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THE THERMAL DECOMPOSITION OF IRON(III) FORMATE

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ABSTRACT

The thermal decomposition of iron(III) formate takes place through competitive formate anion decomposition (to yield $CO+H_2O$) and electron transfer from formate to Fe(III) (to yield Fe(II) formate(s) and CO, CO_2, H_2 and H_2O as gaseous products). The processes are overlapped by reactions that yield HCOH.

INTRODUCTION

The thermolysis of metal carboxylates has attracted the attention of a number of workers [1]. The most studied systems are metal formates, probably because of the inherent simplicity of the anion decomposition products, and also because of its bearing on basic studies of heterogeneous catalysis [2]. Although a number of papers have appeared on the thermal behaviour of metal formates, through the work of Masuda et al. [3–6] the essential features of these reactions were established by Dollimore and Tonge [7] who studied the decomposition of the zinc and manganese(II) salts, and by Iglesia and Boudart [8,9] who studied the decomposition of nickel and copper(II) formates.

In most cases studied so far, the redox chemistry of the metal ion involved is not important, the exceptions being Cu(II), Co(II) and Ni(II) [3], which are reduced to metals according to the stoichiometry

$$M(HCOO)_2(s) \rightarrow M(s) + 2\ CO_2(g) + H_2(g) \qquad (1)$$

(in parallel, lesser amounts of CO also form, see below).

Surprisingly, only a brief reference is found in the literature to the thermolysis of iron(III) formate, in which the formation of γ-Fe_2O_3 and

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Fe_3O_4 is mentioned [10]. This is to be compared with the attention devoted to other iron(III) carboxylates [11,12], which show complex behaviour of the solid upon heating, giving rise to one or more oxidation state change cycles in iron, i.e., Fe(III) → Fe(II) → Fe(III), or even Fe(III) → Fe(II) → Fe(III) → Fe(IV) → Fe(III). The present note is a report on the thermal behaviour of iron(III) formate, showing the influence of redox chemistry of iron(III), of the instability of formate anions and of the reactivity of iron oxides and the gaseous decomposition products of formate, as described by Dollimore and Tonge [7].

EXPERIMENTAL

Iron(III) formate dihydrate was obtained from freshly precipitated iron(III) hydroxide (from ferric nitrate and ammonium hydroxide), by dissolution in excess formic acid, and subsequent crystallization by evaporation in vacuum at 35°C. The product was recrystallized by redissolution in excess formic acid and repeated evaporation. The final solid was washed with water–ethanol mixtures and dried in a desiccator. Analysis for iron: calcd, 24.6%; found, 24.5%. IR spectra and X-ray diffractograms were as expected for ferric formate.

Thermogravimetric measurements were performed in a Mettler Recording Thermoanalyzer 1, with ca. 10 mg samples, between 25 and 500°C, heating rate 6°C min^{-1}, N_2 gas flow 5.6 $\text{dm}^3\ \text{h}^{-1}$. Reference was 8 mg alumina.

Gases evolved were characterized by IR spectroscopy in experiments in which ca. 100 mg of solid were heated up to the desired temperature in an evacuated tube connected to a gas IR cell.

X-ray diffractograms of the solids were registered in a Philips X Ray Generator PW 1130 and vertical goniometer PW 1050.

RESULTS AND DISCUSSION

A typical thermogram is shown in Fig. 1. The main characteristics are: (a) a weight loss with associated endothermic peak, corresponding well to the stoichiometry of the dehydration reaction

$$\text{Fe(HCOO)}_3 \cdot 2\text{H}_2\text{O(s)} \rightarrow \text{Fe(HCOO)}_3\text{(s)} + 2\ \text{H}_2\text{O(g)} \qquad (2)$$

(b) two endothermic weight loss peaks barely separated, centered at 278 and 325°C. The first peak shows complex DTA and DTG profiles reflecting probably the overlap of more than one reaction. The overall weight loss of both peaks agrees reasonably well with either stoichiometry (3) or (4)

$$2\ \text{Fe(HCOO)}_3\text{(s)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + 6\ \text{CO(g)} + 3\ \text{H}_2\text{O(g)} \qquad (3)$$

$$6\ \text{Fe(HCOO)}_3\text{(s)} \rightarrow 2\ \text{Fe}_3\text{O}_4\text{(s)} + 16\ \text{CO(g)} + 2\ \text{CO}_2\text{(g)} + 9\ \text{H}_2\text{O(g)} \qquad (4)$$

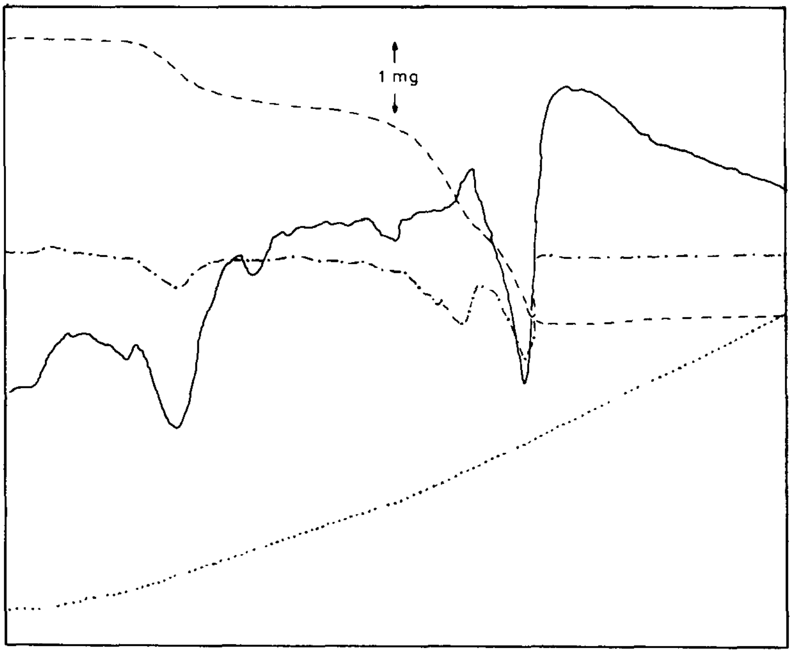


Fig. 1. Typical thermogram of $Fe(HCOO)_3 \cdot 2H_2O$. ——— DTA, — — — TG, -·-·- DTG, ······ T. Experimental conditions: sample weight 5.6 mg, N_2 atmosphere (5.6 $dm^3\ h^{-1}$). Heating rate: 6 °C min^{-1}. For actual T values, refer to Table 1.

(the difference in calculated weight loss is not significant compared with experimental error). The main characteristics of the thermograms are summarized in Table 1.

The analysis of gases evolved at 200 °C indicates that both CO_2 and CO are present, at a ratio of ca. 1.2 : 1.0. Water is also formed, as expected.

X-ray analysis of the solid products obtained at 500 °C shows the presence of both magnetite and hematite in variable ratios depending upon experimental conditions. Hematite is formed, even under nitrogen.

Decomposition of adsorbed formic acid on nickel yields both CO_2 and

TABLE 1

Peak temperature (°C)	% Weight loss	Detected reaction products	Suggested stoichiometry
100	16.0	H_2O	$Fe(HCOO)_3 \cdot 2H_2O \rightarrow$ $2\,H_2O + Fe(HCOO)_3$
278 325	49.9	CO, CO_2, CH_2O, H_2O, (H_2 [a])	See text

[a] H_2 not detected but probably present.

CO [8]. Focusing on the HCOO moiety, two parallel primary reactions have been postulated

$$HCOO - \begin{cases} \rightarrow H + CO_2 \\ \rightarrow OH + CO \end{cases}$$

followed by reactions of the radicals with adsorbed H to yield H_2 or H_2O (the temperature of release may follow other sequences, governed by the adsorption affinity of H_2O, H_2, CO_2 and CO) [13]. The selectivity ratio (i.e. $[CO_2]/[CO]$) ranges between 3.5 and 5.5 for powdered nickel [8,13]. It has also been suggested that the only primary reaction involves CO_2 production, CO being formed from it by dissociation [8]; in support of this, the selectivity ratio has been found to be temperature independent.

The decomposition of nickel formate was also studied, both under isothermal conditions and in temperature-programmed-desorption experiments [9], in the temperature range $200 \pm 25\,^{\circ}C$. The selectivity ratio was found to be roughly constant around 4, being unaltered by conversion temperature, or other experimental variables. Iglesia and Boudart [8,9] thus conclude that the ratio $CO_2 : CO$ is governed by the primary decomposition, rather than by secondary reactions involving gaseous products.

In principle, two types of chemical processes may give rise to decomposition of formates: (a) a redox reaction involving an electron transfer from a formate to the metal ion. This situation seems to be realized in nickel formate; the reaction is however complex and the corresponding stoichiometry is

$$\begin{aligned} Ni(HCOO)_2(s) \rightarrow\ & Ni(s) + 2xCO_2(g) + (2-2x)CO(g) \\ & + (1-x)H_2(g) + xH_2O(g) \end{aligned} \tag{5}$$

with $[x/(1-x)] \simeq 4$. (b) a chemical O–C bond breaking process

$$2\ M(HCOO)_3(s) \rightarrow M_2O_3(s) + 3\ CO(g) + 3\ CO(g) + 3\ H_2(g) \tag{6}$$

further complicated by reactions in the gas phase. This pathway operates in lanthanide formates.

In the case of ferric formate, on this basis, we postulate that the first stage of the decomposition of $Fe(HCOO)_3$ involves reaction (7) in one of its modes with a selectivity that is probably similar to the reported figures.

$$\begin{aligned} Fe(HCOO)_3(s) \rightarrow\ & Fe(HCOO)_2(s) + xCO_2(g) + (1-x)CO(g) \\ & + (1-x)H_2O(g) + [2(x-1)/2]H_2(g) \end{aligned} \tag{7}$$

This reaction overlaps with a mode that does not involve electron transfer from formate to Fe(III).

$$2\ Fe(HCOO)_3(s) \rightarrow Fe_2O_3(s) + 6\ CO(g) + 3\ H_2O(g) \tag{8}$$

The experimental ratio $[CO_2]/[CO]$, i.e $x/[(1-x)+3y]$, where y is the relative probability of pathway (8), is found to be 1.2; thus 15% of the reaction should proceed according to eqn. (7), and this is indeed in agreement with the maximum yields found for Fe_2O_3.

Further, decomposition of ferrous formate is also complex; in agreement with the low stability of wustite, magnetite is formed

$$3\ Fe(HCOO)_2(s) \rightarrow Fe_3O_4(s) + (4+z)CO(g) + (2-z)CO_2(g) + (3-z)H_2(g) + zH_2O(g) \qquad (9)$$

Partial overlap of this reaction in the earlier stages should also decrease the selectivity ratio.

In addition to these solids decomposition reactions, secondary reactions involving the produced gases may also take place:

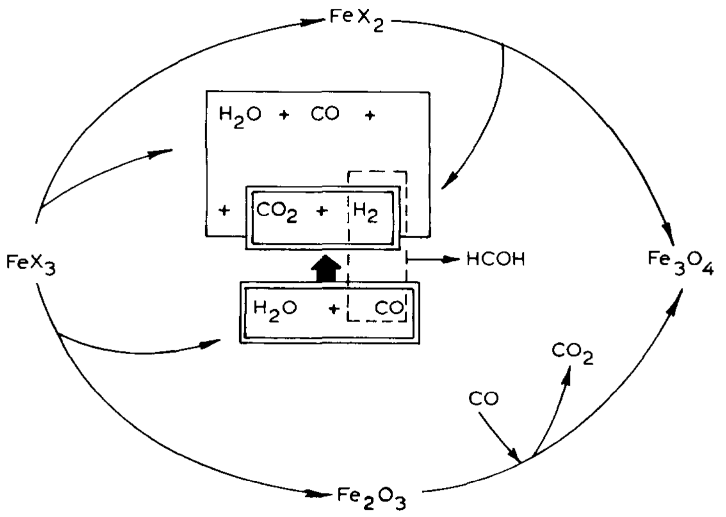
$$3\ Fe_2O_3(s) = CO(g) \rightarrow 2\ Fe_3O_4(s) + CO_2(g) \qquad (10)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad (11)$$

$$CO(g) + H_2(g) \rightarrow HCOH(g) \qquad (12)$$

However, the origin of the formaldehyde is not clear. Thermodynamic data for reaction (12) are $\Delta H^0_{350\,°C} = 21.1$ kJ mol^{-1}; $\Delta G^0_{350\,°C} = 67.3$ kJ mol^{-1} [14]. Thus it must originate in the thermolysis of formate anions, in non-equilibrium quantities. Possible reactions giving rise to CHOH may involve the radicals formed in the early stages of the redox pathway (HCOO, HCO, etc.).

As in any thermal decomposition involving reactions between primary gaseous products and solids, or gas-phase reactions, the actual yield in each reaction product is very sensitive to experimental conditions. Slow heating rates, high gas flows and small sample mass should all minimize reactions (10), (11) and (12).



Scheme 1.

The high amounts of CO_2 in the gaseous products at 200 °C, together with the "ripples" (especially visible in the DTA and DTG traces between 215 and 280 °C, see Fig. 1) in the first decomposition peak indicate that Fe_2O_3 and $Fe(HCOO)_2$ formation and subsequent reduction of Fe_2O_3 by CO overlap. High CO_2 at 200 °C may not be attributed to gas phase reactions (10) and (11), as these become important only at higher temperature (as expected), and especially in experiments with high heating rate and/or low N_2-flow. The interplay of reactions is depicted in Scheme 1.

Thus, the thermal behaviour of ferric formate is controlled by both the reducibility of Fe(III) and the instability of formate anions in trivalent metal ion salts, as shown respectively, in the thermolysis of iron(III) oxalates [11] and of lanthanide formates [6]. Compared with other iron(III) carboxylates, the ease of decomposition of formate precludes quantitative formation of the iron(II) salts. It should be noted however that former studies on iron(III) carboxylates were mostly carried out in an oxidizing atmosphere, which should play a role in the dynamical chemical processes thereby established.

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