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THERMAL STUDIES ON THE ANATION AND DECOMPOSITION OF *TRANS*-FLUOROAQUOBIS(ETHYLENEDIAMINE) AND *TRANS*-FLUOROAQUOBIS(PROPYLENEDIAMINE) DITHIONATE

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ABSTRACT

The anation and decomposition reactions of *trans*$[CrF(H_2O)(aa')_2]S_2O_6$ [aa' = ethylenediamine (en); 1,3-diaminepropane (tmd)] have been studied by means of ATD, TG and DSC techniques. The first and only perfectly defined step is the anation reaction forming the species *cis*$[CrF(S_2O_6)(aa')_2]$. By means of DSC techniques, the enthalpies of reaction and the activation energies of both reactions have been estimated. The electronic spectra of the resultant products suggest *cis* configuration. A second step, preceding total decomposition of the complex, involves

$$cis[CrF(S_2O_6)(aa')_2] \rightarrow cis[CrF(SO_4)(aa')_2] + SO_2$$

which is contaminated by decomposition reactions.

INTRODUCTION

As mentioned in the literature, a large number of thermal studies on the dehydration and anation reactions which may be represented as

$$[MH_2O(N)_5]X_3 \rightarrow [M(X)(N)_5]X_2 + H_2O$$

N being generally NH_3 [1—7], and M = Co, Cr or Ru, have been described.

Studies of complexes with ethylenediamine ligand have also been described, though not generally for the dehydration reaction, but for loss of the amine and substitution of either halogens or pseudohalogens in the presence of catalyzers [8,9]. Few studies have been carried out on the dehydration and anation reactions of complexes of Cr(III) with H_2O and bidentated amines as ligands [10].

Vaughn et al. synthesized for the first time *trans*[$CrF(H_2O)(en)_2](ClO_4)_2$ and *trans*[$CrF(H_2O)(tmd)_2](ClO_4)_2$ [11,12]. From these complexes the corresponding halides were obtained. By heating in the solid state they were transformed into *cis*[$CrF(X)(en)_2]X$ and *trans*[$CrF(X)(tmd)_2]X_2$. Further work by the same authors dealt with analogous reactions with other amino ligands, including mixed ligands (en/tmd; pn/tmd; en/pn) [13,14].

The halides were very soluble in water and, when precipitated, always gave hydrated species in which it was difficult to differentiate coordination water from crystallization water by thermal methods. Testing with several anions, it was found that the dithionate anion produced totally anhydrous salts suitable for thermal studies.

Previous isothermal studies which were carried out at 120—130° C for 12 h, showed a weight loss for the compounds with en and tmd of 4.9% and 4.5%, respectively (1 mole of water represents 4.87% and 4.53%, respectively). At temperatures higher than 140° C the weight loss was considerably increased, showing a loss of SO_2 (detectable by its characteristic odour).

EXPERIMENTAL

Preparation of compounds

trans[$CrF(H_2O)(en)_2](ClO_4)_2$ and *trans*[$CrF(H_2O)(tmd)_2](ClO_4)_2$ were prepared by the usual methods described by Vaughn [11,12]. One g of perchlorate compound was dissolved in a solution of $H_2S_2O_6$ which was previously obtained by passing 2.5 g of $Na_2S_2O_6 \cdot 2\ H_2O$ through an Amberlite IR 120 cationic acid resin. The resultant solution was precipitated with ethanol or acetone, and washed with ethanol and ether. The yield was almost quantitative. Analysis — calcd. for [$CrF(H_2O)(en)_2]S_2O_6$: Cr, 14.09; C, 13.00; N, 15.17; H, 4.87%. Found: Cr, 14.1; C, 13.1; N, 14.8; H, 4.7%. Calcd. for [$CrF(H_2O)(tmd)_2]S_2O_6$: Cr, 13.09; C, 18.13; N, 14.10; H, 5.54%. Found: Cr, 13.2; C, 18.1; N, 14.1; H, 5.5%.

Thermal measurements

Simultaneous differential thermal analyses and thermogravimetry were carried out on about 50 mg (powdered) of the samples at a rate of 5°C min^{-1}, using an STA429 Netzsch thermal analyzer; the samples being kept in a dynamic inert atmosphere. Procedures were similar to those previously described [15,16]. Mass losses were determined by re-weighing the sample after each endothermic peak was passed. Activation energies were determined using the method of Thomas and Clarke [17]. Peak areas were determined by graphical integration, and enthalpy values were calculated using the fusion of metallic tin or indium as a standard. DSC studies were carried out using a Perkin-Elmer differential scanning calorimeter model DSC-2.

Electronic and IR spectra

The electronic spectra were recorded with a Beckman 5230 UV spectrophotometer and the IR spectra were recorded with a Beckman IR 20-A spectrophotometer, using the technique of KBr disk.

RESULTS AND DISCUSSION

The thermogravimetric curve of *trans*$[CrF(H_2O)(en)_2]S_2O_6$ does not show any weight loss until 150°C, appearing then as an inflection at approximately 170°C. This represents a 5% weight loss compared with the theoretical value of 4.87% (assuming the loss of 1 mole of water). Another weight loss is observed at 240°C which represents approximately 18% weight loss compared with the theoretical value of 17.87%, which implies the elimination of 1 mole of SO_2.

The thermogravimetric curve of *trans*$[CrF(H_2O)(tmd)_2]S_2O_6$ is very similar, the only difference being that the separation between the two weight losses is less clear. The three temperatures in this case are: 165, 190 and 240°C. The weight losses are: 4.5% (against 4.55% which implies the loss of 1 mole of water), and 17.4% (against 16.9%, implying the loss of 1 mole of SO_2).

The DSC runs give useful information because the separation between both processes (anation and decomposition of dithionate) is clear (Fig. 1). The DSC curve of *trans*$[CrF(H_2O)(en)_2]S_2O_6$ shows a first endothermic peak of 10.65 ± 0.5 kcal mole^{-1} followed by a small exothermic peak of 0.5 ± 0.05 kcal mole^{-1}. A net change of 10.1 ± 0.5 kcal mole^{-1} is associated with the first decomposition reaction. The DSC of *trans*$[CrF(H_2O)(tmd)_2]S_2O_6$ also shows a first endothermic peak of 9.95 ± 0.6 kcal mole^{-1} followed by an

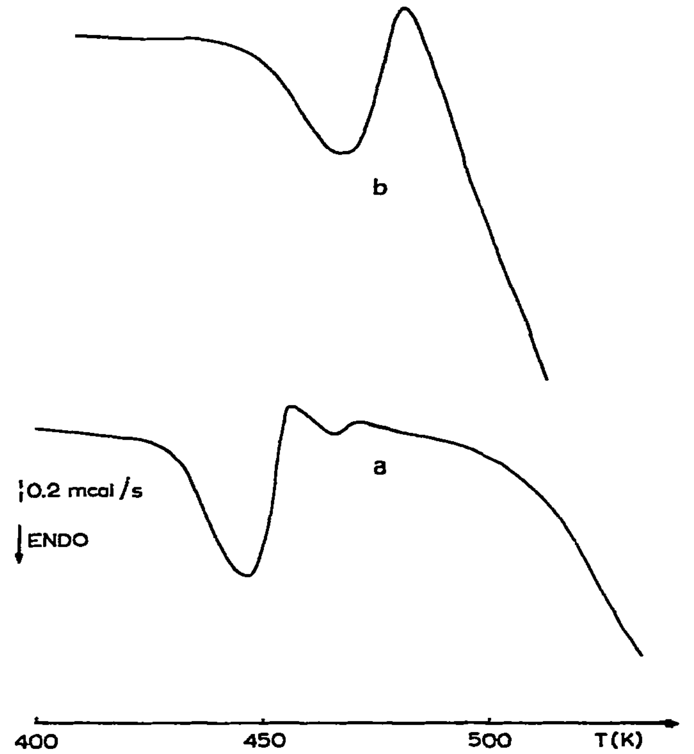

Fig. 1. DSC curves for the decomposition of (a) *trans*$[CrF(H_2O)(en)_2]S_2O_6$ and (b) *trans*-$[CrF(H_2O)(tmd)_2]S_2O_6$.

exothermic peak which could not be numerically valued, since it is overlapped by the endothermic peak of decomposition from dithionate to sulfate. Therefore, a net enthalpy change of 9.9 ± 0.5 kcal mole^{-1} was assigned. The two anation reactions: *trans*[$CrF(H_2O)(aa')_2]S_2O_6 \rightarrow$ *cis*-[$CrF(S_2O_6)(aa')_2$] are in fact the sum of two processes: anation and isomerization. Thus it could have been thought that the two peaks (the first endothermic and the second exothermic) would correspond to each separate process. But this is not so: the analyses, as well as the IR and electronic spectra from the DSC residuals both before and after the small exothermic peak, are totally identical and correspond to a *cis* geometry in an octahedral environment of Cr(III). In fact the isomerization and dehydration are simultaneous. The same effect has been observed in similar processes in which the anion utilized was $M(CN)_4^{2-}$, where M = Ni(II), Pd(II) and Pt(II) [18].

When heated, this *trans* → *cis* isomerization is perfectly demonstrated in two ways. (a) The starting compounds of *trans* geometry show three maxima in the visible spectral zone (between 530 nm and 350 nm) (Table 1) while the residues obtained after heating (DSC or TG) show only two. All the literature data agree that the presence of two definite, symmetrical maxima in this spectral zone is the best evidence of *cis* geometry. Supplementary information may be obtained from refs. 19—21. (b) By means of the IR spectra. The literature points out that the pseudo-octahedral compounds with *trans* geometry and ethylenediamine ligand show only one, very definite band at 1600 cm^{-1}, which is attributed to the vibration of the asymmetric deformation of the NH_2 group. This band is shifted at lower frequencies (1560—1580 cm^{-1}) in the compounds with *cis* geometry and sometimes it splits into two components. When the compounds are heated, this band appears at 1580 cm^{-1} with a less definite shoulder. Therefore, once the presence of *cis* geometry in the anation compounds has been demonstrated, it can be asserted that the decomposition of *trans* complexes [$CrF(H_2O)(aa')_2]S_2O_6$

TABLE 1

Electronic spectra in aqueous solution (0.1 M $HClO_4$)

	λ (nm)			
trans [$CrF(H_2O)(en)_2]S_2O_6$	516		458	367 [a]
trans [$CrF(H_2O)(tmd)_2]S_2O_6$	530		454	374 [a]
After DSC:				
cis [$CrF(S_2O_6)(en)_2$]		505—506		375 [b]
cis [$CrF(S_2O_6)(tmd)_2$]		511—512		375 [b]

[a] Identical maxima as those described in the literature for the cations *trans* [$CrF(H_2O)(en)_2]^{2+}$ and *trans* [$CrF(H_2O)(tmd)_2]^{2+}$ [22].

[b] Identical maxima as those described in the literature for the cations *cis* [$CrF(H_2O)(en)_2]^{2+}$ and *cis* [$CrF(H_2O)(tmd)_2]^{2+}$ [22] due to the great similarity of the aquo and dithionato ligands in the spectrochemical series, and the lability of the dithionato ligand in aqueous solution. A study of this is also reported in refs. 23—25.

takes place in three steps, which may be presented as

$$\text{trans}[\text{CrF}(\text{H}_2\text{O})(\text{aa}')_2]\text{S}_2\text{O}_6 \rightarrow \text{cis}[\text{CrF}(\text{S}_2\text{O}_6)(\text{aa}')_2] + \text{H}_2\text{O} \qquad \text{(I)}$$

$$\text{cis}[\text{CrF}(\text{S}_2\text{O}_6)(\text{aa}')_2] \rightarrow \text{cis}[\text{CrF}(\text{SO}_4)(\text{aa}')_2] + \text{SO}_2 \qquad \text{(II)}$$

$$\text{cis}[\text{CrF}(\text{SO}_4)(\text{aa}')_2] \rightarrow \text{total decomposition} \qquad \text{(III)}$$

Reaction (II) is shown by: (a) a weight loss, corresponding to 1 mole of SO_2, in TG and DSC; (b) the bands of the sulfato coordinated group appear in the IR spectrum; and (c) maximum absorption in the visible spectrum. They actually appear at 525 and 535 nm, respectively. This agrees with the sulfato ligand position in the spectrochemical series (a weaker field than water or the dithionato ion). These results are in good agreement with those obtained for the direct synthesis of *cis*$[CrF(SO_4)(aa')_2]$ [26]. Tables 2 and 3 show the thermal parameters associated with the decomposition reactions (II) and (III).

It is difficult from E_a data to make definite conclusions regarding a possible mechanism. Recently, House [27] has proposed several mechanisms for the thermal reactions of dehydration of solid complexes. For House, the chemical behavior in solid dehydration is often determined by various types of defects. Considering that the formation of a seven-bond complex is unfavorable, based on a crystal field model, in that it requires about 4.26 Dq (with Dq being about 2000 cm^{-1}) for the $[CrF(H_2O)(aa')_2]^{2+}$ [22], which alone would be about 20—25 kcal $mole^{-1}$ and assuming an S_N2 mechanism (hepta-coordination of Cr(III) with a Schottky defect formation in the lattice), the activation energy will be very high. House shows that if an S_N1 mechanism is assumed (penta-coordination of Cr(III) with a Frenkel defect formation) lower values should be obtained. In our case we found 60—70 kcal $mole^{-1}$ values. For House, therefore, the highest values of E_a suggest, preferably, an S_N2 mechanism. For the dehydration to be S_N2, an anion must leave its site in the crystal lattice and enter into the coordination sphere of the metal ion. This is the Schottky type defect and it would be expected that the E_a would increase when the lattice energy increases. Since for a given anion (dithionate) the lattice energy would increase as the cation

TABLE 2

Thermal data for the decomposition of *trans* $[CrF(H_2O)(en)_2]S_2O_6$

Process	Temperature (K)		Mass Loss (%)		E_a (kcal $mole^{-1}$)	ΔH (kcal $mole^{-1}$)
	Initiation	Final	Calcd.	Found		
I	415	470	4.87	4.8—4.9	68.4 ± 3	10.1 ± 0.5
II	470	510	17.87	18.0		

Analysis — calcd. for $[CrF(S_2O_6)(en)_2]$: C, 13.67; N, 15.95; H, 4.55%. Found: C, 13.5; N, 15.7; H, 4.5%. Calcd. for $[CrF(SO_4)(en)_2]$: C, 16.72; N, 19.5; H, 5.57%. Found: C, 15.6; N, 18.2; H, 5.6%.

TABLE 3

Thermal data for the decompositon of *trans* $[CrF(H_2O)(tmd)_2]S_2O_6$

Process	Temp. (K)		Mass loss (%)		E_a (kcal mole^{-1})	ΔH (kcal mole^{-1})
	Initiation	Final	Calcd.	Found		
I	430	475	4.53	4.5	61.31 ± 3	9.95 ± 0.5
II	475	515	16.88	17.4		

Analysis — Calcd. for $[CrF(S_2O_6)(tmd)_2]$: C, 18.99; N, 14.77; H, 5.27%. Found: C, 18.8; N, 14.6; H, 5.3%. Calcd. for $[CrF(SO_4)(tmd)_2]$: C, 22.85; N, 17.77; H, 6.34%. Found: C, 21.6; N, 15.9; H, 6.1%.

size decreases, the ethylenediamine compound should have the highest lattice energy and, therefore, the highest E_a.

The actual values found are 68 and 61 kcal mole^{-1} for en and tmd complexes, respectively. Naturally, in this case, the presence of *trans* → *cis* isomerization may disturb the interpretation of the results and consequently it will be necessary to study reactions of the type *trans* → *trans*, or *cis* → *cis*.

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