Thermochimica Acta, 10 (1974) 73–83

THE THERMAL BEHAVIOUR OF SOME RHODIUM COMPLEXES

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(Received 21 April 1974)

ABSTRACT

The thermal behaviour of several complexes of rhodium has been investigated. Complexes containing nitrogen ligands readily decompose to the oxide, Rh_2O_3. Complexes with phosphorus and arsenic ligands decompose to the same oxide of rhodium, although difficulty is encountered in removing all the phosphorus and arsenic. The suitability of the decomposition to Rh_2O_3 as an analytical technique for rhodium is discussed.

INTRODUCTION

Several studies on the thermal decomposition of rhodium compounds have reported that the complexes decompose to metallic rhodium. Duval[1] noted that the rhodium complexes containing thionalide and 2-mercaptobenzoxazole decompose to rhodium metal in a form which resists oxidation up to 1000°C. This observation is particularly striking as Duval also reports that when rhodium metal is heated, oxygen uptake occurs above 662°C. The reason for the non-oxidation of the rhodium metal obtained by the decomposition of complexes is not apparent.

Kitchens and Bear[2–4] in a series of articles have discussed the thermal behaviour of some rhodium(II) carboxylates and have found that, on heating to 400°C, the complexes decompose to rhodium metal. Although the thermogravimetric studies were carried out in a nitrogen atmosphere, the authors mention that no oxide is formed even if the decomposition is performed in air.

The decomposition of several rhodium complexes to an oxide of rhodium and not to the metal is reported in this paper. Decomposition to the oxide is stoichiometric and the suitability of this technique as a method of analysis for rhodium is discussed.

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EXPERIMENTAL

The complexes used in this study were prepared as described previously[5–7]. The thermogravimetric (TG) curves were recorded on a Stanton Instruments Model T RQ 1 thermobalance employing a heating rate of 4 °C min^{-1}. Sample sizes were in the range of 40–50 mg. Provision for excluding air from the samples was not made.

Simultaneous thermogravimetric–differential thermal analysis (TG/DTA) curves were recorded on a Rigaku Thermoflex (differential thermogravimetric equipment) using a platinum–rhodium thermocouple. A heating rate of 5 °C min^{-1} and DTA ranges of either ± 100 or $\pm 250\ \mu V$ were employed. The size of sample taken was between 8 and 10 mg and an approximately equal quantity of Al_2O_3 was used as a DTA reference. All samples were heated in air.

RESULTS AND DISCUSSION

Complexes with bidentate nitrogen donors

Thermograms for the four complexes, $[Rh(CO)(L\text{–}L)HX_2]$, (where L–L = phen or dipy and X = Cl or Br) are given in Fig. 1. All complexes begin decomposing at

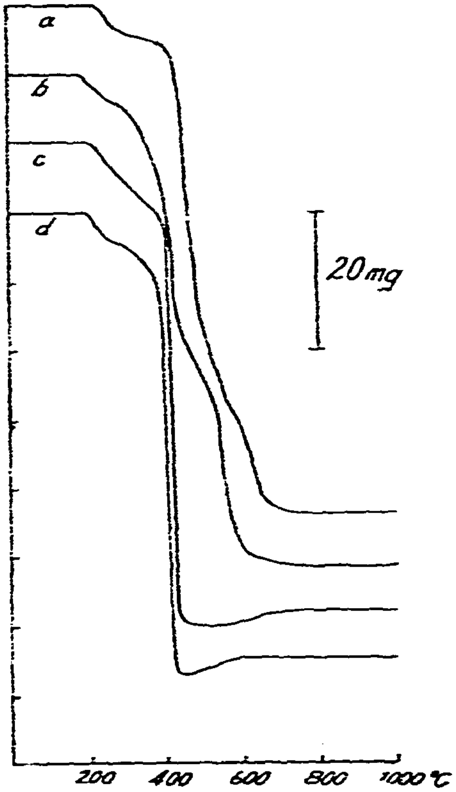


Fig. 1. TG curves for (a) $Rh(CO)(phen)HBr_2$; (b) $Rh(CO)(dipy)HBr_2$; (c) $Rh(CO)(phen)HCl_2$; (d) $Rh(CO)(dipy)HCl_2$.

about 200 °C and decomposition occurs as a single step. In all cases, a constant mass region was not obtained until 800 °C. For [Rh(CO)(phen)HBr$_2$], loss of weight to 800 °C amounted to some 73.3% of the complex. This value is significantly lower than that expected for complete decomposition to rhodium metal (78.2%). The infrared spectrum of the grey residue showed bands at 652(s), 605(s), 548(m), 508(w), 500(w) and 460(m) cm^{-1} which can be assigned to rhodium–oxygen stretching frequencies. Rhodium sesquioxide, Rh_2O_3, is the oxide of rhodium which is thermally stable at this temperature[8]. The mass of residue calculated on the basis of formation of this oxide (Table 1) is very close to the value found for this compound. Similar results for the other dipy and phen compounds (Fig. 1) suggest that decomposition to the oxide occurred in these cases, too. Once again, there is excellent agreement between the calculated percentage of oxide and the percentage of residue.

TABLE 1

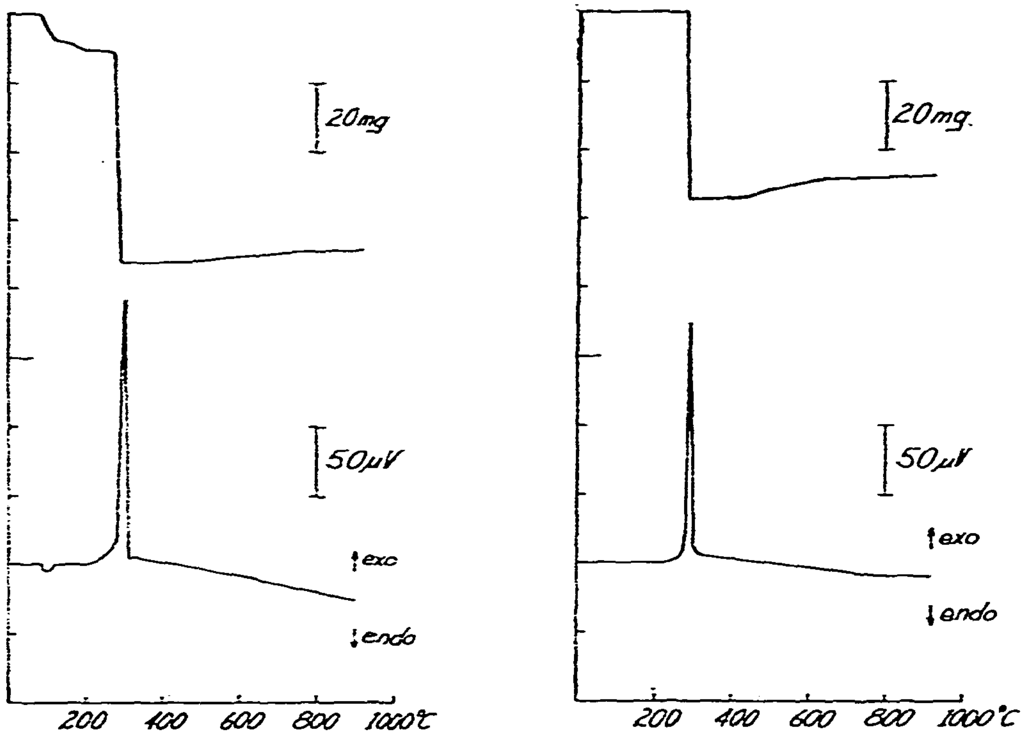
RESIDUE MASSES FOR DIPYRIDYL AND PHENANTHROLINE COMPLEXES

Complex	*% ash*	*calc. Rh_2O_3*	*calc. %Rh*
Rh(CO)(phen)HCl$_2$	32.4	33.1	26.8
Rh(CO)(phen)HBr$_2$	26.7	26.9	21.8
Rh(CO)(dipy)HCl$_2$	35.0	35.4	28.7
Rh(CO)(dipy)HBr$_2$	28.5	28.3	22.9
$Rh_2(C_6H_5COO)_4 \cdot 2(CH_3)_2CO$	31.6	31.5	25.6
$Rh_2(C_2H_5COO)_4$	52.8	51.0	41.3

The thermograms for the four complexes provide little information about the method of decomposition. All complexes decompose in a one-step process, although the rate of decomposition increases rapidly in the 300–400 °C range. The thermograms show that the chloro complexes are less stable than their bromo analogues. Decomposition for the chloro complexes is complete by about 450 °C, whereas the bromo complexes slowly decompose up to about 800 °C, oxygen uptake occurring as the ligands are removed.

The observation that a rhodium oxide is formed in the decomposition of these complexes is contrary to the results of Duval[1]. Duval claims that the metal formed by the decomposition of complexes resists oxidation even at 1000 °C. The present study did not reveal any cases where oxidation of the rhodium failed to occur.

Kitchens and Bear have reported that rhodium(II) carboxylates decompose to rhodium metal when heated in a nitrogen stream[4]. Rhodium(II) propionate and rhodium(II) benzoate, as its diacetone adduct, have been reinvestigated in this study and simultaneous TG/DTA curves are given in Fig. 2. Both complexes decompose to rhodium oxide when heated in air. A powder pattern on the residue from rhodium(II) propionate showed principal lines at 2.62(s), 2.56(m), 1.49(m), the relative intensities of the lines being given in parentheses. The tabulated principal lines for Rh_2O_3 are 2.62(100), 2.57(40) and 1.50(35) (ref. 9). From this information, it can be reasonably inferred that Rh_2O_3 is formed on thermal decomposition of rhodium(II) propionate in air. The similarity in the 400–700 cm^{-1} region of the infrared spectrum of the residue from rhodium(II) propionate with the spectra of the residues of all other compounds studied in this work suggest that the thermal decomposition in air of rhodium complexes produces rhodium(III) oxide, Rh_2O_3, and not rhodium metal.



(a) (b)

Fig. 2. (a) TG/DTA curves for $[Rh_2(C_6H_5COO)_4]\cdot 2(CH_3)_2CO$. (b) TG/DTA curves for $[Rh_2(C_2H_5COO)_4]$.

Figure 2 shows that, at 280°C, both the benzoate and propionate complexes undergo rapid decomposition. As the amount of residue at this point does not correspond to that expected for rhodium metal, some oxidation has presumably occurred. Above 400°C, the residue increases in mass until the stoichiometric amount of Rh_2O_3 is obtained (Table 2). A strong exotherm occurs in the DTA curves of both samples at 280°C. The exotherm is associated with the decomposition of the complex. There may be some contribution to the exotherm from the oxidation of the organic fragments which result from the breakdown of the carboxylate ligands. From the studies of Kitchens and Bear and the present study, it would seem that in an inert atmosphere, the complexes decompose to rhodium metal, whereas decomposition to Rh_2O_3 occurs in an oxidising atmosphere.

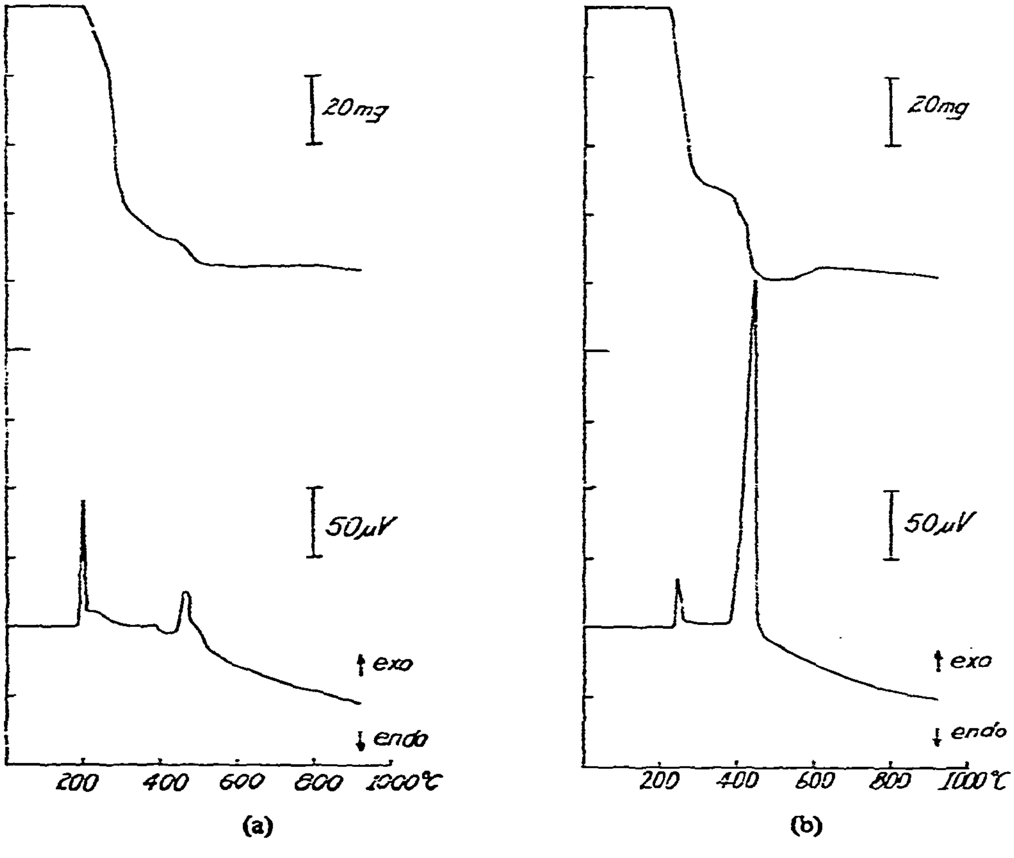
TABLE 2

RESIDUE MASSES FOR PHOSPHINE AND ARSINE COMPLEXES

Complex	*% ash*	*calc. Rh_2O_3*	*calc. %Rh*
$Rh(CO)(PPh_3)_2Cl$	18.7	18.4	14.9
$Rh(CO)(AsPh_3)_2Cl$	16.0	16.3	13.2
$[Rh(diars)_2Cl_2]Cl$	17.0	16.3	13.2
$[Rh(diars)_2Br_2]Br$	13.5	13.9	11.3
$[Rh(8\text{-}dppq)_2Cl_2]Cl \cdot 2H_2O$	16.0	14.6	11.8
$[Rh(8\text{-}dppq)_2Br_2]Br \cdot 2H_2O$	13.8	12.6	10.2
$[Rh(8\text{-}dpaq)_2Cl_2]Cl \cdot 2H_2O$	13.5	13.2	10.7
$[Rh(8\text{-}dpaq)_2Br_2]Br \cdot 2H_2O$	11.2	11.6	9.4

Complexes with phosphorus and arsenic donors

All complexes containing phosphorus or arsenic as donor ligands decompose to the stoichiometric amount of Rh_2O_3, although difficulty is encountered in some situations in removing all the phosphorus or arsenic from the residue. Two complexes of rhodium(I), viz. $[Rh(CO)(EPh_3)_2Cl]$ (E = P, As), were studied and the joint TG/DTA curves are given in Fig. 3. Complexes of rhodium(III) which were studied have



(a) (b)

Fig. 3. (a) TG/DTA curves for $Rh(CO)(PPh_3)_2Cl$. (b). TG/DTA curves for $Rh(CO)(AsPh_3)_2Cl$.

the general formula $[Rh(L\text{–}L)_2X_2]X\cdot 2H_2O$ (X = Cl, Br.). The bidentate ligands used were *o*-phenylenebis(dimethylarsine) (diars), 8-diphenylarsinoquinoline (8-dpaq) and 8-diphenylphosphinoquinoline (8-dppq). Figure 4 contains the TG curves for the diars complexes and simultaneous TG/DTA curves for the 8-dppq and 8-dpaq complexes are given in Fig. 5.

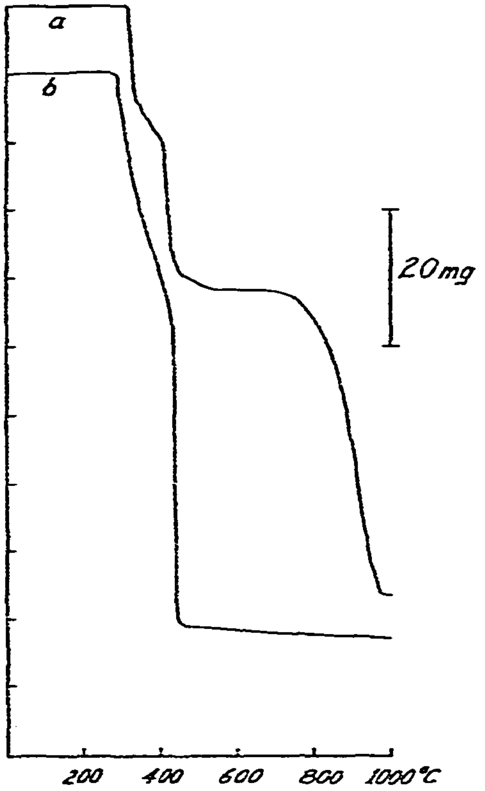
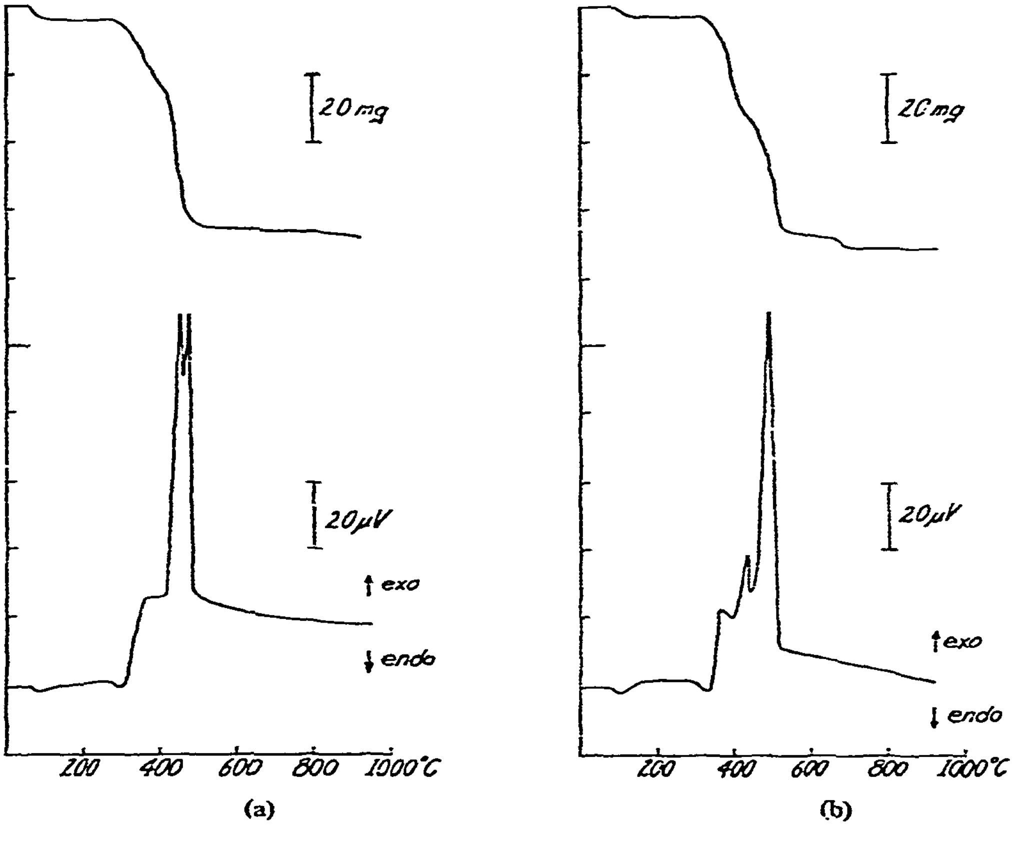


Fig. 4. TG curves for (a) $[Rh(diars)_2Br_2]Br$ and (b) $[Rh(diars)_2Cl_2]Cl$.

The two rhodium(I) complexes, $[Rh(CO)(EPh_3)_2Cl]$ (E = P, As), have similar decomposition patterns (Fig. 3). There is an initial rapid decomposition in the 200–400 °C region which is probably due to the removal of all ligands except phosphorus or arsenic. It appears that the residue contains a significant amount of phosphorus or arsenic at 920 °C. Infrared spectra of samples of these complexes heated to 920 °C show the presence of phosphorus–oxygen (ca. 1100 cm^{-1}) or arsenic–oxygen (ca. 800 cm^{-1}) stretching frequencies. However, if the samples are maintained at 920 °C for about 1 h, slow volatilization of the phosphorus or arsenic occurs (Fig. 6) and the final mass of the residue corresponds to the stoichiometric amount of Rh_2O_3.

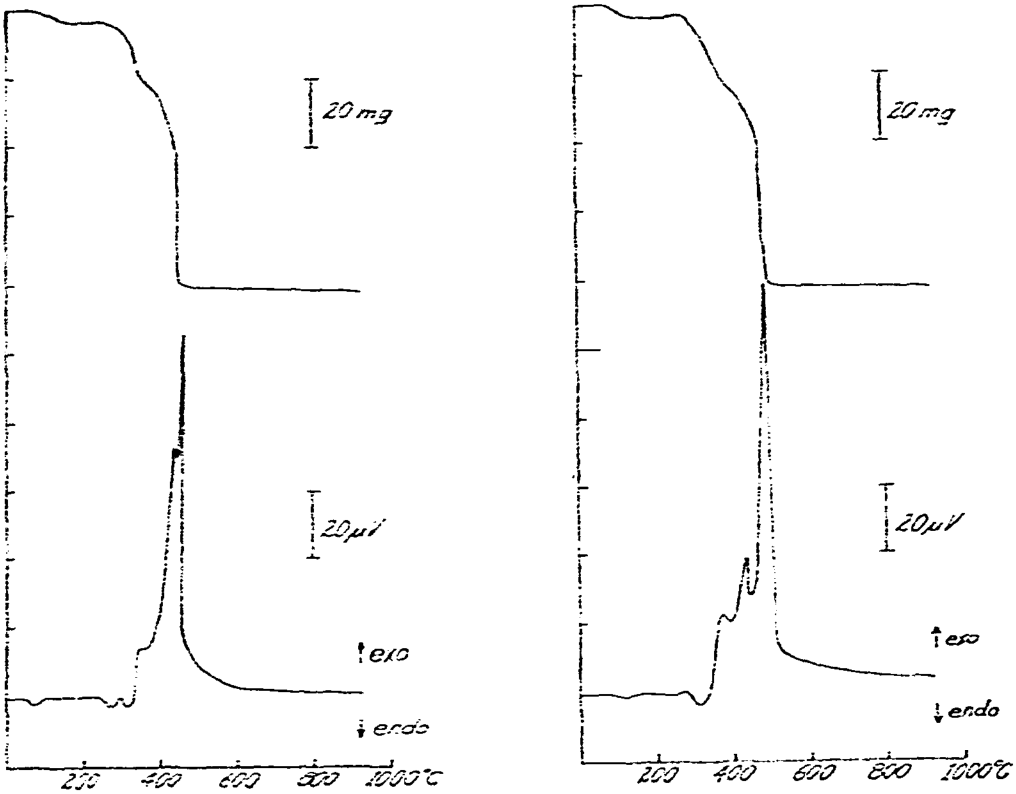
The DTA curve of the phosphine complex shows a sharp exotherm at 200 °C, a broad exotherm at 460 °C and a very broad endotherm from 500–920 °C. The first exotherm is associated with the decomposition of the sample, while the broad nature of the second exotherm would suggest that it is due to some oxidation process, probably oxidation of both rhodium and phosphorus. The slow volatilization of the remaining phosphorus would account for the broad endotherm. A different DTA curve is found for the arsine complex (Fig. 3b). There is an initial exotherm associated with decomposition and this is followed by a sharp and extremely strong exotherm which seems to be due to further decomposition. The final broad endotherm is caused by the removal of the remaining arsenic.

There is a distinct difference in the mode of decomposition of the two diars complexes (Fig. 4). The chloro complex decomposes in a single step between 280 and 500 °C to give the metal oxide from about 700 °C. This is markedly different from the bromo complex which decomposes in two steps, a constant mass region occurring between 550 and 640 °C. To obtain some information about the mode of decomposition of the bromo complex, a sample was heated to 550 °C and its infrared spectrum recorded. The spectrum was virtually featureless except for a weak and broad absorption centered around 800 cm^{-1}, which can be assigned to an arsenic–oxygen stretching frequency. Testing the residue for bromine proved positive. Thus the first part of the decomposition appears to be the loss of carbon and hydrogen together with some bromine or arsenic to give the observed mass decrease. The second step must involve the loss of the remaining arsenic and bromine, together with oxygen uptake, to



(a) (b)

Fig. 5.



(c) (d)

Fig. 5. (a) TG/DTA curves for [Rh(dppq)$_2$Cl$_2$]Cl·2H$_2$O. (b) TG/DTA curves for [Rh(dppq)$_2$Br$_2$]Br·2H$_2$O. (c) TG/DTA curves for [Rh(dpaq)$_2$Cl$_2$]Cl·2H$_2$O. (d) TG/DTA curves for [Rh(dpaq)$_2$Br$_2$]Br·2H$_2$O.

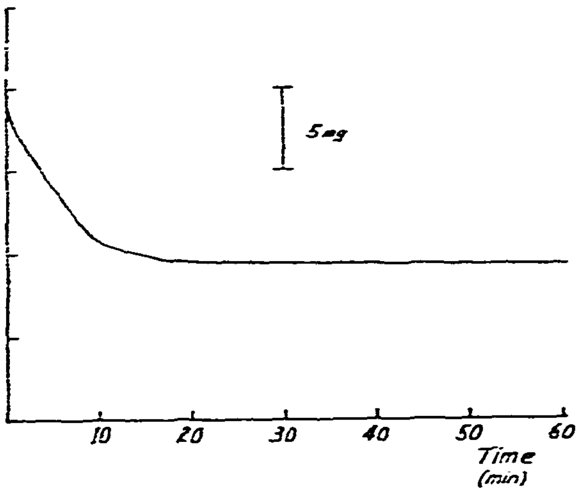


Fig. 6. Decrease in mass with time when the residue from Rh(CO)(PPh$_3$)$_2$Cl is maintained at 920 °C.

produce Rh_2O_3. The higher thermal stability of the bromo complex is in agreement with the observations made on the phenanthroline and dipyridyl complexes discussed earlier.

Complexes containing 8-dpaq and 8-dppq decompose in three steps. Firstly, the lattice water is removed and the decrease in mass suggests that two water molecules are lost (see Table 3). The second step is associated with the loss of the organic fragments plus the halide groups. A distinct odour of quinoline was noted during this step and this suggests that the rhodium–nitrogen and ring carbon–arsenic or phosphorus bonds break before the rhodium-arsenic or rhodium–phosphorus bond. Finally, there is slow volatilization of the oxidized phosphorus or arsenic until the residue of Rh_2O_3 is obtained. The second step in this decomposition is exothermic as shown by the large DTA peak (Fig. 5). The highly exothermic nature of this step may be due to a combination of heat required to break the metal–ligand bonds plus the heat evolved in the consequent oxidation of the organic fragments.

TABLE 3

MASS DECREASE DUE TO LOSS OF WATER

Complex	*found %*	*calc. %*
$[Rh(8\text{-dppq})_2Cl_2]Cl$	4.6	4.1
$[Rh(8\text{-dppq})_2Br_2]Br$	3.6	3.6
$[Rh(8\text{-dpaq})_2Cl_2]Cl$	3.8	3.8
$[Rh(8\text{-dpaq})_2Br_2]Br$	3.2	3.3

Application as an analytical technique for rhodium

Literature methods for the analysis of rhodium are long and complicated. Erdey[10] gives two gravimetric methods, one of which involves precipitation of the rhodium as its hydroxide, and for the other, the precipitate is in the form of $K_3[Rh(NO_2)_6]$. Both methods necessitate ignition of the solid in a hydrogen atmosphere and the resulting ash is weighed as rhodium metal. A colorimetric method has been described by Gardner and Hues[11]. The need to find a suitable colorimetric standard is the disadvantage of this technique. Methods such as precipitation reactions (using hydrogen sulphide or 2-mercaptobenzothiazole), electrogravimetric determinations and direct potentiometry are listed[12]. The majority of these methods are complicated. From the results of the thermal studies described in the previous two sections of this paper, it would appear that a more simple approach to the analysis of rhodium complexes is to decompose the complexes in air and weigh the residue as Rh_2O_3. Evidence for the formation of this oxide comes from powder pattern data and infrared spectra.

The following procedure for rhodium analysis has been tried on a variety of complexes and has been found to be successful. Samples for analysis are weighed in silica crucibles and heated in a furnace for 4 to 5 h, up to temperatures of 900–950 °C. The ash from this decomposition is weighed as Rh_2O_3. Relatively small amounts of sample can be used, as accurate results were obtained with only 8 to 10 mg of the final ash.

Table 4 lists the results from a series of investigations. The first three columns of the table contain the results of separate determinations, whilst the final two columns compare the mean of the determinations with the expected percentage oxide. An investigation of the latter two columns demonstrates the accuracy of the technique. Results are reproducible as shown by the values obtained from different determinations. Difficulty can sometimes be encountered with the removal of phosphorus or arsenic from the samples. Prolonged heating of the ash may cause some decomposition of the rhodium oxide producing low results. With care, however, reproducible results can be achieved with phosphorus or arsenic ligands.

TABLE 4

ANALYTICAL RESULTS

Complex	*found % oxide*			*mean*	*calc. % oxide*
	1	*2*	*3*		*Rh_2O_3*
$Rh(CO)(phen)HCl_2$	32.7	32.0	32.1	32.3	33.1
$Rh(CO)(phen)HBr_2$	26.1	26.7	26.4	26.4	27.0
$Rh(CO)(dipy)HCl_2$	34.8	34.8	34.4	34.7	35.4
$Rh(CO)(dipy)HBr_2$	27.8	27.5	28.0	27.8	28.3
$[NEt_4][Rh(CO)(C_6H_7N)I_4]$[a]	14.7	14.0		14.4	14.7
$[Rh(diars)_2Br_2]Br$	13.6	13.5	13.6	13.6	13.9
$[Rh(8\text{-}dmaq)_2Br_2]Br$[b]	14.7	14.5		14.6	15.7
$Rh(CO)(PPh_3)_2Cl$	18.7	19.5		19.1	18.4
$Rh(CO)(AsPh_3)_2Cl$	17.3	16.0		16.6	16.3

[a] C_6H_7N = aniline. [b] 8-dmaq = 8-dimethylarsinoquinoline.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. S. Woodburn of the Ballarat Institute of Advanced Education for running simultaneous TG/DTA curves. They are indebted also to Mrs. E. Krankovits of La Trobe University for her many helpful discussions.

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