Oxidation of Ferrous Ions in Aqueous Solutions by Cobalt-60 Gamma Rays. III. The Effect of Cupric Ion in Air-free Acidic Solutions

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(Received September 15, 1961)

The effect of cupric ion on the radiolysis of an air-free ferrous acidic solution is usually assumed to be due to the reaction[1]

$$Cu^{2+} + H = Cu^{+} + H^{+} \tag{10}$$

competing with the reaction

$$Fe^{2+} + H^{+} + H = Fe^{3+} + H_2 \tag{3}$$

Therefore, the oxidized ferric ion is re-reduced by the reaction

$$Fe^{3+} + Cu^{+} = F^{2+} + Cu^{2+} \tag{11}$$

On the other hand, it was established in Part II[2] that the reaction

$$Fe^{3+} + H = Fe^{2+} + H^{+} \tag{4}$$

can not be ignored in some cases. The oxidation rate of the ferrous ion in a mixture of ferrous and ferric ions was evaluated by the equation

$$G(\mathrm{Fe^{III}}) = 2G(\mathrm{H_2}) + \frac{2G(\mathrm{H})}{1+\dfrac{k_4(\mathrm{Fe^{III}})}{k_3(\mathrm{Fe^{II}})}} \tag{iii}$$

where k is the rate constant of the respective reactions[2,3]. In the present paper, the contribution of reaction 10 in the ferrous-cupric system will be discussed for the analogous equation.

Experimental

Nitrogen-saturated ferrous ammonium sulfate solutions in sulfuric acid, containing some amounts of cupric sulfate, were irradiated by a 10 kc. cobalt-60 gamma ray source, and the amount of ferric ion was measured by optical density at 304 mμ by the usual methods, presented in Part II[2]. All the solutions for Figs. 1 and 3 contained 0.04 M ferrous salt in 0.8 N sulfuric acid. All the solutions for Fig. 4 contained 0.04 M ferrous salt in various concentrations of sulfuric acid. The concentration of cupric sulfate in all the solutions for Fig. 2 was as large as five times that of ferrous salt in 0.8 N sulfuric acid.

Results and Discussion

The Effect of the Cupric Concentration.— The $G(\mathrm{Fe^{III}})$ of the 0.04 M ferrous ammonium

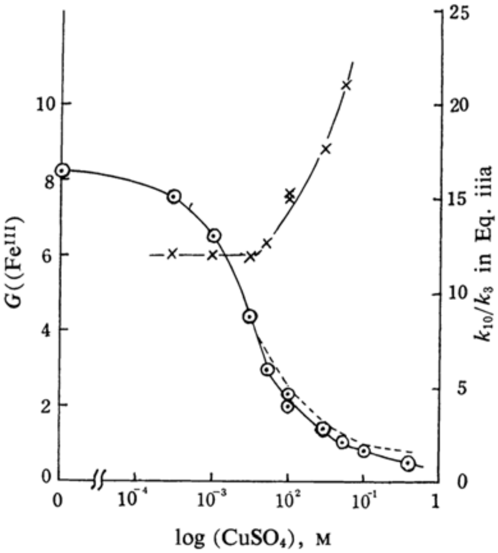

Fig. 1. Effect of cupric sulfate concentration on $G(\mathrm{Fe^{III}})$ (⊙) and k_{10}/k_3 in Eq. iiia (×) in air-free 0.04 M ferrous ammonium sulfate solution of 0.8 N sulfuric acid.

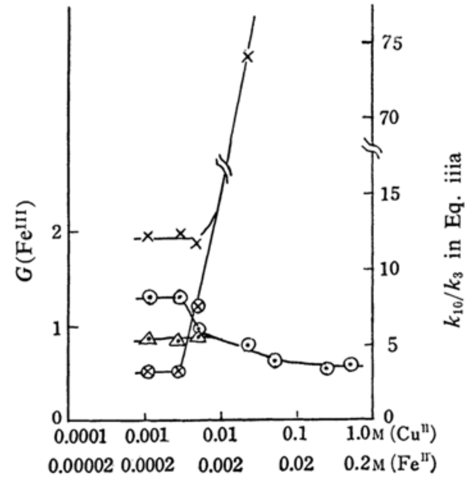

Fig. 2. Effect of concentration of ferrous and cupric sulfate ($(\mathrm{Cu^{II}})/(\mathrm{Fe^{II}})=5$) on $G(\mathrm{Fe^{III}})$ at initial dose (⊙) and 2×10^5 r (△) and the corresponding k_{10}/k_3 in Eq. iiia (⊗) and (×) respectively, in air-free 0.8 N sulfuric acidic solutions.

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[1] E. J. Hart, *Radiation Research*, **2**, 33 (1955).

[2] H. Hotta and S. Ohno, This Bulletin, **34**, 1640 (1961).

[3] W. G. Rothschild and A. O. Allen, *Radiation Research*, **8**, 101 (1958).

sulfate solutions in 0.8 N sulfuric acid is shown by the circles in Fig. 1 as a function of the cupric concentration. Furthermore, in order to confirm the effect of the cupric concentration, the $G(\mathrm{Fe^{III}})$ of the 0.8 N sulfuric acidic solutions, containing amounts of cupric sulfate as large as five times that of ferrous ammonium sulfate, was studied, as is shown in Fig. 2. Since the $G(\mathrm{Fe^{III}})$ for the dilute solutions in this case decreased above 1×10^5 r, the values at the initial dose and 2×10^5 r were plotted as the circles and triangles respectively in Fig. 2.

When the effect of the cupric ions is assumed as has been mentioned in the introduction, the oxidation rate of the ferrous ions in a mixture of ferrous and cupric ions can be expressed by the equation

$$G(\mathrm{Fe^{III}})=2G(\mathrm{H_2})+\frac{2G(\mathrm{H})}{1+\dfrac{k_{10}(\mathrm{Cu^{II}})}{k_3(\mathrm{Fe^{II}})}} \qquad \text{(iiia)}$$

which is like Eq. iii. Therefore, the apparent ratio of the reaction rates, k_{10}/k_3, can be estimated from the observed $G(\mathrm{Fe^{III}})$ as is plotted as crosses in Figs. 1 and 2. These ratios increase sharply in the cupric solutions more concentrated than 0.004 M in Fig. 2 as well as in Fig. 1. If this ratio is consistently 12 over the whole range, the $G(\mathrm{Fe^{III}})$ can be shown as the dotted line in Fig. 1. This fact shows that the apparent ratio of the reaction rates, k_{10}/k_3, is 12 in the present reaction scheme, and that some reactions must be considered in a concentrated cupric solution in addition to the above scheme. The smaller value of the ratio than 12, corresponding to the initial $G(\mathrm{Fe^{III}})$ in Fig. 2, may be due to the effect of the slight residual oxygen.

The smallest $G(\mathrm{Fe^{III}})$ for the present reaction scheme should be 0.78 from Eq. iiia. The smaller observed value than 0.78 can be interpreted at first glance by the so-called "track effect", that is, the reaction of the cupric ion with the hydrogen atom, which has the fate of combining with another hydrogen atom or a OH radical outside of the track. Although this may be partially correct in the very concentrated cupric solution, the above cupric concentration, 0.004 M, at which something begins to happen, is too dilute for such a track effect. This suggests that the capture reaction of the cupric ion with the thermerized electron,

$$\mathrm{Cu^{2+}} + \mathrm{e} = \mathrm{Cu^{+}} \qquad (12)$$

must be considered, in addition to reaction 10, in the cupric solution more concentrated than 0.004 M.

All the solutions plotted in Fig. 1 gave the constant $G(\mathrm{Fe^{III}})$ up to 1.2×10^6 r, but they were not always constant at higher doses as is shown in Fig. 3, in which the oxidation rate of ferrous ions in 0.04 M ferrous ammonium sulfate solutions of 0.8 N sulfuric acid containing a) 0.004 M, b) 0.04 M and c) 0.4 M cupric sulfate, is shown to be up to 10^8 r. The decrease of the $G(\mathrm{Fe^{III}})$ at high doses is expected from Eq. iiia as a result of the decrease in the amount of ferrous ion. Furthermore, at high doses, the reaction between the ferric ions and the thermerized electrons like reaction 12, as has been pointed out by Dobson and Hughes⁴⁾, and the effect of the accumulated hydrogen molecules in the system may also be effective. The constancy of $G(\mathrm{Fe^{III}})$ (=0.48) for solution c up to 7×10^7 r is due to the complete predominance of reactions 10 and 12 in the highly concentrated cupric solution.

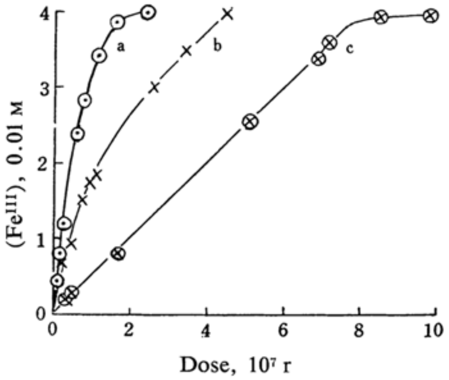

Fig. 3. Oxidation of ferrous ion in air-free 0.04M ferrous ammonium sulfate solutions of 0.8 N sulfuric acid containing a) 0.004 M (⊙), b) 0.04 M (×) and c) 0.4 M (⊗) cupric sulfate.

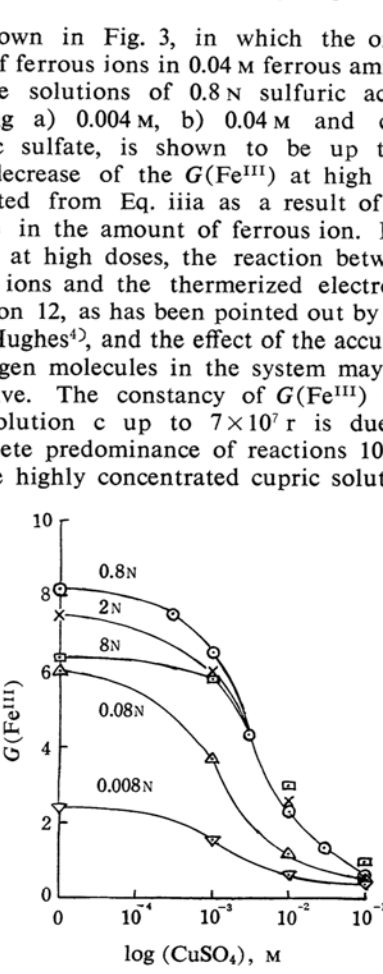

Fig. 4. Effect of concentration of cupric sulfate on $G(\mathrm{Fe^{III}})$ for air-free 0.04 M ferrous ammonium sulfate solutions in 0.008 N (▽), 0.08 N (△), 0.8 N (⊙), 2 N (×) and 8 N (⊡) sulfuric acid, respectively.

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4) G. Dobson and G. Hughes, *Trans. Faraday Soc.*, **57**, 1117 (1961).

TABLE I. k_{10}/k_3 AS A FUNCTION OF H_2SO_4 CONCENTRATION

H_2SO_4 N	Assumed value[3] of G(H)	Assumed value[5] of $G(H_2)$	k_{10}/k_3	
			Apparent from Eq. iiia	Intrinsic for $(Cu^{2+})/(Fe^{2+})$
0.8	3.7	0.39	12	270
0.08	3.5	0.40	57	200
0.008	3.2	0.44	330	210

TABLE II. k_4/k_3 AS A FUNCTION OF SOLUTE CONCENTRATION

H_2SO_4 N	Initial concentration of ferrous salt M	k_4/k_3	
		Apparent from Eq. iii	Intrinsic for $(Fe^{3+})/(Fe^{II})$
0.01	0.001	7.2[3]	9
0.8	0.001	0.08[3]	11
0.8	0.04	0.67[2]	20

TABLE III. $G(Fe^{III})$ FOR CONCENTRATED SULFURIC ACID SOLUTIONS

Composition, M			$G(Fe^{III})$ for energy absorbed	
H_2SO_4	$Fe(NH_4)_2(SO_4)_2$	$CuSO_4$	by total soln.	by water
0.4	0.04	0	8.20	8.20
1	0.04	0	7.50	8.24
4	0.04	0	6.35	9.32
0.4	0.04	0.001	6.51	6.51
1	0.04	0.001	5.96	6.54
4	0.04	0.001	5.80	8.52

The Effect of the Sulfuric Acid Concentration. —The $G(Fe^{III})$ of the 0.04 M ferrous ammonium sulfate solutions in 0.008, 0.08, 0.8, 2 and 8 N sulfuric acid respectively is shown in Fig. 4 as a function of the cupric sulfate concentration.

When the G(H) and $G(H_2)$ for various sulfuric acidic solutions are assumed as listed in Table I[3,5], the apparent ratios of reaction rates, k_{10}/k_3, for these solutions containing 0.001 M cupric sulfate as evaluated from Eq. iiia depend on the concentrations of sulfuric acid as listed in the same table. On the other hand, the apparent ratio of reaction rates, k_4/k_3, for the 0.001 M ferrous sulfate solution in 0.01 and 0.8 N sulfuric acid (containing no cupric ion), observed by Rothschild and Allen[3], has the same tendency as the present ratio, k_{10}/k_3, and apparently is somewhat at variance with our previous value[2], as listed in Table II. A detailed discussion of these problems will appear in the next section.

In Fig. 4, the $G(Fe^{III})$ in 2 and 8 N sulfuric acid is also smaller for no and 0.001 M cupric solutions than for those of 0.8 N. However, when it is assumed that energy absorbed by sulfuric acid is dissipated without chemical change, the $G(Fe^{III})$ for energy absorbed only by water in 2 N sulfuric acid is quite equal to that in 0.8 N acid, and the same $G(Fe^{III})$ in 8 N acid is larger than in 0.8 N acid, as is shown in Table III. This indicates that the present assumption is not correct in 8 N sulfuric acid. In fact, there was some smell in the irradiated solution in 8 N sulfuric acid.

The Intrinsic Ratio of the Reaction Rates for k_4/k_3 and k_{10}/k_3. — As was mentioned in Part II[2], ions are not always free, but also form many complexes with solutes and solvents in a solution, and the reactivity with hydrogen atom depends on their state. Therefore, in Part II, as a result of the estimation of the concentration for the ith ferric complex, c_i, the relative reduction rate of the respective species by hydrogen atom, $k_4{}^i$, to that of reaction 3 was evaluated by the equations

$$\frac{k_4(Fe^{III})}{k_3(Fe^{II})}=\frac{1}{k_3(Fe^{2+})}\sum(c_i)k_4{}^i \qquad \text{(iv)}$$

and

$$(Fe^{III})=\sum(c_i) \qquad \text{(vi)}$$

where (Fe^{II}) and (Fe^{III}) represent the total concentration of ferrous and ferric species, and (Fe^{2+}) and (Fe^{3+}), the concentration of their respective free ions, in the present paper. In Eq. iv, the ratio of reaction rates for the respective complexes, $k_4{}^i/k_3$, is now defined as the intrinsic ratio.

When the concentration of respective ferric complexes in a solution is estimated on the same assumption as in Part II[2], the intrinsic ratio of the reduction rate of free ferric ion,

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[5] D. M. Donald and N. Miller, *Radiation Research*, **9**, 487 (1958).

namely, precisely reaction 4 to the oxidation rate of ferrous ion, is evaluated as in Table II for various solutions. In the present evaluation, the perfect dissociation, that is, $(\mathrm{Fe^{II}})=(\mathrm{Fe^{2+}})$, is assumed for the ferrous ion. This assumption was not very significant in Part II, for the relative value was discussed in relation to results in solutions containing almost equal amounts of solute (almost the same ionic strength). In the present cases, the dissociation degree of ferrous sulfate should be somewhat different. When the true concentration of the free ferrous ions is put in Eq. iv[6] on the assumption that the undissociated molecules are not reactive with hydrogen atoms, the intrinsic ratio of the reduction rate of the free ferric ions to the oxidation rate of the free ferrous ions by the hydrogen atoms is reduced to 7 from the values in Table II for all the present cases. Therefore, it is concluded that the correction factor for the free ferrous ions in Eq. iv is one-third for the result for the 0.04 ferrous ammonium sulfate solution of 0.8 N sulfuric acid; that is, all the intrinsic ratios for the reduction rates of ferric complexes, as listed in Table IV in Part II[2], should be corrected as in Table IV.

TABLE IV. RELATIVE RATE CONSTANTS FOR R+H AT ROOM TEMPERATURE

R	Relative rate constant
$\mathrm{Fe^{2+}}$	1*
$\mathrm{Fe^{3+}}$	7
$\mathrm{(FeCl)^{2+}}$	1100
$\mathrm{(FeBr)^{2+}}$	1000
$\mathrm{(FeSO_4)^{+}}$	<1
$\mathrm{(FeF)^{2+}}$	≈ 0
$\mathrm{Cu^{2+}}$	270

* For $\mathrm{Fe^{2+} + H + H^{+} = Fe^{3+} + H_2}$

Since the dissociation constant of cupric sulfate is 0.0045 M[7] and the dissociation degree of 0.04 M ferrous sulfate is one-third, as deduced above, the intrinsic ratio of the reduction rate of the free cupric ions to the oxidation rate of the free ferrous ions by the hydrogen atom, k_{10}^{1}/k_3, is evaluated as in Table I, as for ferric ion, from the equation

$$\frac{k_{10}(\mathrm{Cu^{II}})}{k_3(\mathrm{Fe^{II}})}=\frac{k_{10}^{1}(\mathrm{Cu^{2+}})}{k_3(\mathrm{Fe^{2+}})}+\frac{k_{10}^{2}(\mathrm{CuSO_4})}{k_3(\mathrm{Fe^{2+}})} \qquad \text{(vii)}$$

For the evaluation, k_{10}^{2}/k_3 is almost zero; this means that the undissociated cupric sulfate molecules are not reduced by the hydrogen atoms. The first value in Table I (270) is the most reliable. Therefore, the ratio of the reduction rates of the free cupric ion to the free ferric ion is about 40. The same ratio is obtained as 22 by other investigators[8,9].

As shown in Tables I and II, the apparent ratio can be consolidated by the intrinsic ratio defined by Eqs. iv and vii.

Another possibility for the dependence of the apparent ratio, k_{10}/k_3, on the concentration of cupric sulfate as shown in Figs. 1 and 2 is that it is due to the dependence of its dissociation degree. However, it is easily seen that its dissociation degree is not so sensitive in 0.8 N sulfuric acid.

Although the contribution of reaction 4 in the ferrous-cupric system is ignored in the above discussion, it could be expressed as

$$G(\mathrm{Fe^{III}})=2G(\mathrm{H_2})+\frac{2G(\mathrm{H})}{1+\dfrac{k_4(\mathrm{Fe^{III}})}{k_3(\mathrm{Fe^{II}})}+\dfrac{k_{10}(\mathrm{Cu^{II}})}{k_3(\mathrm{Fe^{II}})}} \qquad \text{(viii)}$$

However, when the apparent value for k_4/k_3 and k_{10}/k_3 in Tables I and II and the concentration of ferric ions at the initial stage are inserted into this equation, such a disregard is permissible.

Summary

The yield of ferric ions in the air-free ferrous acidic solutions by cobalt-60 gamma rays is reduced in the presence of cupric ion due to their reduction by the hydrogen atoms. The decrement depends on the composition of the solutions. That is, the apparent ratio of this reduction rate to the oxidation rate of the ferrous ions, estimated directly from the observed ferric yield by Eq. iiia increases with the decrease in acidity. On the other hand, the similar ratio for the reduction rate of ferric ions apparently varies according to the composition of the solutions. However, when these apparent ratios are analyzed by a fine composition of the solutions or reduced to the reaction rate for the fine species in solutions, the intrinsic ratios of the reduction rate of the free ferric and cupric ions to the oxidation rate of the free ferrous ions, by the hydrogen atoms, are 7 and 270 respectively and are independent of the composition of the solutions. On the other hand, the direct capture reaction of the cupric ions with the thermerized electrons is effective, in addition to the above reduction reaction with the hydrogen atoms, in the cupric solutions more concentrated than 0.004 M.

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[6] "Gmelins Handbuch der Anorganischen Chemie", 59, Fe(B), p. 430.

[7] W. D. Bale, E. W. Davies and C. B. Monk, *Trans. Faraday Soc.*, 52, 816 (1956).

[8] P. Riesz and E. J. Hart, *J. Phys. Chem.*, 63, 858 (1959).

[9] J. H. Baxendale and D. H. Smithies, *Z. physik. Chem.*, 7, 242 (1956).