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STUDIES ON THE THERMAL DECOMPOSITION OF FERRIC ACETATE

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ABSTRACT

The thermal decomposition of ferric acetate, $Fe(CH_3COO)_3$, has been investigated using thermogravimetry (TG), differential thermal analysis (DTA), the conventional method involving the measurement of the volume of gaseous products evolved during decomposition and the X-ray diffraction technique. Analysis of the kinetic data obtained both by the conventional method and the polythermal decomposition using thermogravimetry gave nearly the same activation energy for the decomposition of ferric acetate. The endothermic peaks at 278 and 328 °C appear to be due to the decomposition accompanied by the desorption of acetone and carbon dioxide, respectively.

INTRODUCTION

A survey of the literature reveals that not much information on stoichiometric ferric acetate, $Fe(CH_3COO)_3$, has been reported so far, while information on the preparation as well as thermal data for the decomposition of basic ferric acetate, $Fe(CH_3COO)_2(OH)$, are available[1,2]. Further, the decomposition product of ferric acetate is γ-Fe_2O_3 which made it interesting to investigate the decomposition of ferric acetate and characterise the decomposition products by X-ray diffraction.

EXPERIMENTAL

Preparation of ferric acetate

Ferric hydroxide obtained as a precipitate by the addition of ammonia to a solution of $FeCl_3 \cdot 6H_2O$ was dried at 120 °C for 15 h. The oxide was crushed to fine powder and heated at 500 °C for 5 h, to remove the adsorbed water. The anhydrous ferric oxide was leached with a sufficient amount of acetic acid by refluxing for 15 h. The ferric acetate solution was separated from insoluble ferric oxide by filtration in a dry atmosphere to remove excess acetic acid. Ferric acetate thus obtained was a rose coloured fine powder. The IR spectrum of the compound exhibited absorption peaks at 1590, 1430, 1220, 1020 and 657 cm^{-1} as expected of a transition metal acetate[3]. The absence of absorption bands in the region 3000 to 2500 cm^{-1} confirms the compound to be

$Fe(CH_3COO)_3$ and not the basic acetate. The iron in the ferric acetate was estimated by titrating against standard $K_2Cr_2O_7$ using n-phenylanthranilic acid as the indicator and the acetate to metal ratio was found to be 3. Thermogravimetry gave the expected weight loss according to the following reaction

$$2Fe(CH_3COO)_3 \rightarrow Fe_2O_3 + 3CH_3COCH_3 + 3CO_2$$

Kinetic study of the thermal decomposition of ferric acetate

Isothermal studies. A pyrex glass tube provided with a thermocouple well around which the ferric acetate could be packed was used to study the kinetics of the isothermal decomposition of ferric acetate. The temperature of the sample was measured with the help of a thermocouple inserted in the thermocouple-well. The rate of decomposition at each temperature was followed by measuring the volume of carbon dioxide evolved. The volumes of carbon dioxide evolved as a function of time are represented in Fig. 1 for decomposition at various temperatures.

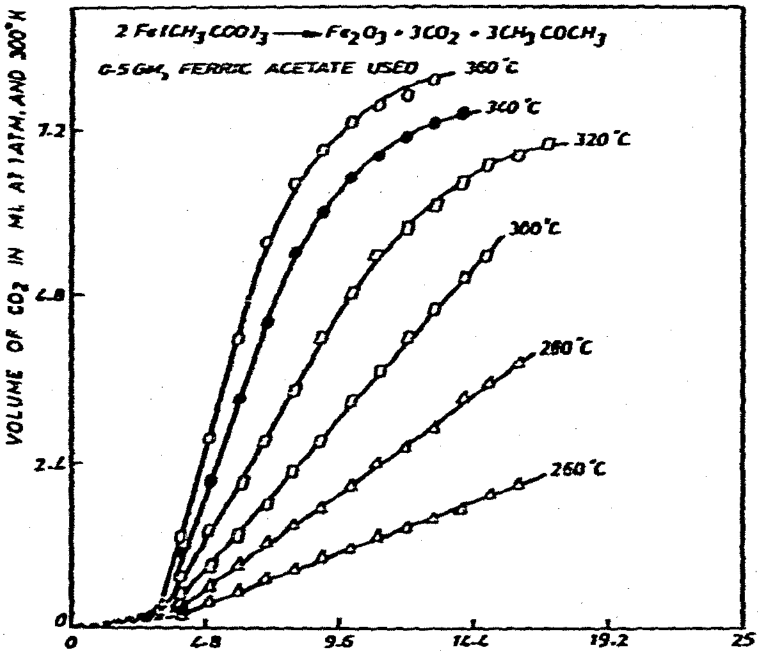

Fig. 1. Thermal decomposition of ferric acetate.

Polythermal studies. Thermogravimetric studies were made in air using a Stanton recording thermobalance at a linear heating rate of 6 °C min^{-1} with 100 mg samples in the crucible container.

Differential thermal analysis. The differential thermal analyses were carried out in air and nitrogen on a Netzsch differential thermal analyser employing a constant weight of 135 mg of the sample. Ignited alumina was used as a reference material.

X-ray diffraction studies. The residue left after the decomposition of $Fe(CH_3COO)_3$ was characterised by the X-ray powder diffraction method. A Debye-Scherrer camera of 114.6 mm diameter was used and the powder patterns were obtained employing iron filtered CoK_α radiation.

RESULTS AND DISCUSSION

The results of the isothermal decomposition of ferric acetate are represented in Fig. 1. There is an initial period of induction at every temperature followed by a steep rise in the volume of carbon dioxide evolved, till most of the reaction is over. The slope measured in the initial region when the steep rise began was taken as the initial rate at a particular temperature. The slope was converted in terms of moles of carbon dioxide evolved per unit time and the logarithm of this initial rate was plotted against the reciprocal of temperature as shown in Fig. 2. The value of the activation energy for the formation of carbon dioxide from ferric acetate was found to be 15.1 kcal mol^{-1}. Since 3 moles of carbon dioxide are formed from 2 moles of ferric acetate, the activation energy for the decomposition of ferric acetate is 22.7 kcal mol^{-1}.

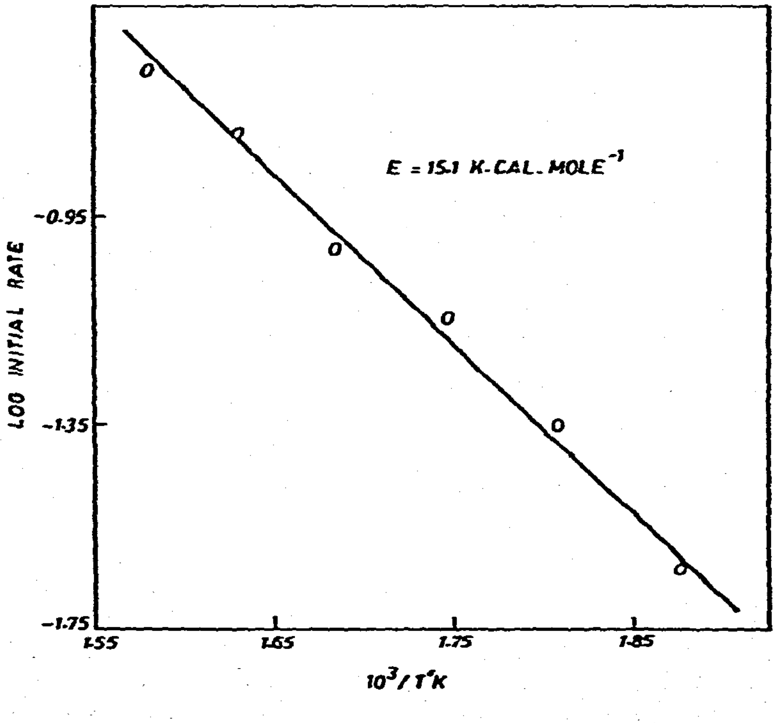

Fig. 2. Arrhenius plot for the thermal decomposition of ferric acetate.

The results obtained in the study of the polythermal decomposition of ferric acetate showed that the decomposition started at 180 °C and was complete at 300 °C. Basic ferric acetate as reported in the literature[2] loses water rapidly up to 242 °C. The inception of reaction and final temperature of decomposition of ferric acetate are much higher than those for the basic ferric acetate which reflects the thermal stability of the former over the latter.

The kinetic observations made during the polythermal decomposition of the salt were analysed using the Coats–Redfern[4] relationship and the results are presented in Fig. 3. The quantities corresponding to Y are plotted against $1/T$ according to the two expressions:

$$Y = -\log \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \quad \text{for} \quad n = 0, 2, 3$$

$$\text{and} \quad Y = -\log \frac{-\log(1-\alpha)}{T^2} \quad \text{for} \quad n = 1$$

where α is the fraction of acetate decomposed at time t and n is the order of reaction. The plot for $n = 1$, fits very well with the Arrhenius relationship for a wide range of values of α giving an activation energy equal to 26.4 kcal mol^{-1} for the decomposition of ferric acetate.

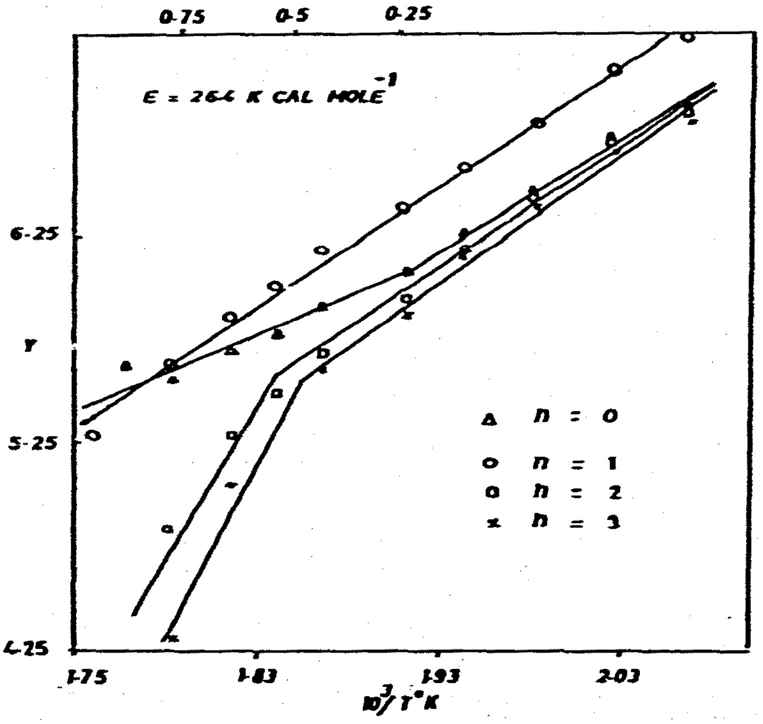

Fig. 3. Arrhenius plot for the decomposition of ferric acetate by thermogravimetry.

Formation of γ-Fe_2O_3 (maghemite) by thermal decomposition of ferric acetate

Differential thermal analysis of the compound in air and nitrogen gave two different types of curves as shown in Fig. 4. Since the ferric acetate does not contain any water the small endothermic peak at 175 °C appears to indicate the inception of decomposition. By thermogravimetric analysis ferric acetate was found to lose weight at about 180 °C. The two endothermic peaks one at about 278 °C and the other at 328 °C may be ascribed to the decomposition of the salt accompanied by the desorption of acetone and carbon dioxide, respectively. This is in agreement with the stronger adsorption of carbon dioxide in comparison to that of acetone which was observed during a study of inhibition of ketonisation of acetic acid on iron oxide by the products, acetone and carbon dioxide[5]. The residue left after the decomposition when the temperature was kept below 340 °C and above 500 °C showed on X-ray analysis (Table 1) that they were γ-Fe_2O_3 and α-Fe_2O_3, respectively. The exothermicity represented by a broad peak (350–500 °C) is due to the quantitative transformation of metastable γ-Fe_2O_3 (maghemite) to stable α-Fe_2O_3 (hematite)[6]. This exothermic peak was found to be totally absent when the analysis is done in a nitrogen atmosphere. Further, the residue analysed by XRD after heating the ferric acetate to about 800 °C in nitrogen showed the presence of γ-Fe_2O_3 only.

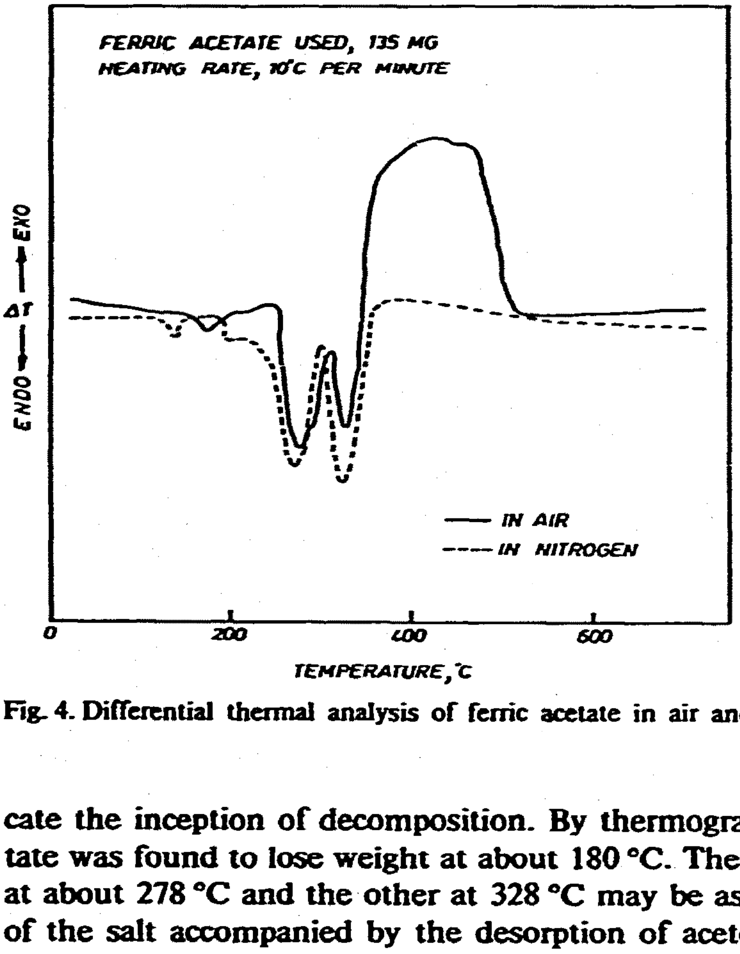

Fig. 4. Differential thermal analysis of ferric acetate in air and in nitrogen.

TABLE I

X-RAY DIFFRACTION DATA FOR α-Fe_2O_3 AND γ-Fe_2O_3 IN Å

α-Fe_2O_3				*γ-Fe_2O_3*			
Reported d-values	*Intensity*[a]	*Experimental d-values*	*Intensity*	*Reported d-values*	*Intensity*	*Experimental d-values*	*Intensity*
3.66	MS	3.65	MS	4.81	MS	4.82	W
2.69	VVS	2.69	VVS	2.94	VS	2.94	S
2.51	S	2.51	VS	2.77	MS	2.77	W
2.20	MS	2.20	MS	2.51	VVS	2.51	VVS
1.84	S	1.84	S	2.08	VS	2.07	MS
1.69	VS	1.69	VS	1.82	S	1.81	MS
1.59	VW	1.59	W	1.70	MS	1.71	W
1.48	MS	1.48	S	1.60	VS	1.61	S
1.45	MS	1.45	S	1.47	VS	1.47	VS
1.40	—	—	—	1.32	W	1.32	VW

[a] VVS = very very strong; VS = very strong; MS = moderately strong; S = strong; W = weak; VW = very weak.

The presence of oxygen seems to be a very important factor for the transformation of γ-Fe_2O_3 to α-Fe_2O_3. In the inert atmosphere γ-Fe_2O_3 is stable even at a temperature as high as 800 °C. The decomposition temperature of ferric acetate in nitrogen atmosphere is raised to about 200 °C which is indicated by an endothermic peak. The small amount of endothermicity observed at about 140 °C may be due to the desorption of adsorbed oxygen from the compound by the inflow of nitrogen.

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