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Note

THERMAL DECOMPOSITION OF DERIVATIVES OF ORGANOCOBALT(III)

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In recent years, we have principally studied the electrochemical oxidation of complexes of organocobalt(III) containing equatorial ligands with a delocalized electronic structure (derivatives of $(\text{dmg-H})_2$, salen, bae, salophen, salpn, salcn) [1–4].

In the literature, little information exists concerning the thermal behavior of these compounds [5,6].

With the aim of contributing to the knowledge of the thermal stability, especially of the Co–C bond, and to propose mechanisms for their thermal decomposition, these complexes were studied using conventional methods and thermogravimetry (TG).

EXPERIMENTAL

The hexacoordinated complexes were prepared in methanol according to the following reactions [7]

$$\text{L} + \text{Co(II)} + \text{NaOH} \overset{N_2}{\rightarrow} [\text{Co(II)L}]$$

$$[\text{Co(II)L}] + \text{BH}_4^- + \text{OH}^- \overset{N_2}{\rightarrow} [\text{Co(I)L}]^-$$

$$[\text{Co(I)L}]^- + \text{RX} + \text{H}_2\text{O} \overset{N_2}{\rightarrow} [\text{RCo(III)L} \cdot \text{H}_2\text{O}]$$

The pentacoordinated complexes were obtained in tetrahydrofuran according to the reactions [8,9]

$$[\text{Co(II)L}] + \text{Na/Hg} \overset{N_2}{\rightarrow} \text{Na}[\text{Co(I)L}] + \text{Hg}$$

$$\text{Na}[\text{Co(I)L}] + \text{RX} \overset{N_2}{\rightarrow} [\text{RCo(III)L}]$$

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The microanalyses of these complexes show a relative error of less than 0.5% for N and H and < 2% for C with respect to the theoretical composition.

TG curves, to a maximum temperature of 800°C, were obtained on a Perkin-Elmer (model 765-1) thermobalance. Samples of approximately 0.8 mg were used, heated at a rate of 5°C min^{-1} in air at atmospheric pressure.

RESULTS AND DISCUSSION

The thermal decomposition of the complexes studied, as well as the kinetics of decomposition, follow characteristic pathways, depending on the nature of the ligands, as can be seen from the TG curves of Fig. 1.

An analysis of the TG curves, in conjunction with the results of conventional analyses, permits the following mechanisms of thermal decomposition to be suggested for these complexes.

(1) [MeCo (dmgH)$_2 \cdot H_2O$]

Three consecutive steps are observed in the thermal decomposition of this complex. The experimental data suggest:

(a) 150–250°C: loss of H_2O, CH_3 and $2HNO_2$. The elimination of HNO_2

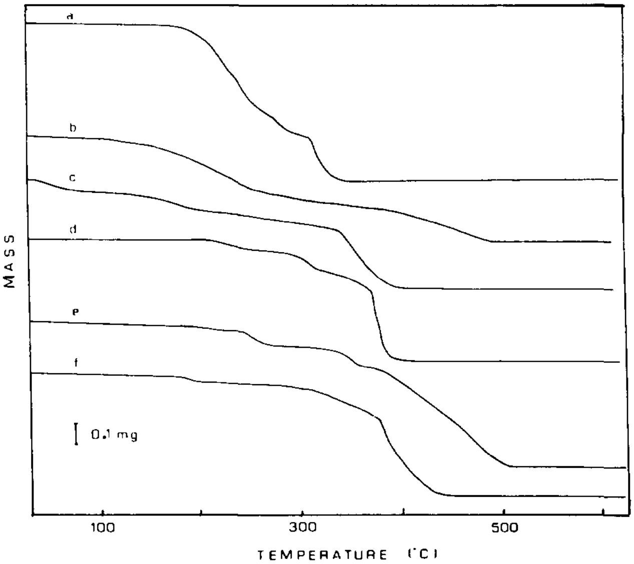


Fig. 1. TG curves of the complexes [RCo(III) (L)B] obtained with a platinum crucible without cover. Heating rate: 5°C min^{-1}. (a) [MeCo(dmgH)$_2 \cdot H_2O$] (0.969 mg); (b) {MeCo[(DO)(DOH)en]$\cdot H_2O$}BΦ_4 (0.777 mg); (c) [MeCo(bae)$\cdot H_2O$] (0.735 mg); (d) [MeCo(salen)] (0.873 mg); (e) [MeCo(salpn)] (0.914 mg); (f) [MeCo(salophen)] (0.782 mg).

at this stage was confirmed by the test with sulfanilic acid and α-naphthylamine. The formation of HNO_2 appears to be favored by the structure of the complex, since it was not detected in the decomposition of dimethylglyoxime;

(b) 250–310°C: partial loss of the ligand C_4H_6;

(c) 310–360°C: loss of the rest of the ligand $(CH_3CN)_2$ as CO_2 and HNO_2, with the formation of Co_3O_4, which was confirmed by X-ray analysis of the thermal decomposition product.

(2) $\{MeCo[(DO)(DOH)en]\cdot H_2O\}B\Phi_4$

Two consecutive steps are observed in the TG curve of this complex. The first weight loss, which occurs until approximately 350°C, is attributed to the elimination of the methyl group and water coordinated to the cobalt and probably to the decomposition of the tetraphenylborate ion. The decomposition of the tetraphenylborate ion in this step is in agreement with the results of Wendlandt for the thermal decomposition of salts of this anion, where the formation of cobalt metaborate is complete only above 700°C [10]. The second weight loss, in the temperature range 350–510°C, is assigned to the thermal decomposition of the equatorial ligand, whose liberation of HNO_2 was observed at temperatures above 400°C.

(3) $[MeCo(bae)\cdot H_2O]$

The thermal decomposition of this complex occurs in four steps, with the last being rapid. The first weight loss occurs up to about 90°C and is attributed to the loss of the coordinated water [11]. The second weight loss occurs between 90 and 200°C and is probably due to the loss of CH_3 and C_2H_4 groups. The third step, which occurs in the temperature range 200–340°C, consists of the loss of HNO_2 as the decomposition product due to the loss of the nitrogens. The last step of the decomposition, occurring between 340 and 400°C, is attributed to the loss of the rest of the ligand with the formation of Co_3O_4.

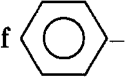
(4) $[MeCo(salen)]$

The thermal decomposition of the complex occurs in four stages, the last being rapid. The first weight loss occurs between 170 and 250°C and is attributed to the elimination of the methyl group [12]. The second and third weight losses, which occurs at 250–320 and 320–375°C, respectively, suggest the consecutive loss of two CH_3CN groups, with the nitrogen in the third step being lost as HNO_2. The last stage of thermal decomposition, is ascribed to the loss of $2C_6H_4$ in the form of CO_2 and H_2O and the simultaneous formation of Co_3O_4.

(5) [MeCo(salpn)]

Three consecutive stages, all of slow kinetics, are observed for the thermal decomposition of this complex. The first weight loss occurs in the temperature range 100–290°C and is probably due to the loss of CH_3 and C_2H_4. The second weight loss observed between 290 and 370°C, appears to be due to the elimination of CH_3CN. The last weight loss, observed between 370 and 530°C, is probably due to the decomposition of the rest of the ligand, with the formation of Co_3O_4. In this step, the remaining nitrogen is lost as HNO_2, as detected in this temperature range.

(6) [MeCo(salophen)]

The thermal decomposition of this complex occurs in three consecutive stages, the last being fast. In the second stage, there is evidence of a loss in two steps. The first weight loss occurs between 160 and 220°C and is attributed to the elimination of the CH_3 group bonded to the cobalt atom. The second loss, observed between 220 and 375°C, is probably due to the elimination of –N. The last stage, observed between 375 and 460°C, is ascribed to the loss of the rest of the equatorial ligand. In both steps, the nitrogen is lost as HNO_2 as verified in these temperature ranges by testing with sulfanilic acid and α-naphthylamine.

CONCLUSION

The kinetics and the number of stages of decomposition of these complexes depend on the equatorial ligand. The results suggest, for almost all the complexes, the following order of loss of groups: water, methyl group, groups derived from the amine, the rest of the equatorial ligand, with the formation of Co_3O_4, confirmed by X-ray diffraction. The tetraphenylborate anion gives cobalt metaborate as the final product. The nitrogen of the equatorial ligand is lost, partially or totally, in the form of HNO_2.

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