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Mössbauer Study of the Thermal Decomposition of Alkali Tris(oxalato)ferrates(III)

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The thermal decomposition of alkali (Li,Na,K,Cs,NH_4) tris(oxalato)ferrates(III) has been studied at different temperatures up to 700°C using Mössbauer, infrared spectroscopy, and thermogravimetric techniques. The formation of different intermediates has been observed during thermal decomposition. The decomposition in these complexes starts at different temperatures, i.e., at 200°C in the case of lithium, cesium, and ammonium ferrate(III), 250°C in the case of sodium, and 270°C in the case of potassium tris(oxalato)ferrate(III). The intermediates, i.e., $Fe^{II}C_2O_4$, $K_6Fe_2^{II}(ox)_5$. and $Cs_2Fe^{II}(ox)_2(H_2O)_2$, are formed during thermal decomposition of lithium, potassium, and cesium tris(oxalato)ferrates(III), respectively. In the case of sodium and ammonium tris(oxalato)ferrates(III), the decomposition occurs without reduction to the iron(II) state and leads directly to α-Fe_2O_3. © 1985 Academic Press, Inc.

Introduction

Tanaka *et al.* (*1, 2*) reported the formation of an intermediate $K_2Fe^{II}(ox)_2$ during thermal dissociation of potassium tris(oxalato)ferrate(III) by means of infrared, thermogravimetric, and polarographic techniques. Bancroft *et al.* (*3*) studied the thermal decomposition of potassium tris (oxalato)ferrate(III) both in air and *in vacuo* using Mössbauer spectroscopy and reported the formation of $K_6Fe_2^{II}(ox)_5$ as an intermediate, also supported by Medvinskii and Poskevnev (*4*). In our earlier communications (*5–7*), the effect of change of the outer cation (Li^+, Na^+, K^+, Cs^+, and NH_4^+) on the Mössbauer parameters of the products from photolysis in solid and solution phases has been reported. In the present investigation our interest is to observe the effect of outer monovalent cations (Li^+, Na^+, K^+, Cs^+, and NH_4^+) on the intermediates, products, particle size, and thermal decomposition temperature of alkali tris(oxalato)ferrates(III) employing Mössbauer and infrared spectroscopy and thermogravimetric techniques.

Experimental

The methods of preparation and chemical analysis of alkali tris(oxalato)ferrates(III) have been described in our earlier publication (*7*). For thermal decomposition all the

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complexes (Li, Na, K, Cs, and NH_4) were heated in a silica crucible in a tubular furnace at difference temperatures, i.e., 100, 200, 300, 500, and 700°C, for 4 hr in air and at intermediate temperatures for short times. The temperature of the furnace was measured by using a Chromel–Alumel thermocouple connected to a portable potentiometer (Toshniwal Industries, Ltd., India). The rate of heating was kept 10°C/min. The variation in temperature was ±5°C.

The experimental detail of Mössbauer investigation has been reported in our earlier publications (*5–7*). Mössbauer spectra were fitted by Lorentzian lines on the ICL-2960 computer at the Indian Institute of Technology, Delhi.

To record the infrared spectrum 2% of the samples were mixed with potassium bromide and the spectra were recorded on the MOM-2000 spectrophotometer (Hungarian Optical Works) in the range 4000–700 cm^{-1}. Thermogravimetric analysis was carried out on a TGA instrument (FCI, India). The rate of heating was kept to 10°C/min.

Results and Discussion

The Mössbauer spectra of alkali tris(oxalato)ferrates(III) at room temperature consist of a single broad absorption band due to electron spin relaxation effect (*8*). Mössbauer parameters of these complexes heated at different temperatures are given in Table I. The isomer shift values at room temperature show that these are high spin complexes with the (+3) oxidation state of iron having octahedral symmetry. The isomer shift value increases in going from the more electronegative lithium to the less electronegative cesium cations in the alkali tris(oxalato)ferrates(III) (*7*).

The infrared spectra of alkali tris(oxalato)ferrates(III) (Li, Na, K, Cs, and NH_4) show a broadband in the range 3300–3450 cm^{-1} due to the presence of $\nu(OH)$, a broadband in the range 1650–1630 cm^{-1} due to $\nu_{asy}(C{=}O)$, and bands in the ranges 1400–1430 and 1260–1320 cm^{-1} due to $\nu_{sym}(C{=}O)$. All these values indicate the presence of coordinated oxalate groups (*9*). In the case of ammonium tris(oxalato)ferrate(III) a broadband at 3050 cm^{-1} has been observed due to $\nu(N–H)$.

The number of water molecules in the complexes have been calculated from weight losses in TGA and elemental analysis.

Lithium Tris(oxalato)ferrate(III) Pentahydrate ($LiFe(ox)_3 \cdot 5H_2O$)

Mössbauer, infrared, and thermogravimetric analysis show that dehydration is complete at 200°C and decomposition starts at 200°C. Mössbauer parameters (Table I) of sample heated 200°C for 15 min indicate the formation of ferrous oxalate (*10*). After heating for 3 hr, further decomposition to α-Fe_2O_3 took place as shown by the Mössbauer results. Mössbauer parameters show how different types of particle sizes in products are formed (Table I). These results agree with the results reported by Kündig and co-workers (*11*). The infrared spectrum shows bands at 1650 and 1335 cm^{-1} due to lithium oxalate (*13*). The Mössbauer spectrum of sample heated at 300°C indicates the formation of α-Fe_2O_3 and the infrared spectrum shows the presence of lithium oxalate and lithium carbonate. However, on heating up to 700°C, the particle size of α-Fe_2O_3 changes and the presence of lithium carbonate is observed. These investigations have also been supported with TGA studies.

Sodium Tris(oxalato)ferrate(III) Tetrahydrate($Na_3Fe(OX)_3 \cdot 4H_2O$)

Mössbauer and infrared spectra of sodium tris(oxalato)ferrate(III) tetrahydrate show complete dehydration at 200°C. The value of the isomer shift increases from 0.15 to 0.21 mm sec^{-1} due to dehydration.

TABLE I

MÖSSBAUER DATA OF PRODUCTS FROM THERMAL DECOMPOSITION OF ALKALI TRIS(OXALATO)FERRATES(III)

Complex		250°C (room temp)	200°C (15 min)	200°C	300°C (15 min)	300°C	500°C	700°C
$Li_3Fe(ox)_35H_2O$	$\delta^{a,b}$	0.03 ± 0.03	1.06 ± 0.03	0.37 ± 0.03	0.037 ± 0.03	0.37 ± 0.03	0.37 ± 0.03	0.33 ± 0.03
	Δ^b	0	1.46 ± 0.03	0.20 ± 0.05	0.27 ± 0.03	0.28 ± 0.03	0.59 ± 0.03	0.59 ± 0.03
				$H_I = 501^c$	$H_I = 504$	$H_I = 511$		
$Na_3Fe(ox)_3 \cdot 4H_2O$	δ	0.15 ± 0.03	0.21 ± 0.03	0.21 ± 0.03	0.35 ± 0.03	0.36 ± 0.03	0.34 ± 0.06	0.36 ± 0.03
	Δ	0	0	0	0.68 ± 0.03	0.67 ± 0.03	0.20 ± 0.06	0.60 ± 0.03
							$H_I = 480$	
$K_3Fe(ox)_3 \cdot 3H_2O$	δ	0.26 ± 0.03	0.29 ± 0.03	0.29 ± 0.03	$\delta_1 = 1.23 \pm 0.03$	0.31± 0.03	0.29 ± 0.06	0.28 ± 0.06
	Δ	0	0	0	$\delta_2 = 0.31 \pm 0.03$			
					$\Delta_1 = 0.96 \pm 0.03$	0.72 ± 0.03	0.22 ± 0.06	0.17 ± 0.06
					$\Delta_2 = 0.71 \pm 0.03$	—	$H_I = 505$	$H_I = 488$
$Cs_3Fe(ox)_3 \cdot 2H_2O$	δ	0.39 ± 0.03	1.29 ± 0.03	0.36 ± 0.06	0.32 ± 0.03	0.32 ± 0.03	0.34 ± 0.06	0.42 ± 0.06
	Δ	0	2.30 ± 0.03	0.21 ± 0.06	0.26 ± 0.03	0.28 ± 0.06	0.28 ± 0.06	0.18 ± 0.06
				$H_I = 480$	$H_I = 485$	$H_I = 488$	$H_I = 499$	$H_I = 509$
$(NH_4)_3Fe(ox)_33H_2O$	δ	0.21 ± 0.03	0.32 ± 0.03	0.33 ± 0.03	0.30 ± 0.03	0.30 ± 0.03	0.41 ± 0.06	0.45 ± 0.06
	Δ	0	0.93 ± 0.03	0.95 ± 0.03	0.69 ± 0.03	0.67 ± 0.03	0.18 ± 0.06	0.18 ± 0.06
							$H_I = 501$	$H_I = 499$

[a] With respect to natural iron.

[b] In mm sec^{-1}.

[c] H_I indicates internal magnetic field in KOe, with an uncertainty of ±KOe.

The Mössbauer spectrum and TGA show that decomposition starts at 260°C. The Mössbauer spectrum of a sample heated at this temperature shows a broadband due to the original complex and also shows a doublet having isomer shift, 0.33-mm sec^{-1}, and quadruple splitting, 0.66 mm sec^{-1}, due to α-Fe_2O_3. The infrared spectrum shows the presence of bands at 1330 and 1640 cm^{-1} due to sodium oxalate (*12*); the Mössbauer spectrum of sample heated up to 700°C indicates the presence of α-Fe_2O_3 and the IR spectrum shows sodium oxalate. The particle size of α-Fe_2O_3 changes on heating up to 700°C (Table I). The decomposition of sodium tris(oxalato)ferrate(III) starts without reduction to the iron(II) state and leads to the formation of α-Fe_2O_3.

Potassium Tris(oxalato)ferrate(III) Trihydrate($K_3Fe(ox)_3 \cdot 3H_2O$)

The isomer shift increases from 0.26 mm sec^{-1} at room temperature to 0.29 mm sec^{-1} at 200°C due to dehydration, which shows that dehydration effects the *s*-electron density at the iron nucleus. This is also supported by infrared studies. The Mössbauer spectrum and TGA show that decomposition starts at 270°C. The values of the isomer shift (1.23 mm sec^{-1}) and quadrupole splitting (3.96 mm sec^{-1}) indicate the formation of K_6Fe_2 $(ox)_5$ as an intermediate species (*14*). On heating to higher temperature, the Mössbauer spectrum shows a doublet due to α-Fe_2O_3 (Table I). These investigations have been supported by TGA and infrared studies. The IR shows the formation of potassium oxalate at 300°C; on heating at 700°C, it changes to potassium carbonate, which is stable at 700°C.

Cesium Tris(oxalato)ferrate(III) Dihydrate($Cs_3Fe(ox)_32H_2O$)

Infrared and TGA studies of the sample show that dehydration is not complete at 200°C. But its decomposition starts at 200°C. Mössbauer and infrared spectra show the presence of $Cs_2Fe^{II}(ox)_2(H_2O)_2$, the intermediate product formed. Mössbauer parameters of sample heated at 200°C for 15 min agree with values reported in the literature (*14*). On heating at higher temperatures up to 700°C, large particles (>15 nm) of α-Fe_2O_3 are formed (Table I). The infrared spectrum shows the absence of oxalate and carbonate frequencies at 700°C, indicating their complete decomposition to oxides. The TGA shows that decomposition starts at 200°C with a weight loss of 7.6% (calculated 7.7%) for the formation of $Cs_2Fe(ox)_2(H_2O)_2$ in air.

Ammonium Tris(oxalato)ferrate(III) Trihydrate $(NH_4)_3Fe(ox)_3 3H_2O$

TGA indicates complete dehydration at 160°C, showing a loss of 11.8% (calculated 12.6%) and shows that the anhydrous complex is stable up to 200°C. Mössbauer parameters of the complex heated at 200°C for 15 min show a singlet due to a parent complex along with a doublet having the values of isomer shift and quadrupole splitting, 0.32 and 0.83 mm sec^{-1}, respectively, indicating the formation of α-Fe_2O_3. Broadbent and co-workers (*15*) have reported the formation of α-Fe_2O_3 at 200°C. Infrared spectroscopy shows the absence of oxalate and carbonate groups. Mössbauer investigations show that the particle size of Fe_2O_3 increases (>15 nm) on heating up to 700°C.

The above observations reveal that different intermediates are formed during thermal decomposition of alkali tri(oxalato) ferrate(III) and that α-Fe_2O_3 is the final product. The decomposition starts at different temperatures in these complexes. In case of lithium tris(oxalato)ferrate(III), reduction of iron(III) to iron(II) occurs at 200°C and iron(II) oxalate is formed as an intermediate. The decomposition starts at 260°C in the case of sodium tris(oxalato)ferrate(III). In the case of potassium tris(oxalato)ferrate(III), decomposition also starts at 270°C and the intermediate ($K_6Fe_2^{II}(ox)_5$) is observed. In the case of cesium tris(oxalato)ferrate(III) the reduction of iron(III) to iron(II) occurs at 200°C giving rise to the formation of $Cs_2Fe^{II}(ox)_2(H_2O)_2$ as an intermediate. The decomposition also starts at 200°C in the case of ammonium tris(oxalato)ferrate(III). Thus different cations (Li^+, Na^+, K^+, Cs^+, and NH_4^+) give rise to different intermediates, products, and thermal decomposition temperatures, of alkali tris(oxalato)ferrates(III). The temperature of decomposition for lithium, cesium, and ammonium tris(oxalato)ferrate(III) is lower than that of sodium and potassium tris(oxalato)ferrate(III).

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