Studies on the *G*($Fe^{3+}\rightarrow Fe^{2+}$)-value in the Radiolysis Caused by $^{6}Li(n,\alpha)T$ Reaction in Lithium Tris(oxalato)ferrate(III)

Junko Akashi, Tomoko Kojima, Yoshio Uchida, and Hirotoshi Sano*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukasawa, Setagaya, Tokyo 158

(Received October 13, 1984)

The *G*-values for the reduction of iron(III) to iron(II) state caused by $^{6}Li(n,\alpha)T$ reaction in $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ and in anhydrated $Li_3[Fe(C_2O_4)_3]$ were determined by taking into account the saturation of the effect of increasing neutron fluence. The contribution of the fast neutrons and γ-rays in a nuclear reactor to the reduction was estimated by using a cadmium tube, and by using the results estimated in the ^{60}Co γ-ray irradiation, respectively. The *G*($Fe^{3+}\rightarrow Fe^{2+}$)-value in the radiolysis caused by $^{6}Li(n,\alpha)T$ reacation in $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ is larger than that in the γ-ray radiolysis, and is also larger than the *G*-value for anhydrated $Li_3[Fe(C_2O_4)_3]$, suggesting that the radiolysis of the water of crystallization contributes to the reduction of the iron(III) species.

It has been pointed out elsewhere that the chemical effects of EC decay in several ^{57}Co-doped coordination compounds are considered to be caused by a nucleogenic local radiolysis in the compound.[1] In our previous papers,[2,3] the reduction of the iron(III) species to the iron(II) species in lithium tris(oxalato)ferrate(III) by thermal-neutron irradiation was studied by means of Mössbauer spectroscopy. The reducing effets were attributed to a radiolytic process caused by the $^{6}Li(n,\alpha)T$ reaction.

The present paper describes the details of the effects of the $^{6}Li(n,\alpha)T$ reaction on the hydrated and anhydrated lithium tris(oxalato)ferrate(III), including an estimation of the *G*-values for reductions in those systems which are important for a better understanding of the processes caused by the $^{6}Li(n,\alpha)T$ reaction in connection to the chemical effects in the blanket materials in a fusion reactor. In order to estimate the *G*-value, the dependence of the areal intensity ratio of iron(III) to iron(II) in the Mössbauer spectra were studied on the irradiation time and on the thermal-neutron fluence rate. The effects of the fast neutrons and γ-rays concomitant in the reactor on the reduction were also determined.

Experimental

Hydrated lithium tris(oxalato)ferrate(III), $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$, sodium tris(oxalato)ferrate(III), $Na_3[Fe(C_2O_4)_3]\cdot 5H_2O$ and potassium tris(oxalato)ferrate(III), $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ were synthesized in the conventional ways.

The particle size of the samples was furnished to 200—300 mesh throughout the present work. Anhydrated $Li_3[Fe(C_2O_4)_3]$ was prepared by heating the $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ at 400 K for 10-30 min in air.

Each 100 mg of the sample heat-sealed under nitrogen in a polyethylene envelope was irradiated either within or without a 0.5-mm thick cadmium tube in a 100-kW TRIGA MarkII reactor at the Institute for Atomic Energy, Rikkyo University.

The irradiated samples were kept in liquid nitrogen until the Mössbauer spectroscopic measurements were carried out. Mössbauer spectra were recorded with a constant-acceleration type spectrometer at 80 K. Isomer-shift values were reported with respect to metallic iron foil.

γ-Ray irradiations were carried out using a ^{60}Co-source, at the Institute of Physical and Chemical Researches, at a dose rate of 9,780 rad min^{-1} (H_2O).

Results and discussion

The Mössbauer spectrum of a sample irradiated at a thermal-neutron fluence rate of 5×10^{11} n s^{-1} cm^{-2} and at a fast-neutron fluence rate of 4.5×10^{10} n s^{-1} cm^{-2} for 2 h within the cadmium tube, which absorbs neutrons with the energy of less than 0.4 eV, is shown in Fig. 1 (b). The spectra of the sample irradiated at the same fluence rates of thermal and fast neutrons for 4 h within the cadmium tube are compared in Fig. 1 (c). A distinctive change is not found in the irradiated sample compared with the spectrum of the non-irradiated sample (Fig. 1 (a)), except for a small peak component ascribed to iron(II) species as found in Fig. 1 (c). In the spectrum shown in Fig. 1 (c), the areal intensity ratio of iron(II) to the total iron species is estimated to be less than 0.09. As shown in Fig. 1 (d), the ratio in the spectrum of the neutron-irradiated $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ in the same irradiation conditions as in the case of Fig. 1(c) is estimated to be 0.67. The ratio is much larger without the cadmium tube than that obtained within the tube as found in Fig. 1(c), suggesting that the reduction of iron(III) to iron(II) observed in the neutron-irradiated $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ is mainly attributed to the effect of thermal neutrons. Figures 2 (a) and (b) show the Mössbauer spectra of $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ subjected to γ-rays of the total dose of 4×10^{7} rad and 1.0×10^{8} rad, respectively, at a dose rate of 9,780 rad min^{-1} (H_2O). Although the total dose in the reactor for the experiment of Fig. 2 (a) is estimated to be about 7 times larger than that in the irradiation conditions used for Fig. 1 (c), it is still not as remarkable a

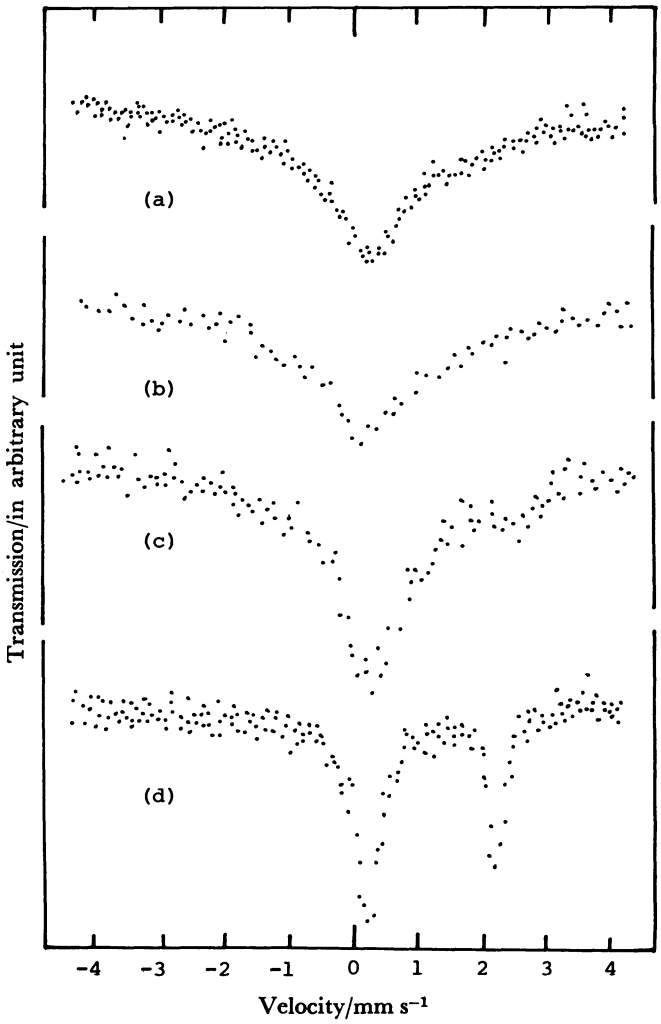

Fig. 1. Mössbauer spectra at 80 K of (a) unirradiated, (b) neutron-irradiated within a cadmium tube, (2 h), (c) neutron-irradiated within a cadmium tube, (4 h), and (d) neutron-irradiated without a cadmium tube, (4 h), $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$. (thermal neutron fluence rate: 5×10^{11} n s^{-1} cm^{-2} fast neutron fluence rate: 4.5×10^{10} n s^{-1} cm^{-2}).

TABLE 1. G-VALUES FOR REDUCTION OF TRIS(OXALATO)-FERRATE(III) CRYSTALS BY ^{60}Co γ-RAY IRRADIATIONS

Compound	$G(Fe^{3+}\rightarrow Fe^{2+})$
$Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$	8.4
$Na_3[Fe(C_2O_4)_3]\cdot 5H_2O$	10.1
$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$	15.1
$(NH_4)_3[Fe(C_2O_4)_3]\cdot 2H_2O$	16.1
$Li_3[Fe(C_2O_4)_3]$	7.3

TABLE 2. AREAL INTENSITY RATIOS OF IRON(III) SPECIES TO TOTAL IRON SPECIES IN SEVERAL IRRADIATION CONDITIONS IN LITHIUM TRIS(OXALATO)FERRATE(III)

Fluence rate n s^{-1} cm^{-2}	Irradiation time h				
	0.5	1	2	4	6
5×10^{11}	0.82	0.64	0.44 0.45*	0.34	—
1.2×10^{12}	—	—	0.32 0.33*	0.05	0.01

* Irradiated at 200 K, others at an ambient temperature in a reactor.

reduction in Fig. 2 (a) as is found in Fig. 1 (c). Based on the linear dependence of the areal-intensity ratio of the iron(II) species to the total iron species in the spectra on the γ-ray irradiation time, the G-value for the reduction of iron(III) in $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ caused by the γ-ray irradiation is estimated to be 8.4.

The $G(Fe^{3+}\rightarrow Fe^{2+})$-value for γ-ray-irradiated potassium, sodium and ammonium salts obtained in a similar way are listed in Table 1, together with that of the lithium salt for the sake of comparison. The value for the lithium salt is a little smaller than those for the potassium, sodium and ammonium salts.

As in the case of Fig. 1 (d), the neutron-irradiated potassium and sodium tris(oxalato)ferrate(III) at the same neutron irradiation condition also show little contribution of the iron(II) species as found in Fig. 3, which is similar to the result found in ammonium salt reported in the previous result.[2] The results indicate that the G-value is negligibly small for the reduction caused by γ-rays in the lithium tris(oxalato)ferrate(III) during irradiation in the reactor for 4 h at the same neutron fluence rate as in the case of Fig. 1 (d).

The areal-intensity ratios of the iron(III) to the total iron species in several neutron-irradiation conditions for $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ are listed in Table 2.

The ratio in the neutron-irradiated $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ at an ambient temperature in the reactor is similar to that in the sample irradiated at 200 K (as cited in Table 2), indicating that the restoration of the iron(III) species through the thermal annealing during and after the $^6Li(n,\alpha)T$ reaction is negligibly small in the system. The ratios for neutron-irradiated $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ decrease linearly neither with increased irradiation time nor with total neutron-fluence, which can be explained by assuming the presence of a saturation process in the reduction, *i.e.*, the iron(II) species produced by the $^6Li(n,\alpha)T$ reaction is practically not affected by the thermal-neutron irradiation. By simply applying the first-order reaction rate, the number of iron(III) atoms affected by the $^6Li(n,\alpha)T$ reaction is expected to follow the equations,

$$dN/d(nt) = -kN, \quad N=N_0\exp(-knt)$$

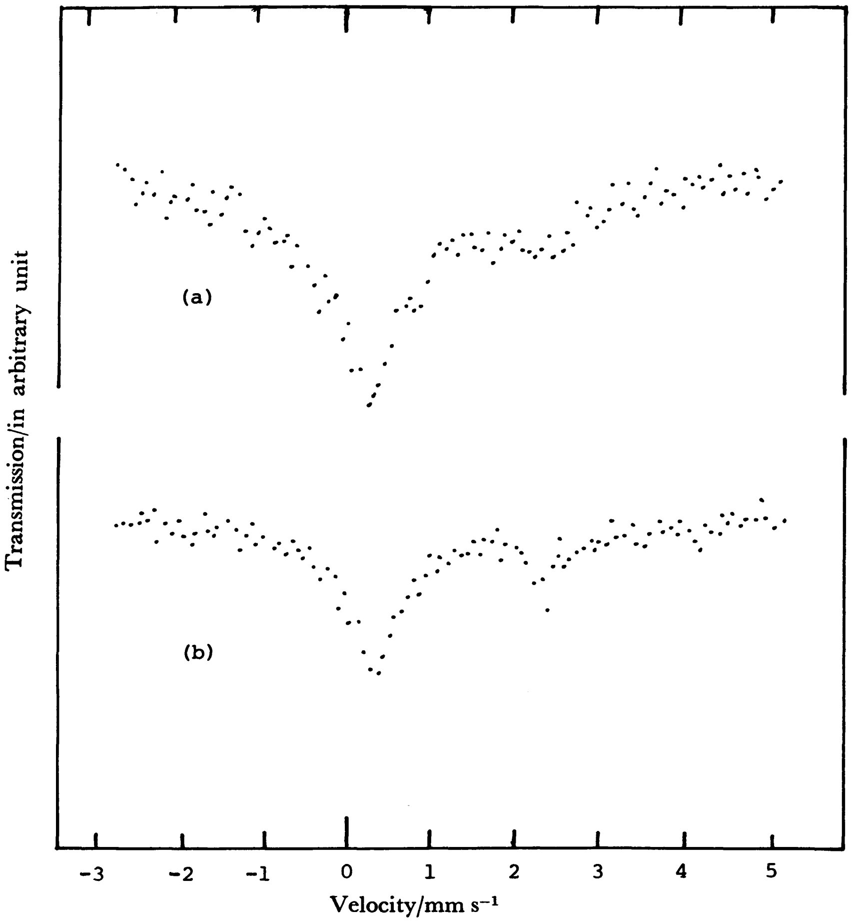

Fig. 2. Mössbauer spectra at 80 K of (a) γ-irradiated (4×10^7 rad) and (b) γ-irradiated (1.0×10^8 rad) $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$.

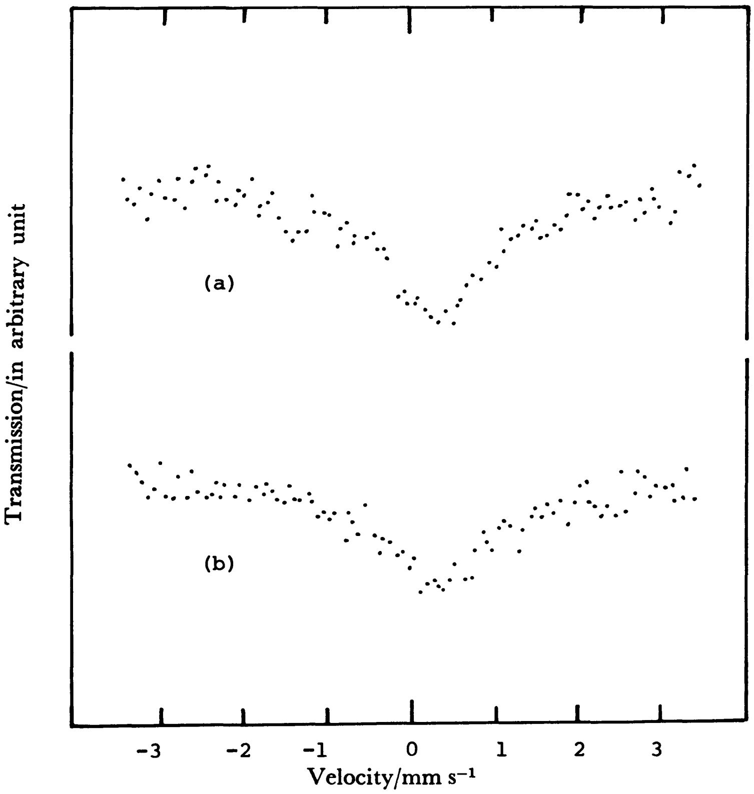

Fig. 3. Mössbauer spectra at 80 K of neutron-irradiated (5×10^{11} n s^{-1} cm^{-2}, 4 h) (a) $Na_3[Fe(C_2O_4)_3]\cdot5H_2O$ and (b) $K_3[Fe(C_2O_4)_3]\cdot3H_2O$.

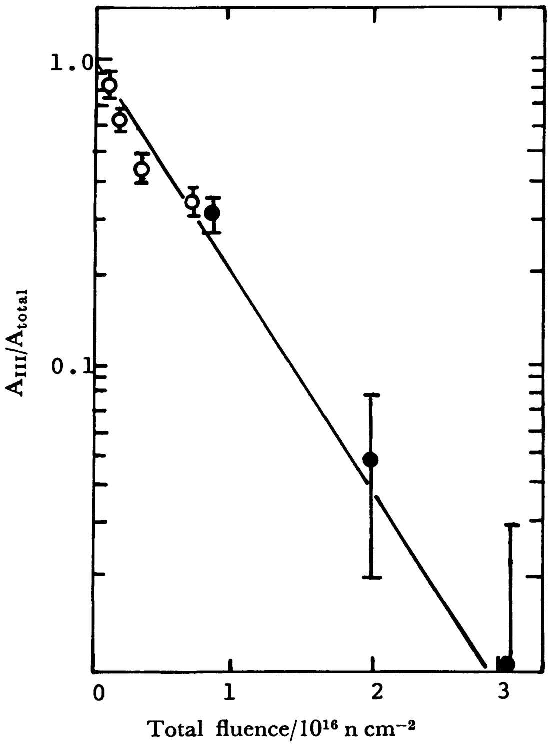

Fig. 4. Areal intensity ratio of Fe(III) to total iron species against thermal neutron fluence in Mössbauer spectra of $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$.

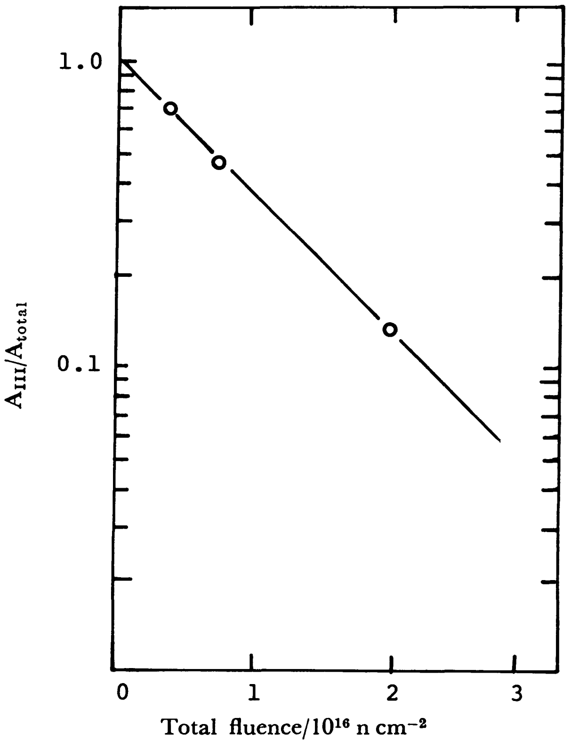

Fig. 5. Areal intensity ratio of Fe(III) to total iron species against thermal neutron fluence in Mössbauer spectra of $Li_3[Fe(C_2O_4)_3]$.

where N: the number of the iron(III) species.
n: thermal neutron fluence rate.
t: irradiation time.
k: rate constant.
N_0: initial number of the iron(III) species.

As a plot of the logarithm of the ratio of the iron(III) species to the total iron species gives practically a straight line against the increased neutron fluence, as shown in Fig. 4. The hypothetical equation seems to be useful to interpret the experimental results. The overall $G(Fe^{3+}\rightarrow Fe^{2+})$-value for the reduction in $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$ caused by the $^6Li(n,\alpha)T$ reaction is estimated to be 18.2 from the gradient of the line in Fig. 4. The G-value for the reduction of an anhydrated compound caused by the $^6Li(n,\alpha)T$ reaction is estimated to be 10.1 based on a similar plot, as shown in Fig. 5.

The G-value corresponds to about half of that obtained for the hydrated one, even after the small increases in the concentrations of iron and lithium compared with those in the hydrated compound. The results imply that the hydrated compound should more easily be subjected to the reduction caused by the $^6Li(n,\alpha)T$ reaction than the anhydrated one, and that the radiolytic products of water of crystallization should play an important role in the reduction of iron(III) to iron(II).

The small deviations of the experimental points from the line found in Fig. 4, may be ascribed to the possible decrease of water of crystallization in the sample during the irradiation at the accumulated fluence values. The G-value for the reduction caused by the $^6Li(n,\alpha)T$ reaction is estimated to be 19.9 from the line component derived from the data in the lower fluence region. These obtained G-values are summerized in Table 3.

Table 3. G-values for the reduction of the iron caused by the $^6Li(n,\alpha)T$ reaction in lithium tris(oxalato)ferrate(III)s

Compound	$G(Fe^{3+}\rightarrow Fe^{2+})$	
$Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$	19.9	estimated from areal intensity of the Mössbauer spectrum in early stage of irradiation
	18.2	estimated from log plot as shown in Fig. 4
$Li_3[Fe(C_2O_4)_3]$	10.1	estimated from log plot as shown in Fig. 5

The $G(Fe^{3+}\rightarrow Fe^{2+})$-value for the hydrated lithium tris(oxalato)ferrate(III) in the $^6Li(n,\alpha)T$ reaction is about 2 times larger than that in the γ-ray-radiolysis using a ^{60}Co source, as shown in Tables 1 and 3. The difference should be attributed to the high values of the linear energy transfer (LET) of alpha and tritium particles emitted by the ^{6}Li(n,α)T reaction. The results reveal that a higher density of electrons and excited species, such as radicals or ions, produced by the high-energy particles is more effective in causing the reduction of the iron(III) to the iron(II) species in lithium tris(oxalato)ferrate(III).

References

1) H. Sano, M. Harada, and K. Endo, *Bull. Chem. Soc. Jpn.*, **51**, 2583 (1978).

2) J. Akashi, M. Katada, and H. Sano, *Chem. Lett.*, **1982** 785.

3) J. Akashi, Y. Uchida, T. Kojima, M. Katada, and H. Sano, *Bull. Chem. Soc. Jpn.*, **57**, 1076 (1984).