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THERMAL DECOMPOSITION OF METAL COMPLEXES

II. MIXED COMPLEXES OF IRON(II) IODIDE WITH 1,10-PHENANTHROLINE, AND 4,7-DISUBSTITUTED-1,10-PHENANTHROLINES

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ABSTRACT

The thermal behavior of the Fe(II) iodide mixed complexes with 1,10-phenanthroline and 4,7-disubstituted phenanthrolines in nitrogen atmosphere is investigated.

In order to determine to what extent small changes in ligand field symmetries influence the "activation energy" E_a^*, this energy is determined. The results are discussed in relation to the changes of the σ and π bonds.

INTRODUCTION

The structural change effects of a ligand in a complex induced by its partial substitution with another ligand have been investigated in solution[1,2] and in the solid state[3–5]. Mixed complexes may be involved in many analytical[6], inorganic[7] and biological[8,9] problems, but in any event a transmission of electronic effects through the central metal atom seems interesting. Thermochemistry of solid transition metal complexes has also been used to estimate the relative strengths of the metal–ligand bonds by means of the "activation energy" E_a^* (ref. 10). For the presence of transport phenomena occurring in the solid state, it is necessary that the total decomposition rate be controlled by the chemical process proper[11].

Previously[12] we have studied the correlation between the substituent effects on the Fe–N bond of tris-phenanthroline complexes and the changes of E_a^*. This thermochemical parameter was measured in order to determine to what extent small changes in ligand field symmetries would influence its value. In particular we consider the effects of 4,7-substituted phenanthroline ligands on the bond of iron(II) with 1,10-phenanthroline.

Earlier, Taylor and Schilt[13] measured the formal oxidation–reduction potentials and discussed the visible absorption spectra of these mixed complexes to discover whether the substituent effect involves additivity or not.

EXPERIMENTAL

All the complexing agents were obtained from Schuchardt (München) and used as received. The complexes of this study: bis(1,10-phenanthroline)-4,7-dimethyl-1,10-phenanthroline iron(II) iodide [FeA_2BI_2], bis(1,10-phenanthroline)-4,7-diphenyl-1,10-phenanthroline iron(II) iodide [FeA_2CI_2], bis(4,7-dimethyl-1,10-phenanthroline)-1,10-phenanthroline iron(II) iodide [FeB_2AI_2] and bis(4,7-diphenyl-1,10-phenanthroline)-1,10-phenanthroline iron(II) iodide [FeC_2AI_2] were prepared as described in literature[13] and dehydrated in vacuum.

The simultaneous TG, DTG, and DTA were performed with a Mettler vacuum thermoanalyzer in a flowing nitrogen atmosphere ($10\ l\ h^{-1}$). The sample weight amounted to about 25 mg. 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[14].

RESULTS AND DISCUSSION

The mixed complexes investigated in this study decompose according to the following reaction scheme:

$$FeA_2BI_2(s) \rightarrow FeABI_2(s) + A(g) \rightarrow FeBI_2(s) + A(g)$$

$$FeA_2CI_2(s) \rightarrow FeACI_2(s) + A(g) \rightarrow FeCI_2(s) + A(g)$$

$$FeB_2AI_2(s) \rightarrow FeB_2I_2(s) + A(g) \rightarrow FeBI_2(s) + B(g)$$

$$FeC_2AI_2(s) \rightarrow FeC_2I_2(s) + A(g) \rightarrow \text{undefinable decomposition}$$

In Table 1 we report the values of E_a^* and n related to the first thermal decomposition reaction, which involves the loss of one mole of A. These values were com-

TABLE 1

"REACTION ORDER" n, "ACTIVATION ENERGY" E_a^* FOR THE LOSS OF THE FIRST MOLE OF THE LIGAND IN THE THERMAL DECOMPOSITION OF Fe(II) MIXED COMPLEXES WITH 4,7-SUBSTITUTED-1,10-PHENANTROLINES IN COMPARISON WITH THE TRIS 1,10-PHENANTROLINE COMPLEX

Complex	*n*	E_a^* *(kcal mol⁻¹)*	*Linear correlation coefficient for* E_a^*
FeA_3I_2[a]	0.7	22	0.999
FeA_2BI_2	0.7	40	0.999
FeA_2CI_2	0.7	28	0.999
FeB_2AI_2	0.7	53	0.999
FeC_2AI_2	0.7	32	0.999

[a] From ref. 12.

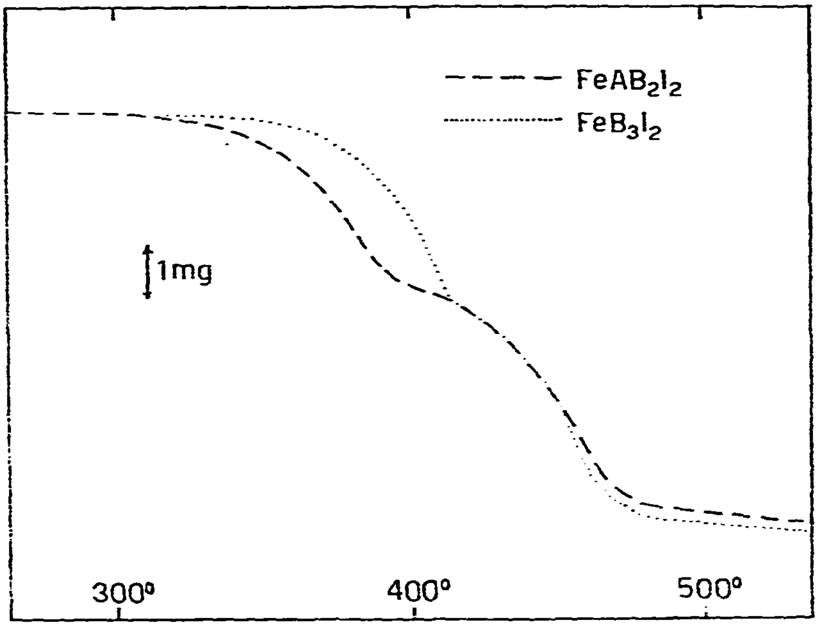

Fig. 1. TG curves of FeB_2AI_2 (18.3 mg) and of FeB_3I_2 (15.7 mg); heating rate 4 °C min^{-1}.

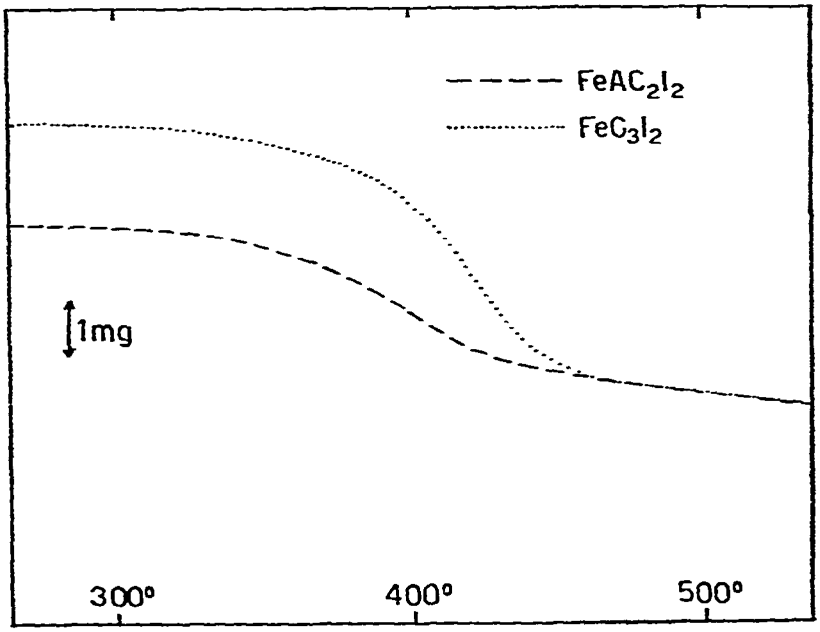

Fig. 2. TG curves of FeC_2AI_2 (17.9 mg) and of FeC_3I_2 (21.2 mg); heating rate 4°C min^{-1}.

pared with the E_a^* and n values obtained in the case of the thermal decomposition of the simple complex FeA_3I_2. In Figs. 1 and 2 we can see that, after the loss of A, the mixed complexes FeB_2AI_2 and FeC_2AI_2 have the same outline of the thermoanalytical curves of the bis complexes FeB_2I_2 and FeC_2I_2 obtained after the decomposition of the tris complexes. At $\phi = 4$°C min^{-1} the complexes FeA_2BI_2 and FeA_2CI_2, seem to lose the two moles of A with a single step; at $\phi = 0.5$°C min^{-1}, two steps are observed, as shown in Fig. 3. Under the latter conditions it was possible to obtain the mixed complexes $FeACI_2$ and $FeABI_2$, which are not reported in literature.

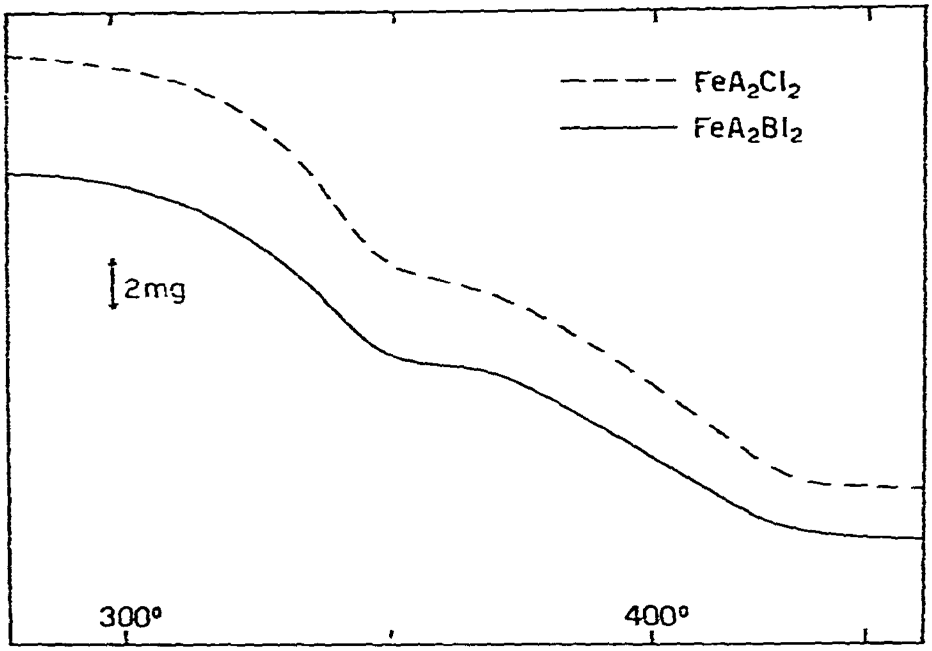

Fig. 3. TG curves of FeA_2BI_2 (41.4 mg) and FeA_2CI_2 (48.9 mg); heating rate 0.5°C min^{-1}.

The thermal behavior of the mixed complexes investigated may be explained if the overall process of the first decomposition reaction involves the breaking of the Fe–N bond with the release of the gaseous product and the formation of a new complex which is 6-fold coordinated with the accomodation of the iodine ions into the coordination sphere. In fact, since the reaction order n experimentally found is about 0.7, it is possible to assert that the rate determining process is the breaking of the Fe–N bond[11]. On the ground of the experimental results we observe that the 4,7-substitution on the ligand causes stronger Fe–N bonds in the 1,10-phenanthroline mixed complexes than in the simple ones. To explain this fact we must consider the important role of the π-bond in the structure of the complexes of Fe(II) with α,α'-diimine ligands. In this case, we must look upon the change of the strength of the bonds Fe–N of 1,10-phenanthroline, in relation to the presence of the phenanthroline substituted ligands which tend to increase the large density on the iron ion. That is, we can think that the introduction of one or two 4,7-disubstituted ligand molecules reinforces the σ-bond, but at the same time, as a consequence of back-donation between dπ orbitals of the iron ion and pπ* of 1,10-phenanthroline we note an increase in the strength of the π bond in the mixed complex compared with that of the simple one with regard to the Fe–1,10-phenanthroline bond. In fact, Fe(II) bound to one or two moles of substituted ligand in mixed complexes reaches an optimal value in the effective charge, through the σ and π bonds, and therefore it becomes a better π-donator for 1,10-phenanthroline compared to the simple complex.

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REFERENCES

1 M. T. Beck, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold, London, 1970, Ch. 8.
2 Y. Marcus and I. Eliezer, *Coord. Chem. Rev.*, 4 (1969) 273.
3 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Amine Complexes*, Elsevier, Amsterdam, 1967.
4 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc. A*, (1967) 925.
5 G. Beech, S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc. A*, (1967) 929.
6 I. D. Alimarin and V. I. Shlenskaya, *Pure Appl. Chem.*, 21 (4) (1970) 461.
7 N. E. Jackobs and D. W. Margerum, *Inorg. Chem.*, 6 (1967) 2038.
8 A. S. Mildvan and M. Coln, *J. Biol. Chem.*, 241 (1966) 1178.
9 B. L. Vallee, T. L. Coombs and R. J. P. Williams, *J. Amer. Chem. Soc.*, 80 (1958) 397.
10 G. Beech, *J. Chem. Soc. A*, (1969) 1903.
11 E. Jóna, V. Jesenák, T. Šramko and J. Gazo, *J. Thermal. Anal.*, 5 (1973) 57.
12 R. P. Bonomo, S. Gurrieri, S. Musumeci, E. Rizzarelli and G. Siracusa, *Thermochim. Acta*, 9 (1974) 373.
13 P. J. Taylor and A. A. Schilt, *Inorg. Chim. Acta*, 5 (1971) 691.
14 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.