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Thermal decomposition of vanadyl Schiff-base compounds

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Abstract

The thermal stability and thermal decomposition of several Schiff bases coordinated to vanadyl, VO (Schiff base), were studied by thermogravimetry and conventional gas chromatographic and X-ray analyses. The kinetics, the number of steps and, in particular, the final temperature of decomposition of these complexes depend on the equatorial ligand.

INTRODUCTION

The preparation, characterization and electrochemical behaviour of several Schiff-base complexes containing transition metals have been studied [1–6]. Schiff bases with delocalized electronic structures (derivatives of $(dmgH)_2$, salen, bae, salophen, salpn and salcn) are coordinated to cobalt: salen = bis(salicylidenato)ethylenediamine; 7,7-DM-salen = bis(7,7′-dimethylsalicylidenato)ethylenediamine; 1,2-salpn = bis(salicylidenato)-1,2-propylenediamine; ethoxy-salen = bis(3,3′-diethoxylsalicylidenato)ethylenediamine; ethoxy-1,2-salpn = bis(3,3′-diethoxylsalicylidenato)-1,2-propylenediamine; 1,2-salbn = bis(salicylidenato)-1,2-butadienediamine; 1,4-salbn = bis(salicylidenato)-1,4-butadienediamine; salophen = bis(salicylidenato)-*o*-phenylenediamine.

Recently, we have extended these studies to complexes of other transition metals, including vanadium [7], chromium [8], copper [9] and uranium [10]. We have described the thermal stability of some methylcobalt complexes (derivatives of $(dmgH)_2$, (do)(doH)en, bae, salen, salpn and salophen) and of other organocobalt(bae) compounds [11,12].

This work is intended to contribute to our knowledge of the thermal

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stability of vanadyl compounds (derivatives of salen, ethoxy-salen, 1,2-salpn, ethoxy-1,2-salpn, 1,2-salbn, 1,4-salbn, 7.7-DM-salen and salophen) and to propose mechanisms for their thermal decomposition. Therefore, thermogravimetry (TG) and conventional gas chromatographic and X-ray analyses were used.

EXPERIMENTAL

The Schiff bases were prepared by the condensation reaction of a diamine and the appropriate carbonyl compound [13].

The vanadyl complexes of the Schiff bases were all synthesized by the same general procedure [7] according to:

$$\text{Schiff base} + \text{NaOAc} \rightarrow (\text{Schiff base})^{2-} + 2\text{HOAc} + 2\text{Na}^{+}$$

$$\text{VO}^{2+} + (\text{Schiff base})^{2-} \rightarrow [\text{VO}(\text{Schiff base})]$$

An aqueous solution of vanadyl sulphate (5 mmol) was added to a stirred methanol solution of the Schiff base (5 mmol) and sodium acetate (11 mmol). The resulting mixture was refluxed with stirring for 4 h. After cooling slowly to room temperature, the reaction mixture was held at 0°C for 12 h. The precipitate was filtered, washed twice with 20 ml of distilled water and twice with 10 ml of methanol and dried in a desiccator over silica under vacuum at room temperature for 72 h. When necessary the compounds were recrystallized from acetonitrile.

TG curves, from room temperature up to 700°C, were obtained on a Perkin–Elmer TGS-2 thermobalance. Samples of approximately 0.6 mg were used, heated at a rate of 20°C min^{-1} in air at atmospheric pressure.

In order to detect the formation of HNO_2 tests with sulphanilic acid and α-naphthylamine were made. A gas chromatograph, Varian model 1400, and an X-ray diffractometer Carl Zeiss Jena model HZG-4, were employed respectively to analyse the gas and residual material produced by the thermal decomposition.

RESULTS AND DISCUSSION

The thermal decomposition of the complexes studied in this work, 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.

The conventional chemical analysis did not detect any HNO_2 formation for any of the compounds studied, although it has been observed in the decomposition of some analogous compounds [11]. On the other hand, nitrile derivatives were detected by gas chromatographic analysis. The final product of the thermal decomposition is a pure vanadium oxide or a mixture of oxides of different oxidation states, as determined from the TG

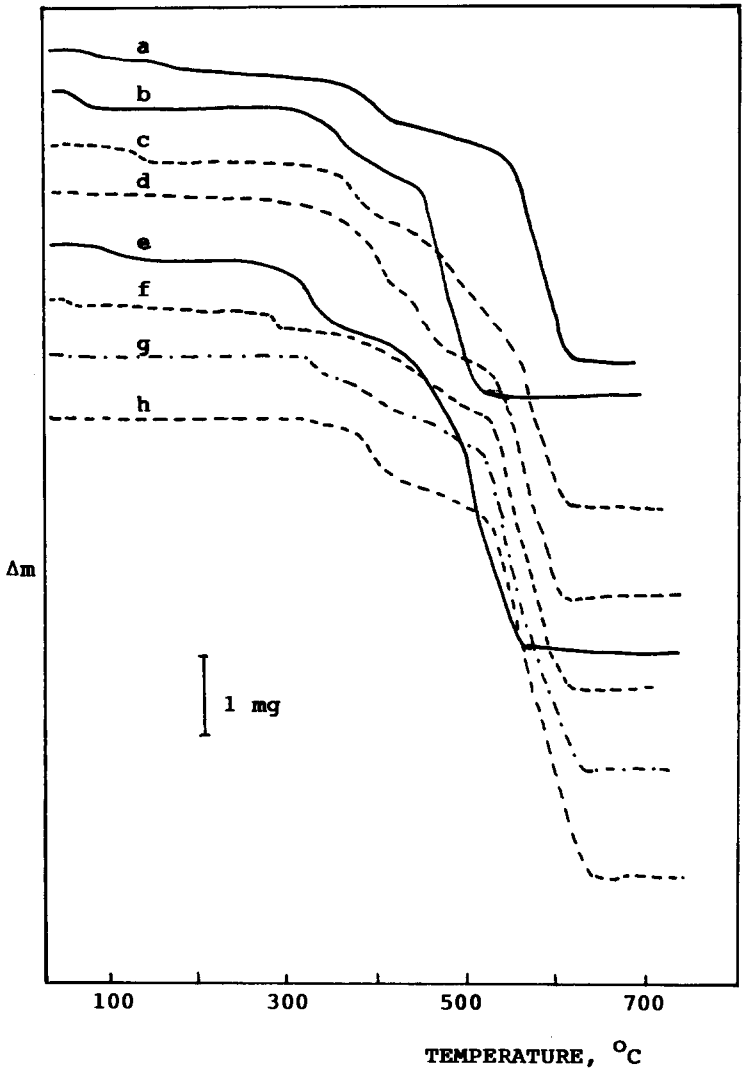

Fig. 1. TG curves. Key: curve a, VO(1,2-salbn)·nH_2O; curve b, VO(salophen)·nH_2O; curve c, VO(ethoxy-1,2-salpn)·nH_2O; curve d, VO(1,2-salpn)·nH_2O; curve e, VO(ethoxy-salen)·nH_2O; curve f, VO(1,4-salbn)·nH_2O; curve g, VO (DM-salen); curve h, VO(salen).

curves. However, only the more stable oxide, V_2O_5, was detected by X-ray analysis because of the reaction between the thermal decomposition products and oxygen from the air.

An analysis of the TG curves in conjunction with the results of the other analyses, permit the following thermal decomposition mechanisms to be suggested for these compounds.

VO(salen) (curve h in Fig. 1)

Two consecutive steps are observed in the thermal decomposition of this complex. The experimental data suggest (a) 310–460°C, partial loss of the equatorial ligand as confirmed by gas chromatographic analysis; (b) 466–640°C, loss of the rest of the equatorial ligand and the formation of V_2O_5 plus loss of a little VO_2 in a fast step.

VO(DM-salen) (curve g in Fig. 1)

This compound presents two consecutive steps in the TG curve, the last being fast. The first mass loss, which occurs between 310 and approximately 510°C, is attributed to the elimination of the C_3H_7CN as a partial decomposition of the equatorial ligand. The second mass loss, in the range 510–630°C, is assigned to the thermal decomposition of the rest of the equatorial ligand with the formation of VO.

VO(ethoxy-salen) · nH_2O *(curve e in Fig. 1)*

The thermal decomposition of this complex occurs in three steps, the last being fast. The first mass loss occurs up to about 115°C and is attributed to the loss of the hydration water. The second mass loss occurs between 240 and 360°C, and is probably due to the loss of coordinated water and CH_3CN. The presence of a molecule of coordinated water bonded between the two ethoxy groups was confirmed by X-ray diffractometry [14]. The last mass loss, in the range 360–670°C, is attributed to the elimination of the rest of the equatorial ligand. The residue is probably VO_3, which decomposes slowly at temperatures above 600°C, as can be seen in the TG curves.

VO(1,2-salpn) · nH_2O *(curve d in Fig. 1)*

Four consecutive steps are observed for the thermal decomposition of this compound, the last being fast. The first step occurs up to 275°C and is related to the loss of hydration water. The second mass loss observed between 275 and 415°C, is attributed to the elimination of C_3H_5CN group. The third mass loss occurs in the range 415–460°C and is probably due to the loss of CH_3CN group. Finally, the last weight loss occurs between 460 and 620°C and is assigned to the loss of the rest of the equatorial ligand with the formation of a mixture of VO_2 and V_2O_3.

VO(ethoxy-1,2-salpn) · nH_2O *(curve c in Fig. 1)*

This compound presents three consecutive steps in the TG curve, the second being slow. The first mass loss, which occurs between 80 and 135°C corresponds to the elimination of the hydration water. The second mass loss observed in the temperature range 290–435°C is attributed to the elimination of C_2H_5CN group which belongs to the equatorial ligand. The last decomposition step, in the range 435–620°C, is assigned to the loss of the rest of the equatorial ligand with the formation of V_2O_3.

VO(1,2-salbn) · nH_2O *(curve a in Fig. 1)*

The thermal decomposition of this compound occurs in three consecutive steps, with the last being fast. Hydration water is lost in the first step of the decomposition until about 180°C. The second mass loss occurs in the range 180–400°C and is attributed to the elimination of CH_3CN group. The last mass loss, in the range 400–625°C, is due to the thermal decomposition of the remainder of the equatorial ligand. The residue is V_2O_5.

VO(1,4-salbn) · nH_2O *(curve f in Fig. 1)*

Three consecutive steps are observed in the thermal decomposition of this compound, the last being fast. In the first step, from room temperature is 280°C, hydration water is lost. The second mass loss occurs between 280 and 515°C and corresponds to the elimination of C_3H_7CN group. The last step of the thermal decomposition, which occurs in the range 515–615°C, is ascribed to the loss of the equatorial ligand with the formation of a mixture of V_2O_5 and VO_2.

VO(salophen) · nH_2O *(curve b in Fig. 1)*

This complex decomposes thermally in three consecutive steps, the last being fast. The loss of the hydration water up to 70°C is proposed as the first mass loss. In the second step, in the range 300–400°C, phenylen group is lost. Finally, the rest of the equatorial ligand is lost between 400 and 525°C with the formation of a mixture of V_2O_5 and VO_3.

CONCLUSION

The kinetics, the number of steps and, in particular, the final temperature of decomposition of these complexes depend on the equatorial ligand. The results suggest, for almost all the compounds, the following order of loss of groups: hydration water (generally $n < 1$), nitrile group as identified by gas chromatography and the rest of the equatorial ligand, with formation of pure vanadium oxide or a mixture of vanadium oxides of different oxidation states. However, only the more stable oxide, V_2O_5, was detected by X-ray analysis.

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