THE THERMOLYSIS OF SOME TRANSITION METAL CHELATES WITH 2-(o-HYDROXYPHENYL)-BENZOXAZOLE

by

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The use of 2-(o-hydroxyphenyl)-benzoxazole (HPB) for the gravimetric determination of cadmium was introduced by WALTER AND FREISER[1]. They found that the chelating agent was fairly selective for cadmium ions and that the metal chelate possessed excellent thermal properties. In fact, there was no color change when the chelate was heated up to 275° in a capillary tube and no sign of melting even at 300°.

Further use of this reagent was made by BYRN AND ROBERTSON[2] who found that copper(II) ions could be selectively precipitated in the presence of ethylenediaminetetraacetic acid as a masking agent. The copper chelate, in this case, was dried at 130–140°.

CHARLES AND FREISER[3] have shown that a number of other metal ions are also precipitated by HPB. The Cu(II), Ni, Zn and Co(II) HPB chelates showed no evidence of melting or decomposition at 300°, the highest temperature they tried. They found, however, that the lead HPB chelate began to decompose at about 280°, but did not melt at 300°.

In view of the excellent thermal stability of this class of chelates and the potential uses of this reagent for the determination of Cd and Cu(II), it was of interest to study the HPB chelates of Cd, Cu(II), Co(II) and Ni on the thermobalance.

EXPERIMENTAL

Reagents

2-(o-Hydroxyphenyl)-benzoxazole was obtained from Eastman Organic Chemicals, Rochester, N. Y

All other chemicals were of reagent grade quality.

Thermobalance

The thermobalance used had been previously described[4] A heating rate of 5.4°/min was used

Preparation of metal chelates

The cadmium HPB chelate was prepared as previously described[1].

The copper HPB chelate was prepared as previously described[2]

The other metal HPB chelates were prepared as previously described[3]

All of the metal HPB chelates were air dried at room temperature (25–20°) for at least 24 h before thermal decomposition on the thermobalance

DISCUSSION

The thermal decomposition curves are shown in Fig. 1 with the metal chelate stability temperatures and minimum oxide level temperatures given in Table I. In general, the metal chelates possessed excellent thermal properties. After a slight weight loss due

References p. 640

to absorbed moisture, the metal chelates began to decompose in the 165 to 285° temperature range. These results reveal that the metal chelates can be dried at fairly high temperatures before decomposition takes place. The metal oxide level temperatures began in the 500 to 595° temperature range. However, it would not be advantageous to ignite the metal chelates to the oxides because they possess favorable gravimetric factors and excellent thermal stabilities.

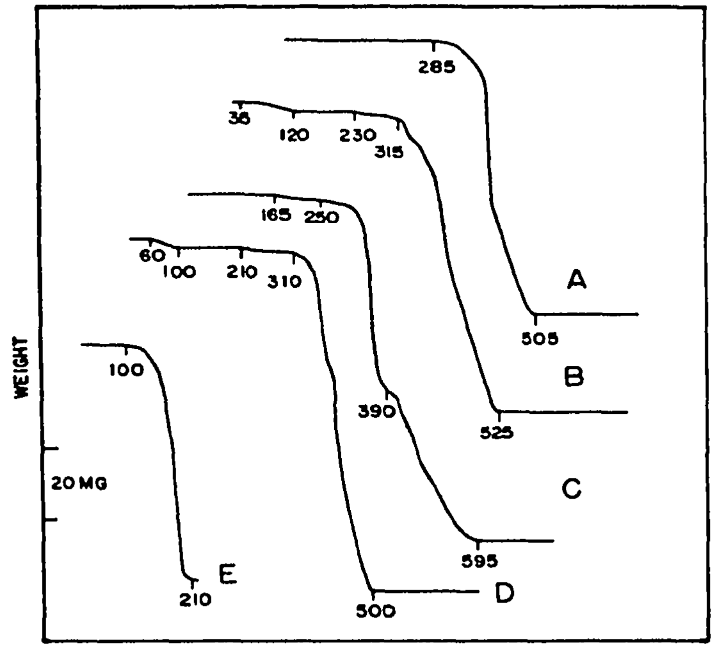

Fig. 1 The thermal decomposition of the metal HPB chelates.
A Cadmium HPB chelate
B Nickel HPB chelate
C Copper(II) HPB chelate
D Cobalt(II) HPB chelate
E HPB

TABLE I

THERMAL PROPERTIES OF METAL 2-(o-HYDROXYPHENYL) BENZOXAZOLE CHELATES

Metal	*Chelate stability temp.* °C	*Minimum oxide level temp.* °C
HPB	<100	—
Cadmium	<285	>505
Copper(II)	<165	>525
Cobalt(II)	<210	>500
Nickel	<230	>525

References p. 640

2-(o-Hydroxyphenyl)-benzoxazole

The reagent was first studied on the thermobalance to determine its thermal properties. If the reagent possessed a favorable sublimation temperature or boiling point, it may be possible to remove any coprecipitated reagent in the metal chelates by heating. However, this was not found to be the case.

The reagent began to lose weight at 100°. Beyond this temperature the weight loss was rapid, resulting in a small amount of carbonaceous matter in the thermobalance pan at 210°. The melting point of the compound was 124–126°, hence, there was some weight loss before it melted.

Cadmium HPB chelate

The air dried cadmium HPB chelate was stable up to 285°. Beyond this temperature, the chelate decomposed rapidly, giving the CdO level at 505°. From the thermal decomposition curve, the drying temperature of 130–140° previously suggested[1] appears justified. However, higher temperatures may be employed if necessary. The cadmium chelate was the most stable of all of the HPB metal chelates studied in this investigation.

Copper(II) HPB chelate

The copper HPB chelate was stable up to 165°. Beyond this temperature, a slight weight loss occurred, becoming more rapid above 250°, and finally giving the CuO level at 595°. Again, the drying temperature of 130–140° appears to be justified[2]. The Cu HPB chelate was the least stable of all of the metal chelates studied.

Nickel HPB chelate

The thermal decomposition curve of the nickel HPB chelate revealed that a small amount of water was retained by the chelate after air drying. This water began to come off at 35° and was completely lost at 120°. From 120 to 230° a horizontal weight level appeared which corresponded to the anhydrous chelate. At 230° the chelate began to lose weight slowly. Beyond 315°, however, the chelate decomposed rapidly, giving the NiO level at 525°.

Cobalt(II) HPB chelate

The thermal decomposition curve of the Co HPB chelate was almost identical to that of the Ni chelate. Absorbed water began to come off at 60° and was completely lost at 100°. The anhydrous chelate was stable between 100 and 210°. Beyond 210°, however, the chelate began to decompose slowly. Above 310° the decomposition became quite rapid to give the Co_3O_4 level beginning at 500°.

SUMMARY

The thermal decomposition of the 2-(o-hydroxyphenyl)-benzoxazole chelates of Cd, Cu(II), Co(II), and Ni were studied on the thermobalance. The metal chelates possessed excellent thermal properties. The first weight losses for the chelates appeared in the 165 to 285° temperature range. The minimum metal oxide levels appeared in the 500 to 595° temperature range.

REFERENCES

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Received October 14th, 1957