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Thermogravimetric Pyrolysis of Cupferron Complexes of Scandium, Yttrium, and Rare Earth Elements

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The thermogravimetric pyrolysis of the scandium, yttrium, and the rare earth cupferrates was determined. It was found that it is not necessary to ignite the complexes to 900° C. but that the oxide level is reached at 500° to 600° C. The construction and operation of a simple thermobalance are described.

THE use of cupferron (ammonium salt of *N*-nitroso-phenylhydroxylamine) as a precipitant for the rare earth elements has recently been investigated (*5*). It was found that the rare earth elements—lanthanum, cerium(III), praseodymium, neodymium, samarium, and gadolinium—were quantitatively precipitated from solution at a pH of 3 to 4. As the precipitates were contaminated with an excess of cupferron, they were ignited and weighed as the corresponding oxides. This study was undertaken to determine the optimum temperature limits for the ignition to the oxide and also to investigate any intermediate products that may be formed during the decomposition.

EXPERIMENTAL

Reagents. Cupferron was obtained from the G. F. Smith Chemical Co., Columbus, Ohio, and the Matheson, Coleman, Bell Co., East Rutherford, N. J. It was used without further purification.

The rare earths were obtained as the oxides of better than 99% purity from Research Chemicals, Inc., Burbank, Calif., and the Lindsay Chemical Co., West Chicago, Ill. As the contaminants were other rare earth elements, no further purification was necessary.

Scandium oxide of 99.8% purity was obtained from A. D. Mackay, Inc., New York, N. Y.

Yttrium chloride of 99% purity was obtained from Research Chemicals, Inc., Burbank, Calif.

All other reagents were of analytical reagent grade.

Thermobalance. In a recent book, Duval (*1*) summarizes the development of the thermobalance. He found that if a standard beam balance were used, the vibration soon dulled the knife edges and could also result in the beam's being displaced from the center position. These difficulties were overcome by the use of a multiple-range, precision torque balance. The balance was converted into a thermobalance as shown in Figure 1. The torque balance, 0 to 100 mg. in range, was made by the Vereenigde Draadfabrieken, Nijmegen, Holland. The smallest scale division was 0.2 mg.; thus, weighings could be made to ±0.1 mg. The sample was placed in a platinum boat, 1 cm. in diameter, suspended by a platinum wire, in a Vycor glass tube, 2.5 cm. in diameter and about 25 cm. in length. This tube was connected to the balance by a ₮ 29/42 joint at *B*. The furnace, *A*, was constructed by first winding 15 feet of No. 22 gage, Nichrome alloy V, resistance wire (1.01 ohms per foot), into a coil $^1/_8$ inch in diameter, then winding this coil onto the asbestos-covered tube at about $^1/_4$-inch spacings. The completed windings were covered adequately with asbestos insulation.

The heating rate of the furnace was controlled by a 6 revolutions-per-day 110-volt synchronous motor connected to the shaft of a Powerstat. The heating rate was linear from 35° to 950° C., at about 4.5° per minute. A slower heating rate could be obtained by decreasing the input voltage into the motor-driven Powerstat.

The temperature of the furnace was measured by an iron-constantan thermocouple, *T*, using an ice bath as the reference junction. The potential of the thermocouple was detected by a Gray portable potentiometer, Model E-3042-S, made by the Gray Instrument Co., Philadelphia, Pa. The thermocouple was calibrated against the freezing point and boiling point of water, and the freezing points of cadmium metal and potassium chloride. The electromotive force of the thermocouple could be read to within ±0.05 mv., which corresponds to about ±1°.

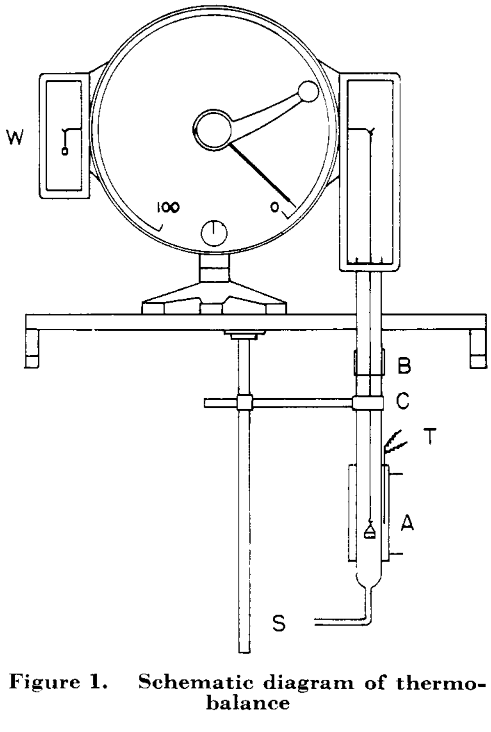

Figure 1. Schematic diagram of thermobalance

It was found that during the pyrolysis of the cupferron complexes, the decomposition products adhered to the sides of the tube and the suspending wire. To prevent this difficulty, a suction was applied to the tube, *S*, which allowed a slow stream of air to pass over the sample. No adverse effects could be detected by the balance. Usually, a bubble count of 3 per second was used.

The accuracy and reproducibility of the thermobalance compared favorably with the Chevenard recording balance (*1*). This was shown by the thermal decomposition of $Na_2HPO_4.12H_2O$. The resultant curve agreed to within 1% of that previously determined.

Procedure. The cupferron complexes of scandium, yttrium, and the rare earth elements were prepared as previously described (*5*). The complexes with scandium and yttrium have not been previously reported, although Pokras (*4*) noted that cupferron precipitated scandium quantitatively from a neutral solution. Coprecipitation was observed as with the rare earth complexes as the ratios of metal to cupferron found were slightly greater than 1 to 3. All of the precipitates were dried at room temperature for at least 24 hours before being pyrolyzed on the thermobalance.

The decomposition of the complexes was carried out by placing 100 to 200 mg. of the dried complex in the platinum boat and suspending it in the furnace. Since the torque balance has a range of 0 to 100 mg., a counterweight was attached at *W*. The motor-driven Powerstat was set at 0 volts, and the input voltage was adjusted to 60 volts by means of another Powerstat. After the rate of air flow through the furnace was adjusted, the weight of the sample in the boat was determined, and the synchronous motor was started. Readings on the balance and the potentiometer were taken at short intervals until a temperature of about 800° C. was reached. Each decomposition took about 3.5 hours to complete. At least two runs were made of each complex with agreement to within 1%.

DISCUSSION

The pyrolysis curves are shown in Figures 2 and 3. The curves of lanthanum, praseodymium, neodymium, samarium, and scandium are similar in appearance. The thermal stabilities of these rare earth cupferrates are remarkably higher than those of any other cupferrates so far determined. Previously reported iron(III) and copper(II) cupferrates were stable to 98° and 118° C., respectively (*3*). In the case of the rare earth cupferrates, the first decomposition begins at about 150° to 180° C. where there is a small break in the curve and then a plateau extending to about 280° to 290° C. This break has also been observed in the case of aluminum cupferrate (*2*) but at a corresponding lower temperature. Another decomposition then occurs and a slight plateau is again formed, which decomposes to the oxide at 450° to 600° C. As far as could be determined, the intermediate plateaus do not correspond to any stoichiometric compositions and are probably mixtures. The melting points of the rare earth cupferrates are from 182° to 188° C., very close to the point where the first decomposition occurs.

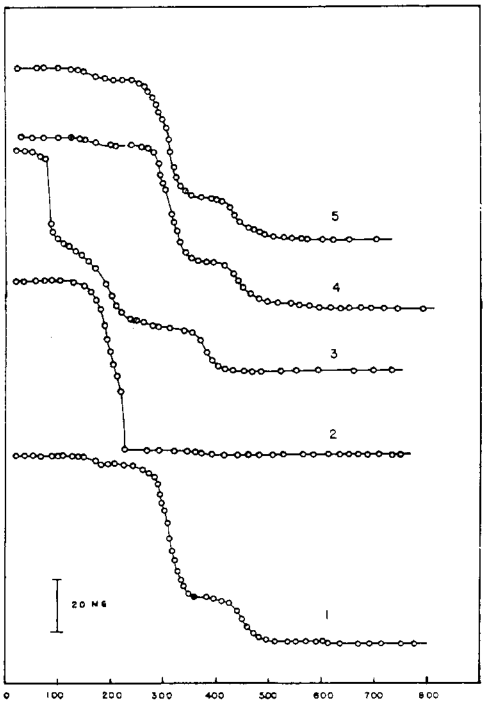

Figure 2. Pyrolysis curves of rare earth cupferrates

1. **Lanthanum cupferrate**
2. **Cerium(III) cupferrate**
3. **Cerium(IV) cupferrate**
4. **Praseodymium cupferrate**
5. **Neodymium cupferrate**

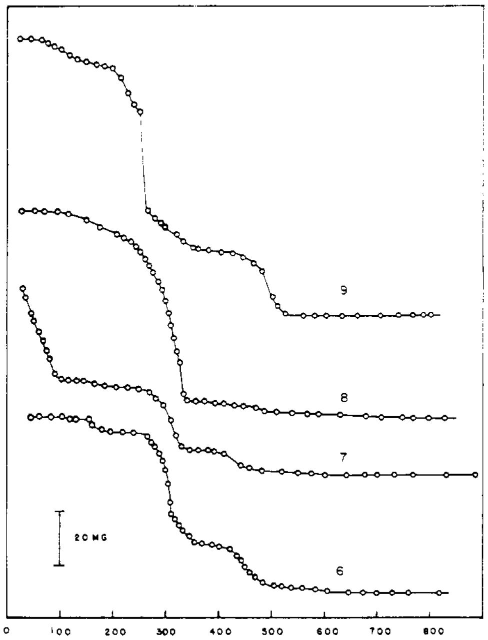

Figure 3. Pyrolysis curves of scandium, yttrium, and rare earth cupferrates

6. **Samarium cupferrate**
7. **Gadolinium cupferrate**
8. **Yttrium cupferrate**
9. **Scandium cupferrate**

The pyrolysis curves for cerium(III) and yttrium are similar. No intermediate plateaus were observed, the decomposition proceeding directly to the corresponding oxides.

The least stable of the complexes seem to be those of cerium(IV) and gadolinium. When anhydrous, they begin to decompose at room temperature. This would probably be expected of cerium(IV) because of its tendency to revert to the lower oxidation state, but the instability of the gadolinium complex cannot be explained.

CONCLUSION

It hardly seems necessary to ignite the cupferron complexes to 900° C. as previously described. This temperature is far too high, as the oxide level is reached at 500° to 600° C. The intermediate products formed in the case of the lanthanum, praseodymium, neodymium, samarium, gadolinium, and scandium complexes are being further investigated.

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