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THERMAL AND CHROMATOGRAPHIC BEHAVIOUR OF Ru(III) AND Rh(III) COMPLEXES WITH IMINODIACETIC ACID

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ABSTRACT

A method has been developed to study the thermal (DTA, TG) and chromatographic behaviour of the complexes formed between Ru(III) and Rh(III) and iminodiacetic acid (IDA). Above 100°C the dehydration of the isolated compounds is detected while the decarboxylation process depends fundamentally on the number of free carboxylic groups. In the cases where the COOH groups predominate on the coordinated COO^-, the release of CO_2 takes place in two different steps, the first one above 270°C and the second at 400°C. Liberation of CO occurs from 550–600°C. Only in the above case the formation of other gases as methane, ethane, ethylene and traces of ammonia and hydrogen is observed.

INTRODUCTION

In the last few years, the synthesis of and the coordination compounds formed between platinum group metals and several polycarboxylic sequestrant agents have been carried out in our laboratories. An important part of this investigation was concerned with study of the thermal properties of the isolated substances using differential thermal analysis (DTA) and thermogravimetry (TG)[1–3]. By simultaneous combination of these techniques it is possible to obtain some physical data in order to discern the structures and properties of the complexes, such as dehydration temperatures, position of water molecules, decarboxylation and pyrolysis processes and magnitudes of the weight losses. In fact, an approximate knowledge of the thermal evolution of the referred compounds and, indirectly, of the metal–ligand bond nature was achieved.

Nevertheless and because of the great complexity of the thermal decomposition processes in coordination compounds of this type, the exclusive use of the above techniques is not sufficient due to the uncertainty of the composition of the released gases. In order to know whether a weight loss corresponding to an observed peak on the DTA curve is due to the release of one or more gases, a combined study of previous methods with gas chromatography (GC) is essential. The validity of this statement has recently been proved carrying out the thermal decomposition of complexes formed between 3*d* transition metals and 1,2-diamino-cyclohexanetetra-acetic acid (DCTA)[4]. In this way, it was shown that the release of carbon dioxide does not correspond in many cases with the minimums observed by DTA while the decarboxylation processes are detected at wide temperature ranges.

We present here the thermal and chromatographic behaviour of Ru(III) and Rh(III) complexes with IDA (YH_2). Where possible, the solid intermediate products formed in the decomposition process have been identified. The synthesis and characterization of the compounds studied in this investigation have been previously reported[5, 6].

EXPERIMENTAL

The thermal decomposition (DTA, TG) was studied using Aminco 4-4442A and Cahn electrobalance RG instruments, respectively. The experiments were carried out under helium atmosphere at normal pressure (60 ml min^{-1}) employing a heating rate of 10°C min^{-1}. Chromel–alumel and Pt/Pt/Rh-thermocouples were used to measure the temperature changes and α-Al_2O_3 was employed as the reference material in the DTA measurements (s.d.: ± 5°C).

The employed Hewlett-Packard 5700/A gas chromatograph was connected with the DTA and TG instruments, using also helium as carrying gas. The metallic columns were filled with solid Porapak Q (80–100 mesh, length of 2 m and 1/8 in. diameter).

The retention indexes for the GC column are shown in Table I. The temperature of the oven was 100°C and that of the detector 150°C.

TABLE I

RELATIVE RETENTION INDEXES OF THE PORAPAK Q[a] COLUMN

All data refer to the column described in this work and are given with respect to water.

Compound	*Retention index*
Hydrogen	0.27
Carbon monoxide	0.30
Methane	0.37
Carbon dioxide	0.49
Ethylene	0.69
Ethane	0.83
Water	1.00 (1.23 min)
Formaldehyde	1.75
Acetaldehyde	2.36

[a] The oven and detector temperatures were 100 and 150°C, respectively; helium flux, 30 ml min^{-1}; column length, 2m; column diameter, 1/8 in.

RESULTS AND DISCUSSION

$Na[Ru(YH)_2Cl_2] \cdot H_2O$

The DTA curve of this compound (Fig. 1) shows some different endothermic peaks between 50 and 900°C. The first minimum detected as a very sharp peak at 150°C is due to the elimination of the hydration water molecule, extreme which has been confirmed by heating the compound at 100°C and study the infrared spectra and TG diagram. The weight loss obtained by this procedure is 3.84% (theoretical w.l. for a water molecule per mol of compound, 3.78%). Immediately above 200°C a strong endothermic effect occurs with a minimum at 230°C probably due to the decarboxylation of two free –COOH groups of the coordinated IDA molecules (experimental w.l., 20.31%). Next to 400°C an endothermic splitted peak of medium intensity presumably represents the combined effect of a second decarboxylation and the release of other small amounts of different gases detected by GC. In this respect, the calculated w.l. from the TG curve (19.92%) coincides quite well with that of two coordinated COO^- groups (18.45%). Finally, in all the compounds studied in this work a strong and sharp endothermic peak is recorded next to 800°C, probably due to the total pyrolysis of the substances.

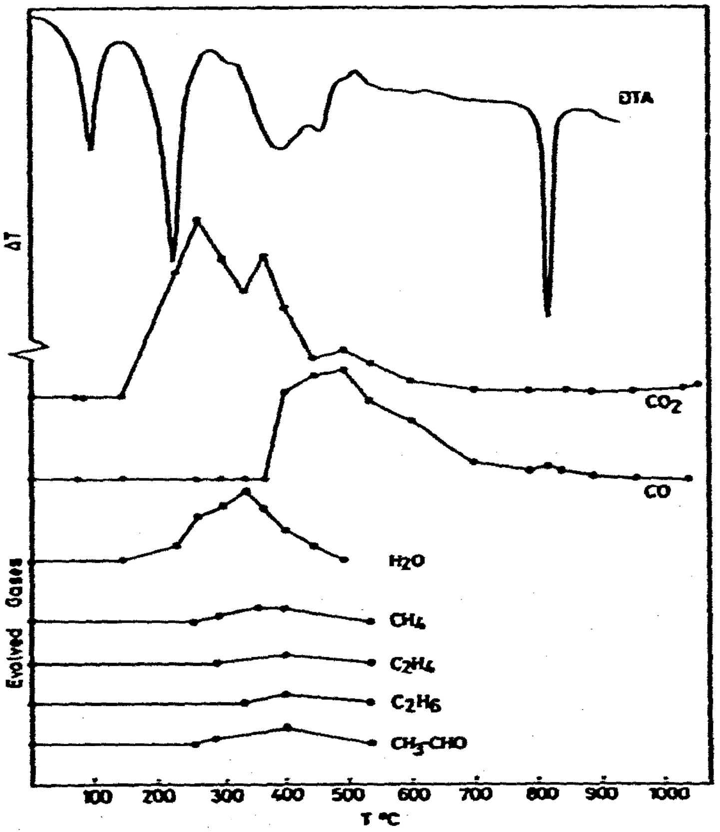

Fig. 1. Thermal and chromatographic behaviour of $Na[Ru(YH)_2Cl_2] \cdot H_2O$.

The evolution of the liberated gases in the decomposition against temperature is shown in Fig. 1. As can be observed the decarboxylation begins at a temperature slightly above 150°C with a maximum release of CO_2 corresponding with the second endothermic effect of the DTA curve (230°C). At 370°C a new liberation of CO_2 coincides with the first minimum of the third endothermic peak observed in the DTA curve.

The evolution of CO clearly shows that this gas is not released until 370°C, with a maximum between 400–500°C (second peak of the endothermic effect of DTA curve).

All the arguments developed so far support the assumption that decarboxylation takes place in two clearly different steps, the first corresponding to the exclusive release of CO_2 and the latter to formation of CO.

Other gases as methane, ethane, ethylene and acetaldehyde are detected at temperatures near 400°C. Although in a recent work[7] on the decomposition of an IDA complex a weight loss attributed to the liberation of ammonia is supposed, we have been able to demonstrate through some experiments performed with this and other compounds that ammonia is only detected in small quantities at temperatures coinciding with the second process of decarboxylation even when columns specially designed for its detection have been used.

The analysis of the final solid residue is according to the presence of Na_2CO_3, NaCl and RuO_3.

$Na[Ru(YH)(YH_2)Cl_3] \cdot 8H_2O$ *(I)* and $Na[Rh(YH)(YH_2)Cl_3] \cdot 2H_2O$ *(II)*

Because of their essential structural analogy these two compounds have been studied together. In both cases, there are more free carboxylic than carboxylate groups, being the IDA mono and bidentate ligand in each one of the complexes. The remaining positions of the distorted octahedral complex are occupied by chlorine atoms.

The DTA diagrams of compounds I and II are presented in Fig. 2, curves a and b, respectively. The forms of the diagrams are similar but different from that of the diacid ruthenium compound already described.

Compound I (curve a) shows a first strong endothermic effect beginning at 120°C due to the dehydration process. The temperature of this effect is abnormally high compared with those observed for the other studied compounds and for the similar complex of Rh (curve b, 85°C), which is probably due to the elevated number of water molecules present in compound I.

The decarboxylation process begins for both compounds at temperatures next to 230°C, showing the corresponding DTA diagrams several endothermic effects observed up to temperatures of 600°C.

The chromatographic analysis shows a maximum release of CO_2 at 270°C resulting from the simultaneous decomposition of the two free carboxylic groups of one of the IDA molecules. The potentiometric study of the compound formed at 275°C confirms the presence of only one –COOH group in both compounds. At 420°C,

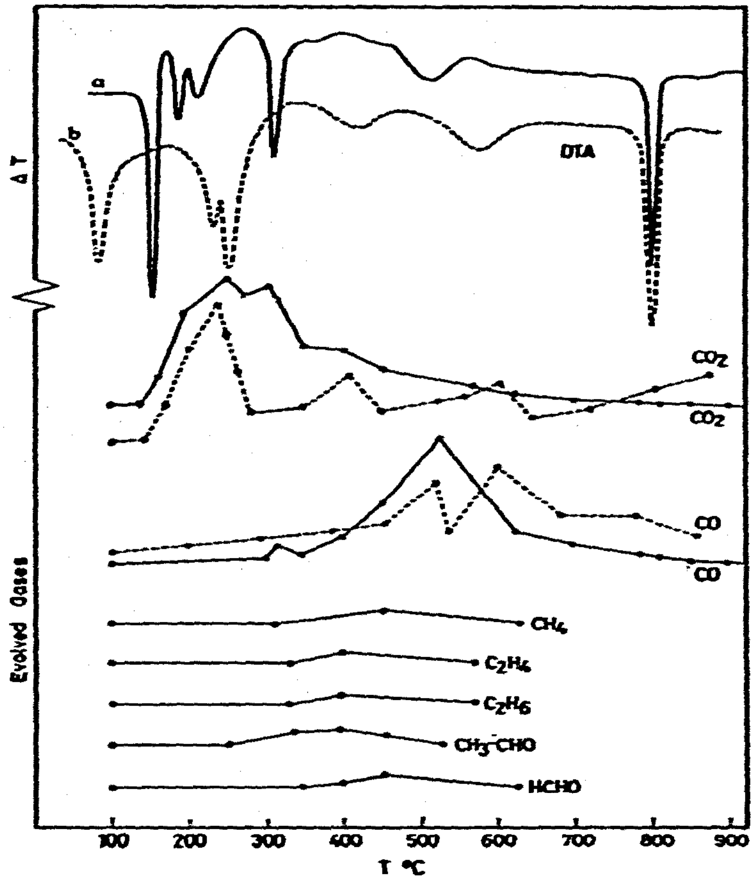

Fig. 2. Thermal and chromatographic study of $Na[Ru(YH)(YH_2)Cl_3] \cdot 8H_2O$ (curve a) and $Na[Rh(YH)(YH_2)Cl_3] \cdot 2H_2O$ (curve b).

a second small liberation of CO_2 is detected while the release of CO begins. The respective diagrams show that maximum formation of CO takes place between 550 and 650°C. The second liberation of CO_2 might be due to the decomposition of the remaining free COOH group. This statement is supported by the different nature of the mentioned COOH group. In this way, Schwarzenbach et al.[8] show the similar acidic nature of two COOH groups in triacid compounds 1:2 formed between Ca, Sr and Ba and ligands $R-N(CH_2-COOH)_2$, while the third free carboxylic group has a very different p*K* value. On the other hand, the distance N . . . COOH in this last case is considerably shorter than in the case of the two others, so that the corresponding group will be more strongly bonded. In a previous work[2] we have likewise demonstrated that the decarboxylation processes of the free COOH groups are detected at lower temperatures than the coordinated COO^- groups, mainly responsible for the CO liberation at high temperatures.

At a temperature (430°C) between the main decarboxylation processes, other gases as methane, ethane, ethylene, acetaldehyde and traces of ammonia are detected. The maximum release coincides with the broad endothermic effect observed at 450°C.

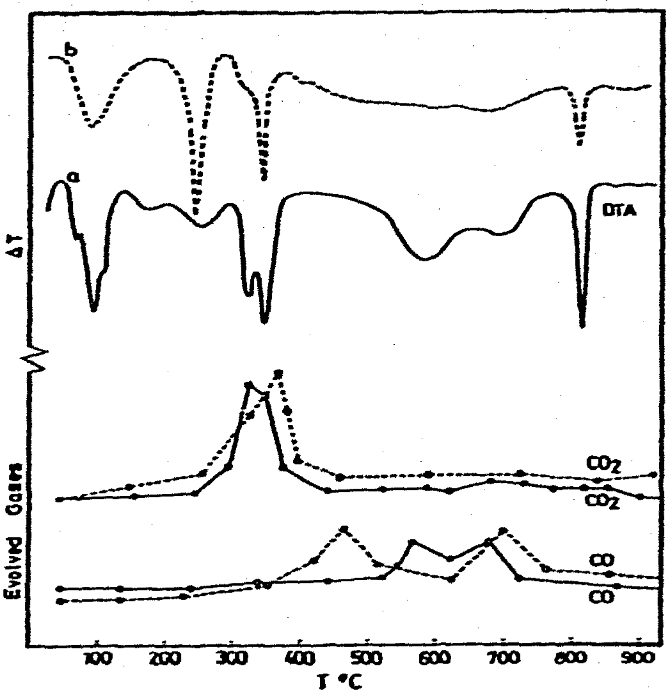

Fig. 3. Thermal and chromatographic study of $Na[Rh(Y)(YH)Cl]\cdot 2H_2O$ (curve a) and $Na[Rh(YH)_2(OH)_2]\cdot H_2O$ (curve b).

$Na[Rh(Y)(YH)Cl]\cdot 2H_2O$

This is the only isolated substance in which the bonded COO^- groups predominate over the free carboxylic ones. As a consequence of this particular structural form, the DTA–GC study is quite different (Fig. 3, curve a). Actually an endothermic effect is detected at 100°C as a result of the dehydration of the substance. The decarboxylation processes are clearly differentiated and take place at temperatures considerably higher than those of the other studied compounds. In this way, CO_2 is suddenly released at 340°C, in a very narrow temperature range (30°C). CO is not produced until 550°C and take place over a wide interval up to 700°C. In this compound only traces of the other gases are observed.

$Na[Rh(YH)_2(OH)_2]\cdot H_2O$

Figure 3b presents the study of the thermal decomposition of this substance. At 100°C, the DTA curve shows an endothermic effect of medium intensity due to the loss of the hydration water molecule. The following quite intense effect at 240°C is particularly interesting, given that at this temperature the beginning of the decarboxylation process is not yet observed. The elemental analysis and potentiometric study of the heated substance (250°C) show the disappearance of the coordinated hydroxylic groups and the coordination of some COO^- groups. For these reasons the referred effect has been attributed to a molecular rearrangement resulting from the elimination of the bonded OH groups.

At 340°C the release of CO_2 suddenly takes place in a similar form to that studied in the previous compound while carbon monoxide is formed in two successive steps (460 and 700°C) at intervals which coincide with the endothermic effects registered in the DTA diagram. The detected amounts of other gases are very small.

CONCLUSIONS

From the study carried out the following conclusions can be drawn:

(1) The dehydration process of the coordination compounds studied is observed by a sharp endothermic effect at temperatures near 100°C in the cases where there are a few water molecules. The same effect is recorded at higher temperatures when the number of water molecules is greater.

(2) The DTA diagram of the isolated rhodium hydroxycompound is according to the structural rearrangement of the complex, presumably due to the coordination of some free carboxylic groups, as a result of the elimination of bonded OH groups.

(3) The decarboxylation processes depend fundamentally on the number of coordinated carboxylate groups. Thus, in those compounds where these groups predominate, a single loss of CO_2 is usually detected at temperatures of 300–350°C while the release of CO occurs in a wide temperature range (500–700°C). If the number of free carboxylic groups is greater than that of the coordinated COO^-, the release of CO_2 takes place in two different steps, the first one at temperatures just above 270°C and the second at 400°C. CO is released from 550–600°C.

(4) In the cases where the number of free carboxylic groups is higher, the formation of methane, ethane, ethylene, formaldehyde, acetaldehyde and traces of ammonia and hydrogen is always observed. In the cases where the coordinated groups predominate, only slight traces of the above gases are observed.

(5) Finally, a sharp and intense endothermic effect is produced in all cases at 800°C, due to the total pyrolysis of the substances.

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