Oxidation of Ferrous Ions in the Aqueous Ferrous-Cupric System. I. Effect of Cobalt-60 Gamma-Rays

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(Received August 27, 1959)

An irradiation facility with a 10 kilocurie Co-60 gamma-ray source has been in operation at Japan Atomic Energy Research Institute since 1958[1]. Although the characteristics of the source, especially the distribution of radiation intensity around the hollow cylindrical source had to be measured for the public use of this facility, a chemical dosimeter for high dose, which was to be used as the standard, was not studied in Japan. The dose rate inside the present source is about $2\times 10^6\ r$/hr.

For this purpose, the properties of various aqueous solutions were examined to find a suitable chemical dosimeter for high doses. In general, a chemical dosimeter must have certain properties, namely, linearity, reliability, stability, easy standardization and so on[2]. It is concluded from the present experiments that a chemical dosimeter for high doses must have the following properties in addition to the above ones.

The first conclusion is that the oxygen-dependent reaction is not preferable, owing to the restriction of oxygen solubility like ferrous or benzene aqueous solution[3,4]. That is, all components of the system must have great solubility, which determines the upper limit of the appriciable dose. Moreover, the product to be measured should have no secondary reaction such as re-redox reaction and decomposition. Re-redox reactions are considered even for ferric[5] and cerous[6] ions, respectively. Since the temperature of solutions irradiated at a high dose rate is apt to be raised owing to the absorption of radiation energy, it is desirable for the *G*-value to be independent of temperature[7].

It is difficult to find an ideal system having all the above properties. The ceric dosimeter is usually recommended for this purpose, but demands the most careful distillation of water. Moreover, the reagent contains some rare earths occasionally. The ferrous-cupric dosimeter[8] is another one used for high doses. This dosimeter can easily be made from pure and cheap reagents, but this matter is not being so exhaustively studied at present. Therefore, the authors studied the aqueous ferrous-cupric system in detail, and give the results of some discussions concerning it in the present paper.

Experimental

Triply distilled water was used as usual, but chemical reagents of special grade were used without further purification. The aqueous solutions were irradiated in a test tube of hard glass (Hario Glass) by a 10 kilocurie Co-60 gamma-ray source at the Irradiation Laboratory of Japan Atomic Energy Research Institute at room temperature (ca. 25°C). The solutions were saturated with either oxygen or nitrogen, and sometimes irradiated without any treatment, which is called hereafter the non-treated solution. The concentration of oxygen in distilled water, which was treated similarly with the solution, was measured at 25°C by the Winkler method[9] as listed in Table I. The solubility of oxygen in water is 1.2×10^{-3} M in the handbook[10].

In the present experiment, as mentioned previously[4], the dose was changed not by the irradiation time, but by irradiation for one hour at

TABLE I. INITIAL CONCENTRATIONS OF OXYGEN AND FERRIC ION AT 25°C IN 10^{-3} M

Treatment	Oxygen in water	Ferric ion in ferrous-cupric system		
		(0)*	(10^{-3})*	(10^{-2})*
N_2-saturated	0.019	0.2	0.2	0.2
Non-treated	0.37	0.2	1.3	1.6
O_2-saturated	1.2	0.2	2.1	2.3

Note: The concentration of cupric ion is listed in ( )*.

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[1] A. Danno, M. Omura, H. Hotta, H. Hirakawa, G. Tsuchihashi and I. Yamaguchi, "The 7th Conf. Hot Lab. and Equipment", Session 6, Cleveland, Ohio, 1959.

[2] G. V. Taplin, "Radiation Dosimetry", Ed. by G. J. Hine and G. L. Brownell, Chap. 8 Academic Press, New York (1956).

[3] P. V. Phung and M. Burton, *Radiation Research*, 7, 199 (1957).

[4] H. Hotta and A. Terakawa, This Bulletin, to be published.

[5] T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc.*, A211, 127 (1952).

[6] J. T. Harian and E. J. Hart, *Radiation Research*, 9, 127 (1958).

[7] H. Hotta and K. Shimada, This Bulletin, to be published.

[8] E. P. Hart and P. D. Walsh, *Radiation Research*, 1, 342 (1954).

[9] Am. Public Health Assoc., "Standard Methods for the Examination of Water, Sewage and Industrial Wastes", Am. Public Health Assoc., New York (1955), p. 252.

[10] N. A. Lange, "Handbook of Chemistry", Handbook Publishers, Sandusky, Ohio (1956), p. 1093.

TABLE II. YIELD OF FERRIC ION IN VARIOUS SOLUTIONS

Run	Solute in M			Treatment	G-value	
	Ferrous ammonium sulfate	Cupric sulfate	Sulfuric acid		at low dose	at high dose
a	0.04	0	0.4	O_2-saturated	15.60 ± 0.06	8.16 ± 0.03
b	0.04	0	0.4	Non-treated	15.55 ± 0.02	7.94 ± 0.31
c	0.04	0	0.4	N_2-saturated	8.07 ± 0.12	
d	0.04	0.001	0.4	O_2-saturated	14.2	6.44 ± 0.2
e	0.04	0.001	0.4	Non-treated	6.50 ± 0.15	
f	0.04	0.001	0.4	N_2-saturated	6.51 ± 0.07	
g	0.04	0.01	0.4	O_2-saturated	2.60 ± 0.14	
h	0.04	0.01	0.4	Non-treated	$2.4\ \pm0.05$	
i	0.04	0.01	0.4	N_2-saturated	2.34 ± 0.08	

various positions, namely, various dose rates. Therefore, the abscissa of all figures gives a value of the dose in r as well as a value of the dose rate in r/hr. The deviation of the observed values from the curve is partially due to the uncertainty of the absolute dose rate at a respective position, for samples were not irradiated at a fixed position as is usually done. The absolute dose rate was determined by the ceric dosimeter, which was corrected up to about $1.4\times10^5 r$ by the oxygen-saturated ferrous dosimeter.

The amount of ferric ion was measured by optical density at 304 mμ ($\varepsilon=2205$ at 25°C). It should be noticed that the ferrous ion was fairly oxidized due to the addition of cupric ions in the presence of oxygen without irradiation as listed in Table I, in which the mean initial concentration of ferric ions in the irradiated solutions is shown[11].

Results

Ferrous Solutions.—The result of aqueous 0.04 M ferrous ammonium sulfate solution containing 0.8 N sulfuric acid and 0.001 M sodium chloride for a) oxygen-saturated, b) non-treated and c) nitrogen-saturated cases are shown in Fig. 1. Their G-value is listed with the composition of the solution in Table II. 0.001 M sodium chloride was added as a stabilizer as usual.

Ferrous-cupric Solutions. — The results of aqueous 0.04 M ferrous ammonium sulfate solution containing 0.8 N sulfuric acid and 0.001 M cupric sulfate for the above three treatments, d), e) and f), are shown in Fig. 2. Moreover, the results of the similar solution containing 0.01 M cupric sulfate for the same three treatments, g), h) and i), are shown in Fig. 3. Their G-value is also listed with the composition of the solution in Table II. The data below about $4\times10^4 r$ were unreliable.

The present results indicate that the non-treated solution is useful as a chemical dosimeter for high doses with good accuracy at

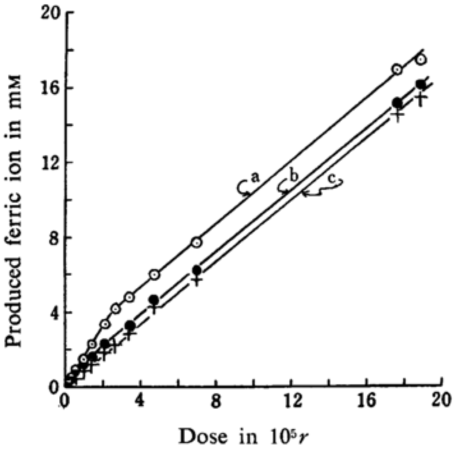

Fig. 1. The oxidation of ferrous ion in 0.04 M ferrous sulfate acidic aqueous solution for (a) oxygen-saturated, (b) non-treated and (c) nitrogen-saturated cases.

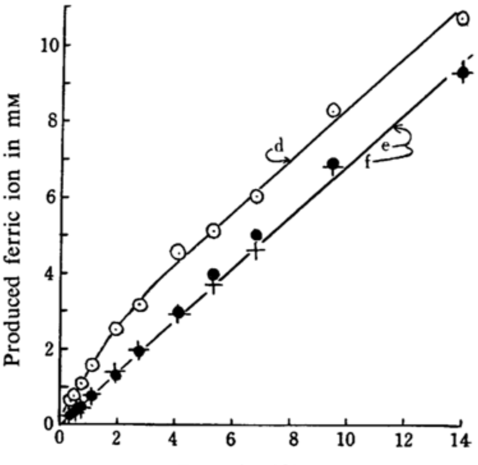

Fig. 2. The oxidation of ferrous ion in 0.04 M ferrous sulfate-0.001 M cupric sulfate acidic aqueous solution for (d) oxygen-saturated (⊙), (e) non-treated (●) and (f) nitrogen-saturated (+) cases.

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[11] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XIV, Longmans, London (1935), p. 267.

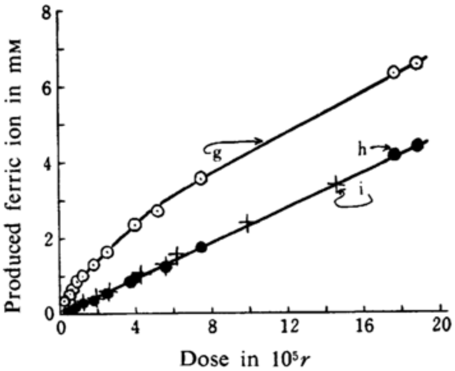

Fig. 3. The oxidation of ferrous ion in 0.04 M ferrous sulfate-0.01 M cupric sulfate acidic aqueous solution for (g) oxygen-saturated (⊙), (h) non-treated (●) and (i) nitrogen-saturated (+) cases.

least up to $2\times10^6 r$ from $4\times10^4 r$. However, the G-value is dependent on the composition of the solution[12].

Discussion

For the primary chemical effects of ionizing radiation on aqueous system,

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ H \text{ and } OH \qquad (0)$$

the yield of the above products per eV., namely, their G-value by Co-60 gamma-rays in the 0.8 N sulfuric acid aqueous system is considered to be $G(H_2)=0.39$, $G(H_2O_2)=0.78$, $G(H)=3.70$ and $G(OH)=2.92$, respectively[13]. The G-value of the following reactions, which is shown in parentheses at the right of each equation, is estimated from the above values. The suffix of G denotes the order of reactions included in the G-value. For example, $G_{2,1}$ means the total G-value of reaction 2 and reaction 1.

The action of OH and H_2O_2 in ferrous solution is

$$Fe^{2+}+OH=Fe^{3+}+OH^- \qquad (G_1=2.92) \qquad (1)$$

and

$$Fe^{2+}+H_2O_2=Fe^{3+}+OH^-+OH \qquad (G_{2,1}=2\times0.78) \qquad (2)$$

However, the action of the H atom is very different according to the condition as follows.

Yield of Ferric Ion in the Absence of Oxygen.—In the absence of oxygen, the action of the H atom in the acidic solution is

$$H+H^+=H_2^+ \qquad (G_3=3.70) \qquad (3)$$

and then

$$Fe^{2+}+H_2^+=Fe^3+H_2 \qquad (G_4=3.70) \qquad (4)$$

Therefore, the total yield of ferric ion in the absence of oxygen is equal to $G_1+G_{2,1}+G_4=8.18$, as usual. In fact, the observed values at high dose for solutions a), b) and c) in Table I are in good agreement with this value.

In the presence of cupric ion, it reduces the yield of ferric ion by the reaction

$$Cu^2+H=Cu^++H^+ \qquad (5)$$

and then

$$Fe^3+Cu^+=Fe^{2+}+Cu^{2+} \qquad (G_5=G_6) \qquad (6)$$

Reaction 5 competes with reaction 4 within $G_4+G_5=3.70$. Even if the cuprous ion reacts with OH or H_2O_2 in addition to reaction 6, the effect of these reactions on the yield of the ferric ion is equivalent to reaction 6. Therefore, these effect are represented by G_6.

According to the above interpretation, the G_5 for solutions f) and i) are 0.85 and 2.9, respectively. On the assumption that

$$G_4/G_5=k_4K_3(H^+)(Fe^{2+})/k_5(Cu^{2+}) \qquad (i)$$

as pointed out by Hart[12], where k, K and parentheses denote rate constant, equilibrium constant and concentration, respectively, the ratios obtained, $k_4K_3(H^+)/k_5$ are 0.084 and 0.069 for solutions f) and i), respectively. If K_3 is assumed to be 100 l./mol. according to Hart[12], the ratio, k_4/k_5 is estimated to be about 10^{-3}. It is confirmed from this value that the cupric ion is very reactive for the H atom in comparison with the ferrous ion.

Yield of Ferric Ions in the Presence of Oxygen.—In the presence of oxygen, the action of H atom in the acidic solution is

$$H+O_2=HO_2 \qquad (7)$$

$$Fe^{2+}+HO_2=Fe^{3+}+HO_2^- \qquad (8)$$

and then

$$HO_2^-+H^+=H_2O_2 \quad (G_{7,8,9,2,1}=3\times3.70) \qquad (9)$$

Therefore, the total yield of ferric ions in the presence of oxygen is equal to $G_1+G_{2,1}+G_{7,8,9,2,1}=15.58$, as usual.

In the ferrous and cupric solution, reaction 8 competes with reaction 5 and the reaction

$$Cu^{2+}+HO_2=Cu^++H^++O_2 \qquad (10)$$

and the rate of the consumption of oxygen by reaction 8 is expressed by the equation

$$G(-O_2)_8=G(H) \times\frac{1}{1+\dfrac{k_5(Cu^{2+})}{k_7(O_2)}}\times\frac{1}{1+\dfrac{k_{10}(Cu^{2+})}{k_8(Fe^{2+})}} \qquad (ii)$$

as pointed out by Hart[12]. Therefore, the circumstance of these reactions is complicated.

On the other hand, if $\varDelta G$ is considered to be the difference between the observed G-value, G°, and the ideal one, G^1, obtained on the

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

[13] A. O. Allen, 1st Intern. Conf. Peaceful Uses of Atomic Energy", Vol. 7, Geneva, (1956), p. 514.

assumption that cupric ion scavenges all H atoms, it is expressed as

$$\Delta G = G^{\circ} - G^{1} = 4G_8 \qquad \text{(iii)}$$

and

$$G^{1} = G_1 + G_{2,1} - G_{5+10} = 0.78$$

Therefore, the consumption of oxygen against the dose in solutions d) and g) is estimated from Eq. iii as shown in Fig. 4. The respective G-value of the elementary reactions at the initial stage for both solutions is obtained from the initial slope in Fig. 4 as listed in Table III.

TABLE III. YIELD OF ELEMENTARY REACTIONS AT THE INITIAL STAGE FOR OXYGEN-SATURATED FERROUS-CUPRIC SOLUTIONS

Run	Cupric ion	G_8	G_{5+10}	G°
d	10^{-3} M	3.34	0.34	14.22
g	10^{-2} M	2.64	1.06	11.34

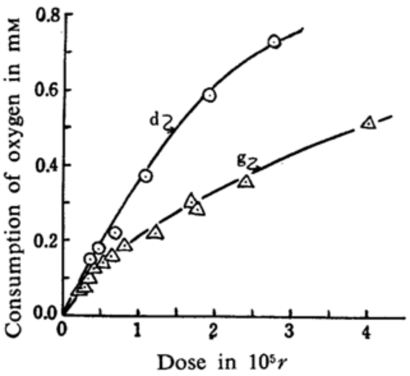

Fig. 4. The consumption of oxygen in oxygen-saturated 0.04 M ferrous sulfate acidic aqueous solution containing (d) 0.001 M and (g) 0.01 M cupric sulfate.

The linearity of the curve at the initial stage in Fig. 4 indicates that the ratios, $k_5(\mathrm{Cu}^{2+})/k_7(\mathrm{O}_2)$ and $k_{10}(\mathrm{Cu}^{2+})/k_8(\mathrm{Fe}^{2+})$ should be constant at this stage in Eq. ii, that is,

$$\frac{k_{10}}{k_8} = \frac{G_{10}(\mathrm{Fe}^{2+})}{G_8(\mathrm{Cu}^{2+})} \qquad \text{(iv)}$$

When the contribution of reaction 5 is assumed to be comparatively slight, $G_{10} \approx G_{5+10}$, in solution d), in which the concentration of cupric ions is low, the ratio, k_{10}/k_8 is estimated to be smaller than 4 from Eq. iv on using the values in Table III. According to Hart[12], the ratio, k_{10}/k_8 is about 50 for the aqueous solution of 10^{-3} M ferrous sulfate and 0.01 N sulfuric acid containing cupric ions between 10^{-6} M and 10^{-3} M. The disagreement between them may be the pH of the solution.

From the present experiment, 10^{-3} M cupric ion is sufficient to suppress the effect of oxygen dissolved naturally. However, it can not be concluded directly from this fact that oxygen is not concerned with the reaction in solution e). It is because the concentration of $\mathrm{HO_2}$ radical should be sufficient for a ferrous ion to react with this radical from the result of solution b), and the G-value of reaction 10 is not so great as to suppress reaction 8 even in solution d) as listed in Table III. Therefore, it can not be understood why there is no difference between solutions e) and f) in spite of the above condition. However, if the cupric ion scavenges $\mathrm{HO_2^-}$ ion by the reaction

$$\mathrm{Cu^{2+} + HO_2^- = Cu^+ + HO_2} \qquad (11)$$

and then $\mathrm{HO_2}$ radical or $\mathrm{H_2O_2}$ molecule by reaction 9 reacts with ferrous and cupric ions as mentioned already, the effect of oxygen, namely, the difference between reactions 4 and 8 can be actually disregarded. The initial concentration of oxygen in solution e), supposed from Table I, is smaller than the concentration of oxygen at the bend point of solution a), supposed from Fig. 1 and Table I.

Summary

The oxidation of ferrous ion in ferrous-cupric acidic aqueous solution by Co-60 gamma-rays was studied in order to find a good chemical dosimeter for high doses. Consequently, it is found that the non-treated solution containing the 10^{-3} M cupric ion is useful for this purpose, for this amount of cupric ions is sufficient to suppress the effect of oxygen, and that the G-value of the ferrous-cupric system is dependent on the composition of the solution. The suppression can be explained by the scavenging of the $\mathrm{HO_2^-}$ ion by cupric ions. Furthermore, some discussions regarding the system are given in the present paper.

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