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On the Thermal Analysis of Ferricenium μ-Oxo-bis[trichloroferrate(III)]

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Abstract

Mössbauer spectroscopic studies on the title complex and that of its pyridinium analogue are reported on samples of these materials previously heated in the temperature range 18–200 °C. The title complex is shown to be reduced to a mixture of iron(II) compounds at 200 °C. The use of ferrocenium as a smoke suppressant appears to have no advantage over that of ferrocene, as it is converted to ferrocene when heated in air in the presence of light.

Introduction

The structure of ferricenium μ-oxo-bis[trichloroferrate(III)], (**A**), has recently been reported both by ourselves [1] and others [2, 3]. The initial interests in this structure both for its own sake [1] and for its use as a model compound for the important non-haem oxygen transport proteins myohaemerythrin and haemerythrin [3, 4]. There was further interest as ferrocene is used as a smoke suppressant in polymers (e.g. PVC), but the volatility of ferrocene can lead to its gradual loss from the polymer. Ferrocenium salts are also said to be active as smoke suppressants [3].

Thermal analysis in air of **A** has been reported using DTA, TG and DTG methods [3]. A three stage degradation mechanism for the complex in air was indicated.

We have carried out DTA and Mössbauer spectroscopic studies on the temperature dependence of **A**, both in the presence and absence of air in the temperature range 18–200 °C. In addition we have performed similar studies on pyridinium μ-oxo bis-[trichloroferrate(III)] pyridine to attempt to isolate the role of the ferricinium. We report the results of these investigations here.

Results and Discussion

Heating Studies of Ferricenium μ-Oxo-bis[trichloroferrate(III)] (A)

Compound **A** displays rather unusual properties on heating which are in disagreement with the work of Aharoni and Litt [5] who stated that no decomposition occurs below 300 °C.

We shall first discuss the results of heating **A** in air. The Mössbauer data for the heated samples of A are presented in Table I, and the spectrum of the sample heated to 200 °C is shown in Fig. 1. The DTA curve for **A** is in Fig. 2 and that of ferrocene

TABLE I. Mössbauer Parameters at 77 K for Ferricenium μ-Oxo-bis[trichloroferrate(III)][a]

Temperature (°C)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ[b] (mm s^{-1})	Absorption area (%)
50	0.30(1)	1.18(2)	0.20(1)	77(2)
	0.45(3)	0.00[c]	0.25(3)	23(2)
100	0.30(1)	1.22(2)	0.17(2)	51(2)
	0.47(2)	0.00[c]	0.30(1)	49(2)
150	1.27(2)	2.56(2)	0.15(1)	50(2)
	0.43(2)	0.00[c]	0.29(3)	50(2)
200 (Residue)	1.20(2)	0.97(2)	0.18(1)	58(3)
	1.24(1)	2.60(2)	0.24(1)	42(3)
Sublimate	0.52(1)	2.36(1)	0.13(1)	100

[a] Taken from samples heated to the respective temperature in air and allowed to cool to room temperature before the spectra were recorded. [b] Half width at half height. [c] Site fitted as a single peak.

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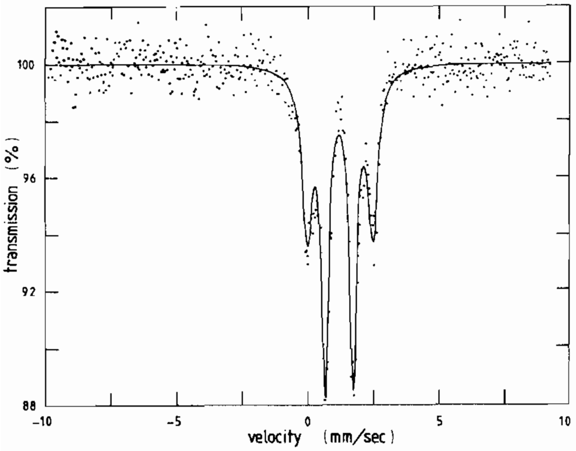


Fig. 1. Mössbauer spectrum (^{57}Fe) of **A** residue at 77 K after heating to 200 °C in air and cooling to R.T. Spectrum recorded at 77 K.

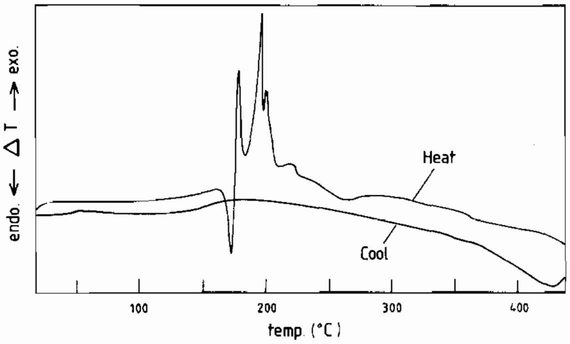


Fig. 2. DTA thermal analysis curves for **A**, heating rate 20 °C min^{-1} in air.

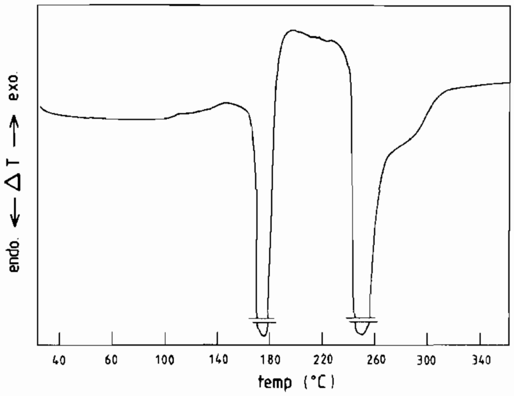


Fig. 3. DTA thermal analysis curve for ferrocene.

itself in Fig. 3. Our DTA (18–500 °C) data is essentially the same as that of Carty *et al.* [3]; our cooling curve indicates that none of the changes that occurred during heating are reversible. Carty *et al.* [3] have explained the endotherm to be due to the sublimation of ferrocene. We agree with this finding, as a similar endotherm takes place in the DTA of ferrocene (Fig. 3). This endotherm around 174 °C is the melting point of ferrocene (172–173.5 °C). Therefore electron exchange (of some kind) must have occurred in the ferricenium species before this, to convert the ferricenium to ferrocene. (We shall discuss this later.) The exothermic peaks occurring above this temperature in **A** are accompanied by the sublimation of yellow–orange needlelike crystals which Mössbauer spectroscopy confirms to be ferrocene (Table I).

The large endothermic peak in the ferrocene analysis at 249 °C is the boiling point of ferrocene and occurs as only a slight depression in the DTA of **A**, as most of the ferrocene has already sublimed by the time this temperature is reached. In fact the Mössbauer data shows two high spin iron(II) environments in the material heated to 200 °C (Fig. 1) with no trace of either ferrocene or ferricenium. The iron(II) sites have parameters that are somewhat similar to those of $FeCl_2 \cdot nH_2O$ ($n = 0, 1, 2$) [6–8]. The Mössbauer results demonstrate that compound **A** is stable to 100 °C as there is little change in the parameters measured from heating between 50 and 100 °C. Also, by taking zero and first layer precession photographs of a crystal from a sample that had been heated to 100 °C and comparing with the original photographs from samples that were not treated, no change in intensity or distribution of the spots was observable.

At 150 °C the first evidence of iron(II) is present and the Mössbauer parameters, $\delta = 1.27$ mm s^{-1}, $\Delta = 2.56$ mm s^{-1}, are similar to the second site in the 200 °C Mössbauer spectrum. The other site is still a ferricenium site, although now it accounts for 50% of the absorption area of the spectrum, as opposed to 23% beforehand. This latter value of absorption area is what would be expected for a compound containing four iron atoms of which two are of one kind (in the μ-oxo-bis[trichloroferrate(II)] ion) and the other two are in the theoretically identical ferricenium environments. Usually it is necessary to grind crystals to ensure that orientation effects are not present in Mössbauer spectra. Our previously reported Mössbauer data on **A** were collected on a carefully ground non orientated sample. Here we used a crystalline sample to enable the X-ray diffraction work to be carried out and were surprised to find that the Mössbauer data were (after heating the sample) of the correct intensity. One possible explanation is that the crystal shape altered during heating.

Entirely different behaviour is evidenced if the heating studies are carried out *in vacuo*. Here there is no sublimation of ferrocene (Table II). However, their is a large increase of absorption under the ferricenium in the Mössbauer spectrum at 200 °C (Fig. 4) which may indicate some changes in this material.

TABLE II. Mössbauer Parameters at 77 K for Ferricenium μ-Oxo-bis[trichloroferrate(III)][a]

Temperature (℃)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ[b] (mm s^{-1})	Absorption area (%)
100	0.48(2)	0.00[c]	0.19(2)	21(3)
	0.31(1)	1.17(2)	0.18(1)	79(3)
150	0.42(2)	0.00[c]	0.25(1)	54(4)
	0.28(2)	1.10(3)	0.21(2)	46(4)
200	0.42(2)	0.00[c]	0.26(2)	68(2)
	0.32(2)	1.12(3)	0.20(2)	32(2)

[a] Taken from samples heated to the respective temperature and cooled to room temperature *in vacuo*. [b] Half width at half height. [c] Site fitted as a single peak.

TABLE III. Mössbauer Parameters at 77 K for Pyridinium μ-Oxo-bis[trichloroferrate(III)] Pyridine[a]

Temperature (℃)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ[b] (mm s^{-1})	ΔH_{eff}	Absorption area (%)
100	0.33(2)	1.24(2)	0.31(3)		100
150	0.34(2)	1.19(2)	0.18(1)		42(2)
	0.37(1)	0.00[c]	0.40(1)		58(2)
200	0.33(1)	0.00[c]	0.28(1)		34(2)
	0.48(1)	0.02(1)	0.28(1)	17.34(1)	61(2)
	0.34(2)	1.29(3)	0.11(3)		5(2)
78 K[d]	0.343	1.29			

[a] Taken from samples heated to the respective temperature and cooled at room temperature. [b] Half width at half height. [c] Site fitted as a single peak. [d] Data from ref. 11.

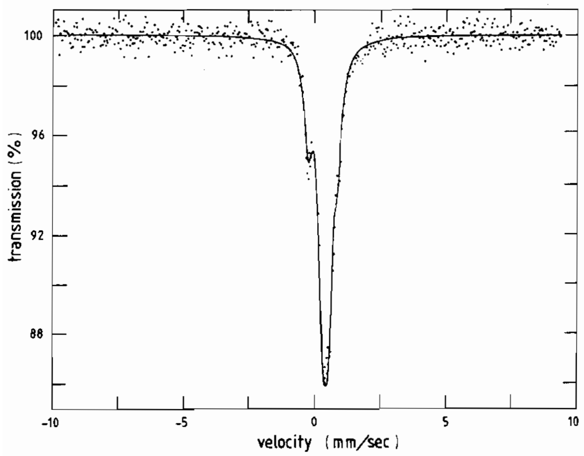


Fig. 4. Mössbauer spectrum (^{57}Fe) of A after heating to 200 ℃ and cooling to R.T. *in vacuo*. Spectrum recorded at 77 K).

The sublimation of ferrocene and production of two iron(II) sites also did not occur in a sample heated to 150 ℃ in the absence of light. The Mössbauer parameters for this sample are $\delta = 0.49(2)$, $\Delta = 0.00$, $\Gamma^* = 0.18(2)$ and $\delta = 0.32(2)$, $\Delta = 1.17(1)$, $\Gamma^* = 0.19(1)$ mm s^{-1}, with percentage absorption areas of 21% and 79%, respectively (* half width at half height).

Heating Studies of Pyridinium μ-Oxo-bis[trichloroferrate(III)] Pyridine

Heating the pyridinium species to 100 ℃ causes little change in the Mössbauer parameters (Table III). Although at 150 ℃ two sites are noted, the first site is reminiscent of the μ-oxo-bridge, $\delta = 0.34$ and $\Delta = 1.19$ mm s^{-1}, although the asymmetry is more marked; the second is in the region characteristic of iron(III), $\delta = 0.37$ and $\Delta = 0.00$ mm s^{-1}, the lack of any observable quadrupole splitting showing that the iron(III) ion is in a symmetric electronic environment.

The spectrum at 200 ℃ shows a marked magnetic splitting (Table III, Fig. 5), which also displays a quadrupole splitting. The parameters of this site, $\delta = 0.48$ and $\Delta H_{eff} = 17.344$ mm s^{-1} are characteristic of Fe$_3$O$_4$ [9] The other two sites are (a) that of a high spin iron(III) similar to that mentioned previously and (b) a small percentage absorption area of a site with $\delta = 0.34$ and $\Delta = 1.29$ mm s^{-1} which is in the right range to be the remnants of the μ-oxo-bridged species.

No iron(II) is observed in any of the heated samples of the pyridinium complex. This observation we interpret to mean that the presence of ferricenium is necessary before reduction can occur with μ-oxo-bis[trichloroferrate(III)].

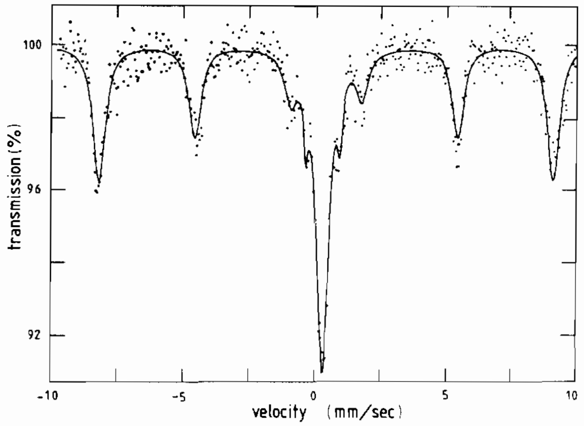
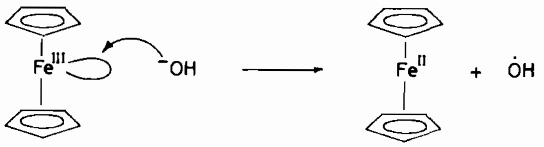


Fig. 5. Mössbauer spectrum (^{57}Fe) of pyridinium μ-oxo-bis[trichloroferrate(III)] pyridine heated to 200 °C and cooled to R.T. Spectrum recorded at 77 K.

Conclusions

The sublimation of ferrocene and subsequent production of two iron(II) sites on heating appears to be due to the presence of the ferricenium cation as this behaviour is not evidenced when the ferricenium is replaced by the pyridinium cation. Indeed pyridinium substitution appears to cause oxidation in air, which is to be normally expected. The iron reduction in air on heating the ferrocenium species in oxygen and/or water is light dependent, the reaction not occurring in the absence of these, and therefore may be due to a light induced radical on heating.

The type of reaction we favour to reduce the ferricenium to ferrocene is one in which a radical forms possibly involving H_2O. Then H_2O splits into hydroxyl ions and H^+ on the surface of A. The hydroxyl ions then react with ferrocenium (possibly induced by light) as follows



The ferrocene so produced would be reoxidized in a reaction with the anion μ-oxo-bis[trichloroferrate(III)] of the typc

$$4(C_5H_5)_2Fe + 2(Fe_2Cl_6O)^{2-} \longrightarrow$$

$$4[(C_5H_5)_2Fe]^+ + 4FeCl_2 + 2O^{2-} + 4\ Cl^-$$

The evidence for $FeCl_2$ comes both from the Mössbauer spectrum of the residue from A heated to 200 °C and from the work of Carty *et al.* [3]. They report an endotherm in their DTA at $T = 671-700$ °C, this they attribute to iron(II) chloride reported to occur in the range 671–674 °C [10].

The fact that ferrocene sublimes out suggests to us that ferrocenium offers no great improvement over ferrocene as a smoke repellent unless water and air can be removed.

Experimental

Materials

Ferrocene (Aldrich) was recrystallized from pentane. $FeCl_3$ (anhydrous) (Aldrich) was used without further purification. All solvents were analar grade. Pyridine (BDH) was distilled before use. Analyses were performed by the University of Manchester Microanalytical Laboratory. Ferricenium μ-oxo-bis[trichloroferrate(III) was prepared as described previously [1, 5]. Analyses were adequate. Pyridinium μ-oxo-bis[trichloroferrate(III)] pyridine was prepared by the method of Drew *et al.* [11], again analyses were adequate.

Differential Thermal Analysis

Thermal analysis curves were carried out on a Dupont 900 instrument using an air atmosphere, with glass beads as a reference at a heating rate of 20 °C/min starting at room temperature, using ferrocene as a standard analysis.

Mössbauer Spectroscopy

Mössbauer spectra were recorded as previously described [12] on solid samples at 77 K. The samples were previously heated in air or vacuum to the required temperature and allowed to cool to room temperature before mounting in cells.

X-ray Crystallography

X-ray analyses were carried out on a Buerger precession camera.

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