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THERMAL DECOMPOSITION OF METAL COMPLEXES

I. COMPLEXES OF IRON(II) IODIDE WITH 1,10-PHENANTHROLINE, 4,7-DIMETHYL-1,10-PHENANTHROLINE AND 4,7-DIPHENYL-1,10-PHENANTHROLINE

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ABSTRACT

The thermoanalytical behaviour of the tris complexes of 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline with Fe(II) iodide is discussed. In conversion of the tris into the bis complexes, the reaction rate is controlled by the metal–ligand bond cleavage so that the "activation energy" can be regarded as an indirect measure of the bond strength.

INTRODUCTION

Though many papers regarding the thermal decomposition of solid coordination compounds have been published[1], as yet no conclusive experimental information exists about the possibility of a correlation between the parameters which can be obtained by means of thermoanalytical techniques and thermodynamic quantities or the strengths of the metal–ligand bond.

The following facts are to be considered:

(1) The reaction rate of a thermal decomposition at solid state may be chemically or physically controlled and it is not always possible to interpret the energy term in a chemical context[2].

(2) There are uncertainties and perplexities in the choice of the thermochemical parameters at solid state (such as starting temperature of reaction, activation energy, enthalpic change...), which are suitable for comparison[3].

(3) Appropriate comparisons cannot be made between parameters referring to homogeneous reactions and parameters referring to heterogeneous reactions[4].

The thermal decomposition of transition metal complexes with α,α'-diimmine has been investigated by means of different techniques chiefly for analytical or preparative purposes[5–11].

Now we consider the influence of the substituent on the activation energy of thermal decomposition of the tris complexes of iron(II) iodide with 1,10-phenanthroline (Phen), 4,7-dimethyl-1,10-phenanthroline (4,7dmphen) and 4,7-diphenyl-

1,10-phenanthroline (4,7dϕphen) under non-isothermal conditions and in a controlled atmosphere.

The thermal decomposition comparisons are possible because these complexes have an octahedral structure as Epstein found on the basis of Mössbauer spectra[12].

We consider, for reactions in the solid state, the "activation energy" as defined by Redfern[2] as the average excess energy which a reactant molecule must have in order to react. This parameter should be dependent on the Fe–N bond strength rather than on the enthalpic change including the differences in the chrystal-packing forces of the decomposition product[13].

EXPERIMENTAL

The complexes used in this study were prepared following the procedures reported in the literature[14] and dehydrated in vacuum.

The simultaneous TG, DTG and DTA were performed with a Mettler vacuum thermoanalyzer in dynamic air and in dynamic nitrogen atmosphere (10 l h^{-1}).

The sample weight amounted to about 20 mg and the particle size was 150–200 mesh. The heating rates were 0.5; 1; 1.5; 2 and 4°C min^{-1}. A Mettler Model T-TD3 crucible holder, 0.3-ml platinum microcrucibles, and thermically inactive Al_2O_3 as reference material were used. The reaction order n and the "activation energy" E_a^* were determined by the Freeman and Carroll method[15].

RESULTS AND DISCUSSION

Thermal analysis in dynamic air atmosphere

Under these experimental conditions thermal decomposition of the complexes investigated occurs in a single step with oxidation processes by air, and the pathway of the thermoanalytical plots does not permit the establishment of the stoichiometry of the decomposition reactions. No significant and diversifying effect is observed in the temperature of the decomposition ($Fe(Phen)_3I_2$: 250°C; $Fe(4,7dmphen)_3I_2$: 274°C; $Fe(4,7d\phi phen)_3I_2$: 274°C) which begins dependent on the substituent of the ligand. It seems evident in this case that this parameter cannot be correlated with the thermal stability and does not permit considerations on the chemical structure of the complexes.

Thermal analysis in dynamic nitrogen atmosphere

The complexes under investigation decompose, under these conditions, by degrees as indicated by the steps of the TG curves (Figs. 1–3) and by the peaks of the DTG and DTA curves. The weight decrease for each observed step corresponds stoichiometrically with the loss of one mole of the ligand.

The complexes decompose according to the equations:

$$Fe(Phen)_3I_2(s) \rightarrow Fe(Phen)_2I_2(s) + Phen(g) \rightarrow Fe(Phen)I_2(s) + Phen(g)$$

$$\begin{aligned} \mathrm{Fe(4{,}7dmphen)_3I_2(s)} &\rightarrow \mathrm{Fe(4{,}7dmphen)_2I_2(s)} + \mathrm{4{,}7dmphen\ (g)} \rightarrow \\ &\rightarrow \mathrm{Fe(4{,}7dmphen)I_2(s)} + \mathrm{4{,}7dmphen\ (g)} \\ \mathrm{Fe(4{,}7d\phi phen)_3I_2(s)} &\rightarrow \mathrm{Fe(4{,}7d\phi phen)_2I_2(s)} + \mathrm{4{,}7d\phi phen\ (g)} \rightarrow \\ &\rightarrow \text{indefinable decomposition} \end{aligned}$$

Observing the thermal curves it is evident that the mono-complexes decompose rather slowly in comparison with the corresponding tris and bis complexes. This behaviour may be due to an octahedral polymeric structure containing bridging halogens as ascertained by Wilde et al.[11] for similar complexes, on the ground of the

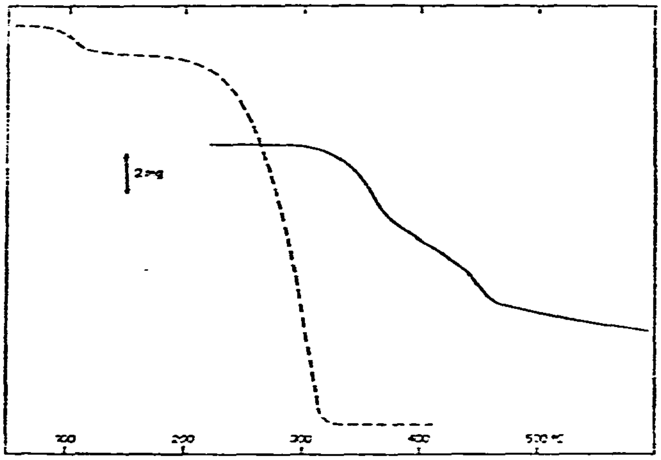

Fig. 1. TG curves of $Fe(Phen)_3I_2$ (full line; weight of reactant 17.9 mg; heating rate 4 °C min^{-1}) and of 1,10-phenanthroline (dotted line; weight of reactant 19.6 mg; heating rate 4 °C min^{-1}; the melting and the loss of 1 mole of water are simultaneous).

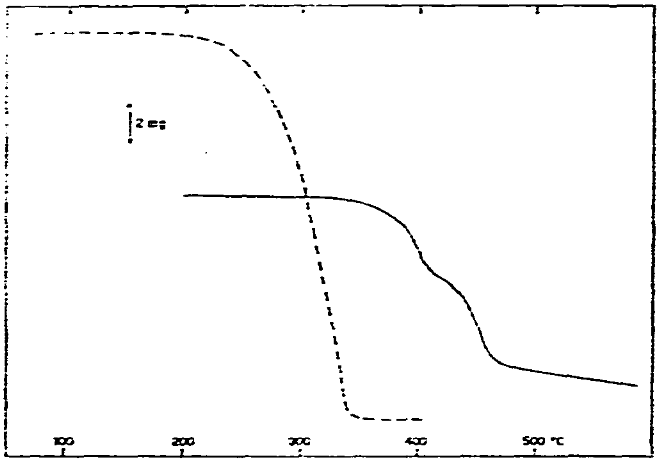

Fig. 2. TG curves of $Fe(4,7dmphen)_3I_2$ (full line; weight of reactant 15.7 mg; heating rate 4 °C min^{-1}) and of 4,7-dimethyl-1,10-phenanthroline (dotted line; weight of reactant 20.1 mg; heating rate 4 °C min^{-1}).

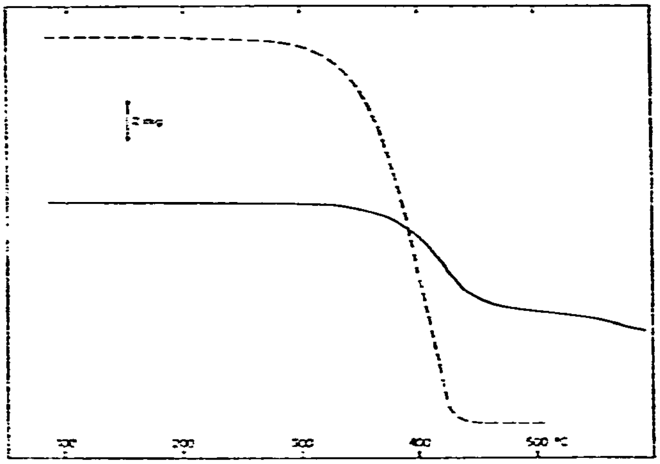

Fig. 3. TG curves of Fe(4,7dϕphen)$_3$I$_2$ (full line; weight of reactant 21.2 mg; heating rate 4 °C min^{-1}) and of 4,7-diphenyl-1,10-phenanthroline (dotted line; weight of reactant 19.2 mg; heating rate 4 °C min^{-1}).

halogen IR frequencies which are lower than the frequency of the terminal halogen

An exothermic peak is observed at 265 °C just before the first weight loss for Fe(4,7dmphen)$_3$I$_2$, a more evident one at 280 °C for Fe(4,7dϕphen)$_3$I$_2$ and none for Fe(Phen)$_3$I$_2$. We exclude that the peak can be a result of the dissociation of the complex with formation of liquid ligand since the vaporizing E_a^* values determined for the free ligand (Phen: 17.9 kcal mol^{-1}; 4,7dmphen: 15.5 kcal mol^{-1}; 4,7dϕphen: 20.5 kcal mol^{-1}) are considerably lower than the E_a^* values obtained for the first step of the decomposition of the corresponding complexes (Table 1) and therefore the weight loss is not due to the transition of the liquid ligand into vapor phase. The peak could be explained admitting the rotation of the 4,7-substituted groups. Since all the complexes begin to decompose at a temperature higher than the vaporizing temperature of the corresponding ligand (Figs. 1–3); the rate of their thermal decomposition in the first step appears to be determined by the dissociation of the ligand from the

TABLE 1

THERMOCHEMICAL DATA OBTAINED FROM THERMOANALYTICAL CURVES FOR THE LOSS OF THE FIRST MOLE OF THE LIGAND

T_i = starting temperature; n = reaction order; and E_a^* = activation energy.

Complex	T_i (°C)	n	E_a^* (*kcal mol^{-1}*)	*Linear correlation coefficient for E_a^**
Fe(phen)$_3$I$_2$	300	0.7	22	0.999
Fe(4,7-dmphen)$_3$I$_2$	360	0.7	63	0.999
Fe(4,7-dϕphen)$_3$I$_2$	385	0.7	39	0.999

complex rather than by the vaporization of the ligand itself, thereby leaving the coordination sphere of the complex.

The high E_a^* values found to turn the tris into the bis complexes (Table 1) are justified since this reaction involves a ${}^1A_1 \rightarrow {}^5T_2$ transition[16] with a diminishment in symmetry and a decrease of the ligand-field stabilization energy.

The E_a^* values mentioned above indicate that the thermal stability of the complexes studied increases in the order:

$$\mathrm{Fe(Phen)_3I_2 < Fe(4{,}7d\phi phen)_3I_2 < Fe(4{,}7dmphen)_3I_2}$$

In comparison with $\mathrm{Fe(Phen)_3I_2}$ this increase was justified for the 4,7-dimethyl substituted compound because of electron donating effects but not for the 4,7-diphenyl substituted compound since the phenyl rings are not coplanar with the phenanthrolinic system at room temperature. The rotation of the phenyl rings, indicated by the DTA peak, should overcome the molecular overcrowding, and decrease the twisting angles between the plane of the chelate ring and that of the phenyl groups with a consequent increase of the bonding properties of the α,α'-diimminic system.

In treating the substituent effect of the tris α,α'-diimmine iron(II) complexes, Krumholz[17] asserted that there is no simple relation between the spectral shifts and the electronic properties or the relative position of substituents on the ligand.

From the results obtained in this study it seems possible to relate the electronic properties of the substituent with the E_a^* values; moreover the substitution in the phenanthrolinic system causes more remarkable changes in the E_a^* parameter than in the Mössbauer spectral shifts[18] and in the pK values[19].

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