$1.5 \times 10^7$
$k_6$	$\text{HO}_2 + \text{Fe}^{2+}$	$3.0 \times 10^7 \times [\text{H}^+]$
$k_8$	$\text{OH} + \text{Fe}^{2+}$	$3.2 \times 10^8$
$k_9$	$e^- + \text{O}_2$	$1.9 \times 10^{10}$
$k_{10}$	$e^- + \text{Cu}^{2+}$	$3.0 \times 10^{10}$
$k_{11}$	$\text{OH} + \text{Cu}^{2+}$	$3.5 \times 10^8$
$k_{12}$	$\text{H} + \text{H}$	$1.4 \times 10^{10}$
$k_{13}$	$\text{OH} + \text{OH}$	$0.6 \times 10^{10}$
$k_{14}$	$\text{H} + \text{OH}$	$2.0 \times 10^{10}$
$k_{15}$	$\text{H} + \text{HO}_2$	$2.0 \times 10^{10}$
$k_{16}$	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	$1.1 \times 10^{10}$
$k_{17}$	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$4.7 \times 10^9$
$k_{18}$	$\text{OH} + \text{HSO}_4^- (\text{SO}_4^{2-}) \rightarrow \text{OH}^- + \text{HSO}_4 (\text{SO}_4^-)$	$4 \times 10^5$

<sup>a</sup> Except for  $k_5$  and  $k_6$ , literature references for other rate constants may be found in the rate constant compilations of Anbar and Neta.<sup>14</sup> The value of  $k_5$  is that reported by S. H. Baxendale, *Radiat. Res.*, **17**, 312 (1962);  $k_6$  was evaluated experimentally and from the known  $k_5/k_6$  ratio<sup>3</sup> at  $[\text{H}^+] = 0.01 M$ . The values of  $k_{12}$  and  $k_{13}$  are averages of two or more literature values.

*The Role of the Solvated Electron and the Effect of Hydrogen Ion Concentration.* Although water and aqueous solutions are the most investigated systems in modern radiation chemical research, some of the specific primary processes which occur during the radiolysis of

(16) W. R. Balkwell and S. B. Oldham, USNRDL-TR-903 (1966).

water are not yet fully understood. Specifically, a degree of uncertainty still exists concerning the mechanism of formation of the radiolytically produced hydrogen atoms, *i.e.*, whether some of the hydrogen atoms observed in the radiolysis of aqueous systems are produced from the direct dissociation of water molecules,<sup>15,17,18</sup> or whether all hydrogen atoms result from the reaction between solvated electrons and hydrogen ions as indicated in reaction 2. Allan and Scholes,<sup>15</sup> for example, believed on the basis of experiments involving organic solutes that hydrogen atoms are formed directly from single excited molecules with  $G(\text{H}) \sim 0.6$ . Lifschitz,<sup>19</sup> on the other hand, concluded on the basis of isotope effect experiments that even the so-called "residual" hydrogen atoms could not possibly result from the dissociation of one single water molecule, but must require a reaction involving separate water "molecules," supporting thereby the hypothesis that all hydrogen atoms are produced by sequences such as



*i.e.*, the initial ionization of the water molecule to form the H<sub>2</sub>O<sup>+</sup> and e<sup>-</sup> ion pairs, followed by the reaction of the electron with a hydrated hydrogen ion to form the free hydrogen atom. This latter possibility has not been supported by our experimental results, and consequently the 100 eV yield of the primary hydrogen atoms in acid solutions<sup>20</sup> is a reflection of the primary yields of both hydrogen atoms and solvated electrons with  $g_{\text{H}}^0 = 0.6$ ,  $g_e = g_{\text{H}} - g^0 = 3.1$ .

The concept that both electrons and hydrogen atoms are produced in a highly acidic medium is not inconsistent with the experimental fact that only hydrogen atoms and not solvated electrons are observed in pulse radiolysis experiments involving acidic aqueous systems. Observations in pulse radiolysis experiments, for practical reasons, are made only after the completion of the pulse, *i.e.*, after a time period which is usually on the order of a microsecond. Since the pseudo-first-order rate constant for the conversion of electrons into hydrogen atoms is on the order of  $2 \times 10^9 \text{ sec}^{-1}$  at pH 1, the residual electron concentration will be well below the detection capability of available methods, and solvated electrons have therefore been detected only in alkaline or nearly neutral media. The events of interest to high-intensity radiation chemistry, on the other hand, occur during the pulse period when both reactions 9 and 10 can effectively compete with reaction 2. Consequently, depending on the relative concentrations of the hydrogen and cupric ions in the system, the cuprous ions can be formed directly from electrons without requiring hydrogen atoms as the intermediate species.

At the higher acidities, reaction 6 is enhanced at the expense of reaction 5. Consequently, some of the perhydroxyl radicals will eventually oxidize three equivalents of ferrous ions according to reactions 6 and 7 instead of reducing one equivalent of ferric ions according to reactions 5 and 5a.  $G(\text{Fe}^{3+})$  thus increases with increasing hydrogen ion concentration even at low dose rates as shown in Table II. More importantly, in-

Table II: Low Dose Rate  $G(\text{Fe}^{3+})$  Values ( $G_0$ )<sup>a</sup>

[Cu <sup>2+</sup> ], M	[H] <sup>+</sup> , M	[O <sub>2</sub> ], M	G <sub>0</sub>	Reference
0.01	0.01	0.0012	0.76	4
0.01	0.01	0.00024	0.66	3
0.01	0.04	0.00024	0.80	This work
0.01	0.40	0.00024	1.4	This work
0.01	0.01	0	0.63	4
0.02	0.01	0.00024	0.63	This work
0.05	0.01	0.00024	0.58	This work
0.20	0.01	0.00024	0.57	This work

<sup>a</sup> [Fe<sup>2+</sup>] = 0.001 M.

creased acidity of the irradiated sample will also favor the formation of hydrogen atoms at the expense of the direct formation of the cuprous ions according to eq 2 and 10. As a result, the concentration of both the H and HO<sub>2</sub> radicals will increase with increasing acidity, enhancing the extent of the three radical combination processes responsible for increased  $G(\text{Fe}^{3+})$ , *i.e.*, reactions 12, 15, and 16. As Figure 1 shows, this expectation is indeed borne out by our experiments.

*The Role of the Cu<sup>3+</sup> Ions and the Effect of Cu<sup>2+</sup> Ion Concentration.* The absorption peak at 265 nm observed in the pulse radiolysis of acidic aqueous solutions of cupric salts has been interpreted<sup>21</sup> on the basis of kinetic evidence to be due to the transient Cu<sup>3+</sup> ion. Reactions 11 and 11a are, however, not always included in the reaction network describing the radiation chemistry of aqueous FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> systems. Inasmuch as the overall results of these two reactions are identical with that of reaction 8, such an approach is well justified in the case of low-intensity irradiation experiments where radical combination reactions are negligible. At the high intensities which prevail in our experiments, however, combination of the radiation-produced radicals affects  $G(\text{Fe}^{3+})$  as indicated in eq 22, and consequently, reactions 11 and 11a have been included in our kinetic analysis.

(17) J. Rabani, *J. Amer. Chem. Soc.*, **84**, 868 (1962).

(18) E. Hayon, *Trans. Faraday Soc.*, **60**, 1059 (1964).

(19) C. Lifschitz, *Can. J. Chem.*, **40**, 1903 (1962).

(20) F. S. Dainton and W. S. Watt, *Nature*, **195**, 1294 (1962).

(21) J. H. Baxendale, E. M. Fielden, and J. P. Keene, "Pulse Radiolysis," (Proc. 1st Int. Symp. on Pulse Radiolysis, Manchester, England, 1965) Academic Press, New York, N. Y., 1965 p 218.

The role of cupric ions in the high-intensity radiolysis of the  $\text{FeSO}_4\text{-CuSO}_4\text{-H}_2\text{SO}_4$  is severalfold. Increased cupric ion concentration reduces the extent of hydrogen atom formation as the result of the very large rate constant of reaction 10. In addition, it also will reduce the extent of the various radical combination reactions by the competing processes 4, 5, and 11. Consequently,  $G(\text{Fe}^{3+})$  for systems containing higher concentrations of cupric ions may be expected to show little, if any, dependence on the radiation dose rate. As Figure 2 shows, this conclusion is well supported by our experimental findings.

It is to be noted that even a low dose rate,  $G(\text{Fe}^{3+})$  in the  $\text{FeSO}_4\text{-CuSO}_4\text{-H}_2\text{SO}_4$  system decreases with increasing  $\text{Cu}^{2+}$  concentration.<sup>3,22</sup> Consequently, the low dose rate  $\text{Fe}^{3+}$  yields, *i.e.*,  $G_0$ , have been obtained and are summarized in Table II.

*The Role of Oxygen and Radiation-Induced Decomposition of Hydrogen Peroxide.* Hydrogen peroxide, which can be formed by both eq 13 and 15 through the combination of two OH or the H and  $\text{HO}_2$  radicals, is an important factor responsible for the higher  $G(\text{Fe}^{3+})$  values only in the case of aerated systems. No net change in  $G(\text{Fe}^{3+})$  is expected from reaction 13. Reaction 15 is inherently impossible in deaerated systems, and in addition, as Figure 5 shows, is also not a major process in oxygenated systems inasmuch as most of the radiation-produced hydrogen atoms would actually be converted into the  $\text{HO}_2$  species. In all cases, however, the radiation-produced hydrogen peroxide molecules are expected to be decomposed by further irradiation. Consequently,  $\Delta G(\text{Fe}^{3+})$  values calculated omitting this decomposition would be increasingly too high at the higher dose rates as illustrated in Figures 1-3. Calculations including this decomposition reaction, on the other hand, are seen to agree well with the experimental data. Equation 28, obtained on the basis of the experimental results for hydrogen peroxide solutions in the absence of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions thus appears to be also a reasonable approximation under the conditions of our experiment. It is to be pointed out, however, that the importance of the hydrogen peroxide decomposition process increases with increasing dose rate, and the application of eq 28 to experiments at still higher radiation intensities may well result in appreciable discrepancies between the observed and calculated  $G$  values.

Among other factors, the extent of decomposition of  $\text{H}_2\text{O}_2$  is also a function of the pulse rate. Specifically, low repetition rates should lead to  $G(\text{Fe}^{3+})$  values which are higher as it may be evidenced by a comparison of the data reported by Bjerbakke and Sehested<sup>4</sup> with those observed in our experiments.

*The Role of Hydrogen Sesquioxide ( $\text{H}_2\text{O}_3$ ).* Hydrogen sesquioxide, discovered in 1963 by Czapski and Bielski,<sup>23</sup> is formed by the combination of OH and  $\text{HO}_2$  radicals when aerated or oxygenated water is exposed to high-

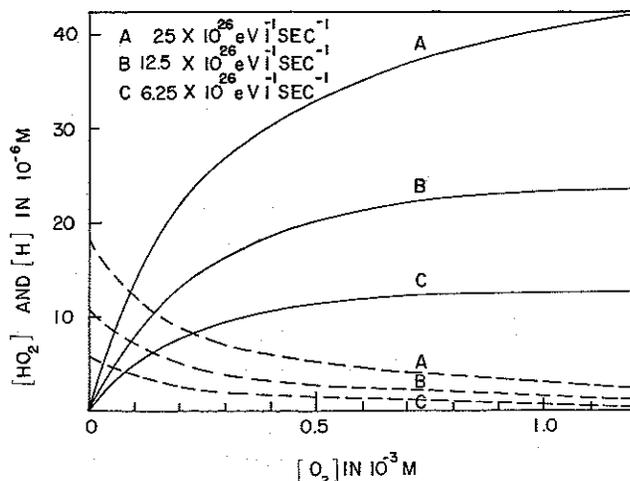
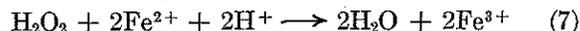
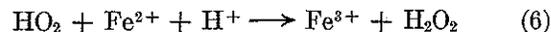
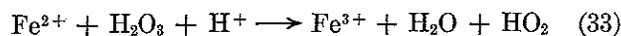


Figure 5. Effect of oxygen on the concn of  $\text{HO}_2$  and H. Radicals (at  $1 \mu\text{sec}$  after initiation of pulse): —,  $[\text{HO}_2]$ ; ---,  $[\text{H}]$ .

intensity radiation. According to these investigators,  $k_{16} = 1.1 \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$  whereas  $k_{17} = k_{16}/2.3 = 4.7 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$ . More recently, Sehested, Rasmussen, and Fricke,<sup>24</sup> using a somewhat different procedure, reported that  $k_{16} + k_{17}$ , which is a function of the pH of the sample, equals  $1.27 \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$  in an acidic medium. In either case, radiation-induced decomposition of  $\text{H}_2\text{O}_3$  has not been explicitly considered, and consequently, the values of  $k_{16}$  represent descriptions of the net rate of formation of  $\text{H}_2\text{O}_3$  under high intensity irradiation conditions.

$\text{H}_2\text{O}_3$  decomposes to form water and molecular oxygen with a pH-dependent first order rate constant on the order of  $1 \text{ sec}^{-1}$ . It therefore mainly reacts with the reducing species in the irradiated medium. In an acidic solution of ferrous sulfate, for example, there is considerable evidence that each molecule of  $\text{H}_2\text{O}_3$  will lead to the oxidation of four ferrous ions, a phenomenon which has been explained on the basis of the following mechanisms<sup>24</sup>



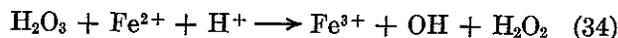
This mechanism is, however, probably of only limited importance in the oxidation of ferrous ions by  $\text{H}_2\text{O}_3$ . If reaction 33 were indeed the principal path for such oxidation processes, the formation of  $\text{H}_2\text{O}_3$  from OH and  $\text{HO}_2$  radicals should not have any effect on  $G(\text{Fe}^{3+})$  inasmuch as the  $\text{HO}_2$  radicals formed in reaction 28 will act mainly as a reducing agent in accordance to reaction 5. Our calculations, on the other hand, show that

(22) D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 657 (1964).

(23) G. Czapski and B. H. J. Bielski, *ibid.*, **67**, 2180 (1963).

(24) K. Sehested, O. L. Rasmussen, and H. Fricke, *ibid.*, **72**, 626 (1968).

H<sub>2</sub>O<sub>3</sub> is the principal species responsible for the very high  $G(\text{Fe}^{3+})$  values in oxygenated aqueous FeSO<sub>4</sub>-CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> systems. Indeed, good agreements between calculation and experiment are obtained if each molecule of H<sub>2</sub>O<sub>3</sub> is assumed to oxidize in full four ferrous ions. An alternate path must therefore be considered. We believe this to be



followed by the oxidation of three additional Fe<sup>2+</sup> ions by OH and H<sub>2</sub>O<sub>2</sub> according to reactions 7 and 8.

At least in principle, determination of the validity of reaction 34 may be afforded by performing H<sub>2</sub>O<sub>3</sub> under high intensity irradiation conditions followed by direct observation of the radical species formed when the H<sub>2</sub>O<sub>3</sub> so produced is allowed to react with a solution of FeSO<sub>4</sub>. Alternatively, the preformed H<sub>2</sub>O<sub>3</sub> may be allowed to react with an acidic aqueous solution containing both CuSO<sub>4</sub> and FeSO<sub>4</sub> in which  $[\text{Cu}^{2+}]/[\text{Fe}^{2+}] \geq 10$ . The extent of Fe<sup>2+</sup> formation would then provide a direct measure of the relative importance of the two alternative paths indicated by reactions 33 and 34.

*The Effect of Pulse Length.* The time required for the reactions of the H atoms in deaerated samples and that of the HO<sub>2</sub> radicals in the oxygen-containing solutions are all on the order of a few microseconds. The  $G(\text{Fe}^{3+})$  values should, therefore, increase initially with increasing pulse length, reaching a maximum value, and then possibly decrease at even longer pulse lengths as the result of the decomposition of hydrogen peroxide by prolonged irradiation.

Comparative experiments have been carried out at a number of selected pulse lengths. These results are summarized in Table III.

Table III: Effect of Pulse Length on  $G(\text{Fe}^{3+})^a$

[Cu <sup>2+</sup> ], M	[O <sub>2</sub> ], M	Dose rate, 10 <sup>27</sup> eV l. <sup>-1</sup> sec <sup>-1</sup>	Pulse length, 10 <sup>-8</sup> sec	$G(\text{Fe}^{3+})$
0.01	0.0012	1.63	5	1.84
		1.60	2	1.77
0.01	0.00024	2.44	2	1.41
		2.50	1.5	1.17
0.01	0	1.54	5	1.22
		1.41	2	0.98
0.02	0.00024	1.37	2	0.92
		1.31	1	0.84
0.05	0.00024	1.56	2	0.66
		1.44	1	0.62
0.10	0.00024	2.00	2	0.65
		2.00	1	0.65

<sup>a</sup>  $[\text{Fe}^{2+}] = 0.001 \text{ M}$ .

*$G(\text{Fe}^{3+})$  at Very High Dose Rates.* According to our calculations, the maximum  $G(\text{Fe}^{3+})$  value which can be reached is approximately 4. At the very highest dose rates, recombination of the H and OH radicals to form water, hydrogen peroxide, and molecular hydrogen assumes increasing importance, and may indeed even lead to decreases from the maximum value. It would be interesting to examine the validity of this conclusion in experiments using the very intense pulses from machines such as the field-emission sources.

*Acknowledgment.* The authors are indebted to Dr. E. J. Hart of the Argonne National Laboratory for his valuable advice, Dr. Raymond D. Cooper, Mr. Christopher W. Rees, Mr. James M. Caspersen, Mr. George Dewey, Mr. Christopher Hursh, and Mr. Leon Gricus at the Linear Accelerator Branch of the U. S. Army Natick Laboratories for experimental support.