Thermal Studies on *Trans*-lmidazolium Tetrachlorobis (Imidazole) Ruthenate(III) Dihydrate and Rhodate(III) Dihydrate

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Thermal studies (TG, DTG and DTA) in static air showed that *trans*-imidazolium tetrachlorobis(imidazole) ruthenate(III) dihydrate, $(ImH)[RuCl_4 (Im)_2]\cdot2H_2O$ loses two molecules of water within 200°C, followed by two steps decomposition to give unstable intermediates. At 565°C the weight loss conforms to formation of thermally reduced transient RuCl and finally there is gain in weight due to formation of nonstoichiometric oxide. *Trans*-imidazoliumtetrachlorobis (imidazole) rhodate(III) dihydrate becomes anhydrous around 230°C followed by two steps decomposition to several intermediates and forms spongy Rh metal at 500°C (mass loss: found 80%; calculated 78.8%) and beyond it there is weight gain due to oxide formation. The activation energies for the dehydration and two steps decomposition reactions were calculated by Freeman and Carrol's method and the respective values for ruthenium(III) and rhodium(III) complexes were 20.1, 38.3, 153.2, 277.2 kJ mol^{-1} and 27.1, 76.6, 98.1 kJ mol^{-1}. The tentative mechanism for thermal decomposition has been proposed.

Key Words: Thermal decomposition, TG-DTA, DTG, Imidazolium-imidazole, Ruthenium(III), Rhodium(III), Activation energy.

INTRODUCTION

Because of their biological significance the complexes of transition metals with imidazole and substituted imidazoles are extensively studied. In many metalloenzymes the metal ligand bond occurs through the imidazole of the histidine moiety of the proteins. Since 1970 there has been a spurt of interest in the imidazole complexes of the platinum metals[1-4]. Studies of the antitumour activities of complexes[5] like $(ImH)[RuCl_4(Im)_2]$ and $(ImH)_2[RuCl_5(Im)]$ revealed that the interactions take place at the DNA level. According to hard and soft principle nitrogen is a hard donor but due to high polarizability of the ring in imidazole it behaves as a borderline base and a weak π-acceptor[6]. However, in presence of alkyl substituents the basicity increases. In continuation of our earlier

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work on synthesis and characterization[7] of $(ImH)[RuCl_4(Im)_2] \cdot 2H_2O$ and $(ImH)[RhCl_4(Im)_2] \cdot 2H_2O$, we report here the relative thermal stability and the pattern of the thermal decomposition, activation energies of dehydration and decomposition steps as well as the tentative mechanism of decomposition of the above complexes.

EXPERIMENTAL

The complexes were prepared as described earlier[7]. TG, DTG and DTA were recorded at 10°C min^{-1} in static air in a Shimadzu DT-30 thermal analyzer.

RESULTS AND DISCUSSION

The TG curve of Ru(III) compound (Fig. 1) exhibits the beginning of mass loss at 125°C and at 150°C indicating the removal of the first molecule of water (mass loss: found, 4%; calculated, 3.7%) at 200°C; an 8% mass loss indicates the removal of the second water molecule(calculated mass loss 7.4%). This corresponds to the DTG peak between 220° and 285°C. A small and broad endothermic peak in the DTA profile in the range 125°–290°C ($\Delta T_{min} = 160$°C) corroborates this dehydration reaction. The weight loss is gradual from 260° up to 560°C with one broad DTG peak. This is followed by sharp exothermic DTA peaks between
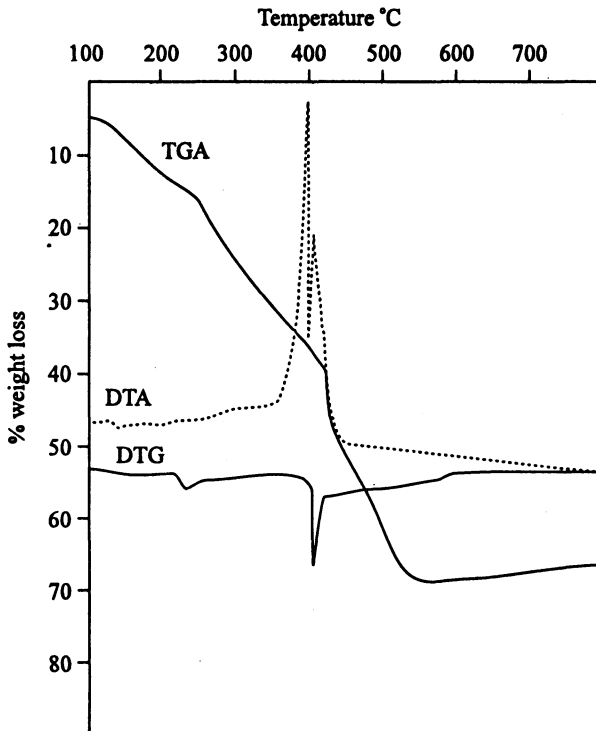

Fig. 1.   Thermogram of $(ImH)[RuCl_4(Im)_2] \cdot 2H_2O$ in air.

330° and 430°C (ΔT_{min} = 375°, 385° and 390°C). Above 556°C there is 70% mass loss, indicative of formation of thermally reduced transient RuCl and finally there is gain in weight due to formation of non-stoichiometric oxide.

The TG profile (ImH)[RhCl$_4$(Im)$_2$]·2H$_2$O (Fig. 2) shows 4% mass loss at 70°C, which continues up to 230°C. This corresponds to the DTG peak between 200° and 280°C, conforming to the loss of two molecules of water (mass loss: found, 7%; calculated, 7.4%). A sharp endothermic peak between 220° and 250°C corresponds to this dehydration step. Therefore, mass loss occurs gradually with two major inflexions indicated by DTG peaks in the range 400°–420°C and 430°–560°C. At 430°C there is 49.2% mass loss indicative of the elimination of the imidazolium ion and two imidazole ligands (calculated mass loss 49.6%). A large exothermic peak in the DTA curve between 340° and 415°C (ΔT_{min} = 410°C) corroborates this decomposition. At 500°C, the 80% mass loss indicates the removal of four chloride ligands (calculated mass loss 78.8%). A large exothermic peak in the range of 415°–600°C (ΔT_{min} = 420°C) lends support to this change. Beyond 600°C there is gradual increase in weight due to formation of oxide of uncertain composition.
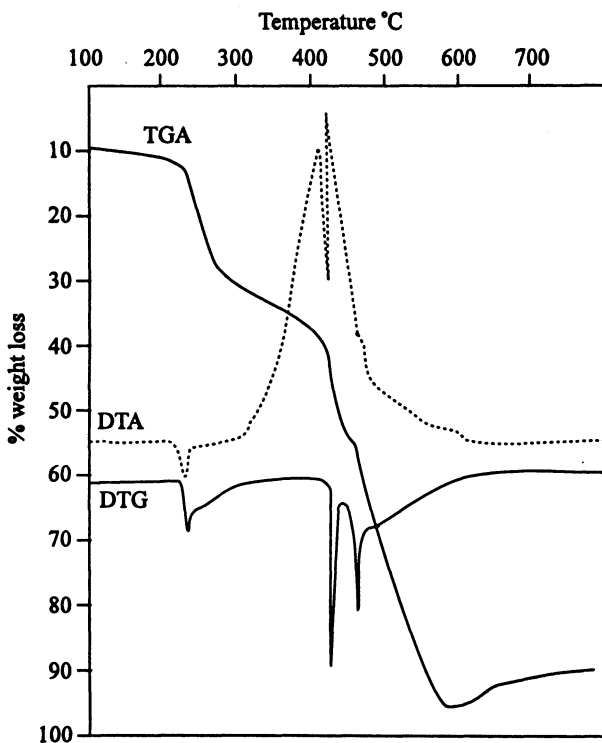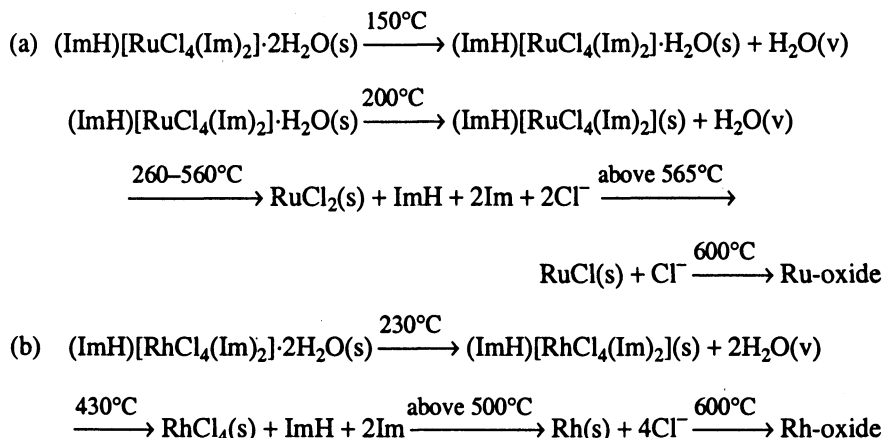

Fig. 2.   Thermogram of (ImH)[RhCl$_4$(Im)$_2$]·2H$_2$O in air.

In view of the results obtained above, the following tentative mechanism may be suggested for the dehydration and decomposition of the complexes in air.

(a) $(ImH)[RuCl_4(Im)_2] \cdot 2H_2O(s) \xrightarrow{150^\circ C} (ImH)[RuCl_4(Im)_2] \cdot H_2O(s) + H_2O(v)$

  $(ImH)[RuCl_4(Im)_2] \cdot H_2O(s) \xrightarrow{200^\circ C} (ImH)[RuCl_4(Im)_2](s) + H_2O(v)$

  $\xrightarrow{260-560^\circ C} RuCl_2(s) + ImH + 2Im + 2Cl^- \xrightarrow{above \ 565^\circ C}$

  $RuCl(s) + Cl^- \xrightarrow{600^\circ C} Ru\text{-oxide}$

(b) $(ImH)[RhCl_4(Im)_2] \cdot 2H_2O(s) \xrightarrow{230^\circ C} (ImH)[RhCl_4(Im)_2](s) + 2H_2O(v)$

  $\xrightarrow{430^\circ C} RhCl_4(s) + ImH + 2Im \xrightarrow{above \ 500^\circ C} Rh(s) + 4Cl^- \xrightarrow{600^\circ C} Rh\text{-oxide}$

Using the thermogravimetric data, the activation energy (E*) of decomposition of these complexes was evaluated by adopting the Freeman and Carrol's technique[8], the advantage of this method is that in one single step both the energy of activation and order of the reaction can be calculated. The relationship between the weight change, temperature and activation energy is given by

$$\frac{(-E^*/2.3R) \, \Delta(T^{-1})}{\Delta \log W_r} = -x + \frac{\Delta \log dW/dt}{\Delta \log W_r}$$

where, $W_r = W_e - W$, W_e = weight at the completion of the reaction
    W = total weight loss at time t and
    R = gas constant (8.3256 kJ mol^{-1})
Calculation of E* from the above equation consists of the following steps:
  (i) Plot of weight loss (W) against time (t), the slope of which gives dW/dt.
  (ii) Plot of log dW/dt against log W_r at the points corresponding to curve (i), the slope of which gives $\Delta \log (dW/dt)/\Delta \log W_r$
  (iii) Plot of T^{-1} against log W_r at the points corresponding to curve (i), the slope of which gives $\Delta T^{-1}/\Delta \log W_r$
  (iv) Finally, plot of $[\Delta \log dW/dt/\Delta \log Wr]$ against $\Delta T^{-1}/\Delta \log Wr$, the slope of which gives $(\pm)E^*/2.3R$, where from the activation energy can be calculated.

The values of activation energy for the two steps dehydration and decomposition for $(ImH)[RuCl_4(Im)_2] \cdot 2H_2O$ were 20.1, 38.3, 153.2 and 277.2 kJ mol^{-1} while for $(ImH)[RhCl_4(Im)_2] \cdot 2H_2O$ the corresponding values were 27.1, 76.6 and 98.1 kJ mol^{-1} respectively. It was observed that the activation energy of dehydration and thermal decomposition for the d^5 Ru(III) complex were higher than the d^6 Rh(III) complex for the same sets of ligands, although their electronegativities and ionic radii were comparable[9]. The likely reasons for this would be:

(a) for electronic reason, the half filled d^5 configuration of Ru(III) is quite stable;

(b) generally, Ru(III) has more affinity towards N-donors[10] compared to Rh(III) or Os(III).

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