

A kinetic and mechanistic study of the isothermal decomposition of ferric oxalate hydrate

Andrew K. Galwey^a and Mohamed A. Mohamed^b

^a *School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (UK)*

^b *Department of Chemistry, Faculty of Science, Qena (Egypt)*

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Abstract

We report a kinetic and mechanistic study of the isothermal decomposition of ferric oxalate hydrate $[\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4.6\text{H}_2\text{O}]$. The principal products of reaction between 410 and 450 K are carbon dioxide and ferrous oxalate which retains a small proportion (approx. 10%) of the ferric salt. From microscopic studies, it was concluded that reaction was not accompanied by melting. Yield–time curves were sigmoid shaped providing evidence that this is a nucleation and growth process occurring in the solid state. Data did not fit a single-rate equation but was satisfactorily expressed in two stages: the acceleratory first half fitted the Avrami–Erofe'ev equation ($n = 2$) and the second half fitted the contracting cube equation. The activation energies were relatively low for this type of reaction, 107 ± 8 and $120 \pm 10 \text{ kJ mol}^{-1}$ respectively.

The reaction mechanism is discussed and it is concluded that the rate is controlled either by electron transfer or rupture of the C—C bond in the anion. The participation of water retained in the solid through intermediate formation of oxalic acid is discussed.

INTRODUCTION

The thermal decomposition of metal salts of oxalic acid, especially those for the transition metals, have been the subject of numerous investigations by different workers [1]. Many of these studies have been concerned with non-isothermal kinetic measurements, including thermogravimetric (TG) and differential thermal analysis (DTA) [2–5] and there have also been a number of isothermal studies reported [6–8] together with discussions of the mechanism of oxalate ($\text{C}_2\text{O}_4^{2-}$) breakdown [9].

Several studies in the field have been concerned with the decompositions of iron oxalates [10–12]. On heating, ferrous oxalate dihydrate first undergoes endothermic dehydration at approx. 435 K, followed by anion breakdown at approx. 635 K, also endothermic in an inert atmosphere or

Correspondence to: M.A. Mohamed, Department of Chemistry, Faculty of Science, Qena, Egypt.

vacuum. The residual product is probably FeO, but this readily disproportionates to Fe₃O₄ and metallic iron. Ferric oxalate, the subject of the present paper, has, however, attracted less interest. Broadbent et al. [10] used TG, DTA and X-ray powder diffraction measurements to investigate the decompositions of ferric oxalate, sodium ferric oxalate and ammonium ferric oxalate. Thermal analysis of ferric oxalate detected an initial small endotherm, ascribed to partial dehydration, before the two main endotherms, identified as decomposition of ferric oxalate to ferrous oxalate which later decomposes to FeO. Ammonium ferric oxalate yielded Fe, FeO and Fe₃O₄, while potassium ferric oxalate gave Fe₂O₃ and K₂C₂O₄. These workers concluded that the mechanisms of the breakdown of certain complex oxalates, in the solid state, are similar to the mechanism of photochemical decomposition of dissolved species [13].

The adsorption characteristics of the residual solids, including ferric oxide, produced by the decomposition of Fe₂(C₂O₄)₃ hydrate were studied by Dollimore and Nicholson [14]. They found that there is a marked difference in surface properties of the products from salt samples heated at approx. 670 K and samples heated to this temperature after previous heat treatment at 460 K. This was attributed to the rapidity with which transformation occurred from amorphous to crystalline modifications of the product Fe₂O₃.

Other studies of the thermal reactions of complex oxalates showed the importance [15] of the gaseous environment in determining the course of decomposition. During reactions in air, exothermic behaviour appeared in the later stages of decomposition, attributed [16] to the catalytic promotion of carbon oxidations by the metal oxides $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ and $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$.

Decomposition of the mono-oxalate complex [FeC₂O₄]⁺ in aqueous solution has been studied at 348 K and it was shown that the rate depended on hydrogen ion concentration. These ions, however, also form the labile polymeric species [Fe₃(C₂O₄)₃]³⁺ which does not undergo measurable thermal decomposition at the same temperature, regardless of the hydrogen concentration.

We have undertaken the present kinetic and mechanistic study of ferric oxalate decomposition for two reasons. Firstly, we were able to find no previous isothermal kinetic study for the decomposition of this salt in the literature although the thermal reactions of many other transition metal oxalates have been reported. Secondly, we have recently completed an isothermal investigation of the rate of ferrous oxalate decomposition [12], known to be a principle product of ferric oxalate breakdown under the conditions of our study. Accordingly the present work was undertaken to enable a comparative study of the two reactants to be completed, including consideration of the role, if any, of cation oxidation or reduction in anion breakdown.

EXPERIMENTAL

Reactant salt

Ferric oxalate hydrate was prepared from freshly precipitated ferric hydroxide and oxalic acid. Ferric ammonium sulphate (40 g) was dissolved in 300 ml deionized water and ammonium hydroxide was slowly added, with stirring, until the solution was slightly alkaline. A gelatinous reddish precipitate of ferric hydroxide was formed and the excess ammonia boiled off. The settled hydroxide was separated by centrifuging and was washed with water until the filtrate was sulphate free. The iron hydroxide was then added slowly, with continuous stirring, to a solution of 24 g oxalic acid (Analytical Reagent grade) dissolved in 300 ml deionized water. The yellow-green precipitate which formed was left in solution for 48 h at 320 K. This was filtered, dried at 373 K and was gently crushed before use in decomposition studies.

This prepared reactant was analysed by combustion analysis for carbon and hydrogen and by atomic absorption and EDTA for iron. The results obtained agreed well with theoretical expectation for a hydrate containing $4.6\text{H}_2\text{O}$, consistent with results quoted in the literature; see Table 1.

TABLE 1

Elemental analysis for ferric oxalate hydrate

	H (%)	C (%)	Fe (%)
Found	2.01	15.53	25.2
Theoretical for $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4.6\text{H}_2\text{O}$	2.02	15.71	24.4

Apparatus

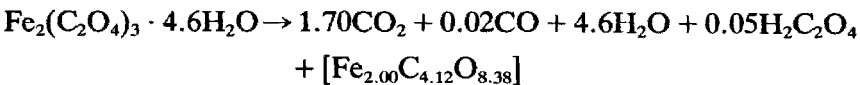
The kinetics of the isothermal (± 1 K) decomposition of ferric oxalate hydrate were studied in a constant-volume pre-evacuated (10^{-4} Torr) glass apparatus through measurements of the pressure of the product permanent gases evolved at suitable time intervals. The reactant temperature was measured and controlled using a chromel–alumel thermocouple located close to the reactant sample but outside the vacuum envelope. Pressure measurements were made using a McLeod gauge and a cold refrigerant trap (175 K) was interposed between the reaction vessel and the gauge to condense product water. The rate studies reported here refer, therefore, to the processes resulting in the evolution of carbon dioxide only with a small yield of carbon monoxide.

RESULTS AND DISCUSSION

Reaction stoichiometry

The mean yield of carbon dioxide was 1.70CO_2 from 30 rate experiments across the temperature interval used for the kinetic studies. This was measured from the final pressure evolved from the completed decomposition of known reactant weights in the calibrated volume of the pre-evacuated apparatus. Yields of carbon monoxide, similarly measured using a 78 K trap, were always small ($<0.02\text{CO}$).

The mean weight loss (also from 30 experiments) was 34.8% of the original reactant weight. This corresponds closely with expectation for the loss of $1.70\text{CO}_2 + 4.6\text{H}_2\text{O}$ from the reactant (34.3%) but is somewhat less than that the 37.3% calculated for the formation of anhydrous ferrous oxalate only. A small sublimate of oxalic acid was formed during salt decomposition, estimated as $0.05\text{H}_2\text{C}_2\text{O}_4$ by titration with standard alkali. The reaction may, therefore, be represented as



The composition of the residue is somewhat different from that expected for ferrous oxalate ($2\text{FeC}_2\text{O}_4$), and this is explained by incomplete decomposition of the ferric salt (approx. 10% retained). This point is discussed further below. No carbonaceous residue was formed in this reaction; the solid products dissolved completely in dilute hydrochloric acid.

Attempts to prepare the anhydrous salt were unsuccessful; some decomposition accompanied dehydration even in vacuum at temperatures as low as 400 K.

Thermogravimetric and differential thermal analysis

TG analysis for the prepared reactant identified two weight-loss steps. The first, between 390 and 465 K, indicated an overlap of two rate processes: salt dehydration and decomposition to ferrous oxalate. Again the weight loss (33%) was less than theoretical expectation (37.3%). The second step resulted in a further 34.5% weight loss identified as ferrous oxalate decomposition. DTA detected two endotherms at 458 and 623 K clearly attributable to the same rate processes.

Reaction kinetics

Our kinetic study of the isothermal decomposition of ferric oxalate hydrate was completed between 410 and 450 K. A representative selection

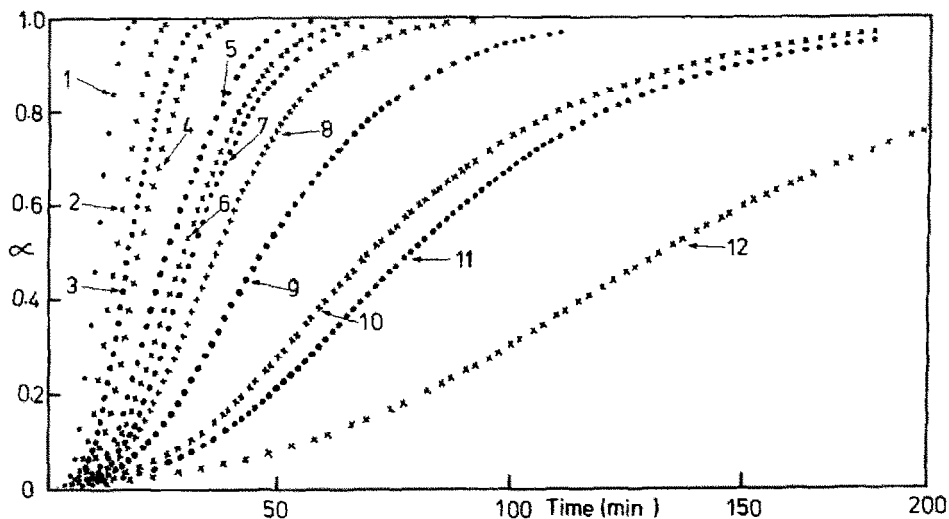


Fig. 1. Representative fractional reaction (α) against time plots for the isothermal decomposition of ferric oxalate hydrate at selected temperatures: 1, 450; 2, 445; 3, 440; 4, 436; 5, 432; 6, 430; 7, 428.5; 8, 425; 9, 422.5; 10, 417; 11, 415; and 12, 410 K.

of fractional reaction (α) versus time curves are shown in Fig. 1. The yield (CO_2)–time curves were sigmoid shaped, with the short acceleratory process completed at $\alpha \approx 0.25$, followed by a relatively longer deceleratory phase. The main reaction was preceded by the rapid evolution of a small amount of gas, 2% at 5 min. This was subtracted from data used for the kinetic analyses [17]: $\alpha' = (\alpha - 0.02)/0.98$.

The obedience of our isothermal yield–time measurements was tested to those rate equations that have found application in kinetic studies of solid-state decompositions [1]. No expression capable of representing the overall reaction could be found, and the second half of the reaction was invariably slower than the requirements of the various equations used. Accordingly, the kinetic behaviour was expressed in two parts [7]. The first half of the reaction obeyed the Avrami–Erofe'ev equation ($n = 2$) for $0.03 < \alpha < 0.50$

$$[-\log(1 - \alpha')]^{1/2} = kt \quad (1)$$

Plots of the fit of the data on Fig. 1 to eqn. (1) are shown in Fig. 2. The second half of the reaction was most satisfactorily expressed by the contracting cube equation, eqn. (2), for $0.50 < \alpha < 0.95$

$$1 - (1 - \alpha')^{1/3} = kt \quad (2)$$

Plots of the fit of the data in Fig. 1 to eqn. (2) are shown in Fig. 3. The calculated activation energies for the first and second parts of the reaction are 107 ± 8 and 120 ± 10 kJ mol^{-1} respectively.

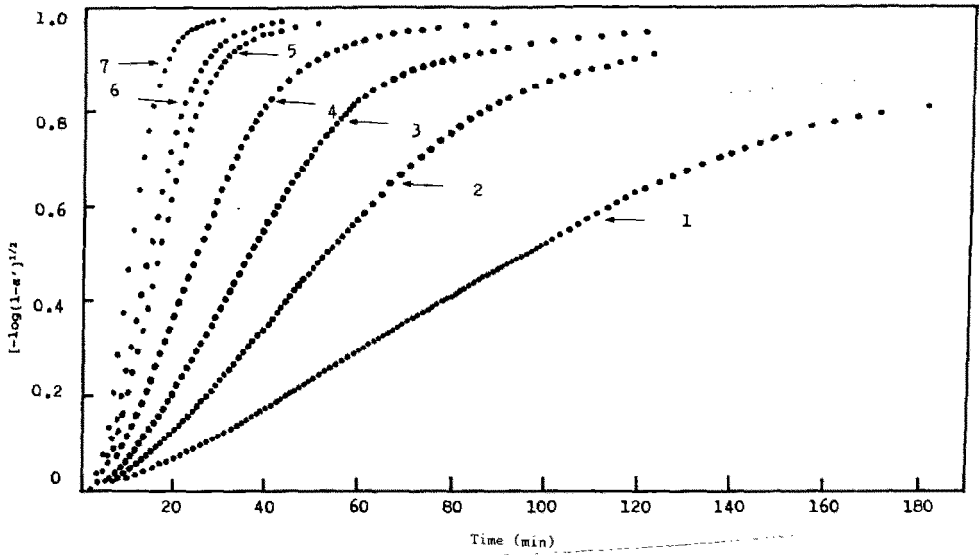


Fig. 2. Plots of $[-\log(1-\alpha')]^{1/2}$ against time for the first half of the ferric oxalate decomposition reaction for the experiments in Fig. 1.

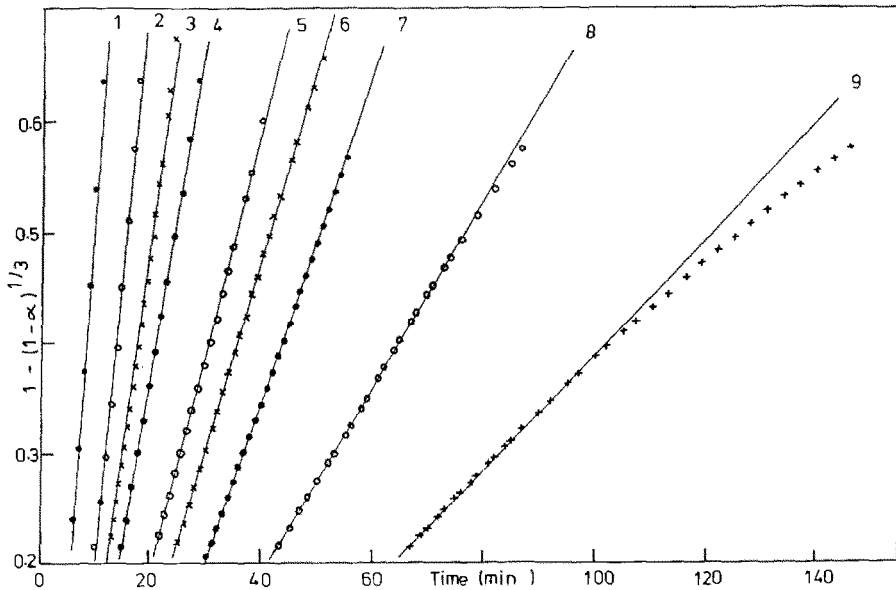


Fig. 3. Plots of $[1 - (1-\alpha')^{1/3}]$ against time for the second half of the ferric oxalate decomposition reactions for data labelled 1–9 (450–422.5 K) in Fig. 1.

Reduction of iron ($Fe^{3+} \rightarrow Fe^{2+}$) during decomposition

The reaction stoichiometry reported above identifies ferrous oxalate as the principle solid product of ferric oxalate decomposition. We report here quantitative measurements, based on three different analytical techniques, which confirm that there is a linear reduction in Fe^{3+} content with α , and it was confirmed that a proportion of the ferric ion (approx. 10%) was retained in the residual products.

Iodometric titration

The amounts of Fe^{3+} present in known weights of reactant, before reaction ($\alpha = 0.00$) and after reaction ($\alpha = 1.00$) and of samples reacted to a range of intermediate measured α values, were determined by iodometric titration using standard sodium thiosulphate (with KI, Cu_2I_2 cat-

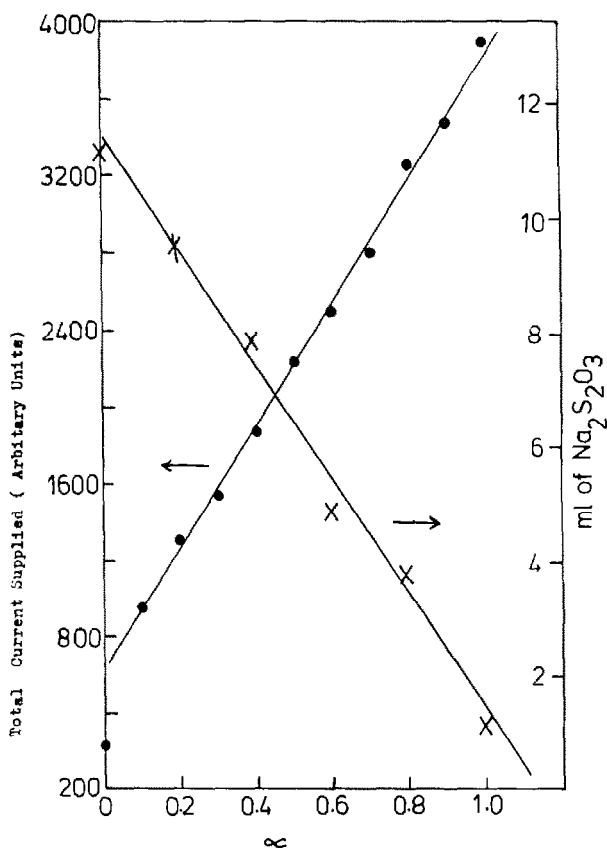


Fig. 4. Evidence of a linear diminution in the amount of ferric ion present with extent of ferric oxalate decomposition, α . On completion of the rate process studied here some Fe^{3+} (approx. 10%) was retained in the product. Data here report results of iodometric titration with $Na_2S_2O_3$ (x) and of anodic oxidation (●).

alyst and starch indicator). There was a linear reduction in the amount of Fe^{3+} with α , see Fig. 4, and on completion of decomposition some 10% of the ferric ion remained in the residue.

Anodic oxidation

The Fe^{3+} iron contents of a series of similarly prepared reactant samples, at known α values ranging from reactant to $\alpha = 1.00$, were determined by anodic oxidation [18]. Each sample was dissolved in a standard mixture containing sulphuric acid, ferric oxalate and ferroin indicator. The time required to oxidize the ferrous iron at 10 mA current (colour change of indicator from red to pale blue) was a measure of the amount of Fe^{2+} present and increased in direct proportionality with α as shown in Fig. 4. Again a small proportion of Fe^{3+} (approx. 10%) remained at $\alpha = 1.00$.

ESR method

The Fe^{3+} contents of a further series of partially decomposed salt samples were measured by the ESR response signals. Again a linear reduction in ferric ion amount with α was found.

Product decomposition

Two isothermal decomposition rate experiments were compared at 612 K using (i) pure ferrous oxalate dihydrate and (ii) the residue from the ferric oxalate reaction (identified as ferrous oxalate containing about 10% of the ferric salt). The α -time plots in Fig. 5 show that the shapes of both curves are similar, but the decomposition rate of the ferric oxalate residue was faster than that of the pure ferrous salt. This could be due to the retention of some Fe^{3+} ions on completion of the lower temperature reaction. The ferric salt is significantly less thermally stable than the ferrous salt. This experiment confirms that Fe_2O_3 is not the residual solid from the decomposition of ferric oxalate, otherwise no volatile product would have been evolved on heating the residue to 612 K.

Electron microscopic observations

The irregular shape of a typical reactant crystallite is shown in Fig. 6(a) which, after partial dehydration, Fig. 6(b), has undergone extensive retexturing to give a porous material permeated by numerous channels through which water has presumably escaped.

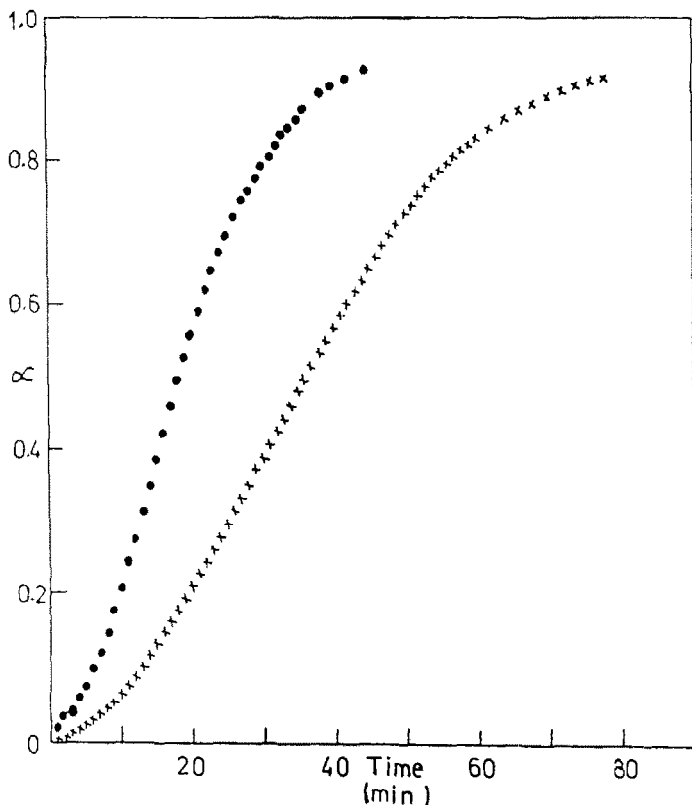
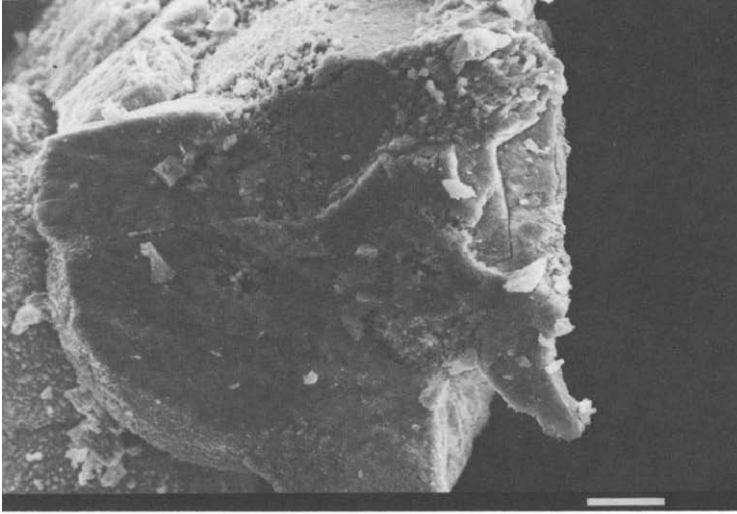


Fig. 5. Comparative α against time curves for the isothermal decompositions at 612 K of ferrous oxalate dihydrate (\times) and the solid product of ferric oxalate hydrate (\bullet) known to retain about 10% Fe^{3+} . The latter reacted more rapidly.

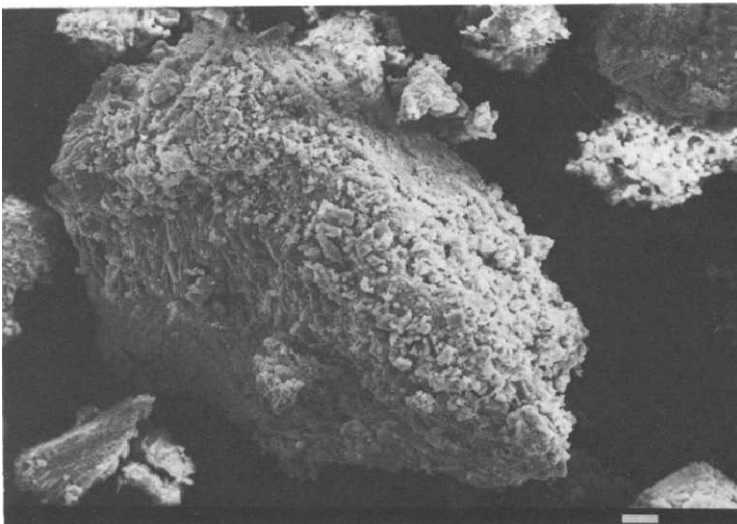
After reaction was established ($\alpha = 0.3$, see Fig. 6(c)), recrystallization has resulted in the development of a lamellar structure [14]. The internal texture of the product is crystalline, see Fig. 6(d) for $\alpha = 1.00$ where the residue was lightly crushed before examination [19]. The well-crystallized product was identified as anhydrous ferrous oxalate. There was no evidence of melting during decomposition.

REACTION MECHANISM

From the above results, we conclude that the ferric oxalate hydrate ($\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4.6\text{H}_2\text{O}$) decomposes between 410 and 450 K to yield principally carbon dioxide and ferrous oxalate that retains a small proportion (approx. 10%) of the ferric salt. From microscopic examinations of the participating solids, we found no evidence of melting. α -Time plots for the isothermal reactions exhibited the sigmoid shape characteristic of



(a)

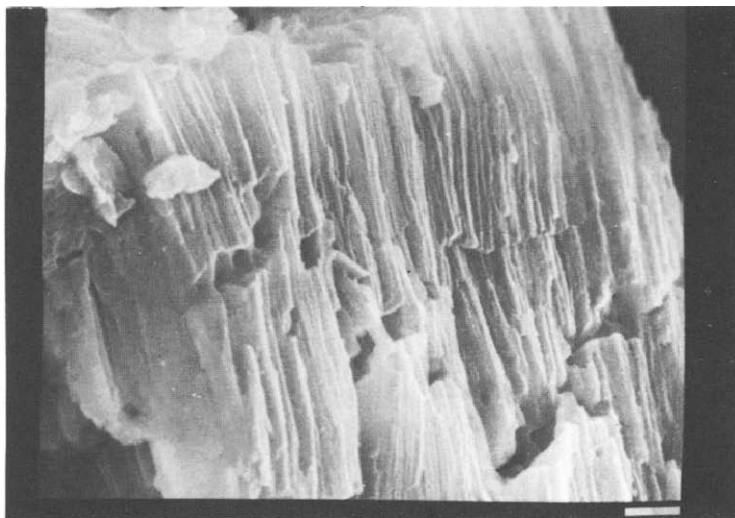


(b)

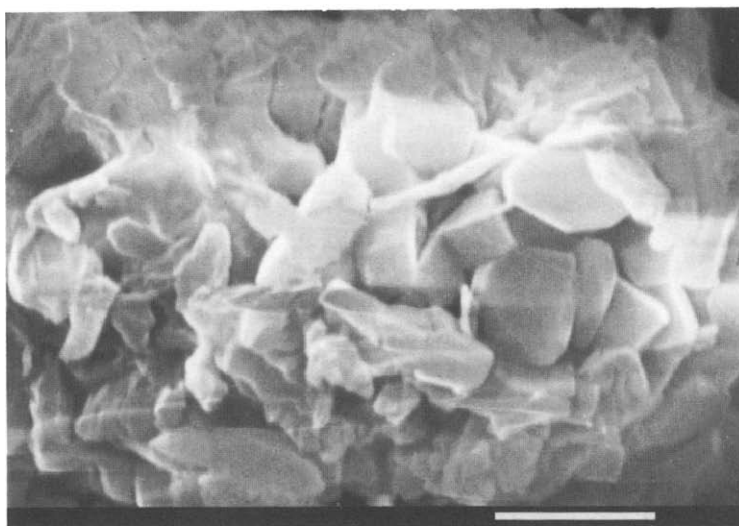
Fig. 6. Scanning electron micrographs showing the textures of ferric oxalate hydrate for (a) the reactant, (b) partially dehydrated salt, (c) partially decomposed salt, $\alpha = 0.3$, and (d) completely decomposed salt ($\alpha = 1.00$) lightly crushed after reaction to reveal internal textures.

nucleation and growth reactions and the activation energy was relatively low.

In our highest temperature experiments, 450 K see Fig. 1, some 90% decomposition of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ was completed in 17 min. These results compare well with observations reported by Dollimore and Nicholson [14] who showed that at 463 K (13 K above our experiment) there was



(c)



(d)

Fig. 6 (continued).

extensive anion breakdown ($0.23 \rightarrow 1.70$ oxalate loss) at between 13 and 16 min for ferric oxalate. Of interest here is their observation that this stage of reaction was accompanied by the loss of almost $2\text{H}_2\text{O}$.

The autocatalytic α -time behaviour (Fig. 1) and the kinetic obedience to rate equations characteristic of solid state processes is evidence that reaction occurs preferentially at a reactant/product interface. The following chemical steps, individually or in concert, are required in the chemical change characterized.

- (i) oxalate oxidation $C_2O_4^{2-} \rightarrow C_2O_4 + 2e^{-}$.
- (ii) oxalate breakdown $C_2O_4 \rightarrow 2CO_2$ (rupture of the C–C link [9]).
- (iii) cation reduction $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$.
- (iv) recrystallization of ferric oxalate \rightarrow ferrous oxalate.
- (v) dehydration $-2H_2O$ (see above and ref. 14).

The electron transfer process (i) + (iii) can be expected to be achieved more readily for the ferric salt than for the (product) ferrous salt due to the greater ease of Fe^{3+} reduction. This is an attractive explanation for the marked difference in the thermal stabilities of the two salts (and the greater reaction rate of ferrous oxalate retaining Fe^{3+} , Fig. 5). This reaction ($Fe^{3+} \rightarrow Fe^{2+}$) does not, however, proceed to completion, but the product ferrous oxalate is capable of accommodating a small proportion of ferric salt. This may arise because two Fe^{3+} ions are required for each $C_2O_4^{2-}$ anion breakdown.

An alternative mechanistic explanation of the reaction, participating with the steps discussed above, identifies the role of water in anion breakdown. We note that a small yield of oxalic acid is sublimed during reaction, that water is evolved ((v) above) and that oxalic acid decomposes at 440 K [20], the temperature of the present study. This mechanism envisages the intervention of $(FeOH)^{2+}$ and $(HOOC)_2$, and is effective as a preferred reaction path if C–C rupture [9] occurs more readily in the acid ($H_2C_2O_4$) than in the anion ($C_2O_4^{2-}$). Subsequently, $(FeOH)^{2+} + HOOC \cdot \rightarrow Fe^{2+} + H_2O + CO_2$. Such a sequence of reactions explains the relative reduction in rate as the decomposition advances towards completion, requiring the application of two rate equations (Figs 2 and 3) because the availability of water is expected to diminish progressively with time at this temperature. The complex mechanism may account for the unusually low activation energy for a reaction of this type. The participation of water is undoubtedly the reason for the small yield of oxalic acid.

The activation energy for ferric oxalate decomposition is very low compared with values for reactions of other metallic oxalates [1]. The present result ($E = 27 \text{ kcal mol}^{-1}$ and $\Delta H(FeO_{3/2}) = -98 \text{ kcal mol}^{-1}$) falls well below the line (on the axis) on Fig. 6 of ref. 21 which correlates magnitudes of E with heat of formation of the appropriate metal oxide. This is consistent with the mechanistic discussion above and with the observation that reaction results in cation reduction only ($Fe^{3+} \rightarrow Fe^{2+}$). In this respect, the behaviour differs from the other decompositions which yield either metal or oxide residues. This mechanism also accounts for the observation that the salt does not dehydrate completely prior to the decomposition reaction.

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