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THERMAL DECOMPOSITION OF SOME RUTHENIUM CARBONYL HYDRIDES

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ABSTRACT

The thermal stability of α-$H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{10}P_2$, $H_4Ru_4(CO)_9P_3$, $H_4Ru_4(CO)_8P_4$ (where P = triphenylphosphine) has been investigated by differential scanning calorimetry and by thermogravimetric analysis under argon dynamic atmosphere.

The TG curves of the triphenylphosphine substituted derivatives of α-$H_4Ru_4(CO)_{12}$ suggest the release of the carbonyl and of the phenyl groups through a not well-defined pattern and overlapping decomposition reactions up to the retention of phosphorus in the residue, while α-$H_4Ru_4(CO)_{12}$ decomposes to metallic ruthenium. The decomposition heat of α-$H_4Ru_4(CO)_{12}$ and the isomerization heat of $H_4Ru_4(CO)_8P_4$ have been evaluated.

INTRODUCTION

Although the preparation of ruthenium carbonyl hydrides and their catalytic activity in the carbonylation and hydrogenation of olefins and of aldehydes have been largely studied, only fragmentary data are available concerning their behaviour on heating. We have examined the thermal behaviour of α-$H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{10}P_2$, $H_4Ru_4(CO)_9P_3$, $H_4Ru_4(CO)_8P_4$, (P = triphenylphosphine) by TG and DSC to obtain some information about their decomposition.

EXPERIMENTAL

Materials

The complexes were prepared according to Piacenti et al.[1] and the results of their elemental analyses were: α-$H_4Ru_4(CO)_{12}$, C 19.43% (calc. 19.36), H 0.50% (calc. 0.54); $H_4Ru_4(CO)_{10}P_2$, C 45.46% (calc. 45.50), H 2.85% (calc. 2.82); $H_4Ru_4(CO)_9P_3$, C 52.30% (calc. 52.28), H 3.95% (calc. 3.41); $H_4Ru_4(CO)_8P_4$, C 57.60% (calc. 57.14), H 3.65% (calc. 3.89).

Apparatus

The thermogravimetric studies were carried out using a Du Pont 950 thermobalance with a dynamic atmosphere of oxygen-free argon flowing, under atmospheric pressure, at 100 ml min^{-1} and with a sample weight of 5–8 mg and a heating rate of 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 in contact with the pan.

The DSC experiments were carried out by a Du Pont 900 thermal analyzer fitted with a DSC cell. The sample ranged in mass from 3 to 5 mg and was contained in an aluminum pan. Experimental conditions were the same as for TG. The DSC cell was calibrated, for quantitative measurements, using the latent heats of fusion of metallic gallium, indium, tin and zinc.

RESULTS

TG curves of the four complexes are given in Fig. 1. As shown all the hydrides examined began to decompose at about 170°C and decomposition occurred in a single step for α-$H_4Ru_4(CO)_{12}$, while the degradation pattern of the triphenyl phosphine-substituted derivatives is complicated and seems to be due to an overlapping of two or more reactions. A constant mass region was obtained at about 250°C for α-$H_4Ru_4(CO)_{12}$ and the amount of residue, 54.6% of the initial weight, corresponds to what was expected for metallic ruthenium (calculated Ru: 54.34%).

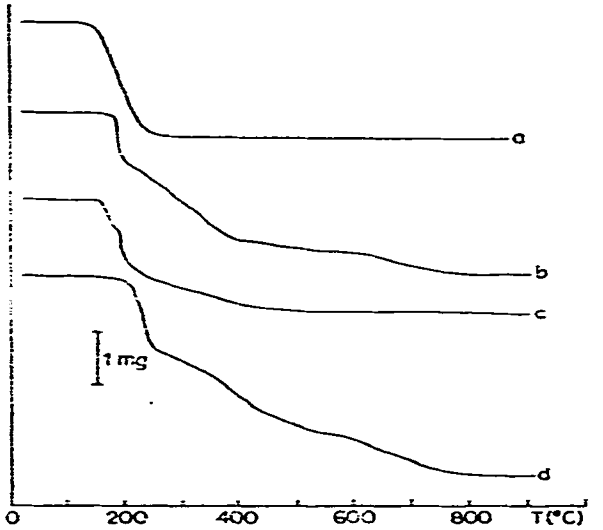

Fig. 1. TG curves for (a) α-$H_4Ru_4(CO)_{12}$; (b) $H_4Ru_4(CO)_{10}P_2$; (c) $H_4Ru_4(CO)_9P_3$; (d) $H_4Ru_4(CO)_8P_4$. (P = triphenylphosphine.)

All complexes containing phosphorus as donor ligands show a constant mass region at about 750–800°C and the amount of residue at this temperature does not correspond to what was expected for metallic ruthenium, but seems to correspond to the total of ruthenium and phosphorus as shown in Table 1. This assumption is plausible because of the difficulty to remove phosphorus from a residue containing noble metals as shown by other authors[2]. A quantitative analysis of phosphorus in the residue from the TG was attempted, but the results were not reproducible.

TABLE 1

TG OF HYDRIDES: COMPARISON OF THE EXPERIMENTAL VALUES OF THE RESIDUE WITH THE EXPECTED AMOUNTS OF Ru AND OF Ru+P

P = triphenylphosphine.

Compound	*Ruthenium*		*Ruthenium + phosphorus*	
	Expected	*Found*	*Expected*	*Found*
α-$H_4Ru_4(CO)_{12}$	54.31	54.60	—	—
$H_4Ru_4(CO)_{10}P_2$	33.25	—	38.44	38.37
$H_4Ru_4(CO)_9P_3$	27.86	—	34.20	33.90
$H_4Ru_4(CO)_8P_4$	23.99	—	31.29	33.70

The DSC curves of the complexes are reported in Fig. 2. The α-$H_4Ru_4(CO)_{12}$ curve shows an endotherm in the range 170–230°C. Assuming that the complex decomposes to metallic ruthenium and carbon monoxide, as is suggested by thermogravimetric analysis, the enthalpy of decomposition may be evaluated from the area of the peak and is found to be $\Delta H_{dec} = 54.03$ kcal mol^{-1}.

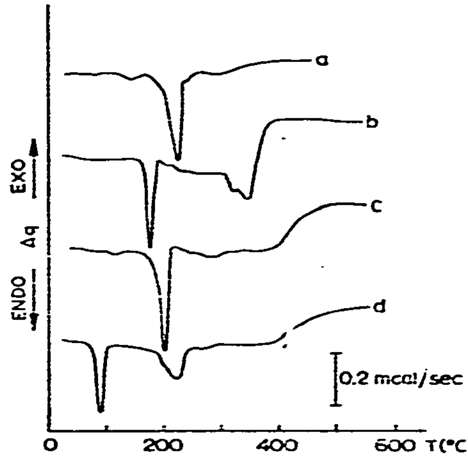

Fig. 2. DSC curves for (a) α-$H_4Ru_4(CO)_{12}$; (b) $H_4Ru_4(CO)_{10}P_2$; (c) $H_4Ru_4(CO)_9P_3$; (d) $H_4Ru_4(CO)_8P_4$. (P = triphenylphosphine.)

$H_4Ru_4(CO)_{10}P_2$ shows a sharp endotherm in the range 165–190°C and another wide broad endotherm in the range 200–480°C, while $H_4Ru_4(CO)_9P_3$ shows a sharp endotherm at 170–200°C followed from a wide broad and not well-defined endotherm in the range 210–400°C.

$H_4Ru_4(CO)_8P_4$ shows two endotherms, the first in the range 75–100 °C and the second in the range 180–240 °C: the first endotherm can be attributed to an isomerization, possibly the formation of different isomeric species, due to the relative position of the phosphines on the ruthenium atoms[1]. From the area of the peak, the isomerization heat has been evaluated and is found to be $\Delta H_{isom} = 14.83$ kcal mol^{-1}. The endotherms occurring near 200 °C in the DSC curves of the triphenylphosphine-substituted derivatives are attributable to the initial decomposition of the complexes, while the wide, broad endotherms are very likely due to a combination of heat required to break metal–ligand bonds plus the heat evolved in a probable intramolecular rearrangement.

It was initially hoped to obtain some data on the strenghth of the metal–phosphorus and on the metal–CO bonds in these compounds, but the complexity of the decomposition does not permit such an evaluation at present.

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