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THERMAL BREAKAGE OF Fe–L BONDS IN $Na_{17}\{Fe(CN)_5L\}\cdot xH_2O$. CORRELATION WITH SOLUTION KINETICS

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ABSTRACT

TG–DTG–DTA data for various solids of the type $Na_n\{Fe(CN)_5L\}\cdot xH_2O$ are reported, L being a pyridinic or pyrazinic derivative. Observed transitions are interpreted and, for the case of neutral L ligands, a correlation is established between ligand release temperature and the energy of the charge transfer $t_{2g}(Fe) \rightarrow {}^*\pi(L)$ transition of the complex ion. The latter is related to the rate of release of the ligand in aqueous solution, thus demonstrating that the bond-breaking process determines the observed trends in reactivity both in the solid phase and in aqueous solution.

INTRODUCTION

At present, a wealth of information is available for the ligand exchange processes in $\{Fe(CN)_5L\}^{n-}$ ions, where L is a pyridinic or pyrazinic derivative [1–6]. It has been thoroughly demonstrated that in reactions of the type

$$\{Fe(CN)_5L\}^{n-} + X \rightarrow \{Fe(CN)_5X\}^{3-} + L^{(n-3)-} \qquad (1)$$

a maximum rate is achieved at high scavenger X concentration [1,4] and the corresponding first-order rate constant, k_{-L}, has been shown to correspond to the process represented by

$$\{Fe(CN)_5L\}^{n-} + H_2O \rightarrow \{Fe(CN)_5H_2O\}^{3-} + L^{(n-3)-} \qquad (2)$$

where water has been included because of its ready availability and lack of experimental evidence for a pentacoordinated species.

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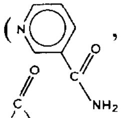
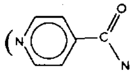
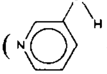
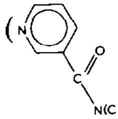
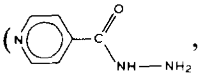
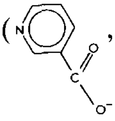
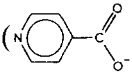
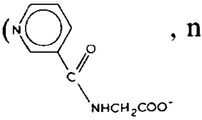
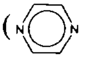
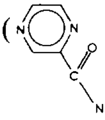
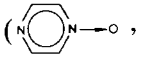
Process (2) is dissociative, of the I_d type in aqueous solution [6], and consequently good correlations have been found between k_{-L} and various parameters which are, in principle, related to the stability of the Fe–L bond, such as Mössbauer isomer shifts in ^{57}Fe, crystal field stabilization on Fe(II), and especially the energy of the charge transfer transition $t_{2g}(\mathrm{Fe}) \rightarrow {}^*\pi(\mathrm{L})$, which places an electron in an antibonding orbital of the ligand and is a measure of the stabilization due to π-back donation from the heterocycle to Fe in the ground state [1,6].

Superimposed on these relations between rate of release and bond energy, the role of water is clearly observed in the kinetics of release of several aliphatic amines [7] and diamines [8]; also, in the case of the release of aromatic amines [4,6], solvation energetics in the activation process causes the reactivity of neutral and anionic ligands to fall in the opposite direction to that expected from simple spectroscopic considerations. We have considered it of interest, therefore, to obtain information on the reactivity of Fe–L bonds in solid salts containing $\{\mathrm{Fe(CN)_5L}\}^{n-}$ ions. For this purpose we have undertaken the study of the thermal decomposition of the sodium salts of these ions in the cases where L = nicotinamide ( , nide), isonicotinamide ( , isonide), nicotinaldehyde ( , nical), coramine or niketamide ( , cora), isonicotinoylhydrazide ( , Hinh), nicotinate anion ( , nic⁻), isonicotinate anion ( , isonic⁻), nicotinoylglycinate anion ( , nicgly⁻), pyrazine ( , pz), pyrazineamide ( , pzide) and pyrazine mono *N*-oxide ( , NOpz).

Previously, the only pertinent available information referred to the pyridine complex salt $\mathrm{Na_3\{Fe(CN)_5py\}\cdot 3\ H_2O}$ studied by Aymonino and coworkers [9]. The present thermogravimetric study was restricted to the lower temperature range (up to 400°C), as the further decomposition of the products formed upon release of ligand L was not of interest for our purposes.

EXPERIMENTAL

Compounds of the type $Na_n\{Fe(CN)_5L\}\cdot xH_2O$ were prepared by reaction of $Na_3\{Fe(CN)_5NH_3\}\cdot 3\ H_2O$ dissolved in water with an adequate excess of L; the solid salt was obtained on addition of an organic solvent or by salting out with NaI. For further details, ref. 10 should be consulted.

Characterization of the complexes was achieved by chemical analyses, and UV–visible, IR, NMR and Mössbauer spectroscopic techniques [3,10,11]. The number of water molecules was determined by chemical analysis and by use of the TG data given below.

DTA–DTG–TG curves were obtained in a Mettler Recording Thermoanalyzer 1 under the following operating conditions: sample weight ~ 10 mg (special care was taken to maintain this condition constant as much as possible), reference weight 14 mg Al_2O_3; heating rate 6°C min^{-1}; atmosphere purified N_2, 6.3 $dm^3\ h^{-1}$; DTA range 50 μV; DTG range 5 mg min^{-1}; TG range 100 mg; temperature range 25–450°C.

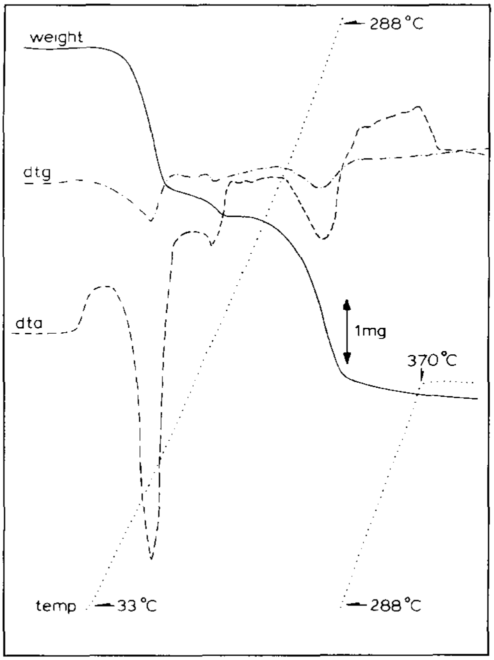


Fig. 1. TG (————), DTA (- - - - - -) and DTG (–·–·–) curves for $Na_3\{Fe(CN)_5nide\}\cdot 6\ H_2O$. Linear heating rate is also shown (· · · · · ·).

RESULTS AND DISCUSSION

Figure 1 shows the thermogram of the nicotinamide complex salt, which is typical of all the thermograms observed for this group of substances. Except for L = nic$^-$, isonic$^-$ and nicgly$^-$ (i.e. for anionic ligands), all compounds lose weight in at least two stages, the first one being attributable to the loss of water (100–130°C); in some cases, this loss is split into two or three stages up to 160°C, indicating the existence of stable lower hydrates. At higher temperatures, ligand L is lost in a transition that is, in many cases, not complicated by other features. Only in the case of L = NOpz and Hinh ligand does decomposition start prior to ligand release, in good agreement with the chemical nature of these compounds. In the case of L = NOpz, decomposition probably involves internal oxidation of Fe(II) to Fe(III) (this redox reaction between the N → O group and a reducing M(II) takes place at room temperature in solution in the case of the stronger reductants V(II) and Cr(II) [12]); in the case of Hinh, the hydrazide group decomposes releasing N_2 (this decomposition mode takes place in the complex at room temperature, albeit rather slowly).

In the case of coramine, the solid was probably impure, with small amounts of $Na_3\{Fe(CN)_5NH_3\} \cdot 3\ H_2O$, due to the difficult crystallization of the cora complex [10]; this is confirmed by carbon analysis. The ligand

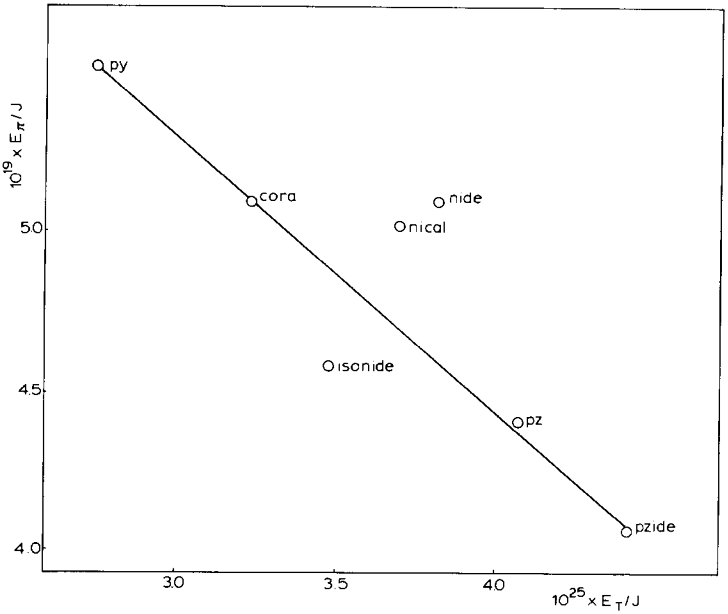


Fig. 2. Correlation between the energy of the $t_{2g}(Fe) \to {}^*\pi(L)$ electronic transition in aqueous solution ($E_\pi = hc/\lambda$) and the thermal energy for bond breakage in solid $Na_3\{Fe(CN)_5L\}$ ($E_T = kT$, where T is the temperature of the maximum in the DTA or DTG curve).

TABLE 1
DTA–TG data for $Na_n\{Fe(CN)_5L\} \cdot xH_2O$ solid salts

Ligand	DTA peak maximum (°C)	Weight loss (%)		Lost product
		Found	Calcd.	
nide	100 (endo)	18.9	18.5	5 H_2O
	160 (endo)	3.6	3.7	1 H_2O
	277 (endo)	24.3	25.0	1 nide
cora	104 (endo)	14.0	14.3	4 H_2O
	235 (endo)	32.0	35.0	1 cora
nic^-	130 (endo)	21.6	21.3	6 H_2O
$isonic^-$	60 (endo)	10.8	10.7	3 H_2O
	120 (endo)	10.8	10.7	3 H_2O
$nicgly^-$	113 (endo)	13.9	13.6	4 H_2O
Hinh	83 (endo) 100 (endo)	20.8	21.6	6 H_2O
	213, 376 (endo)			Decomp. products
isonide	85 (endo)	11.4	11.1	3 H_2O
	125 (endo)	11.7	11.1	3 H_2O
	206 (exo)			?
	252 (endo)	24.6	25.1	1 isonide
nical	92 (endo) 119 (endo)	24.1	23.8	6 H_2O
	268 (endo)	22.0	22.8	1 nical
pz	90 (endo) 100 (endo)	24.5	24.4	6 H_2O
	295 (endo)	16.7	18.1	1 pz
pzide	88 (endo) 117 (endo)	22.2	22.4	6 H_2O
	320 (endo)	26.0	25.3	1 pzide
NOpz	60–82(endo)	17.7	16.3	4 H_2O
	110 (endo)	3.1	4.0	1 H_2O
	202 (exo)			Decomp. products

release temperature can, however, be safely determined for our purposes. The isonicotinamide complex shows a small but consistently reproducible exothermic peak just prior to ligand release; although the origin of the peak is not clear, the ligand release temperature determined in this case must be regarded with caution, as local heating effects due to the exothermic process may shift the DTG peak to nominally lower temperatures.

The thermograms of the complexes of anionic ligands do not show any peak related to ligand loss or decomposition in the temperature range studied; only the dehydration process can be seen at around 100–130°C. The DTA–TG data for the whole set of compounds is given in Table' 1.

In Fig. 2, we have plotted the thermal energy calculated as kT (where T is the temperature at the maximum in the DTG or DTA curve) as a function of the energy of the electronic transition $t_{2g}(\mathrm{Fe}) \rightarrow {}^*\pi(\mathrm{L})$ expressed as $h\nu$; we have included in the plot the point corresponding to the pyridine complex taken from ref. 8. A reasonably good correlation can be seen to exist between both values although neither is directly the Fe–L bond energy, their changes are governed by the changes in the latter, because a common reaction product is formed in the solid phase release, and the visible spectrum has been shown previously [6] to be a measure of the bond stability.

The identity of the products of thermolysis is borne out by the infrared spectra of the residues obtained at 300°C, which are very similar and show bands at 2050, 2025, 595 and 430 cm^{-1}. These bands indicate that $Na_4\{Fe(CN)_6\}$ is formed, probably also with lesser amounts of $Fe_2\{Fe(CN)_6\}$. According to this, the stoichiometry of the ligand release process would be

$$12\ Na_3\{Fe(CN)_5L\} \rightarrow 9\ Na_4\{Fe(CN)_6\} + Fe_2\{Fe(CN)_6\} + 12\ L \qquad (3)$$

In principle, it should be possible to analyze the data in order to obtain kinetic parameters related to the bond breaking event [13,14], but we believe that the inherent uncertainty of DTA–DTG data would make such an attempt unsafe and we prefer to establish the present correlation in terms of more direct magnitudes. Implicit, however, in the correlation is the relationship between ligand release rate constant in solution and ligand release rate constant in the solid phase.

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