

MÖSSBAUER AND DTA STUDIES OF THE DECOMPOSITION OF IRON OXALATES

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Results are reported for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$; various stages in the decomposition are demonstrated. The second compound on decomposition in nitrogen gives rise to finely divided Fe_3O_4 containing a little free metal. The conditions for this are established.

Physicochemical methods throw light on these complex topochemical processes and give data of value in science and technology. We have used the Mössbauer effect as giving much evidence on the elementary stages of reactions [1], together with simultaneous dta and thermogravimetric analyses, which are performed by an apparatus called a derivatograph [2].

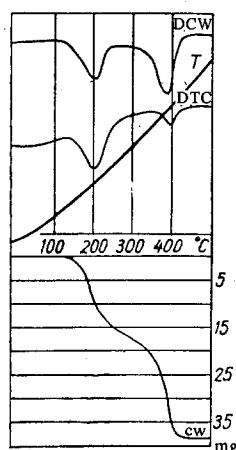


Fig. 1. Recordings for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in nitrogen.

This apparatus records on a single strip of photographic paper the change in weight (CW), the differential weight change (DCW), the temperature (T), and the differential temperature change (DTC) with the temperature increasing uniformly. The sample (70-100 mg) is placed in a platinum crucible fitted at the bottom with a thermocouple. We used a heating rate dT/dt of 10 deg/min, with the apparatus filled with dried nitrogen flowing at 200 cm^3/min . The balance could detect 0.2 mg, giving an error of measurement not exceeding $\pm 1\%$. The temperature was measured to within $\pm 5\%$.

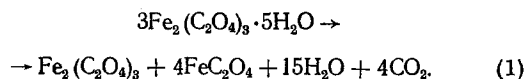
The Mössbauer and X-ray measurements were made on specimens produced in the apparatus at the same dT/dt , the specimen being rapidly cooled to room temperature at or near the turning points. The Mössbauer spectra were recorded with an apparatus of electrodynamic type [3] with Co^{57} in chromium as source.

Figures 1 and 2 show recordings for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$. The DCW and DTC curves for Fe(II) oxalate have minima at 200 and 400°C (Fig. 1), while those for Fe(III) oxalate have minima at 200, 260, and 400°C (Fig. 2).

The DTC curves show that all stages of the decomposition are endothermic. Mössbauer spectro-

scopy [4] was used to examine the phase transitions. Figures 3 and 4 show spectra of the products at various temperatures; the 200 and 400°C curves for Fe(II) oxalate represent the minima on the DCW and DTC curves. The parameters of the Fe(III) curves are given in the figure. X-ray studies were made on specimens heated to 200, 300, and 400°C under analogous conditions.

Curves a of Figs. 3 and 4 show the spectra of the initial compounds: a doublet characteristic of Fe(II) and a single line (unresolved doublet) characteristic of Fe(III) [4]. Fe(III) oxalate at 160°C (Fig. 4b) gives lines corresponding to Fe(II) oxalate; at 200°C and 230°C (Fig. 4d) there is still some residual $\text{Fe}_2(\text{C}_2\text{O}_4)_3$. The presence of Fe(II) oxalate at 200°C was confirmed by X-ray analysis. The Mössbauer spectra and the CW curve at 200°C show that the first minimum on the DTC and DCW curves (Fig. 2) corresponds to



The table gives the % weight loss calculated from the proposed reactions and as actually observed (CW curve), the actual loss at 200°C for Fe(III) oxalate being 30%, whereas (1) gives 31.8%. There is only 1.6% loss at 160°C, although the Mössbauer spectrum indicates the presence of much Fe(II) oxalate, which is due to the delay in gas release.

Fe(II) oxalate at 200°C shows dehydration,

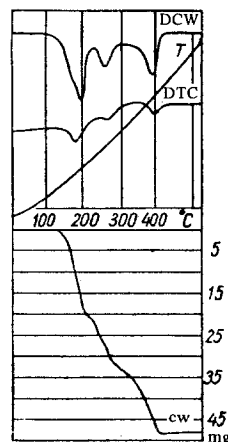
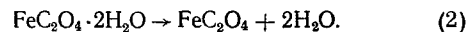


Fig. 2. Recordings for $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ in nitrogen.

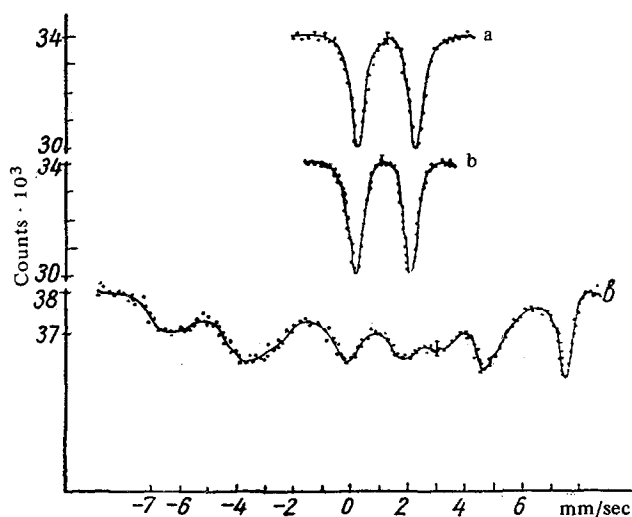


Fig. 3. Room-temperature Mössbauer spectra for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposing in nitrogen: a) initial material, b) and c) decomposition products at 200 and 400° C.

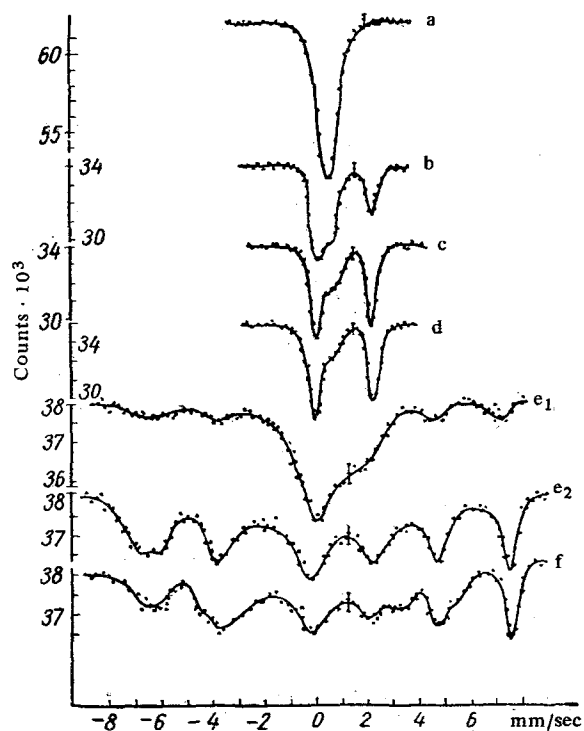


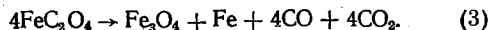
Fig. 4. Mössbauer spectra for $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ decomposing in nitrogen: a) initial material, b)–f) products at 160, 200, 230, 280, and 400° C. The two spectra for 280° C were recorded at: e₁) 77° K, e₂) 300° K; the other spectra were recorded at room temperature.

Temperature and Weight Characteristics of the Pyrolysis of Iron Oxalates

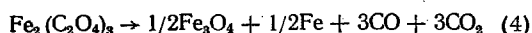
Compound	Temp. range	DCW min.	DTC min.	Supposed reaction	% decomp.	
					calc.	exp.
$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$	130—220	200	190	$3\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{C}_2\text{O}_4)_3 + 4\text{FeC}_2\text{O}_4 + 15\text{H}_2\text{O} + 4\text{CO}_2$	31.8	30
	220—320	260	260	$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \rightarrow 1/2\text{Fe}_3\text{O}_4 + 1/2\text{Fe} + 3\text{CO} + 3\text{CO}_2$	15.4	15
	320—420	395	395	$4\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe} + 4\text{CO} + 4\text{CO}_2$	21.3	24
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	150—250	205	200	$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}$	20.0	20
	300—420	395	400	$4\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe} + 4\text{CO} + 4\text{CO}_2$	39.3	37

The CW curve (Fig. 1) gives 20% loss; (2) predicts 20% loss. Figure 3b shows the Mössbauer spectrum. Fe(II) oxalate is present in the Fe(III) oxalate heated to 160° C, while the above dehydration starts only at 200° C, so the reduction of Fe(III) to Fe(II) (with release of CO_2) precedes the dehydration. It is stated [5] that the conversion of Fe(III) oxalate to Fe(II) oxalate starts at 140° C.

Thus at 200° C we get conversion of Fe(III) oxalate to Fe(II) oxalate and also dehydration of the latter, although some Fe(III) oxalate persists even at 230° C. The DCW and DTC minima at 260° C occur only for Fe(III) oxalate (Fig. 2), but these are best elucidated by first considering the processes corresponding to the minimum at 400° C, which occurs for both compounds. Figures 3c and 4f show the Mössbauer spectra of the products from Fe(III) oxalate and Fe(II) oxalate at this point; these spectra reveal the presence of Fe_3O_4 and metallic iron, which is confirmed by the X-ray results. For instance, the power pattern of $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ heated to 400° C shows lines characteristic of Fe_3O_4 and metallic iron. The product is Fe_2O_3 when Fe(III) oxalate decomposes in air [6], so the 400° C minimum is ascribed to the decomposition of the Fe(II) oxalate produced from the Fe(III) oxalate. The weight loss is 24%, as against 21.3% calculated for $\text{Fe}_2(\text{C}_2\text{O}_4)_3$; the corresponding values for FeC_2O_4 are 37.0% and 39.3%. The reaction at 400° C appears to be



This gives a satisfactory explanation of the third minimum on the DCW and DTC curves for $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, and it also elucidates the relation of the second minimum on those curves to the decomposition of Fe(III) oxalate. There is 15% weight loss due to decomposition of the Fe(III) oxalate remaining after heating to 250° C, while calculation from



gives 15.4%.

However, (4) differs from (3) in giving Fe_3O_4 in a very specific state; Fig. 4e shows the

Mössbauer spectrum from Fe(III) oxalate heated to 280° C, the shape of the curve being very much dependent on the recording temperature. At 300° K (Fig. 4e₁), almost all of the Fe_3O_4 is in the paramagnetic state (one line), while at 77° K (Fig. 4e₂) there are six lines characteristic of Fe_3O_4 in the antiferromagnetic state. Decomposition at 220—320° C gives Fe_3O_4 with a very much lowered Neel point (usual value 900° K), so this Fe_3O_4 must have a particle size less than 100 Å, since this gives [7, 8] a lowered Neel point. This makes it desirable to examine this Fe_3O_4 further, especially as regards catalysis.

The 260° C minimum for Fe(III) oxalate is thus shown by the Mössbauer spectra to represent decomposition of the residual Fe(III) oxalate to give very finely divided Fe_3O_4 , which also contains some metallic iron. Decomposition at 400° C produces no specific features.

The main stages of decomposition for these oxalates are thus established. A special finely divided Fe_3O_4 is produced at 280° C. The results generally illustrate the value of combining dta with Mössbauer spectrometry in research on topochemical reactions.

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