A Mössbauer Study of the Hot-atom Effect of EC Decay in Cobalt(II) Oxalate

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Mössbauer spectroscopy provides unambiguous information about the chemical consequences of nuclear transformations. It is especially useful as a method for studying such effects on a rapid time scale which is inaccessible to classical chemical experimentation. The first excited state in the ^{57}Fe nuclide is populated by the EC decay of ^{57}Co, followed by the emission of a 123 keV. gamma ray from the second excited state. It has been found that the electron shake-off Auger cascade resulting from these precursor events gives rise to iron atoms in both $3d^5$ and $3d^6$ configurations, in cobalt(II) oxide,(1) cobalt(III) acetylacetonate(2) and biscyclopentadienyl cobalt(III) salts(3).

The Mössbauer study of the radiolysis of iron(III) oxalate has shown that iron(II) oxalate is formed as an irradiation product.(4) It has been also reported that the $G(\mathrm{Co}^{2+})$ value in the γ-ray irradiated oxalatocobalt(III) complexes increases with an increase in the

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1) G. K. Wertheim, *Phys. Rev.*, **124**, 764 (1961).

2) G. K. Wertheim, W. R. Kingston and R. H. Herber, *J. Chem. Phys.*, **37**, 687 (1962).

3) G. K. Wertheim and R. H. Herber, ibid., **38**, 2106 (1963).

4) N. Saito, H. Sano, T. Tominaga and F. Ambe, This Bulletin, **38**, 681 (1965).

oxalate ion content of the complexes,⁵⁾ and that ninety percent or more of the radiocobalt atoms are found as cobalt(II) species after the dissolution of the neutron-irradiated oxalatocobalt(III) complexes.⁶⁾ In the present study, the Mössbauer spectrum of ^{57}Fe produced from ^{57}Co in the $CoC_2O_42H_2O$ host crystal will be determined.

Pale pink-colored crystal of cobalt(II) oxalate was made by adding oxalic acid to cobalt(II) nitrate solution (containing 2 millicurie of ^{57}Co). The cobalt content was determined radiochemically. The Mössbauer spectrum was measured with a stainless steel absorber moving at various constant velocities at room temperature. The spectra were also measured with iron(II) oxalate and iron(III) oxalate absorbers, using a ^{57}Co diffused copper foil source.

Typical spectra are shown in Fig. 1. With respect to a stainless steel source, iron(II) oxalate and iron(III) oxalate give isomer shifts of 1.28 and 0.49 mm./sec., and quadrupole splitting of 1.73 and 0.43 mm./sec., respectively. In the case of ^{57}Co-labeled cobalt(II) oxalate, it may be expected that the EC precursor event leaves the daughter ^{57}Fe atom not only in the same oxidation state as that of parent cobalt atom, but also in a different oxidation state from those observed in cobalt(II) oxide, cobalt(III) acetylacetonate and biscyclopentadienyl cobalt(III) salts. However, no evidence for ionic charge states other than 2+ is observed. As may be seen in Fig. 1, the electron configuration around the ^{57}Fe atom produced in the cobalt(II) oxalate crystal is essentially identical to that in ferrous oxalate. This may be explained by assuming that higher charge species—even if formed as a consequence of the prior nuclear event—have been reduced by the oxalate ions in times brief compared to 10^{-7} sec. at room temperature; this is in accordance with the remarkable reducing power of oxalate ions observed in the radiolyses of iron(III) oxalate,⁴⁾ potassium trisoxalatoferrate-(III)⁷⁾ and oxalatocobalt(III) complexes,⁵⁾ and with hot-atom effect of the latter.⁶⁾

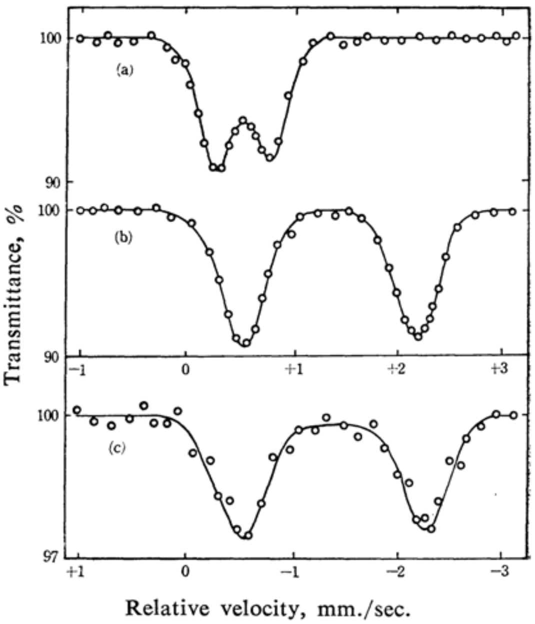

Fig. 1. Mössbauer spectra (at 22°C).

(a) Absorber, $Fe_2(C_2O_4)_35H_2O$; source, ^{57}Co in Cu

(b) Absorber, $FeC_2O_42H_2O$; source, ^{57}Co in Cu (Abscissa is normalized to stainless steel source)

(c) Source, $^{57}CoC_2O_42H_2O$; absorber, stainless steel

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7) H. Sano and T. Fukuroi, Presented at the 17th Annual Meeting of Chemical Society of Japan, Tokyo April, 1964.