A Mössbauer Resonance Absorption Study of the Photolysis and Radiolysis of Ferric Oxalate*[1]

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The technique of the Mössbauer resonance absorption of γ rays has recently been applied to the study of the valence state, structure and nature of the chemical bond of various compounds. Because of the favorable properties of ^{57}Fe for the observation of the resonance absorption spectra, a number of iron compounds have been investigated. However, the Mössbauer resonance absorption technique has not so far been used to investigate the chemical change induced by ionizing radiation or light in iron compounds.[1] Therefore, the present authors have applied this technique to the study of the photolysis and radiolysis of ferric oxalate.

Ferric oxalate, $Fe_2(C_2O_4)_3 \cdot nH_2O$,*[2] was irradiated with ^{60}Co γ rays at an ambient temperature in the presence of air. The total dose was 2×10^8 r. In case of photolysis, the same salt was exposed to the light from a mercury lamp. The resonance absorption of 14.4 KeV. γ rays in irradiated and non-irradiated iron oxalates (as absorbers) was measured with a source of ^{57}Co diffused into copper foil. The source was moved linearly at a constant velocity by means of a mechanical drive. No remarkable change was observed between the spectra obtained with the same absorber at 22°C and at the temperature of liquid nitrogen. Their Mössbauer spectra are shown in Figs. la-lc.

As may be seen in Fig. la, the spectrum of non-irradiated ferric oxalate consists of two lines, at 0.27 and 0.70 mm./sec. (vs. stainless steel). After irradiation with γ rays, the height of both lines is decreased, and new lines appear at about 0.5 and 2.3 mm./sec. (Fig. lb). Since the positions of these new lines nearly correspond to those in the spectrum of non-irradiated ferrous oxalate (Fig. lc), it may be concluded that the electron configuration around the iron atom in ferric oxalate irradiated with γ rays becomes very similar to that in ferrous oxalate (and that, therefore, Fe^{3+} is reduced to Fe^{2+} as the result of radiolysis). The Mössbauer spectrum obtained with ferric oxalate which has undergone photolysis is almost identical in shape with that of γ ray-irradiated sample.*[3]

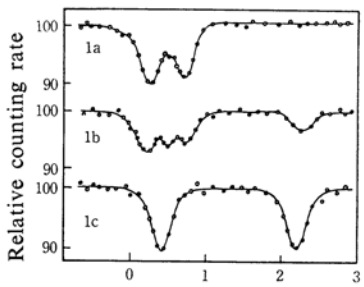

Fig. la-lc. Mössbauer resonance absorption spectra (at 22°C).
la : Non-irradiated ferric oxalate
lb : Irradiated ferric oxalate
lc : Non-irradiated ferrous oxalate

The above conclusion may be confirmed by the investigation of their infrared spectra shown in Figs. 2a-2c. The infrared spectra of irradiated and non-irradiated iron oxalates were measured as a KBr disk by using a Hitachi EPI-510 spectrophotometer. By examining the 750-850 cm^{-1} (O-C-O bending) and 1250-1350 cm^{-1} (C-O

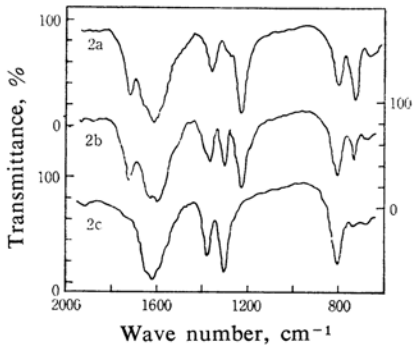

Fig. 2a-2c. Infrared spectra.
2a : Non-irradiated ferric oxalate
2b : Irradiated ferric oxalate
2c : Non-irradiated ferrous oxalate

*1 Presented at the 8th Symposium on Radiochemistry, November, 1964, Osaka.

1) The effect of γ rays on the shape of Mössbauer spectra has been reported only on some tin compounds: A. Y. Aleksandrov et al., *Soviet Physics JETP*, **16**, 1467 (1963).

*2 n=nearly 5.

*3 It is well known that ferric oxalate is decomposed by light to yield ferrous oxalate.

stretching) regions, it may be concluded that the spectrum of irradiated ferric oxalate (Fig. 2b) is obtainable by the superimposition of the spectrum of non-irradiated ferrous oxalate (Fig. 2c) on that of non-irradiated ferric oxalate (Fig. 2a) in adequate proportions.

Further study is now in progress to investigate the possibility of the semiquantitative determination of the Fe^{2+} formed in ferric oxalate in the course of γ radiolysis using the Mössbauer technique.

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