

with hard acids (class a metals). Using this theory, it would appear that the cyanide groups in $[\text{Co}(\text{CN})_5\text{NCSe}]^{3-}$ enhance the hard character of cobalt(III) by the withdrawal of d_π electron density into their vacant π^* orbitals, thereby reinforcing the tendency of the cobalt to bond to the hard nitrogen end of the selenocyanate, while in $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$ the cyanide groups convert the cobalt(III) into a soft metal by strong σ donation of electron density, thereby making the bond to the soft sulfur end of the thiocyanate the preferred one—conclusions which seem to be mutually exclusive.

If the π -bonding explanation of Turco and Pecile¹⁷ is used to rationalize the bonding in the $[\text{M}(\text{bipy})_2(\text{SeCN})_2]$ and $[\text{M}(\text{bipy})(\text{NCS})_2]$ complexes, the con-

(17) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

clusion reached is that the π -bonding factor is of lesser importance in the selenocyanate complexes, whereas, by virtue of the parallel behavior of their infrared frequencies, π bonding would be expected to be of comparable importance for both. In point of fact, the only over-all bonding trend observed is that observed for the selenocyanate complexes which, in all of the complexes prepared thus far, exhibit the "normal" class a N-bonded, class b Se-bonded bonding pattern.

Acknowledgments.—M. Y. A. wishes to thank the Government of the Republic of Iraq for financial support throughout the course of this study. The cooperation of Professors J. C. Bailar, Jr., and T. L. Brown is gratefully acknowledged.

CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED,
MURRAY HILL, NEW JERSEY

Thermal Decomposition of Barium and Strontium Trisoxalatoferates(III)¹

By P. K. GALLAGHER

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Thermogravimetric, differential thermal, and effluent gas analyses were performed on $\text{Ba}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]_2 \cdot 8\text{H}_2\text{O}$ and $\text{Sr}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]_2 \cdot 2\text{H}_2\text{O}$. These results were compared with those of the individual oxalates and with a physical mixture having the same metallic ratio as the complex oxalates. The stoichiometry of the decomposition was found to be highly complex, involving at least four changes in the oxidation state of the iron. At an intermediate stage, a considerable fraction of the total iron has the usual oxidation state of +4.

Introduction

It was suggested by Derbyshire, *et al.*,² that the calcination of a coprecipitated barium-iron(III) oxalate produced stoichiometric barium ferrate(IV) (BaFeO_3). By analysis of the X-ray pattern of this material and comparison with that of barium titanate, they further concluded that barium ferrate(IV) had a cubic perovskite structure at room temperature. Other investigators have prepared a material approaching this composition by calcining the mixed oxides or carbonates and have discussed its properties and possible structure.³⁻⁶ The magnetic and electrical properties of the analogous strontium compound have been more extensively studied.⁷⁻¹⁰ Confirmation of the actual

existence of iron(IV) has been provided by measurements of the Mössbauer effect for the strontium¹¹ and barium¹² compounds. All the aforementioned studies, with exception of those of MacChesney, *et al.*,^{9,11} have employed nonstoichiometric material and, therefore, possible preparation of the stoichiometric compound by simple calcination of the complex oxalate has great interest.

The nature and stoichiometry of the thermal decomposition of such an alkaline earth-iron(III) oxalate is likely to be complex because of the probable changes in the oxidation state of iron. Iron(III) oxalate is readily photoreduced to iron(II) oxalate and such a reduction might occur during the thermal decomposition. The data of Derbyshire² require iron(IV) at 700° while MacChesney⁹ has shown that above about 1000° the iron is predominantly trivalent. In this work, thermogravimetric (t.g.a.), differential thermal (d.t.a.), and effluent gas analysis (e.g.a.) were performed on the individual barium, strontium, and iron(III) oxalates as well as on the coprecipitated barium or strontium trisoxalatoferates(III). Similar experiments were per-

(1) Presented at the Symposium on the Chemical Reactivity of Solids, American Chemical Society, Ann Arbor, Mich., Nov. 12-13, 1964.

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formed on a physical mixture of the appropriate individual oxalates having the same composition, except for water, as the coprecipitated compound. These data are used to elucidate the nature and stoichiometry of the thermal decomposition of these materials and to evaluate the synthesis of barium or strontium ferrate(IV) by this technique.

Experimental

Reagent grade oxalates were used without further purification. Triply distilled de-ionized water was used. The alkaline earth-iron(III) oxalate was prepared by dissolving weighed quantities of the individual oxalates in a minimum of 0.02 *M* oxalic acid at about 80°. The solution was allowed to cool slowly with constant stirring. At approximately 55°, yellow-green crystals began to separate. At room temperature the slurry was filtered and washed with acetone. The preparation was performed in the dark as much as possible and the product stored in dark bottles because the compound has a tendency to darken upon exposure to room light. X-Ray fluorescence analysis of borax beads indicated the ratio of alkaline earth to iron to be 1.50 ± 0.02 .¹³

The t.g.a. apparatus has been described previously.¹⁴ A standard heating rate of 100°/hr. was employed. Samples, 0.1000 g., were arranged in a thin uniform layer which had excellent contact with the furnace atmosphere. The d.t.a. furnace was originally built by P. D. Garn in the manner of Lodding and Hammell.¹⁵ The sample holder was a platinum block and chromel-alumel thermocouples were used. Dynamic gas atmospheres were employed with a heating rate of 600°/hr. The gas stream from the sample side of the d.t.a. apparatus could be led to a Fisher-Hamilton gas partitioner for subsequent gas analysis. The output from the chromatograph was fed to a Perkin-Elmer Model D2 integrator, which printed the integrated value and time of the peak. The results were simultaneously monitored on a Leeds and Northrup Speedomax H AZAR recorder. Helium was used as the carrier gas in both the chromatograph and furnace. In this manner the gas stream was analyzed for nitrogen, oxygen, carbon dioxide, and carbon monoxide at 10-min. intervals. A heating rate of 100°/hr. was employed for the e.g.a.

Samples of iron(III) oxalate and barium and strontium trisoxalato ferrates(III) were heated at a rate of 200°/hr. in air. Small samples were removed at 100° intervals up to 1200° and cooled rapidly. Separate samples of the barium and strontium salts were also heated at 1000° for 60 hr. and allowed to cool slowly with the furnace. X-Ray diffractometer tracings of these samples were made employing a General Electric Model XRD-3 and Cr K α radiation.

Results

For convenience of comparison, the results of the t.g.a. are plotted as the differential (d.t.g.a.) in units of per cent weight loss per minute. This was obtained by calculating the per cent weight loss during 10-min. intervals and plotting this against the average temperature during that interval. The results of the d.t.g.a., d.t.a., and e.g.a. for the compounds are presented in Figures 1-5. Values of per cent weight loss are given in Table I for the t.g.a. experiments in oxygen. The nitrogen atmosphere did not have a significant effect

on the actual values of weight loss; however, there were obvious changes in the temperatures at which some reactions occur.

The physical mixtures of the individual oxalates did not have the same thermal analysis patterns as the coprecipitated material. The separate decompositions of the iron and alkaline earth oxalates were clearly evident. The weight loss near 800° corresponded to the decomposition of three molecules of alkaline earth carbonate, indicating that there has been little if any formation of iron(IV) prior to this temperature. The separate peaks were even more evident in the d.t.a. curves. This dissimilar behavior, along with the formation of the same precipitate over a wide range of starting concentrations, indicates that the precipitate is, in fact, a true compound.

As expected, the X-ray results were not particularly illuminating since in the regions of greatest interest, *i.e.*, regions of change, the particle size was very small and the structures were poorly formed. Consequently even a semiquantitative estimate of the concentration of a component based upon its peak height or area was doubtful. As the particle size grew and the structure annealed, the intensity could vary greatly without a change in concentration. Nevertheless, the X-ray data were of qualitative value and indicated that the alkaline earth carbonates were present in the 500-900° region. The principal peak of the alkaline earth ferrate(IV)^{4,9} appeared from 600 to 700° and gradually shifted with increasing temperature to a value associated with a predominantly iron(III) constant.^{11,12} At 900° the patterns associated with Sr₃Fe₂O_{7-x}¹⁶ and Ba₃Fe₂O_{7-x}¹⁷ predominate. The exact values of the X-ray parameters vary with oxygen content but the values obtained from the calcinations at 1000°, which were allowed to cool slowly, were within experimental error of those of Brisi¹⁶ for the strontium compound and those of Derbyshire, *et al.*,² which were reported for BaFeO₃. No patterns were discernible for iron(III) oxalate samples which had been calcined at less than 500°. At temperatures greater than this the product was hematite.

Discussion

The data for barium and strontium oxalates, shown in Figures 1 and 2, are in good agreement with previous investigations.^{18,19} The stepwise endothermic loss of water, carbon monoxide, and carbon dioxide is straightforward in each case. The oxidation of carbon monoxide to carbon dioxide at the surface and in the pores and interstices of the powder leads to an exothermic peak in oxygen at around 400°. This is typical of oxalate decompositions. The split nature of these exothermic peaks may be due to a partial or local depletion of oxygen during the decomposition. The endothermic phase transition in barium carbonate

(13) This indicates a formula $M_3[Fe(C_2O_4)_3] \cdot xH_2O$, which seems reasonable on the basis of the known stability of trisoxalato ferrate(III) ion. This, however, is in contradiction to Derbyshire, *et al.*,² who implied equal numbers of barium and iron ions in the precipitate. The ratio of 1.5 was obtained for samples in which the starting iron to alkaline earth ratio in solution varied from 0.5 to 2.0 and therefore is clearly the proper value.

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TABLE I
RESULTS OF THE T.G.A. EXPERIMENTS IN OXYGEN

Compound	Temp. range, °C.	Products ^a		% wt. loss	
		Solid	Gas	Obsd. ^b	Calcd.
BaC ₂ O ₄ ·1/2H ₂ O	100-150	BaC ₂ O ₄	1/2H ₂ O	3.1	3.4
	400-525	BaCO ₃	CO	12.2	11.9
	900-1200	BaO	CO ₂	19.0	18.8
SrC ₂ O ₄ ·H ₂ O	100-175	SrC ₂ O ₄	H ₂ O	9.2	9.3
	400-500	SrCO ₃	CO	14.1	14.5
	700-950	SrO	CO ₂	23.4	22.7
Fe ₂ (C ₂ O ₄) ₃ ·6H ₂ O	50-125	Fe ₂ (C ₂ O ₄) ₃ ·3H ₂ O	3H ₂ O	8.1	11.2
	125-170	Fe ₂ (C ₂ O ₄) ₃	3H ₂ O		11.2
	150-350	2FeC ₂ O ₄	2CO ₂	[57.2]	18.2
	225-350	Fe ₂ O ₃	2CO ₂ , 2CO		26.4
Ba ₃ [Fe(C ₂ O ₄) ₃] ₂ ·8H ₂ O	50-175	Ba ₃ [Fe(C ₂ O ₄) ₃] ₂	8H ₂ O	11.1	12.4
	175-300	Ba ₃ Fe ₂ (C ₂ O ₄) ₅	2CO ₂	7.6	7.6
	300-400	3BaCO ₃ , Fe ₂ O ₃	2CO ₂ , 5CO		18.2
	300-800	BaCO ₃ , 2BaFeO _{2.5}	1.4CO ₂ , 0.6CO	[23.8]	5.1
	750-900	Ba ₃ Fe ₂ O _{6.6}	CO ₂	[5.5]	3.8
	>800	Ba ₃ Fe ₂ O ₆	0.3O ₂		0.5
Sr ₃ [Fe(C ₂ O ₄) ₃] ₂ ·2H ₂ O	100-175	Sr ₃ [Fe(C ₂ O ₄) ₃] ₂	2H ₂ O	3.5	3.8
	175-350	Sr ₃ Fe ₂ (C ₂ O ₄) ₅	2CO ₂		9.4
	300-450	3SrCO ₃ , Fe ₂ O ₃	2CO ₂ , 5CO	[32.2]	22.6
	500-650	SrCO ₃ , 2SrFeO _{2.5}	1.4CO ₂ , 0.6CO	5.6	6.3
	700-900	Sr ₃ Fe ₂ O _{6.6}	CO ₂		4.7
	>800	Sr ₃ Fe ₂ O ₆	0.3O ₂	[4.9]	0.5

^a These are based on mechanisms proposed in the Discussion and subject to the limitation described. There is an uptake of oxygen involved in the oxidation of iron(II). ^b The observed values quoted at high temperatures are not necessarily for the temperature span indicated but only include weight losses to the highest temperature indicated in the appropriate figure. Values in brackets are sums for reactions which overlap as indicated in the temperature column.

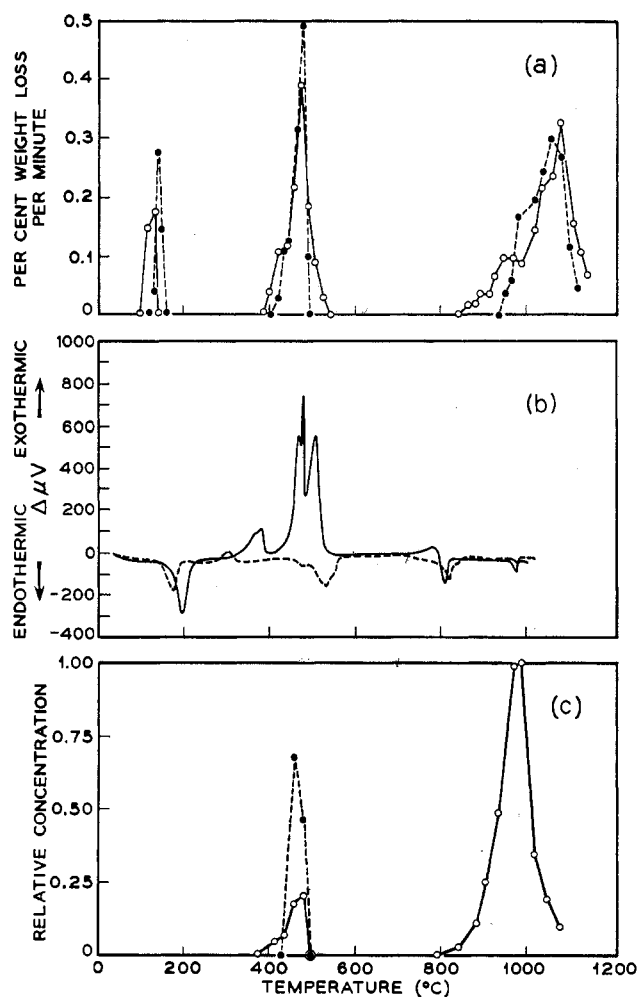


Figure 1.—Thermal analysis of barium oxalate: (a) d.t.g.a. — in O₂, - - - in N₂; (b) d.t.a. — in O₂, - - - in He; (c) e.g.a. — CO₂, - - - CO.

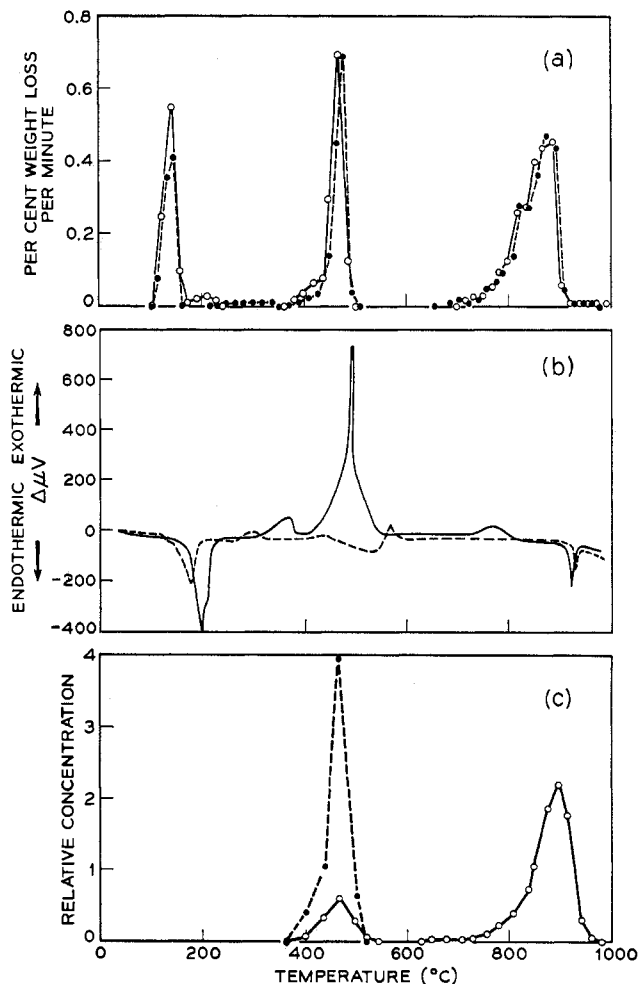


Figure 2.—Thermal analysis of strontium oxalate: (a) d.t.g.a. — in O₂, - - - in N₂; (b) d.t.a. — in O₂, - - - in He; (c) e.g.a. — CO₂, - - - CO.

near 800° is well-known and clearly evident; a similar but smaller peak occurs in the strontium curve. This small peak is closer to the carbonate decomposition, and since the weight loss peak appears asymmetric it may be associated with the loss of carbon dioxide in an unspecified two-step process rather than a phase transition.

Points pertinent to the subsequent discussion are the temperature of anhydrous oxalate and carbonate decompositions, for comparison with mixed and coprecipitated material, and the disproportionation of the carbon monoxide. Carbon monoxide is thermodynamically unstable in this region of temperature but the kinetics of the reaction are normally unfavorable. Apparently there is catalytic action by either the furnace walls or the finely divided carbonate because a significant amount of carbon dioxide is evident in the effluent gases. Failure to detect the carbon, formed by the possible disproportionation, in the t.g.a. experiments is probably the result of either its rapid oxidation upon formation or the suppression of the disproportionation because of the direct oxidation of the carbon monoxide. The exclusion of oxygen, to the extent necessary to prevent the oxidation, was impossible in the t.g.a. apparatus employed due to the hole at the top of the furnace tube for the exit of the sample suspension wire.

The decomposition of iron(III) oxalate is more complex as shown in Figure 3. Much less prior information is available for this compound. Dollimore, *et al.*,²⁰ have performed t.g.a. experiments in air and, although the total weight loss, initial temperature of decomposition, and end product are compatible with this work, the shape of the weight loss curve is markedly different. Figure 3 and the weight loss given in Table I distinctly show the two-step loss of water with the additional loss of a molecule of carbon dioxide simultaneous with or immediately following the last three molecules of water. Dollimore, *et al.*,²⁰ indicate a single unresolved weight loss. Their use of a much larger sample (1.5 g.) may have caused the reduced resolution.

The proposed scheme of decomposition is indicated in Table I. The temperature separation between the loss of water and carbon dioxide is based on the results of the e.g.a. The formation of iron(II) oxalate is inferred from the separation of the carbon dioxide and monoxide peaks near 350°. It is also consistent with the multistep appearance of the d.t.a. and results presented later for the complex oxalates. There is a much more apparent dependence of the decomposition temperature upon atmosphere. The observed decomposition temperature of iron(II) oxalate is compatible with its immediate decomposition upon formation.^{21,22} This would further complicate any possible resolution. Similar reductions have been shown to occur in the decomposition of

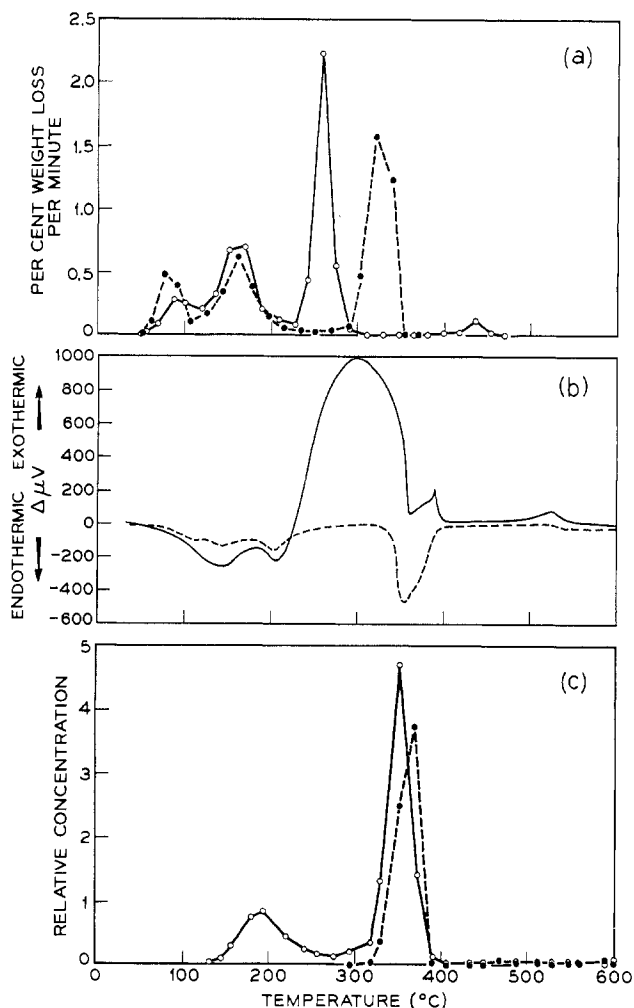


Figure 3.—Thermal analysis of iron(III) oxalate: (a) d.t.g.a. ——— in O₂, - - - - in N₂; (b) d.t.a. ——— in O₂, - - - - in He; (c) e.g.a. ——— CO₂, - - - - CO.

europium(III) oxalate²³ and barium or strontium titanyl oxalates.²⁴

The small weight loss near 450° probably arises from the desorption of gas associated with the crystallization of the amorphous iron(III) oxide. The X-ray results indicated such an ordering process in this temperature range. The exothermic peak which should be associated with this process has very likely been assimilated with the major decomposition peak at the lower temperature. Presumably the lower heating rate enables the distinction in the d.t.g.a. curve.

Figures 4 and 5 present the results of the thermal analysis of the strontium and barium trisoxalatoferates(III), respectively. The proposed scheme of decomposition for both complex oxalates is indicated in Table I. The quoted zones of temperature are naturally not exact. The comparison of calculated and observed weight losses is quite satisfactory in view of the overlapping reactions.

Reactions which lead to the formation of the alkaline earth carbonate and iron(III) oxide are similar to those for the individual oxalates but it is significant

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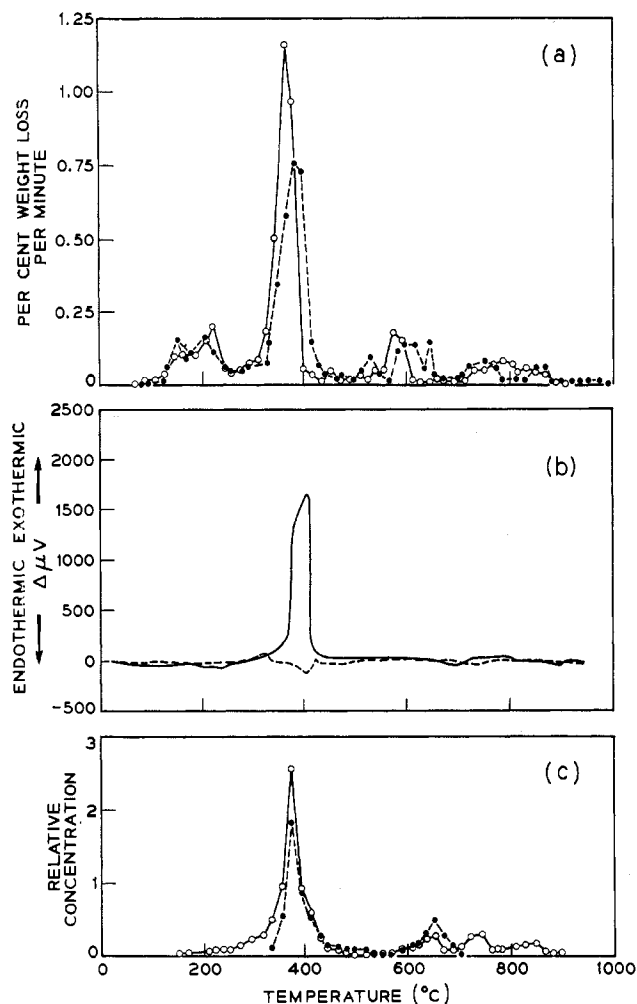


Figure 4.—Thermal analysis of strontium trisoxalatoferate(III): (a) d.t.g.a. ——— in O₂, - - - - in N₂; (b) d.t.a. ——— in O₂, - - - - in He; (c) e.g.a. ——— CO₂, - - - - CO.

that the major decompositions of the iron(II) and alkaline earth oxalate portions occur simultaneously. This decomposition shows as a single peak in all the curves. The subsequent step in Table I is the interesting one in that it leads to the formation of iron(IV). The conversion to iron(IV) is incomplete and in fact only slightly more than one-half of the total iron is oxidized to iron(IV). There is a wide range of solubility of anion vacancies in these compounds.^{9,17,25} In the formation of iron(IV) the necessary oxygen is obtained by distorting the ratio of gases in favor of carbon monoxide, rather than introducing ambient oxygen, because the reaction occurs even in the absence of oxygen,^{9,25} although to a lesser extent. In addition the e.g.a. indicates a significant amount of carbon monoxide in this region. Subsequent loss of oxygen and conversion to the alkaline earth ferrate(III) is slow and would take place over a wide range; however, the heating rate is such that equilibrium is probably not established during this process. The $M_3Fe_2O_{7-x}$ compounds

(25) J. B. MacChesney, J. F. Potter, R. C. Sherwood, and H. J. Williams, Paper FA10, National Meeting of The American Physical Society, New York, N. Y., Jan. 28, 1965; to be published.

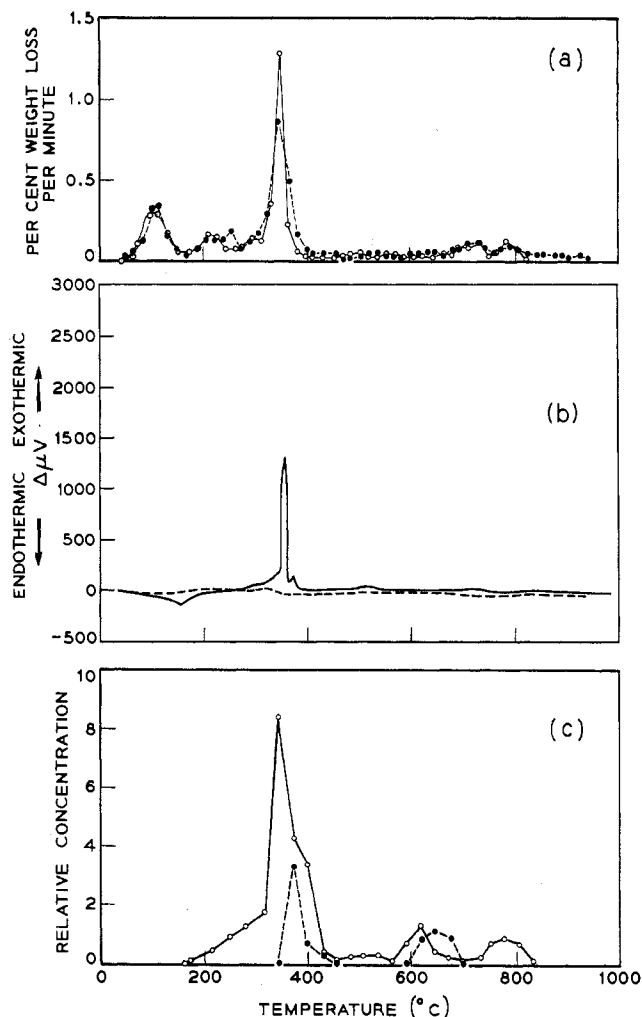


Figure 5.—Thermal analysis of barium trisoxalatoferate(III): (a) d.t.g.a. ——— in O₂, - - - - in N₂; (b) d.t.a. ——— in O₂, - - - - in He; (c) e.g.a. ——— CO₂, - - - - CO.

continue to lose oxygen as the temperature increases. Measurements of the Mössbauer effect during the decomposition of strontium trisoxalatoferate(III) clearly support the frequent changes in oxidation state proposed.²⁶

The results of the X-ray analysis are consistent with the proposed mechanisms of decomposition. The structure of the oxygen-deficient barium ferrate(IV) is hexagonal.^{4,6,12,25} The cubic pattern reported by Derbyshire, *et al.*, is associated with a polymorph of Ba₃Fe₂O_{7-x}.¹⁷ Strontium ferrate(IV) is cubic^{9,10} and undergoes a tetragonal distortion with increasing concentration of anion vacancies.⁹ The Sr₃Fe₂O_{7-x} compound is tetragonal.^{16,17}

Conclusions

Barium and strontium trisoxalatoferates(III) are readily precipitated from a dilute oxalic acid solution. Thermogravimetric, differential thermal, effluent gas, and X-ray diffraction analyses were employed to determine the nature and stoichiometry of the thermal de-

(26) P. K. Gallagher and C. R. Kurkjian, paper presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4-9, 1965; to be published.

composition of these compounds. Comparisons were made with similar analyses of the individual oxalates and appropriate physical mixtures thereof. The results indicate that the oxidation state of the iron changes frequently during the course of the decomposition of the complex oxalates and in the region of 700–900° the principal oxidation state is iron(IV). The components of the mixtures, however, behave independently and do not appear to form significant amounts

of iron(IV) at these temperatures. Unfortunately, decomposition of the complex oxalate does not yield stoichiometric barium or strontium ferrate(IV), as had been previously suggested.²

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CONTRIBUTION FROM RCA LABORATORIES,
PRINCETON, NEW JERSEY

Rare Earth Sesquiselenides and Sesquitellurides with the Sc_2S_3 Structure

BY J. P. DISMUKES AND J. G. WHITE

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The sesquiselenides of Sc, Yb, Tm, Ho, and Y and the sesquitellurides of Tm, Ho, Dy, and Y have the Sc_2S_3 structure which is a superstructure of the NaCl type based on the ordering of cation voids. The tellurides with this structure are stable only over a very narrow range of cation/anion radius ratio, centered at about 0.414. This suggests that the tellurides require both cation–anion and anion–anion contacts to stabilize the structure. The selenides are stable over a wider range of radius ratio, and the relative values of the orthorhombic cell parameters a , b , and c show appreciable deviation from the ideal values 2, $\sqrt{2}$, and $3\sqrt{2}$, respectively, times the NaCl subcell parameter a_0 . Thus, factors other than geometrical considerations are important in determining the stability of the selenides.

Introduction

The rare earth sesquichalcogenides, Ln_2X_3 , of the elements from La to Gd crystallize principally in a defect-type Th_3P_4 structure,¹ of which Ce_2S_3 is a well-known example.² The structures of most of the sesquichalcogenides of the higher atomic number rare earth elements, Tb to Lu, are not well characterized, however. Single crystal data are almost entirely lacking, and even X-ray powder data are not available for many of these compounds of Tb, Ho, and Tm. Although unit cell dimensions for some compounds obtained from X-ray powder data have been reported,^{2–9} only the structures of Yb_2S_3 and Lu_2S_3 ,⁹ both $\alpha\text{-Al}_2\text{O}_3$ type, have been established.

Very recently, however, Haase, Steinfink, and Weiss¹⁰ have shown that Er_2Se_3 and Er_2Te_3 have the Sc_2S_3 -

type structure,¹¹ which is a superstructure of the NaCl type based on the ordering of cation voids. In Sc_2S_3 the unit cell is orthorhombic with $a = 2a_0$, $b = \sqrt{2}a_0$, and $c = 3\sqrt{2}a_0$, where a_0 is the NaCl-type subcell lattice constant. The axes a , b , and c are parallel to the directions $[100]$, $[011]$, and $[01\bar{1}]$, respectively, of the subcell. The fact that Flahaut, *et al.*,⁸ have reported a face-centered cubic subcell for many of the sesquiselenides and sesquitellurides of the higher atomic number rare earth elements suggests that the occurrence either of the Sc_2S_3 structure or of another structure having a NaCl-type subcell is widespread in these compounds. The sesquisulfides of these rare earth elements, however, appear not to have the Sc_2S_3 structure.^{3,4,9,12} Therefore, the present investigation is limited to the occurrence and range of stability of the Sc_2S_3 structure among the sesquiselenides and sesquitellurides of the rare earth elements between Gd and Lu, which also includes Y and Sc because of their chemical similarity.

Experimental

Preparation.—Polycrystalline samples of Sc_2Se_3 and Sc_2Te_3 were prepared by the direct reaction in stoichiometric propor-

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(12) We have prepared the sesquisulfides of all the high atomic number rare earth elements. Tb_2S_3 had the Th_3P_4 structure with $a_0 = 8.333 \text{ \AA}$. Ho_2S_3 and Tm_2S_3 , data for which have not been published to our knowledge, give very complex powder patterns and appear to be isostructural with Er_2S_3 and Y_2S_3 . However, indexing of these compounds on the basis of the monoclinic unit cell suggested by Picon, *et al.*,³ has not yet been tested. The data for Lu_2S_3 agree with that published by Flahaut, *et al.*⁹ Thus none of these compounds appears to have the Sc_2S_3 structure.