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# A Mössbauer Study of the Photolysis of Bis- and Tris-oxalato Iron(III) Complexes in a Solid, Solutions, and Frozen Solutions

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The photolytic reactions of bis- and tris-oxalato iron(III) complexes in a solid, solutions, and frozen solutions were studied by means of $^{57}$Fe Mössbauer spectroscopy. An iron(II) species was observed as a metastable intermediate product in the photolysis of tris(oxalato)ferrate(III) in a solid and solutions. A mechanism with a sequence of iron(II) intermediates was tentatively proposed for the photolysis and subsequent reactions in this compound. The Mössbauer technique was also used to examine whether or not tris(oxalato)ferrate(III) was diluted uniformly with diamagnetic substances in the mixed crystals and frozen solutions.

It has been demonstrated in our earlier work that Mössbauer spectroscopy is a useful tool for detecting the changes in oxidation states and structures induced by radiolysis, photolysis, and pyrolysis in solid iron compounds.[1–6] Recently, we have investigated the photolysis of potassium tris(oxalato)ferrate(III) in a solid and solutions[7] and proposed the possible application of Mössbauer spectroscopy in the photochemistry of metal complexes in the liquid and frozen states.

The object of this article is to present a more complete report of our work concerning the photolysis of potassium tris(oxalato)ferrate(III) in a solid and solutions, together with our recent results on the photolysis of potassium diaquabis(oxalato)ferrate(III) in solutions. In addition, the Mössbauer technique has also been applied to the investigation of whether or not potassium tris(oxalato)ferrate(III) is diluted uniformly with diamagnetic substances in mixed crystals and in frozen solutions.

## Experimental

*Materials.* *Potassium Tris(oxalato)ferrate(III) Trihydrate $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$*: An aqueous solution of a (1 : 3) mixture (by mole ratio) of iron(III) chloride and potassium oxalate was heated for 2 h at 80 °C; after the solution had been cooled, the precipitate was collected and recrystallized three times from water. Found: C, 14.6; H, 1.2%. Calcd for $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$: C, 14.7; H, 1.2%.

*$^{57}$Fe-enriched Potassium Tris(oxalato)ferrate(III) Trihydrate $K_3[^{57}Fe(C_2O_4)_3]\cdot 3H_2O$*: A 0.2 M potassium hydrogenoxalate solution was added to an excess of freshly precipitated $^{57}Fe_2O_3\cdot nH_2O$, after which the mixture was heated for 1 h at 70 °C (1 M = 1 mol dm$^{-3}$). The resulting solution was filtered, and the filtrate was concentrated in a vacuum.[8] Found: C, 14.7; H, 1.0%. Calcd for $K_3[^{57}Fe(C_2O_4)_3]\cdot 3H_2O$: C, 14.6; H, 1.2%.

*$^{57}$Fe-doped Potassium Tris(oxalato)cobaltate(III) Trihydrate $K_3[(^{57}Fe,Co)(C_2O_4)_3]\cdot 3H_2O$*: An aqueous solution containing a (1 : 33) mixture (by weight) of $^{57}$Fe-enriched potassium tris(oxalato)ferrate(III) trihydrate and potassium tris(oxalato)cobaltate(III) trihydrate was quenched quickly in liquid nitrogen, and then the frozen solution was condensed in a vacuum at −21 °C by pumping it through a liquid nitrogen trap.

*$^{57}$Fe-enriched Potassium Diaquabis(oxalato)ferrate(III) ($K[^{57}Fe(C_2O_4)_2(H_2O)_2]$) Solutions*: A (1 : 3) mixture (by mole ratio) of potassium oxalate and oxalic acid in an aqueous solution was added to an excess of freshly precipitated $^{57}Fe_2O_3\cdot nH_2O$; the solution was then filtered after having been heated for 1 h at 70 °C.

*Potassium Diaquabis(oxalato)ferrate(II) $K_2[Fe(C_2O_4)_2(H_2O)_2]$*: This compound was prepared according to the procedures described by Temperly *et al.*[9]

*Potassium μ-Oxalato-bis[bis(oxalato)ferrate(II)] $K_6[Fe_2(C_2O_4)_5]$*: This was prepared by heating potassium tris(oxalato)ferrate(III) for 15 min at 260 °C according to the method described by Bancroft *et al.*[10]

*Photoirradiation.* Samples were exposed either to a 500-W superhigh-pressure mercury lamp (spectral range: 300—600 nm) or to a 30-W low-pressure mercury lamp (253.7 nm). The solid samples were irradiated as crystals spread over a glass plate or adhesive tape, as film coated on an acrylic plate,[11] or as a disk in KCl.

A quartz cell with a 5-mm optical path was used for the irradiation of the solutions. Frozen solutions were irradiated as dipped directly in liquid nitrogen or as contained in acrylic or Teflon holders designed for Mössbauer measurements.

*Freezing of Solutions.* Both irradiated and unirradiated solutions were frozen quickly by one of the following procedures, A—D, prior to Mössbauer measurements:

A) The holder containing the solution was placed on Dry Ice.

B) The holder containing the solution was immersed in liquid nitrogen.

C) Droplets of the solution were added directly to liquid nitrogen.

D) A spatula precooled at 77 K was dipped into the solution so that a small amount was condensed on it, and then it was quickly put into liquid nitrogen. By repeating this procedure, small droplets of the frozen solution were collected in the liquid nitrogen.

By Procedures B—D, we may achieve freezing rates of 5—8 K/s, 10—40 K/s, and 100—250 K/s respectively.

*Measurements of Mössbauer Spectra, Infrared Spectra, and Powder X-Ray Patterns.* The Mössbauer spectra at 77 K and 293 K were measured by using a Hitachi AA-40 or a Shimadzu MEG-2 Mössbauer spectrometer against $^{57}$Co in copper or rhodium foil. Acrylic or Teflon holders (32 mm in diameter) were used for the measurements of the solutions.

The curve-fitting of the spectra thus obtained was performed with a HITAC 8800/8700 computer, assuming that they were composed of absorption peaks in a Lorentzian line shape.

The infrared spectra were recorded on a Hitachi EPI-G2 spectrophotometer (400—4000 cm$^{-1}$ region). The powder X-ray patterns of the (1 : 33) mixture of potassium tris(oxalato)ferrate(III) trihydrate with potassium tris(oxalato)cobaltate(III) trihydrate, and $^{57}$Fe-doped potassium tris(oxalato)cobaltate(III) trihydrate were taken by using a Rigaku Denki Geigerflex and Fe Kα-radiation.

## Results and Discussion

*Photolysis of Potassium Tris(oxalato)ferrate(III) in the Solid Phase.* The Mössbauer spectrum at 77 K of the unirradiated solid potassium tris(oxalato)-ferrate(III) (Product I) in Fig. 1a is composed of a single broad absorption indicative of an electronic spin relaxation effect.[12)] After irradiation at 253.7 nm for 5 h at room temperature, the Mössbauer spectrum (Fig. 1b) represents two sets of quadrupole doublets for an iron(II) species (Product II) and an iron(III) species (Product III) in addition to the broad single absorption of the unreacted parent compound. After the prolonged standing of the photolyzed sample in air, however, the intensities of the iron(III) doublet peaks (Product III) had increased, while those of the iron(II) doublet (Product II) had decreased and the iron(II) doublet (Product II) had disappeared eventually (Fig. 1c).

When smaller amounts of $^{57}$Fe-enriched potassium tris(oxalato)ferrate(III) were irradiated in a solid, in a disk, or on film, two iron(II) species (Products IV and V) other than Product II were obtained as photolysis products, depending on the irradiation conditions (period, temperature, and atmosphere) (Fig. 2).

Table 1 summarizes the Mössbauer parameters of the photolysis products from potassium tris(oxalato)-ferrate(III), together with the identities of those products tentatively deduced on the basis of the results reported previously for the pyrolysis and radiolysis of the same system.[9,10,13,14)]

Among such products, Products V and VI[15)] are fairly unstable intermediates which have not been observed in the earlier work. The Mössbauer parameters and infrared spectra (Fig. 3) reveal that both products, V and VI, cannot be identical with any of the known products, I to IV, nor with any tetrahedral species. Furthermore, from the conceivable structures for Products V and VI, we may rule out the following ones:

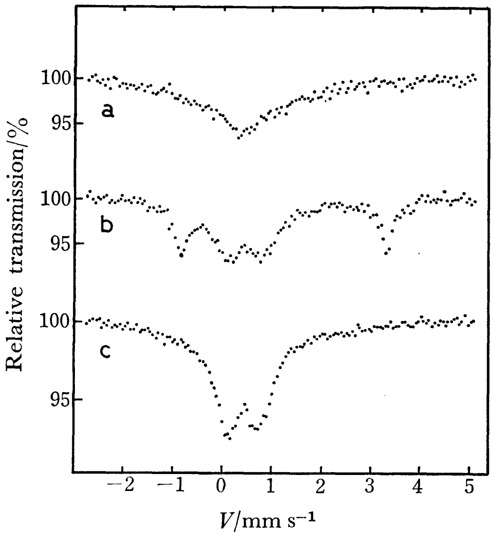


Fig. 1. Mössbauer spectra at 77 K of solid $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, [*V*: velocity]. a) Unirradiated solid sample, b) solid sample irradiated for 5 h with 253.7 nm light, c) irradiated solid sample after standing for 20 d.

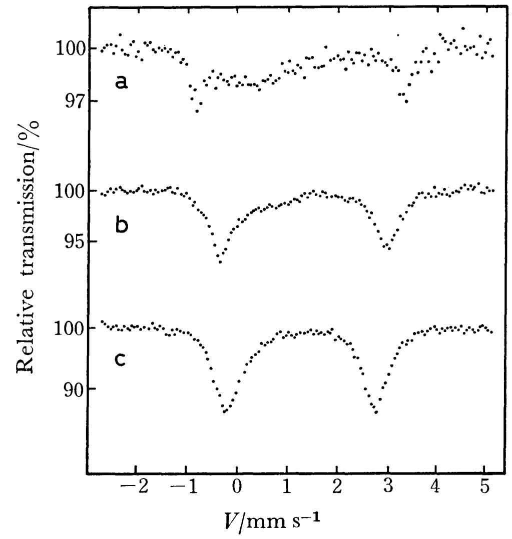


Fig. 2. Mössbauer spectra at 77 K of solid $K_3[^{57}Fe(C_2O_4)_3]\cdot 3H_2O$ (in small amounts) photoirradiated (a) in KCl disk for 3 min at 60 °C in air with 300—600 nm light (Product II), (b) in KCl disk for 2 h at 0 °C in $CO_2$ with 253.7 nm light (Product IV), and (c) in powder for 1 min at 40 °C in air with 300—600 nm light (Product V).

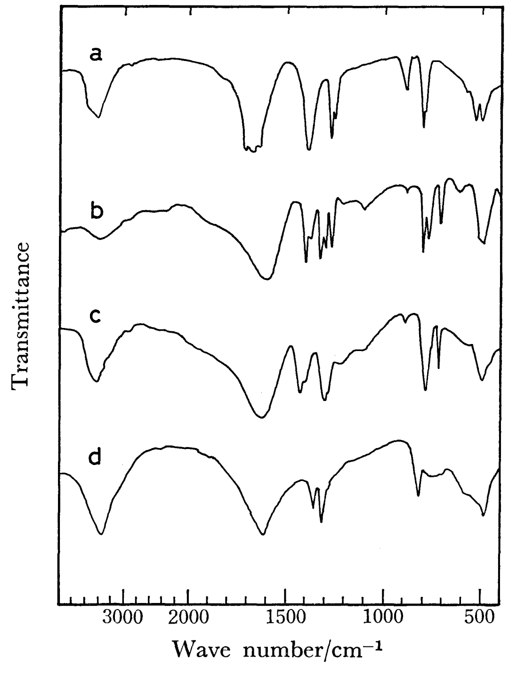


Fig. 3. Infrared spectra of (a) $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, (b) Product II ($K_6[Fe_2(C_2O_4)_5]$), (c) Product V, and (d) $FeC_2O_4\cdot 2H_2O$.

1) $[Fe(C_2O_4)_3]^{4-}$ and $[Fe(C_2O_4)_2(C_2O_4H)(H_2O)]^{3-}$ can be excluded for stoichiometric reasons.

2) $[Fe(H_2O)_6]^{2-}$ and $[Fe(C_2O_4)(H_2O)_4]$ are unlikely because Product VI is stable in solutions containing excess potassium oxalate.

3) Structures with bridging oxalates may also be eliminated because the infrared spectrum of Product

Table 1. Mössbauer parameters of the photolysis products from potassium tris(oxalato)ferrate(III)

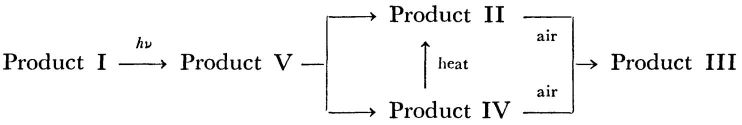
| Product | 77 K |  | 293 K |  | Tentative assignment |
|---|---|---|---|---|---|
|  | $\delta^{a)}$ | $\Delta E_Q$ | $\delta^{a)}$ | $\Delta E_Q$ |  |
|  | mm/s |  | mm/s |  |  |
| Product I | $0.44\pm0.02$ | — | $0.33\pm0.02$ | — | Parent compound |
| Product II | $1.26\pm0.02$ | $4.09\pm0.08$ | $1.16\pm0.02$ | $3.89\pm0.08$ | $[Fe_2^{II}(C_2O_4)_5]^{6-}$ |
| Product III | $0.49\pm0.02$ | $0.70\pm0.03$ | $0.36\pm0.03$ | $0.68\pm0.04$ | $[Fe^{III}(C_2O_4)_2(H_2O)_2]^-$ |
| Product IV | $1.34\pm0.02$ | $3.27\pm0.04$ | $1.22\pm0.02$ | $2.53\pm0.04$ | $[Fe^{II}(C_2O_4)_2(H_2O)_2]^{2-}$ |
| Product V | $1.28\pm0.02$ | $2.94\pm0.03$ | — | — | Metastable iron(II) species |
| Product VI | $1.29\pm0.01$ | $2.91\pm0.01$ | — | — | Metastable iron(II) species |
| Freeze drying (Product V) | $1.29\pm0.02$ | $2.94\pm0.02$ | — | — | Metastable iron(II) species |

a) With respect to the centroid of the spectrum of iron foil at 293 K. Experimental errors are indicated of maximum deviations.

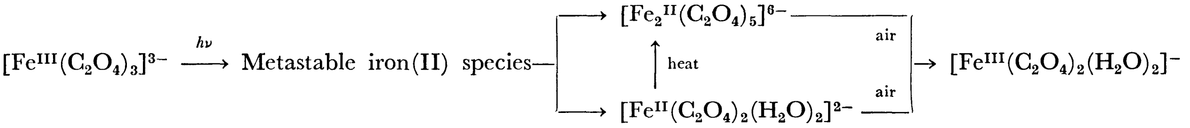
V shows no absorption band in the 1300—1400 cm$^{-1}$ region (characteristic of the iron complexes with oxalate bridging, such as $FeC_2O_4\cdot2H_2O$ and $K_6[Fe_2(C_2O_4)_5]$).

Although further investigation will be necessary for determining the identities of Products V and VI, we may assume tentatively that a geometrical isomer of Product IV ($K_2[Fe(C_2O_4)_2(H_2O)_2]$) remains as one of the possible structures for Product V (and VI).

As has been mentioned above, the formation and subsequent conversion of Products II, III, IV, and V were governed mainly by the photoirradiation conditions. A brief irradiation at a lower temperature generally favors the initial formation of Product V. After prolonged standing, Product V is converted into Products IV and II, which are eventually converted into Product III by oxidation in air. Product II also appears on the heating of Product IV at 120 °C. Thus, the overall mechanism for the formation of such products can be generally accounted for by assuming the following sequence of photolytic and subsequent reactions:



or, in terms of tentative assignments;



*Dilution of Potassium Tris(oxalato)ferrate(III) in Mixed Crystals and Frozen Solutions.* As is shown in Fig. 4a, the Mössbauer spectrum of solid potassium tris(oxalato)ferrate(III) trihydrate consists of a remarkably broadened absorption peak, indicating an electronic spin relaxation effect.[12)] If this compound is diluted uniformly with a diamagnetic substance (*e.g.*, potassium tris(oxalato)cobaltate(III) trihydrate or water), however, a resolved hyperfine structure is observed in the Mössbauer spectrum due to the developing relaxation effect. In fact, the Mössbauer spectrum of $^{57}$Fe-doped potassium tris(oxalato)ferrate(III) trihydrate, $K_3[(^{57}Fe,Co)(C_2O_4)_3]\cdot3H_2O$ (Fig. 4b), indicates a resolved magnetic hyperfine structure and suggests that potassium tris(oxalato)ferrate(III) trihydrate is diluted uniformly in solid potassium tris(oxalato)cobaltate(III) trihydrate. By comparing the powder X-ray pattern of the $^{57}$Fe-doped potassium tris(oxalato)cobaltate(III) with that of a (1 : 33) mixture of potassium tris(oxalato)ferrate(III) trihydrate and potassium tris(oxalato)cobaltate(III) trihydrate, it may be presumed that the $^{57}$Fe-doped potassium tris(oxalato)cobaltate(III) trihydrate is constituted of mixed crystals.

In frozen solutions containing uniformly dispersed iron(III) species, Mössbauer spectra have been reported to show similar hyperfine structures resulting from long spin-relaxation times.[16,17)] Although we have, in this work, measured the Mössbauer spectra of frozen solutions (quenched by Procedure B) at various concentrations (0.002—1 M) of potassium tris(oxalato)ferrate(III), no significant difference was observed in their spectra over the concentration range studied. For example, the Mössbauer spectrum of the 0.005 M potassium tris(oxalato)ferrate(III) solution (Fig. 4c) quenched by Procedure B resembles that of the same compound in the solid state (Fig. 4a) and suggests that microcrystals of the solute were separated on freezing the solutions. However, the Mössbauer spectrum of the 0.005 M potassium tris(oxalato)ferrate(III) solution containing an excess of potassium hydrogenoxalate, frozen quickly by Procedure D

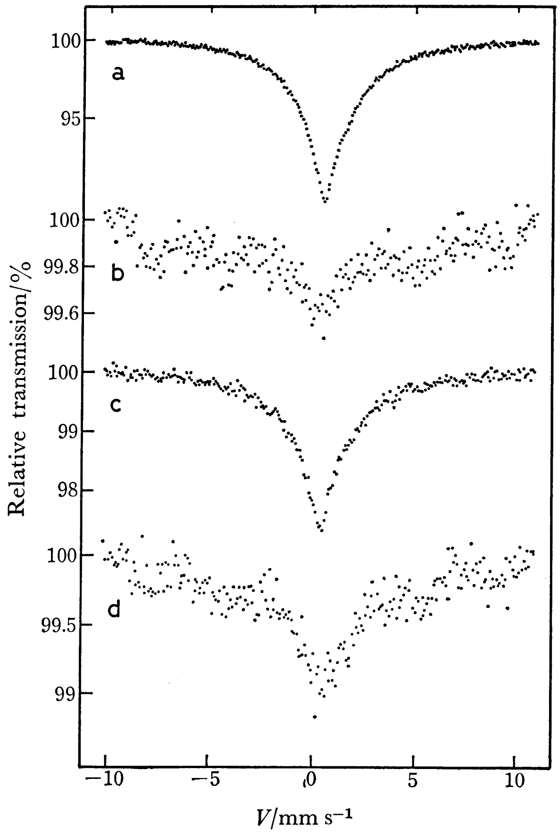


Fig. 4. Mössbauer spectra at 77 K of (a) solid $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, (b) solid $K_3[(^{57}Fe,Co)(C_2O_4)_3]\cdot 3H_2O$, (c) a 0.005 M $K_3[^{57}Fe(C_2O_4)_3]$ solution quenched by procedure B, and (d) a 0.005 M $K_3[^{57}Fe(C_2O_4)_3]$ solution containing an excess of $KHC_2O_4$, quenched quickly by procedure D.

(Fig. 4d), shows the hyperfine structure characteristic of the relaxation effect. Accordingly, it is obvious that the solute is diluted more uniformly in this frozen solution. Thus, the Mössbauer technique can be used to examine whether or not solutes are uniformly diluted in quenched solutions.

*Photolysis of Potassium Tris(oxalato)ferrate(III) in Aqueous Solutions and Frozen Aqueous Solutions.* In Fig. 5 are illustrated the Mössbauer spectra of neutral aqueous solutions of potassium tris(oxalato)ferrate(III) quenched by Procedure B after photoirradiation for 3, 10, and 120 s with a superhigh-pressure mercury lamp. The iron(III) single peak of the parent complex (Product I) tended to disappear, yet the iron(II) doublet (Product VI) became predominant with the increase in the irradiation period. Table 2 summarizes the Mössbauer parameters of the products obtained by the photoirradiation of the solutions, together with the percentage photoreduction for various irradiation periods.

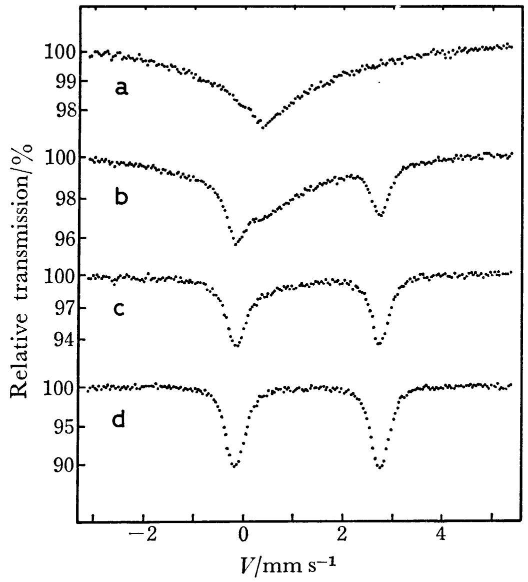


Fig. 5. Mössbauer spectra at 77 K of neutral aqueous solutions of $K_3[^{57}Fe(C_2O_4)_3]$ quenched by procedure B after photoirradiation for various periods. (a) Unirradiated, (b) 3-s irradiated, (c) 10-s irradiated, and (d) 120-s irradiated.

The Mössbauer spectrum of the photoirradiated frozen solutions of potassium tris(oxalato)ferrate(III) also indicates the formation of Product VI (Fig. 6a). On 5-min standing at room temperature after 2-min exposure to the superhigh-pressure mercury lamp, iron(II) oxalate has already started precipitating in an aqueous solution of potassium tris(oxalato)-

Table 2. Mössbauer parameters at 77 K of the photolysis products of 0.02 M $K_3[^{57}Fe(C_2O_4)_3]$ aqueous solutions and the percentage photoreduction for various irradiation periods

| Product | | Period of photoirradiation/s | | | |
|---|---|---|---|---|---|
| | | 0 | 3 | 10 | 120 |
| Iron(III) species (parent) | $\delta^{a)}$/(mm/s) | 0.44(1)[b)] | 0.43(1) | 0.43(4) | — |
| | $\Delta E_Q$/(mm/s) | — | — | — | — |
| | $\Gamma$/(mm/s) | 2.48(5) | 2.41(5) | 2.03(15) | — |
| | $\varepsilon$/% | 2.5(1) | 2.7(1) | 1.2(1) | — |
| Iron(II) species (Product VI) | $\delta^{a)}$/(mm/s) | — | 1.29(1) | 1.29(1) | 1.29(1) |
| | $\Delta E_Q$/(mm/s) | — | 2.91(1) | 2.91(1) | 2.91(1) |
| | $\Gamma$/(mm/s) | — | 0.43(2) | 0.43(1) | 0.44(1) |
| | $\varepsilon$/% | — | 2.4(1) | 6.2(1) | 10.5(2) |
| Percentage of photoreduction/% | | 0 | 17 | 59 | 100 |

a) With respect to the centroid of the spectrum of iron foil at 293 K. b) Figures in parentheses indicate standard deviations in units of the last significant digit. $\Gamma$: Line-width; $\varepsilon$: resonance-effect magnitude.

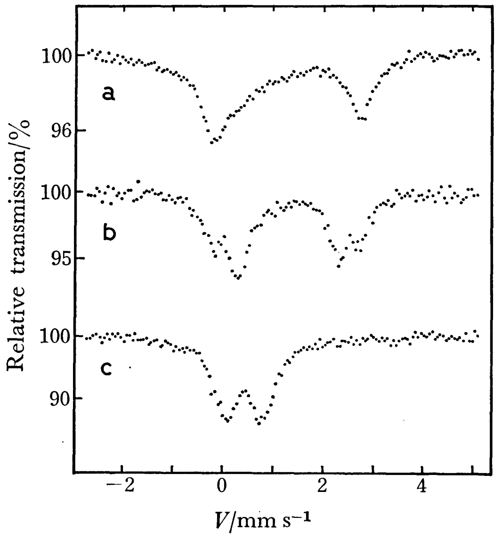


Fig. 6. Mössbauer spectra at 77 K of (a) a photoirradiated frozen aqueous solution of $K_3[^{57}Fe(C_2O_4)_3]$, (b) an aqueous solution of $K_3[^{57}Fe(C_2O_4)_3]$ quenched on 5-min standing at room temperature after photoirradiation, and (c) an aqueous solution of $K_3[^{57}Fe(C_2O_4)_3]$ quenched on prolonged standing at room temperature after photoirradiation.

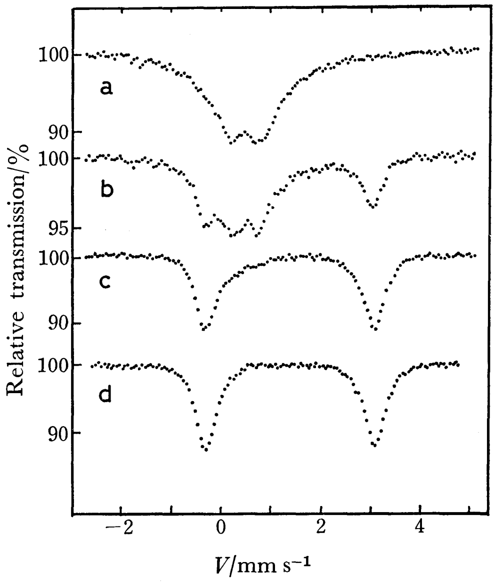


Fig. 7. Mössbauer spectra at 77 K of 0.05 M sulfuric acid solutions of $K_3[^{57}Fe(C_2O_4)_3]$ quenched by procedure A after photoirradiation for (b) 3 s, (c) 10 s, and (d) 60 s. (a): Unirradiated solution.

ferrate(III); Fig. 6b shows the spectrum of this solution quenched quickly. Although Product VI is at first converted into iron(II) oxalate, iron(II) oxalate is in turn oxidized after prolonged standing in air and is dissolved again. The Mössbauer spectrum of the iron(III) species resulting from the oxidation of iron(II) oxalate (Fig. 6c) reveals the formation of potassium diaquabis(oxalato)ferrate(III) and potassium tris(oxalato)ferrate(III).

The Mössbauer parameters and infrared spectra suggest that the product obtained from freeze-drying (at −21 °C) of Product VI may be identical with Product V.

Hence, the photolysis and subsequent reactions of potassium tris(oxalato)ferrate(III) in aqueous solutions presumably proceed as in the following sequence:

$$\begin{tikzcd}
{[Fe(C_2O_4)_3]^{3-}} \arrow[r, "h\nu"] & \begin{array}{c}\text{Metastable iron(II)}\\ \text{species (Product VI)}\end{array} \arrow[r] \arrow[d, "\text{freeze-drying}"] & \begin{array}{c}FeC_2O_4\cdot 2H_2O\\ \text{(precipitate)}\end{array} \arrow[r, "\text{air}"] & {[Fe^{III}(C_2O_4)_2(H_2O)_2]^- \text{ or } [Fe^{III}(C_2O_4)_3]^{3-}} \\
 & \text{Product V} & &
\end{tikzcd}$$

*Photolysis of Potassium Tris(oxalato)ferrate(III) in Sulfuric Acid Solutions.* Based on spectrophotometric measurements, Parker has reported that both monooxalato- and bisoxalato- iron(III) complexes are present in sulfuric acid solutions of potassium tris(oxalato)ferrate(III).[18]

The Mössbauer spectrum obtained in this work of a frozen 0.05 M sulfuric acid solution of potassium tris(oxalato)ferrate(III) reveals a broad singlet absorption of tris(oxalato)ferrate(III) ion in addition to the mono- and bis-oxalato complexes (Fig. 7a). The relative quantities of mono-, bis-, and tris-oxalato complexes in frozen solutions were found to depend on the freezing rate. Figures 7b—d illustrates the Mössbauer spectra of sulfuric acid solutions of potassium tris(oxalato)ferrate(III) frozen by Procedure A after having been irradiated with the superhigh-pressure mercury lamp for 3, 10, and 60 s. It is obvious that the parent complex was reduced to an iron(II) species (Product VII). The Mössbauer parameters of Product VII ($\delta = 1.4$ mm/s, $\Delta E_Q = 3.2—3.4$ mm/s) appear to change slightly with the change in the freezing rate. The percentage photoreduction to the iron(II) species was estimated as being about 30, 70, and 100% for 3-, 10-, and 60-s irradiations respectively. The percentage reduction determined spectrophotochemically by means of the *o*-phenanthroline method[19] was in good agreement with the Mössbauer data.

Since Product VII is unstable, iron(II) oxalate has already appeared in the solution after 120-s photoirradiation. When a frozen-sulfuric-acid solution of potassium tris(oxalato)ferrate(III) has been exposed to light, the Mössbauer spectrum also indicates the formation of Product VII.

*Photolysis of Potassium Diaquabis(oxalato)ferrate(III) in Aqueous Solutions.* Figure 8 demonstrates the Mössbauer spectra of aqueous solutions of potassium diaquabis(oxalato)ferrate(III) frozen by Procedure B after photoirradiation; the percentage photoreduction of the parent complex to iron(II) species increases with the increase in the photoirradiation period. Table

Table 3. Mössbauer parameters at 77 K of the photolysis products of 0.02 M $K[^{57}Fe(C_2O_4)_2(H_2O)_2]$ aqueous solutions for various irradiation periods

| Product | | Period of photoirradiation/s | | | |
|---|---|---|---|---|---|
| | | 0 | 3 | 10 | 60 |
| Iron(III) species (parent) | $\delta^{a)}$/(mm/s) | 0.49 | 0.49 | b) | — |
| | $\Delta E_Q$/(mm/s) | 0.64 | 0.58 | b) | — |
| | $\Gamma$/(mm/s) | 0.54 | 0.53 | b) | — |
| | $\varepsilon$/% | 7.0 | 5.6 | b) | — |
| Iron(II) species (photolysis product) | $\delta^{a)}$/(mm/s) | — | 1.34 | 1.31 | 1.29 |
| | $\Delta E_Q$/(mm/s) | — | 3.21 | 2.88 | 2.83 |
| | $\Gamma$/(mm/s) | — | 0.48 | 0.57 | 0.39 |
| | $\varepsilon$/% | — | 3.3 | 5.5 | 11.0 |

a) With respect to the centroid of the spectrum of iron foil at 293 K. b) Reasonable values were not available.

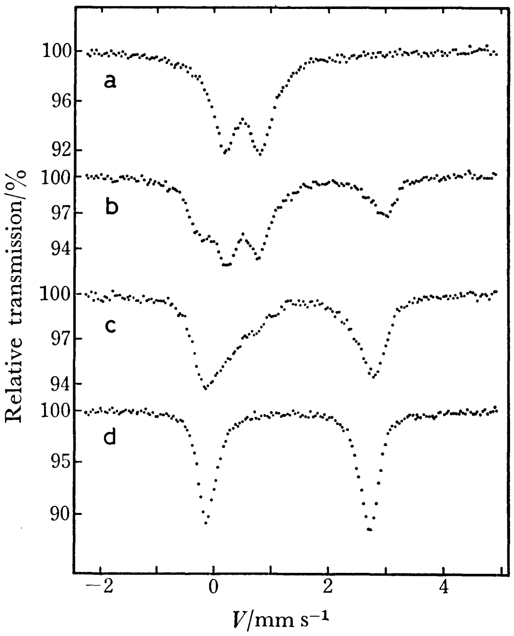


Fig. 8. Mössbauer spectra at 77 K of aqueous solutions of $K[^{57}Fe(C_2O_4)_2(H_2O)_2]$ quenched by procedure B after photoirradiation for (b) 3 s, (c) 10 s, and (d) 60 s. (a): Unirradiated solution.

3 summarizes the Mössbauer parameters obtained from curve-fitting by assuming a quadrupole doublet of the Lorentzian line-shape for the iron(II) species. While the isomer shift and quadrupole splitting of the iron(II) species are decreased with the increase in the irradiation period, the line-width shows anomalous behavior. Although the Mössbauer line-width is, in general, expected to increase with the concentration of iron species,[20] the line-width of the iron(II) species in Fig. 8 does not simply increase with the concentration in terms of the irradiation period; the widths are 0.48, 0.57, and 0.39 mm/s for 3-, 10-, and 60-s irradiations respectively. Such an anomaly can be explained tentatively by assuming that at least two iron(II) species with slightly different parameters are formed in photolysis; one of them is predominant after 3-s irradiation, while the other becomes predominant after 60-s irradiation. Both species can exist after 10-s irradiation. Unfortunately, the Mössbauer spectrum obtained after 10-s irradiation (Fig. 8c) cannot be resolved well by computer curve-fitting because of the broad overlapping absorption of tris(oxalato)ferrate(III), possibly formed by the combination of the parent complex with free oxalate ions.[21]

Further study will be necessary for a complete understanding of the mechanism of the photolysis of diaquabis(oxalato)ferrate(III) in aqueous solutions.

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