Thermochimica Acta, 16 (1976) 89–93

DECOMPOSITION STUDIES OF TRIRUTHENIUM DODECACARBONYL AND TRIOSMIUM DODECACARBONYL

P. BANDITELLI, A. CUCCURU AND F. SODI
Laboratorio di Radioprotezione, Camen, 56010 San Piero a Grado, Pisa (Italy)
(Received 10 November 1975)

ABSTRACT

The thermal behaviour of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been investigated by thermogravimetry, in argon, nitrogen and air dynamic atmosphere and by DTA and DSC in argon.

Meaningful differences were observed between the two complexes: while $Ru_3(CO)_{12}$ in argon and nitrogen atmosphere decomposes to metallic ruthenium and carbon monoxide, $Os_3(CO)_{12}$ sublimates completely before decomposition and a condensation of the vapour was observed on the cold wall of the quartz furnace tube of the TG apparatus. Both the complexes ignite in air dynamic atmosphere but only $Ru_3(CO)_{12}$ shows a residue at the end of the experiment.

The melting heats and entropies, the decomposition heats were evaluated and found to be for $Ru_3(CO)_{12}$: 10.40 kcal mol^{-1}, 24.03 cal deg^{-1} mol^{-1}, 89.45 kcal mol^{-1} and for $Os_3(CO)_{12}$: 10.70 kcal mol^{-1}, 21.37 cal deg^{-1} mol^{-1}, 70.5 kcal mol^{-1}.

INTRODUCTION

The syntheses of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ and their catalytic activities in hydroformilation of olefins have been largely studied but only fragmentary data are available concerning their thermal behaviour. Particularly, the thermal decomposition of these complexes in the solid phase have not yet been completely investigated.

In this paper the decomposition of the two complexes has been investigated by thermoanalytical methods and the melting heats and entropies and the overall decomposition heats were evaluated.

EXPERIMENTAL

Compounds

Triruthenium dodecacarbonyl was prepared according to the method described by Pino, et al.[1], triosmium dodecacarbonyl was obtained by the procedure of Bradford and Nyholm[2]. Both complexes were recrystallized four times from tetrahydrofuran before carrying out the experiments.

Apparatus

The thermogravimetric studies were carried out using a DuPont 950 thermobalance, with a dynamic atmosphere flowing under atmospheric pressure at 100 ml min^{-1}; the gases used were oxygen-free argon and nitrogen, and dry air; the heating rate was 10°C min^{-1}; the sample was contained in an open platinum pan and the temperatures were perceived by a chromel–alumel thermocouple with its sensing junction positioned inside the sample can close to the sample.

The DSC experiments were carried out by a DuPont 990 thermal analyzer equipped with a DSC cell. The sample to be analyzed was placed, under argon atmosphere, in an aluminum container and hermetically sealed to avoid sublimation or evaporation of the complex; the container can withstand at least 3 atm (internal pressure) prior to rupture. The references consisted of an empty sealed aluminum pan and the experimental conditions were as follows: sample mass 1±0.1 mg; heating rate 10°C min^{-1}; atmosphere in the cell: static pure argon.

The DTA experiments were carried out using a DuPont 900 thermal analyzer equipped with a standard cell assembly: samples were placed in disposable glass tubes (2 mm in diameter) into which is inserted the chromel–alumel thermocouple sensing the temperatures and reference consisted of glass beads in contact with the reference thermocouple; the operating conditions were as previously described for DSC experiments.

RESULTS

TG

The TG curves in argon, nitrogen and dry air at atmospheric pressure of the complexes examined are given in Figs. 1, 2, 3, respectively. $Ru_3(CO)_{12}$ in argon decomposes to metallic ruthenium and carbon monoxide, the residue at the end of the decomposition being 47.5% (theor. Ru 47.54), while $Os_3(CO)_{12}$ does not decompose but sublimates completely; the vapours are condensed on the cold wall of the quartz tube of the thermobalance and no residue was observed (Fig. 1).

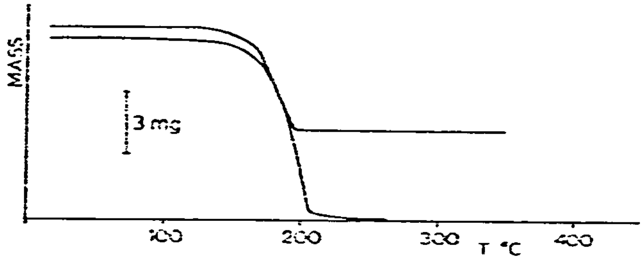

Fig. 1. TG curves in argon atmosphere of (a) $Ru_3(CO)_{12}$ and (b) $Os_3(CO)_{12}$.

Again, if in nitrogen atmosphere, triruthenium dodecacarbonyl decomposes to metallic ruthenium and carbon monoxide (residue 47.45%) as shown in Fig. 2; on the

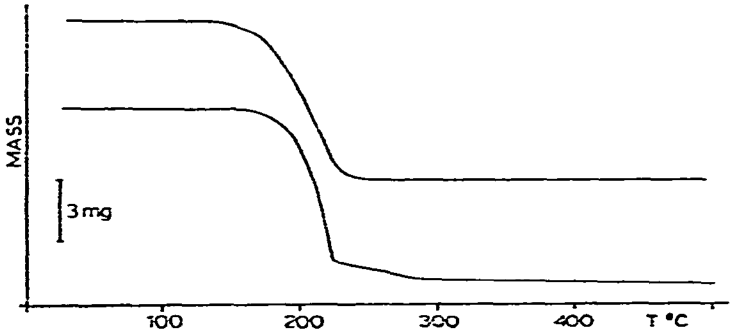

Fig. 2. TG curves in nitrogen atmosphere of (a) $Ru_3(CO)_{12}$ and (b) $Os_3(CO)_{12}$.

contrary triosmium dodecacarbonyl sublimates to a great extent, but partly decomposes to an intermediate (about 10% of the initial weight), whose composition has not been investigated, which slowly degradates to a stable residue. When heated in air, triruthenium dodecacarbonyl begins to decompose at 155 °C and ignites violently giving a residue stable up to 500 °C; in the range 500 to 700 °C the residue shows an increase of its weight due perhaps to a completion of the oxidation; triosmium dodecacarbonyl, too, ignites violently, but a compound is formed which vaporises on heating (Fig. 3).

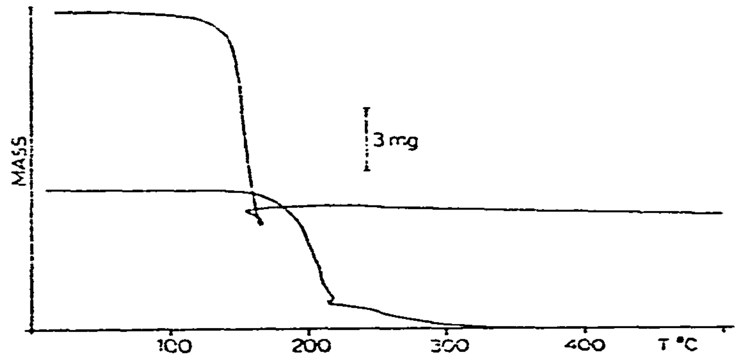

Fig. 3. TG curves in dry air of (a) $Ru_3(CO)_{12}$ and (b) $Os_3(CO)_{12}$.

At least the thermogravimetric curves of $Ru_3(CO)_{12}$ in argon were investigated according to Flynn and Wall[4] in an attempt to obtain the apparent overall activation energy (E_A) and the reaction order (n) for the decomposition. The data obtained ($E_A = 13$ kcal mol^{-1}; $n = 1$) are in good agreement with those reported in the literature for similar carbonyls[5].

DSC and DTA

DTA curves are reported in Fig. 4 and the endothermic transitions indicate that $Ru_3(CO)_{12}$ melts at 155 °C and decomposes at 231 °C while $Os_3(CO)_{12}$ melts at 224 °C and decomposes at 275 °C.

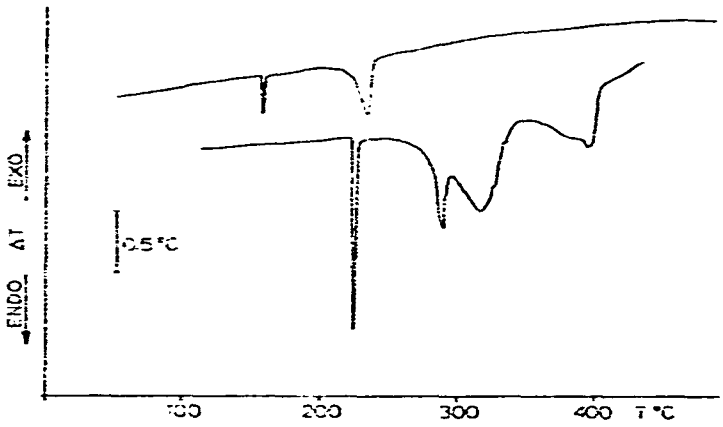

Fig. 4. DTA curves in argon atmosphere of (a) $Ru_3(CO)_{12}$ and (b) $Os_3(CO)_{12}$.

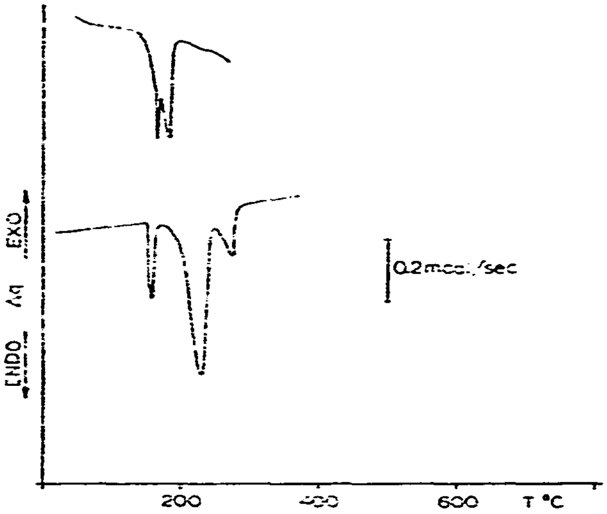

Fig. 5. DSC curves in argon atmosphere of (a) $Ru_3(CO)_{12}$ in open pan and (b) $Ru_3(CO)_{12}$ in sealed pan.

TABLE 1

MELTING HEATS AND ENTROPIES, DECOMPOSITION HEATS OF $Ru_3(CO)_{12}$ AND $Os_3(CO)_{12}$

Complex	*M.p.* (°*C*)	ΔH_m (*kcal mol*$^{-1}$)	ΔS_m (*cal deg*$^{-1}$*mol*$^{-1}$)	ΔH_{dec} (*kcal mol*$^{-1}$)
$Ru_3(CO)_{12}$	155	10.40	24.03	89.45
$Os_3(CO)_{12}$	225	10.70	21.37	70.5[a]

[a] Approximate value.

The literature data[1-3] state that $Ru_3(CO)_{12}$ melts and decomposes at 155°C: such behaviour was also observed by us when operating with a DSC cell using an open pan; but it is sufficient to use a sealed pan, so that the evolved gas may produce a slight overpressure, to separate and distinguish the two phenomena as shown in Fig. 5.

From the DSC curves of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ the melting heat and entropies, the decomposition heats were evaluated and the results are reported in Table 1.

We must specify that the decomposition heat of $Os_3(CO)_{12}$ is approximate because of the difficulty in obtaining a quantitative DSC curve, due to a loss of the sublimated complex from the sealed pan.

REFERENCES

1 G. Braca, G. Sbrana and P. Pino, *Chim. Ind.*, 50 (1968) 121.
2 C. W. Bradford and R. S. Nyholm, *Chem. Commun.*, (1967) 384.
3 I. Wender and P. Pino, *Organic Syntheses via Metal Carbonyls*, Vol. 1, Interscience Publishing, New York, 1968, p. 39.
4 J. H. Flym and L. A. Wall, *J. Res. NBS*, 70A (1966) 6.
5 A. S. Mnukhin, B. Y. Krasilshchik, G. R. Fedorova, A. M. Verbovskii and A. Vereshchagina, *Chem. Abs.*, 73 (1971) 18976 s.