Thermochimica Acta, 12 (1975) 409–411

THERMAL DECOMPOSITION OF THE $H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$ AND $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$ COMPLEXES

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(Received 6 March 1975)

ABSTRACT

The thermal decomposition of $H_4Ru_4(CO)_9P_3$ and of $H_4Ru_4(CO)_8P_4$, where P = tributylphosphine, has been investigated by thermogravimetry and by differential scanning calorimetry in argon dynamic atmosphere.

The TG and DSC curves suggest the release of the carbonyl and butyl groups, but it was not possible to elucidate the intermediate compounds formed in the thermal decomposition. The melting heats and the overall decomposition heats were evaluated.

INTRODUCTION

Although the synthesis of $H_4Ru_4(CO)_9P_3$ and $H_4Ru_4(CO)_8P_4$ (where P = tributylphosphine) and their catalytic activity in the hydrogenation of olefins and aldehydes have been largely studied[1] no data are available concerning their thermal stability. In this paper the decomposition of the two complexes is investigated by thermoanalytical methods, in the hope to obtain some information about their method of dissociation and their thermal properties.

EXPERIMENTAL

Compounds

The complexes were prepared according to Piacenti et al.[2] and their elemental analyses were as follows: $H_4Ru_4(CO)_8P_4$, C 46.95% (theor. 46.65), H 7.84% (theor. 7.83), m.wt. 1395 (theor. 1441.7); $H_4Ru_4(CO)_9P_3$, C 42.64% (theor. 42.64), H 6.73% (theor. 6.76), m.wt. 1298 (theor. 1267.4).

Apparatus

The TG and DSC apparatus and the experimental conditions were the same as previously described[3]; the DSC cell was calibrated for quantitative measurements by running melting curves of metallic gallium, indium, tin and zinc.

RESULTS

The TG and DSC curves of the complexes examined are given in Figs. 1 and 2 respectively.

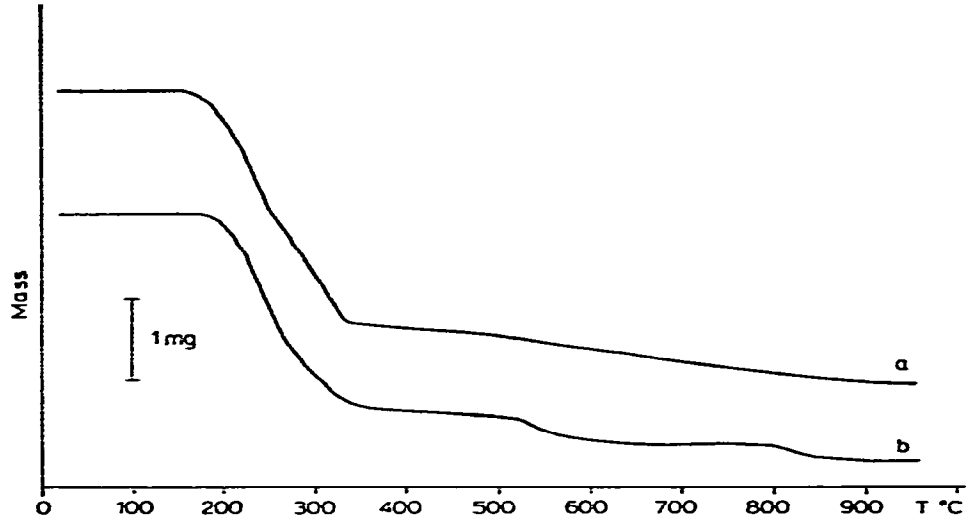

Fig. 1. TG curves of (a) $H_4Ru_4(CO)_9P_3$ and (b) $H_4Ru_4(CO)_8P_4$. P = tributylphosphine.

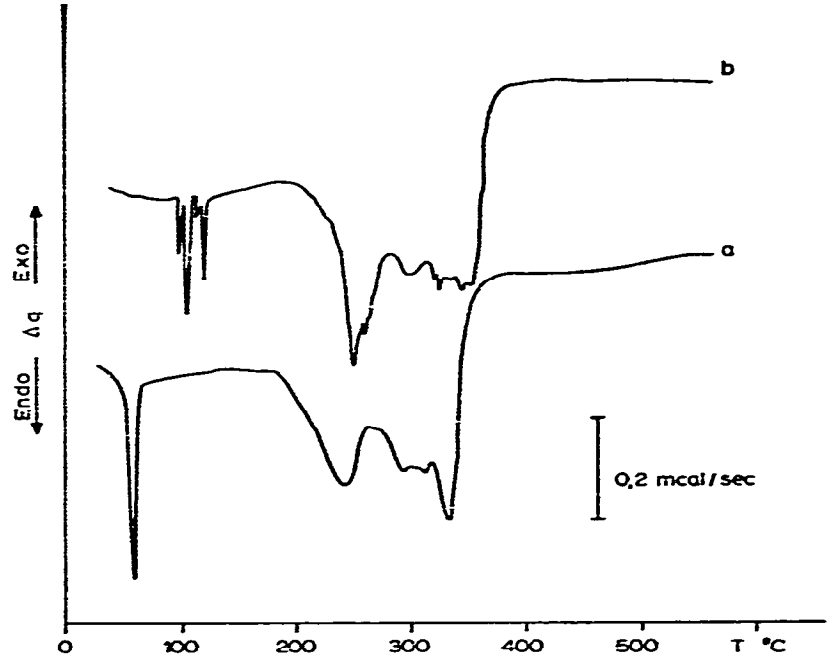

Fig. 2. DSC curves of (a) $H_4Ru_4(CO)_9P_3$ and (b) $H_4Ru_4(CO)_8P_4$. P = tributylphosphine.

As shown, $H_4Ru_4(CO_8)P_4$ began decomposing at about 180°C and $H_4Ru_4(CO)_9P_3$ at about 160°C.

The TG curves are similar in shape and also exhibit a small difference in the temperature range at which the decomposition process takes place. A constant mass region was obtained at about 850°C and the amount of residue at this temperature, does not correspond to the expected for metallic ruthenium but seems to correspond to the total of ruthenium and phosphorus. The residue to the decomposition was indeed 38.2% of the initial weight for $H_4Ru_4(CO)_8P_4$ (calc. ruthenium plus phosphorus 36.6%) and 40.65 of the initial weight for $H_4Ru_4(CO)_9P_3$ (calc. ruthenium plus phosphorus 39.5%). This assumption is plausible because of the difficulty encountered in removing phosphorus from a residue containing noble metals as also shown by other authors[3–4].

The DSC curves indicate endothermic transitions and in the case of $H_4Ru_4(CO)_8P_4$ the first peak, occurring at 100°C is attributable to an isomerization[2] and is followed by a melting peak at 120°C; the decomposition peak begins at 180°C and spreads out over a fairly large temperature range.

The DSC curve of $H_4Ru_4(CO)_9P_3$ shows two endothermic transitions, the first one at 65°C is attributable to melting while the second, which begins at about 160°C and extends over a wide temperature range, is due to the decomposition of the complex. The melting, isomerization and overall decomposition heats are evaluated and are reported in Table 1.

TABLE 1

MELTING, ISOMERIZATION, OVERALL DECOMPOSITION HEATS OF $H_4Ru_4(CO)_8P_4$ AND $H_4Ru_4(CO)_9P_3$

P = tributylphosphine.

Complexes	ΔH_m (*kcal mol*$^{-1}$)	$\Delta H_{is.}$ (*kcal mol*$^{-1}$)	$\Delta H_{dec.}$ (*kcal mol*$^{-1}$)
$H_4Ru_4(CO)_9P_3$	8.65	—	126.7
$H_4Ru_4(CO)_8P_4$	4.60	6.30	199.2

The data obtained correlate well with the data for similar complexes, as reported in a previous paper[3].

ACKNOWLEDGMENT

The authors acknowledge the assistance of Mr. F. Sodi.

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