Mössbauer Study of Solid State Photolysis of Alkali Tris(oxalato)ferrates(III)

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Solid state photolysis of alkali tris(oxalato)ferrates(III) (Li, Na, K, Cs, and NH_4) was studied with mercury radiation in the visible region by means of Mössbauer spectroscopy. The intermediate $K_6[Fe^{II}_2(ox)_5]$ is formed in the case of potassium tris(oxalato)ferrate(III) and $FeC_2O_4 \cdot 2H_2O$ in the case of other alkali tris(oxalato)ferrates-(III)[Li, Na, Cs, and NH_4].

Mössbauer spectroscopy is effective for detecting the change in oxidation state and structure.[1] By means of UV and visible spectroscopy and magnetic susceptibility measurements Wendlandt and Simmons[2] found that iron(II) oxalate is formed during the course of solid state photolysis of potassium tris(oxalato)ferrate(III). Bancroft *et al.*[3] reported the formation of $K_6[Fe^{II}_2(ox)_5]$ as an intermediate, the results contradicting the observation made by Wendlandt and Simmons.[2] Sato and Tominaga[4,5] investigated the photolysis of potassium bis- and tris(oxalato)ferrate(III) in solid state and frozen solutions using Mössbauer spectroscopy, their results supporting those obtained by Bancroft *et al.*[3] They also suggested the formation of metastable iron(II) species during the course of photolysis. In our earlier communication,[6] Mössbauer parameters of alkali tris-(oxalato)ferrates(III) have been reported. The effect of change of cation on the isomer shift values have been observed. In this communication, the effect of change of cation (Li, Na, K, Cs, and NH_4) on the intermediates formed during the course of solid state photolysis of these complexes is reported.

Experimental

Alkali Tris(oxalato)ferrates(III) $M_3[Fe(ox)_3] \cdot 3H_2O$ (M= Li, Na, K). These were prepared by mixing three volumes of 1.5 mol dm^{-3} alkali metal oxalate solution and one volume of 1.5 mol dm^{-3} iron (III) chloride solution with vigrous stirring. The precipitated green product, *i. e.* $M_3[Fe(ox)_3] \cdot 3H_2O$ (M=Li, Na, K), was recrystallized three times from warm water and dried in a current of warm air (45 °C) with a drier.[7] The solid product was stored in the dark in order to avoid chemical change.

Caesium Tris(oxalato)ferrate(III) Trihydrate $Cs_3[Fe(ox)_3] \cdot 3H_2O$. Caesium oxalate was prepared from caesium chloride and oxalic acid. Three volumes of 1.5 mol dm^{-3} caesium oxalate solution and one volume of 1.5 mol dm^{-3} iron (III) chloride solution were mixed with vigrous stirring. The reaction mixture was concentrated on a water bath until crystals of caesium tris (oxalato) ferrate (III) formed. The crystals were recrystallized from warm water and then stored and dried in the dark.

Ammonium Tris(oxalato)ferrate(III) Trihydrate $(NH_4)_3[Fe(ox)_3] \cdot 3H_2O$. This complex was prepared as reported.[8]

The percentage of iron in the alkali tris(oxalato)ferrates (III) was determined by electronic spectroscopy and found to agree with that of the expected value.[9] The percentage of sodium and potassium in sodium- and potassium tris(oxalato)ferrate-(III) trihydrate respectively was determined with a flame photometer.

For photo-irradiation, samples were exposed to medium pressure 125 watts mercury lamp radiations.

A Mössbauer spectrometer MBS-35 (ECIL, India) coupled with MCA-38B with constant acceleration drive was employed to record the spectrum. A 5-mi ^{57}Co (Rh) source was used. The values of isomer shift are reported with respect to naturaliron. All the spectra were recorded at temperature 25±2 °C. A sample containing approximately 10 mg/cm^2 of the natural iron was taken for each measurement. All the spectra have been fitted to Lorentzian line shape using program and fitting procedures[10] on microcomputer 2000 (DCM, India). The intensities of quadrupole doublets are almost equal, the Mössbauer spectra of the tris(oxalato)-ferrates(III) at room temperature being almost symmetrical. Slight deviations might be due to powdered random samples and due to spin lattice relaxation effect.[11]

Results and Discussion

The Mössbauer spectra of alkali tris(oxalato)ferrates-(III) at room temperature (25±2 °C) consist of a single broad absorption band due to an electronic spin relaxation effect.[11] The Mössbauer parameters of alkali tris-(oxalato)ferrates(III) are given in Table 1. The isomer shift value of 0.26 mm s^{-1} for potassium tris(oxalato)-ferrate(III) trihydrate agrees with the reported value.[1,3,4,12-14]

Table 1. Mössbauer parameters of alkali tris(oxalato)ferrates(III)

Name of complex	Isomer shift / mm s^{-1}	Width at half maximum / mm s^{-1}	Percentage absorption
$Li_3Fe(C_2O_4)_3 \cdot 3H_2O$	0.03±0.02	1.39±0.02	6.09
$Na_3Fe(C_2O_4)_3 \cdot 3H_2O$	0.15±0.02	1.37±0.02	2.35
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	0.26±0.02	1.78±0.02	6.12
$Cs_3Fe(C_2O_4)_3 \cdot 3H_2O$	0.39±0.02	0.85±0.02	3.81
$(NH_4)_3Fe(C_2O_4)_3 \cdot 3H_2O$	0.21±0.02	1.16±0.02	2.07

The alkali tris(oxalato)ferrates(III) are high spin complexes having octahedral structure with oxidation state (+3) of iron. The sp^3d^2 hybridization is involued in bonding with the ligands (oxalates). The change in polarization of the alkali metal cation affects the 3s-electron density at the iron nucleus. The more electronegative cation will polarize the oxalato group causing a change in the electron density of the iron. The increase of electronegativity from caesium to lithium decreases the electron density in the 3d-orbital of iron

Table 2. Mössbauer parameters of the products of photolysis from alkali tris(oxalato) ferrates(III)

Product	Isomer shift / mm s^{-1}	Quadrupole splitting / mm s^{-1}	Tentative assignment
Product I	—	—	Parent compounds[a]
Product II	1.16±0.04	3.89±0.04	$K_6[Fe_2^{II}(ox)_5]$
Product III	0.28±0.04	0.68±0.04	$M[Fe^{III}(ox)_2(H_2O)_2]$[b]
Product IV	1.18±0.04	1.80±0.04	$FeC_2O_4\cdot 2H_2O$

a) The values of isomer shift and quadrupole splitting are given in Table 1. b) M=Na, K, Cs.

which affects the shielding of 3s-electron density at iron nucleus. Less electronegative cation would have less effect on the d orbital and the resulting s-electron density at the nucleus would decrease, giving higher isomer shift value. The effect of electronegativity of cation on the value of isomer shift is greater as compared with that in low spin octahedral complexes[15] [hexacyanoferrate(II) and hexacyanoferrate(III)] and high spin tetrahedral complexes[16] [alkalidithioferrate-(III)]. A linear relationship between cationic size and isomer shift has been observed in alkali tris(oxalato)-ferrates(III).[6]

The Mössbauer parameters of alkali tris(oxalato)-ferrates(III) products for the solid state photolysis are given in Table 2. The Mössbauer spectrum of potassium tris(oxalato)ferrate(III), irradiated for 30 h at room temperature (Fig. 1b) shows a broad band with isomer

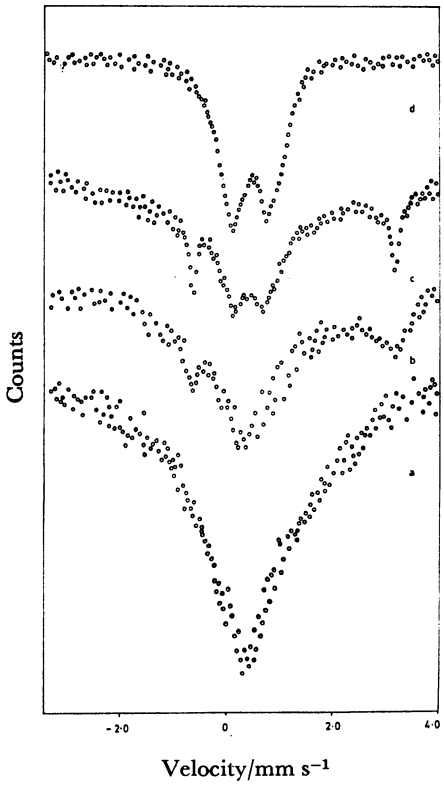

Fig. 1. Mössbauer spectra of potassium tris(oxalato)-ferrate(III) trihydrate at room temperature (25 °C). a: Unirradiated complex, b: irradiated for 30 h, c: irradiated for 60 h, d: irradiated for 200 h and on long standing in air.

shift 0.29 mm s^{-1}, indicating the presence of parent complex and a quadrupole doublet with isomer shift value 1.19 mm s^{-1} and quadrupole splitting value of 3.89 mm s^{-1} indicating the formation of $K_6[Fe_2^{II}(ox)_5]$. The Mössbauer spectrum of potassium tris(oxalato)-ferrate(III) irradiated for 60 h at room temperature (Fig. 1c) represents two sets of quadrupole doublets, one with isomer shift and quadrupole splitting value of 1.16 and 3.89 mm s^{-1}, respectively, indicating the formation of $K_6[Fe_2^{II}(ox)_5]$, and the other with isomer shift and quadrupole splitting values of 0.33 and 0.62 mm s^{-1}, respectively, indicating the formation of $K[Fe^{III}(ox)_2(H_2O)_2]$ species. Wendlandt and Simmons[2] observed the formation of FeC_2O_4 in the solid state photodecomposition of potassium tris-(oxalato)ferrate(III) by means of magnetic susceptibility measurements. However, no such results were obtained on the basis of Mössbauer studies. On further irradiation of the complex, oxidation of $K_6[Fe_2^{II}(ox)_5]$ to $K[Fe^{III}-(ox)_2(H_2O)_2]$ takes place. The isomer shift and quadrupole splitting values of this complex *i. e.* $K[Fe^{III}(ox)_2-(H_2O)_2]$ are 0.32 and 0.65 mm s^{-1}, respectively, showing that the complex has octahedral symmetry with oxidation state (+3). After irradiation with mercury radiations for a period of 200 h (Fig. 1d), the Mössbauer spectrum shows isomer shift and quadrupole splitting values of 0.32 and 0.62 mm s^{-1}, respectively, indicating complete photodecomposition to $K[Fe^{III}(ox)_2(H_2O)_2]$. No change in Mössbauer parameters has been observed on further irradiation. $K_6[Fe_2^{II}(ox)_5]$ is an unstable complex which, after being left to stand in the air for several days, gets oxidized to $K[Fe^{III}(ox)_2(H_2O)_2]$ (product III). It is possible that product III is formed by radiation and aerial oxidation. Sato and Tominaga[5] reported the formation of metastable iron(II) and $[Fe(ox)_2(H_2O)_2]^{2-}$ intermediate. The formation of these species was not observed in our experiments. This might be due to the difference in wavelength and experimental conditions. The mechanism of the solid state photodecomposition of potassium tris(oxalato)ferrate(III) is suggested as follows:

$$\underset{(I)}{K_3[Fe^{III}(ox)_3]} \xrightarrow{h\nu} \underset{(II)}{K_6[Fe_2^{II}(ox)_5]} \xrightarrow[air]{h\nu} \underset{(III)}{K[Fe^{III}(ox)_2(H_2O)_2]}.$$

The Mössbauer spectra of sodium and caesium tris(oxalato)ferrates(III) irradiated for a period of 60, 150, and 200 h are shown in Figs. 2 and 3, respectively. The Mössabauer spectra of these complexes irradiated for 60 h (Figs. 2b and 3b) show a doublet with isomer shift and quadrupole splitting values of 1.22 and 1.82

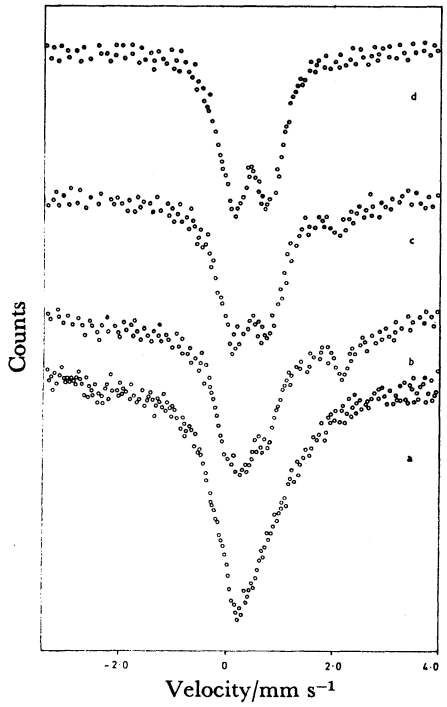

Fig. 2. Mössbauer spectra of sodium tris(oxalato)-ferrate(III) trihydrate at room temperature (25 °C).
a: Unirradiated complex, b: irradiated for 60 h, c: irradiated for 150 h, d: irradiated for 200 h.

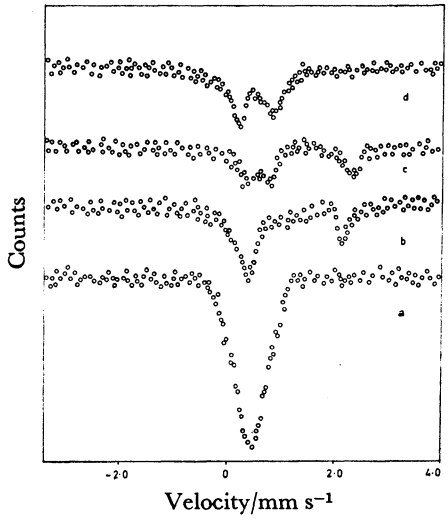

Fig. 3. Mössbauer spectra of caesium tris(oxalato)-ferrate(III) trihydrate at room temperature (25 °C).
a: Unirradiated complex, b: irradiated for 60 h, c: irradiated for 150 h, d: irradiated for 200 h.

mm s^{-1} in the case of sodium tris(oxalato)ferrate(III), and 1.18 and 1.77 mm s^{-1} in the case of caesium tris-(oxalato)ferrate(III). The values of isomer shift and quadrupole splitting are comparable to those reported for iron(II) oxalate dihydrate.[14] The same were observed in the Mössbauer spectrum of iron(II)oxalate-dihydrate (pure A.R.). On further irradiation, the Mössbauer spectrum shows a quadrupole doublet with isomer shift and quadrupole splitting values of 0.30 and 0.66 mm s^{-1} in sodium tris(oxalato)ferrate(III) (Fig. 2c) and 0.28 and 0.66 mm s^{-1} in the case of caesium tris(oxalato)ferrate(III) (Fig. 3c). These values indicate the formation of an octahedral complex with oxidation state(III). When these complexes (Na and Cs) were irradiated for 200 h and left to stand in the air for several hours, the Mössbauer spectrum represents a quadrupole doublet with isomer shift and quadrupole splitting values of 0.28 and 0.68 mm s^{-1} in sodium tris(oxalato)ferrate(III) (Fig. 2d) and 0.29 and 0.68 mm s^{-1} in the case of caesium tris(oxalato)ferrate(III) (Fig. 3d), indicating the formation of $M[Fe^{III}(ox)_2(H_2O)_2]$ complexes (M=Na, Cs). Further irradiation of these complexes shows on change in the Mössbauer spectra. The mechanism of photodecomposition of sodium- and caesium-tris(oxalato)ferrates(III) in solid state might be postulated as follows:

$$M_3[Fe^{III}(ox)_3] \xrightarrow{h\nu} \underset{(IV)}{Fe^{II}(ox)2H_2O} \xrightarrow[air]{h\nu} \underset{(M=Na,\ Cs)}{M[Fe^{III}(ox)_2(H_2O)_2]}.$$

These observations are similar to those for the products obtained by the photolysis of potassium tris(oxalato)-ferrate(III) in acidic solutions.[17] Potassium tris-(oxalato)ferrate(III) is used in actinometer. Photolysis of potassium tris(oxalato)ferrate(III) has extensively been investigated in solution as regards its use in actinometer. The formation of ferrous oxalate is observed in solutions.

In the case of lithium- and ammonium tris(oxalato)-ferrates(III) the Mössbauer spectra of these complexes irradiated for 100 h at room temperature indicate a quadrupole doublet with isomer shift and quadrupole splitting values of 1.20 and 1.77 mm s^{-1} in the case of lithium tris(oxalato)ferrate(III) (Fig. 4b) and 1.22 and 1.74 mm s^{-1} in the case of ammonium tris(oxalato)-

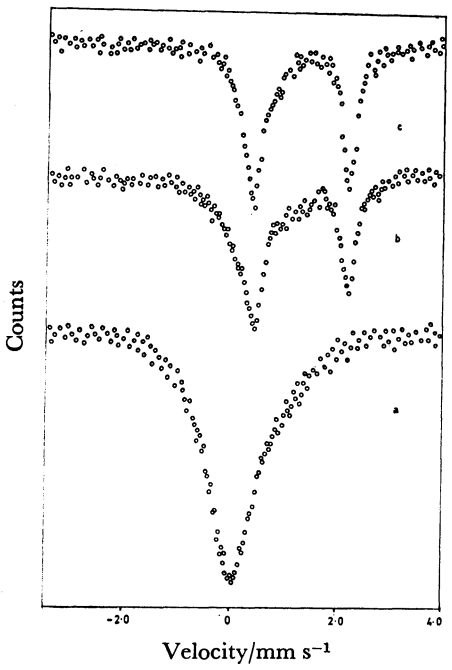

Fig. 4. Mössbauer spectra of lithium tris(oxalato)-ferrate(III) trihydrate at room temperature (25 °C).
a: Unirradiated complex, b: irradiated for 100 h, c: irradiated for 200 h.

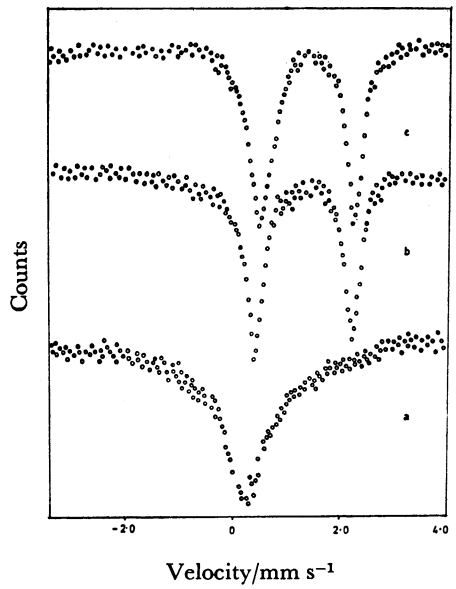

Fig. 5. Mössbauer spectra of Ammonium tris(oxalato)-ferrate(III) trihydrate at room temperature (25 °C).
a: Unirradiated complex, b: irradiated for 100 h, c: irradiated for 200 h.

ferrate(III) (Fig. 5b). On further irradiation upto 200 h (Figs. 4c and 5c) no change in the Mössbauer parameters was observed.

In the photolysis of potassium tris(oxalato)ferrate-(III), the $K_6[Fe_2^{II}(ox)_5]$ intermediate is formed and finally $K[Fe^{III}(ox)_2(H_2O)_2]$ is obtained. In sodium- and caesium tris(oxalato)ferrates(III), iron(II) oxalate has been observed as an intermediate. However, in the case of lithium- and ammonium tris(oxalato)ferrates-(III), iron(II) oxalate is formed upto 200 h of irradiation. It can be concluded that different intermediates are formed during the course of photolysis of alkali tris(oxalato)ferrates(III). The rate of photodecomposition is greater in the case of potassium- and ammonium tris(oxalato)ferrates(III). This might be the reason for the use of potassium tris(oxalato)ferrate(III) in an actinometer.

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