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Mössbauer Spectroscopic Studies of the Effects of the ^{6}Li(n, α)T Reaction in Lithium Tris(oxalato)ferrate(III)

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The chemical effects of the ^{6}Li(n,α)T reaction in lithium tris(oxalato)ferrate(III) crystals were examined by means of Mössbauer spectroscopy. Neutron irradiations were carried out under different conditions in order to clarify the mechanism of the effects. The reduced iron(II) species observed in the spectrum of $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$, subjected to neutron irradiation (8.6×10^{15} n cm^{-2}) at 200 K, shows a larger Q.S. value than that in the spectrum of the sample neutron-irradiated at an ambient temperature (300—320 K) in a reactor, suggesting that the initially produced iron(II) species changes into another iron(II) species during the irradiation at the ambient temperature. A species identical with the initial iron(II) species produced in the neutron irradiation was found to be prepared by the pyrolysis of $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$. A comparison of neutron-irradiated hydrous and anhydrous $Li_3[Fe(C_2O_4)_3]$ suggests that the change in the iron(II) species is influenced by the existence of crystal water.

Mössbauer spectroscopy is one of the most useful tools in studying the chemical states nondestructively in solids. Based on the results of Mössbauer spectroscopic studies, it has been reported that iron(III) oxalate is reduced by γ-ray irradiation and that the results can be interpreted by the formation of iron(II) oxalate,[1] *i.e.*;

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2$$

Temperley suggested that the γ-ray-radiolysis of ammonium and sodium tris(oxalato)ferrate(III) could be explained by assuming this reaction;[2]

$$2M_3[Fe(C_2O_4)_3] \rightarrow 2FeC_2O_4 + 3M_2C_2O_4 \rightarrow 2CO_2,$$

while the iron(II) species observed in the Mössbauer spectrum of γ-ray-irradiated potassium tris(oxalato)ferrate(III) was not definitely assigned to an iron(II) oxalate.[2] Bancroft *et al.* proposed this reaction;

$$2(K_3[Fe(C_2O_4)_3]\cdot 3H_2O) \rightarrow 2K_2[Fe(C_2O_4)_2(H_2O)_2] + K_2C_2O_4 + 2CO_2 + 2H_2O,$$

for the reduction induced by the γ-irradiation of the tris(oxalato)ferrate(III).[3]

Studies of the photo-irradiated potassium tris(oxalato)ferrate(III) by using Mössbauer and infrared absorption spectroscopy have also revealed that several kinds of reduced iron species other than $FeC_2O_4\cdot 2H_2O$ were produced.[4]

Recently, we ourselves reported that a reduced iron(II) species was found in the Mössbauer spectrum taken for the $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ sample subjected to the ^{6}Li(n,α)T reaction,[5] although the mechanism of the formation of iron(II) species had not yet been clarified in detail.

In the present paper, the species produced by the ^{6}Li(n,α)T reaction in lithium tris(oxalato)ferrate(III) were compared with those produced by thermal decomposition in order to clarify the processes caused by the ^{6}Li(n,α)T reaction.

Experimental

$Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ was prepared by a conventional method. The particle size of the sample was adjusted to 200—350 mesh throughout this work. The difference in the effects of the particle size will be shown elsewhere. Thermogravimetry and differential scanning calorimetry were carried out for $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ both in air and under nitrogen. The heating rate was kept at 5 K min^{-1}. Anhydrous $Li_3[Fe(C_2O_4)_3]$ was prepared by allowing the hydrous compound to stand for 10 min in an oven at 450 K in air. The anhydrous compound was kept in a desiccator over P_2O_5 to avoid moisture. The neutron irradiation of each 100-mg portion of the sample heat-sealed in a polyethylene envelope was carried out in a 100-kW Triga Mark II reactor at the Atomic Energy Institute of Rikkyo University. The irradiated samples were kept in liquid nitrogen until IR and Mössbauer measurements has been carried out.

In the thermal decomposition of $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$, a brown powder was obtained by putting the sample in an oven at 525—545 K for 5—10 min, either in air or under nitrogen, while a yellow powder was obtained when the sample was put in an oven at 500—510 K for 5—10 min under nitrogen.

The Mössbauer spectra were determined by using a constant-acceleration-type spectrometer. The isomer-shift values were reported with respect to iron foil. The infrared spctra were taken by the KBr method.

Results and Discussion

Mössbauer spectra of the neutron-irradiated (for 2 h at a fluence rate of 1.2×10^{12} n s^{-1} cm^{-2}) $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ are shown in Fig. 1. The new doublet produced by the ^{6}Li(n,α)T reaction shows a different Q.S. value depending on the temperature during the irradiation. The doublet A in Fig. 1(a), where the neutron irradiation was carried out at 200 K, has a larger Q.S. value (2.63 mm s^{-1}) than that (1.97 mm s^{-1}) of the doublet B shown in Fig. 1(b), where the neutron irradiation was carried out at the ambient temperature in the reactor (roughly estimated to be 300—320 K). The isomer-shift values of these doublets coincide with each other within the limits of experimental error. Figure 1(c) shows the spectrum of the same sample as that shown in Fig. 1(a) after it had been allowed to stand for 5 months at room temperature (295—298 K). The doublet A decreases in intensity, and a doublet appears at the same position as that of the doublet B. The results suggest that an unstable species which has a larger Q.S. value changes into a stable species during the irradiation at the ambient temperature or during storage for a long time at room temperature.

The results of the thermogravimetry and differential

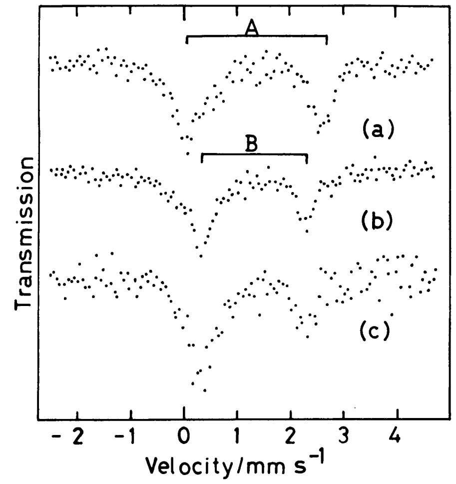

Fig. 1. Mössbauer spectra at 80 K of (a) neutron-irradiated (1.2×10^{12} n s^{-1} cm^{-2}, 2 h, at 200 K) $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$, (b) neutron-irradiated (1.2×10^{12} n s^{-1} cm^{-2}, 2 h, at an ambient temperature) $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$, and (c) neutron-irradiated (1.2×10^{12} n s^{-1} cm^{-2}, 2 h, at 200 K) $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$ after storage for 5 months at room temperature.

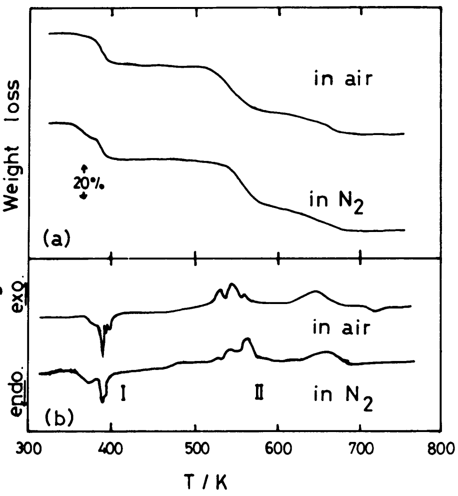

Fig. 2. (a) TG curves for $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$ in air and under nitrogen, and (b) DSC curves for $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$ in air and under nitrogen.

scanning calorimetry of $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$, both in air and under nitrogen, are shown in Fig. 2. As is shown by the TG curves, the hydrous complex evolves 4.5 mol of water endothermically in stage I. The split peak in the DSC curves of dehydration indicates that the water molecules are not held uniformly in the crystal lattice. On the basis of the results, it is concluded that the dehydration ocurrs at a higher temperature in lithium tris(oxalato)ferrate(III) than the temperature reported for the corresponding potassium salt.[6–9)]

For $K_3[Fe(C_2O_4)_3]\cdot3H_2O$, a decomposition reaction such as

$$K_3[Fe(C_2O_4)_3] \rightarrow K_2[Fe(C_2O_4)_2] + 1/2K_2C_2O_4 + CO_2$$

was proposed for the second stage under nitrogen, where one mol of CO_2 was evolved.[6–9)] On the contrary, a weight change corresponding to two moles of CO_2 was observed in stage II of the thermal decomposition of $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$, either in air or under nitrogen.

A Mössbauer spectrum of thermal-decomposition product in stage II in air is shown in Fig. 3(a). When the decomposition occurs at 525—545 K, a doublet ascribed to a high-spin iron(III) species (I.S.=0.44, Q.S.=0.95 mm s^{-1}) is observed. The same species was also found in the spectrum of the sample decomposed under nitrogen in the same temperature range. As the weight loss of the sample in stage II corresponds to two moles of CO_2, the formation of $Li[Fe(III)(C_2O_4)_2]$ may be suggested for this stage.

A Mössbauer spectrum at 80 K of the sample thermally decomposed at 500—510 K under nitrogen is shown in Fig. 3(b). The Mössbauer parameters of the iron(II) species produced thus coincide with those of

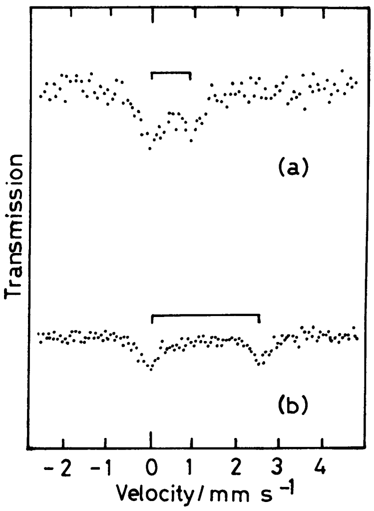

Fig. 3. Mössbauer spectra at 80 K of $Li_3[Fe(C_2O_4)_3]\cdot4.5H_2O$ (a) decomposed at 525—545 K in air, and (b) decomposed at 500—510 K under nitrogen.

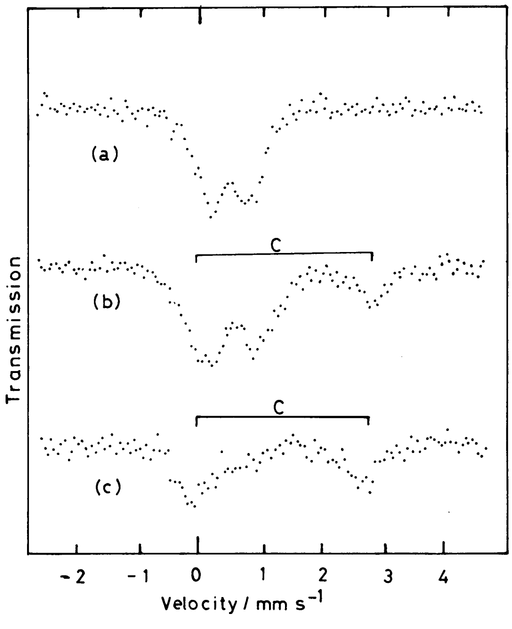

Fig. 4. Mössbauer spectra at 80 K of (a) unirradiated, (b) neutron-irradiated (5×10^{11} n s^{-1} cm^{-2}, 2 h), and (c) neutron-irradiated (1.2×10^{12} n s^{-1} cm^{-2}, 4 h) anhydrous $Li_3[Fe(C_2O_4)_3]$.

the doublet A in Fig. 1. The formation of this yellow product may correspond to a small heat change without any remarkable change in the weight at 465 K under nitrogen. The color change is accompanied by a reduction of iron(III) to iron(II), as is observed in the thermal decomposition of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ at 393 K.⁶⁾

A Mössbauer spectrum at 80 K of anhydrous $Li_3[Fe(C_2O_4)_3]$ is shown in Fig. 4(a). The dehydration of the sample was confirmed by measuring the weight loss of the sample by heating and IR spectrum of the sample; the weight loss of the compound coincides with the theoretical value within 2%. Although the Mössbauer spectrum of $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ consists of a broad single peak due to magnetic relaxation, the spectrum of the anhydrous compound consists of an asymmetric doublet with a narrower line-width. The difference between the Mössbauer spectra of the hydrous and anhydrous lithium tris(oxalato)ferrate(III) implies that the spin-spin relaxation time decreases in the anhydrous compound compared with the hydrous compound because of the decreased average Fe-Fe distance.

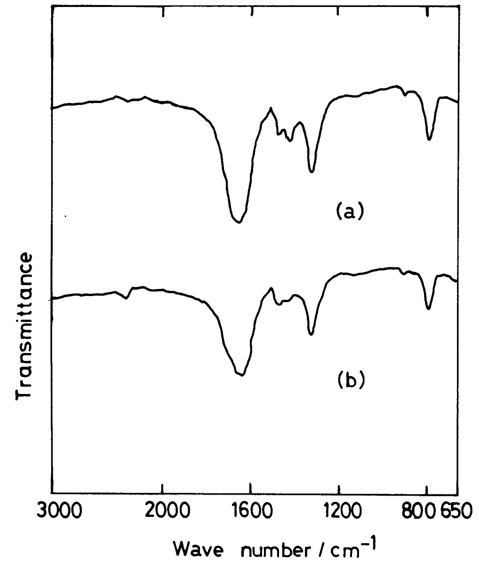

Fig. 5. IR spectra of (a) neutron-irradiated (1.2×10^{12} n s^{-1} cm^{-2}, 4 h) $Li_3[Fe(C_2O_4)_3]$, and (b) thermally decomposed (500—510 K under nitrogen) $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$.

Table 1. Mössbauer parameters of the species A, B, and C shown in Figs. 1 and 4, and of the thermally decomposed $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$

Species	I.S. mm s^{-1}	Q.S. mm s^{-1}
A	1.26	2.63
B	1.32	1.97
C	1.32	2.86
Product after heating at 525—545 K in air	0.44	0.95
Product after heating at 500—510 K under nitrogen	1.30	2.60

A Mössbauer spectrum of neutron-irradiated (5×10^{11} n s^{-1} cm^{-2}, 2 h, at the ambient temperature) anhydrous $Li_3[Fe(C_2O_4)_3]$ is shown in Fig. 4(b). The doublet C (I.S.=1.32, Q.S.=2.86 mm s^{-1}) is ascribed to a high-spin iron(II) species produced by neutron irradiation; it is similar in I.S. value to the doublets A and B. When the anhydrous $Li_3[Fe(C_2O_4)_3]$ is irradiated at a higher neutron fluence rate (1.2×10^{12} n s^{-1} cm^{-2}) and for a longer period (4 h) than those in Fig. 4(b), a species which has the same Mössbauer parameters as the doublet C is obtained as the main product, as is shown in Fig. 4(c). The Mössbauer parameters for the species A, B, and C, shown in Figs. 1 and 4, and the thermally decomposed products are summarized in Table 1 for the sake of comparison. As may be seen in Fig. 5, the IR spectrum of the sample shown in Fig. 4(c) is similar to that of the thermally decomposed product at 500—510 K under nitrogen. Thus, the species produced through the neutron irradiation of $Li_3[Fe(C_2O_4)_3]$ is concluded to be produced also by the thermal decomposition. Although the cause of different Q.S. values of the product in the anhydrous compound has not yet been fully elucidated, the different crystal structure of the anhydrous compound may explain the small difference in the Q.S. value of the new species produced in the original host crystal lattice.

The Fe(II) species produced in the neutron-irradiated $Li_3[Fe(C_2O_4)_3]$ and $Li_3[Fe(C_2O_4)_3]\cdot 4.5H_2O$ are ascribed to a precursor of $[Fe(C_2O_4)_2]^{2-}$ and a hydrous or anhydrous $[Fe(C_2O_4)_2]^{2-}$ species respectively. Since the weight decrease corresponding to one mol of the oxalato ligand is not observed in the neutron irradiation of the sample, decomposed fragment species, such as CO_2, produced from the oxalato ligand seem to remain in the crystal lattice of the irradiated sample.

As the spectral component C remains even after a long period of irradiation of the anhydrous compound, the change in the species A to the species B, shown in Fig. 1(a) and in Fig. 1(b) respectively, can be concluded to be related to the existence of crystal water, for instance, in such a way that the presence of water molecules is involved in stabilizing the species A to B, although further investigations are required to identify those iron(II) species.

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