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A kinetic and mechanistic study of the isothermal decomposition of ferrous oxalate dihydrate

Mohamed A. Mohamed [a] and Andrew K. Galwey [b]

[a] *Department of Chemistry, Faculty of Science, Qena (Egypt)*

[b] *School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (UK)*

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Abstract

A kinetic study has been made of the isothermal decomposition of ferrous oxalate between 596 and 638 K. The principal products of reaction are FeO (which disproportionates to Fe_3O_4 and Fe) and $CO_2 + CO$ (3:2 ratio). Yield–time data for the evolution of the gaseous products obeyed the Avrami–Erofe'ev ($n = 2$) equation, $[-\ln(1-\alpha)]^{1/2} = kt$, characteristic of solid state nucleation and growth reactions. The activation energy calculated for this reaction was 175 ± 7 kJ mol^{-1}. Scanning electron microscopic examinations of partially decomposed salt showed that anion breakdown was not accompanied by reactant melting. The reaction mechanism is discussed. It is concluded that decomposition is initiated rapidly and proceeds as an interface advance process thereafter. The activation energy is comparable with values for decomposition of other oxalates and it is concluded that similar controls on the rate-limiting step apply.

INTRODUCTION

A number of studies, which together have contributed materially towards establishing the theoretical concepts that are applicable to solid state decompositions, have been concerned with the thermal reactions of metal salts of oxalic acid. A review of the reported kinetic characteristics of breakdown reactions of representative oxalates appeared in 1980 [1]. Certain of these well-defined compounds have been the subject of several independent investigations by different groups of workers. Nickel oxalate, for example, was investigated in two particularly detailed kinetic analyses [2, 3] of nucleation and growth behaviour and also in a later [4] microscopic examination of nucleus development. Similarly, silver oxalate has attracted wide interest [5, 6] partly because the rate of reaction is sensitive to methods of preparation [7], ageing, grinding and other pre-treatments [1].

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

Various attempts have been made to identify the factors controlling the stabilities of oxalates and to characterize the parameters that determine the rates of salt breakdown. Boldyrev et al. [8] concluded that, in the decompositions of all oxalates, the first step is the rupture of the C–C bond in the anion $C_2O_4^{2-}$. Depending on the electropositive character of the cation, the subsequent reactions may yield oxide or metal as the residual product (illustrated for divalent transition metals) [9]

$$MC_2O_4 \rightarrow MO + CO_2 + CO$$

$$MC_2O_4 \rightarrow M + 2CO_2$$

The first of these reactions is endothermic in the absence of side reactions.

Acheson and Galwey [10] noted a correlation between the activation energy for the decompositions of oxalates (and also for mellitates) and the heat of formation of the appropriate oxide. Macklen [11] found that the stabilities of four divalent oxalates in nitrogen diminished in the sequence of decreasing electronegativities of the cations $Mn > Fe > Co > Ni$. It was also concluded [12] that in the decomposition of manganese(II) oxalate, the initial oxidation of a small proportion of the cation, $Mn^{2+} \rightarrow Mn^{3+}$, provided the active intermediate that participated in the subsequent salt decomposition. We have recently [13] obtained evidence that the decomposition of copper(II) oxalate proceeds to completion through the intervention of the copper(I) salt, $Cu_2C_2O_4$. These observations indicate that either the strength of the metal–oxygen link or the energy required for an electron transfer step may control the decomposition rates of transition metal oxalates.

There have been several previous studies [9, 11, 14–17] of the decomposition of ferrous oxalate but we could find no previous comprehensive kinetic and mechanistic investigation. Broadbent et al. [14] have reported non-isothermal data for the decomposition of iron oxalates and their complexes. Nicholson [15] reported that the behaviour of $FeC_2O_4 \cdot 2H_2O$ on heating is very sensitive to the presence of traces of oxygen in the prevailing atmosphere. Macklen [16] has identified FeO as the primary product of $FeC_2O_4 \cdot 2H_2O$ breakdown in N_2 or CO_2. Halsey and Pritchard [17], however, working on the same compound, could obtain no evidence of wustite (cubic FeO) formation in a Mossbauer examination of the residual decomposition products.

In a study [18] of the dehydrations of some transition metal oxalates, the enthalpy of $FeC_2O_4 \cdot 2H_2O$ dehydration was measured as 62.3 kJ per mol H_2O, and the decomposition enthalpy was 30.5 kJ mol^{-1}. Water molecules in these compounds are reported [19] to be coordinated directly to the metal ion and therefore the dehydration temperature and enthalpy are dependent on both the nature and the size of the cation.

EXPERIMENTAL

Reactant salt

The ferrous oxalate dihydrate preparation investigated here was an analytical grade material, used without further purification. Elemental analyses (combustion analyses for carbon and hydrogen, and both atomic absorption and EDTA titrations for Fe) gave results that agreed very satisfactorily with theoretical expectation for the dihydrate, see Table 1. Reactant dehydration in vacuum at approx. 390 K for 90 min resulted in a weight loss of 20.1% which is in good agreement with the calculated value for the loss of $2H_2O$, 20.03%.

TABLE 1

Elemental analysis of ferrous oxalate dihydrate

	H (%)	C (%)	Fe (%)
Found	2.29	13.40	31.10
Theoretical for $FeC_2O_4 \cdot 2H_2O$	2.24	13.35	31.04

Apparatus

The kinetics of the isothermal (±1 K) decomposition of the reactant $FeC_2O_4 \cdot 2H_2O$ were studied in a constant volume pre-evacuated (10^{-4} Torr) glass apparatus [19] by measuring the pressure of the product permanent gases evolved at suitable time intervals. The temperature of the heated reactant was recorded and controlled using a chromel–alumel thermocouple located as close to the heated sample as possible, but outside the vacuum envelope. The McLeod pressure gauge was used with a cold refrigerant trap (178 K, liquid/solid acetone) interposed between the reaction vessel and the gauge to condense water and any other easily condensable decomposition products. The rate studies reported here refer, therefore, to the reactions yielding the permanent gases CO and CO_2 only.

Non-isothermal thermogravimetry and differential thermal analysis measurements were performed using a Shimadzu 50 apparatus, heating the samples in nitrogen at 5 K min^{-1}.

Scanning electron microscopic investigations were carried out using a Jeol 35CF instrument. Specimens studied were rendered conducting by precoating with a thin film of Au/Pd prior to examination. To investigate textural changes within the bulk (interior) of the crystallites, partially reacted samples were gently crushed prior to coating, as described elsewhere [20].

RESULTS AND DISCUSSION

Thermogravimetric (TG) and differential thermal analyses (DTA)

Thermal analyses were performed for $FeC_2O_4 \cdot 2H_2O$ to 1073 K in a flowing nitrogen atmosphere; thermal responses are shown in Fig. 1. Thermogravimetric curves show two weight losses. The first reaction, commencing at 390 K, resulted in a 20% weight loss, in accordance with expectation for the evolution of $2H_2O$. Dehydration was completed before the onset of decomposition, which commenced at 593 K and resulted in the loss of a further 38.5% of the reactant weight.

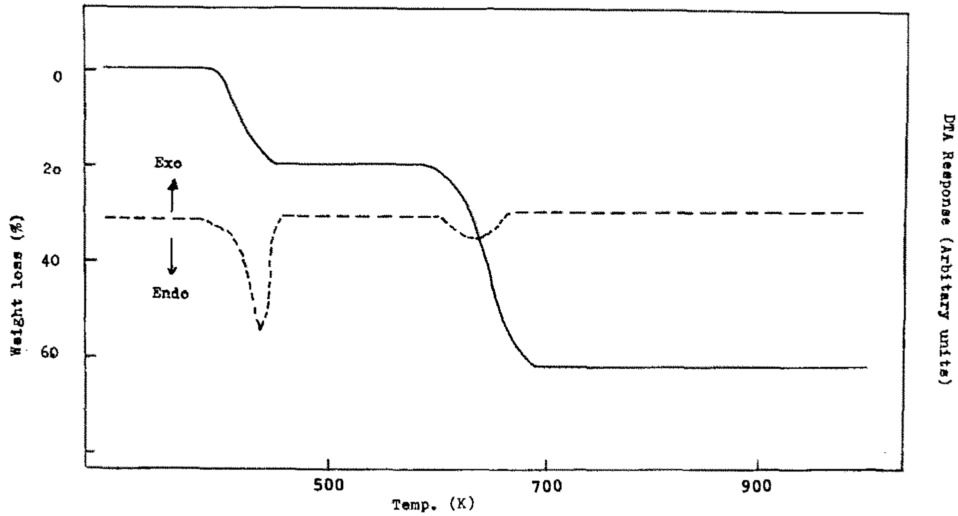


Fig. 1. TG and DTA response peaks for the decomposition of ferrous oxalate dihydrate in flowing nitrogen during heating at 5 K min^{-1}.

DTA analyses of the same salt, again in nitrogen, detected two separated endothermic peaks with maxima at 435 and 636 K. The first was ascribed to dehydration and the second to anion breakdown of the anhydrous ferrous oxalate. The decomposition endotherm at 636 K is in agreement with results reported by Macklen [16] and Nagase et al. [18] but contrasts with the exothermic character of this reaction reported by other workers [9, 21].

Reaction stoichiometry

Yields of product gases, CO and CO_2, were measured from the pressures evolved in the calibrated volume of the pre-evacuated apparatus after the completed decompositions (20 experiments, 596–638 K) with 78 or 178 K cold traps to determine CO and $(CO + CO_2)$ respectively.

Reaction stoichiometry was well represented by

$FeC_2O_4 \rightarrow FeO + 1.14CO_2 + 0.74CO + 0.3C$

The carbon in the residue was determined by combustion analysis. The solid reaction products were shown, by spot tests, to contain very small amounts of Fe^{3+}. The mean weight loss from decomposition, 58.5%, agreed well with the thermogravimetric value reported above. The mean $CO/(CO + CO_2)$ ratio was 0.39, in contrast with the earlier report [15] that CO and CO_2 are produced in equimolar proportions. The presence of Fe_3O_4 in the residual products was confirmed by X-ray diffraction measurements, consistent with an earlier result [9] and expected from disproportionation of FeO which is thermodynamically unstable below 846 K.

Reaction kinetics

Representative fractional reaction (α)–time plots for the evolution of $(CO + CO_2)$ from the decomposition of ferrous oxalate at selected temperatures across the range studied (596–639 K) are shown in Fig. 2. These curves are sigmoid shaped but without an induction period to reaction. The acceleratory stage was rapidly completed initially, leading to a period of almost constant reaction rate. From tests of our kinetic data for obedience to those rate equations most usually applied to reactions of solids [1], the best fit was to the Avrami–Erofe'ev expression

$$[-\ln(1-\alpha)]^{1/2} = kt \qquad (1)$$

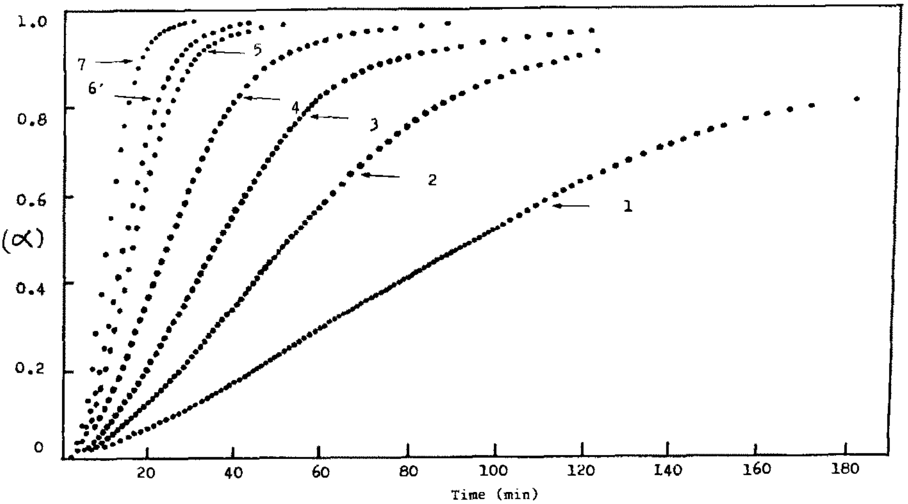


Fig. 2. Representative isothermal plots for thermal decomposition of ferrous oxalate dihydrate at selected temperatures across the range studied: 1, 596; 2, 604; 3, 611; 4, 619; 5, 626; 6, 632; and 7, 639 K.

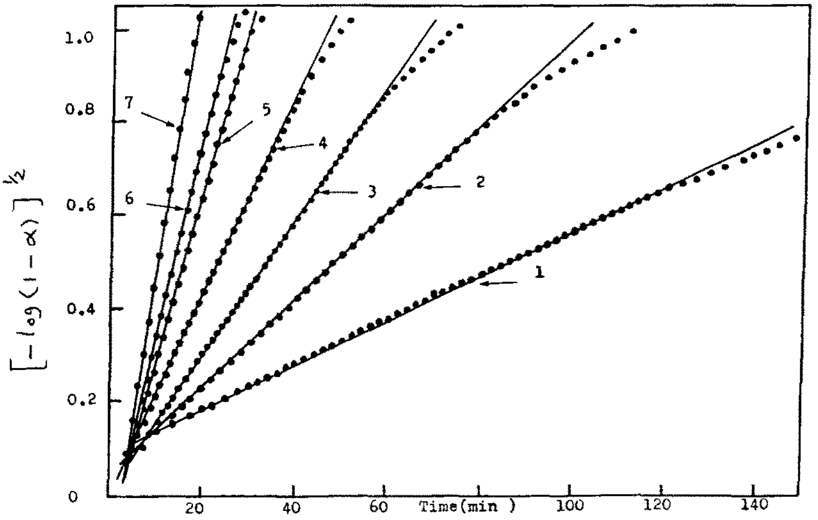


Fig. 3. Plots of $[-\log(1-\alpha)]^{1/2}$ against time for data in Fig. 2.

Equation (1) very satisfactorily represented the data $0.02 < \alpha < 0.87$, Fig. 3, though the reaction rate diminished relatively more slowly during the final stages when $\alpha > 0.87$. Somewhat similar behaviour was shown by decomposition of the ferric salt [22]. The point of convergence of data on Fig. 3 corresponds to $\alpha = 0.02$ at 5 min, the time required to heat the sample to reaction temperature, and confirms the absence of any induction period. It is concluded that a small amount of gas ($\alpha = 0.02$) is rapidly evolved during salt heating, after which the main reaction is established. Rate constants measured for all our kinetic data gave a linear Arrhenius plot from which the calculated activation energy was 175 ± 7 kJ mol^{-1}.

Carbon monoxide formation reaction

Pairs of otherwise identical rate experiments were performed using 78 and 178 K refrigerant traps. The kinetic characteristics of both rate processes, for CO and for ($CO + CO_2$) formation, were closely similar except that the rate of the former was somewhat greater (×1.3) than reactions where both gases were evolved. We conclude, therefore, that relatively greater proportions of CO were formed during the early stages of salt decompositions.

Decomposition of an $FeC_2O_4 + Fe_2(C_2O_4)_3$ (10%) mixture

Comparative kinetic studies were made for ferrous oxalate decomposition and a mixture containing 10% by weight of added ferric oxalate.

Initially the rate of decomposition of the mixture was the more rapid but after some 20% of reaction, the rate of reaction of the pure salt proceeded at the greater rate.

Electron microscopy

Samples of reactant, completely reacted product ($\alpha = 1.00$) and salt decomposed to several intermediate, known α values were examined in

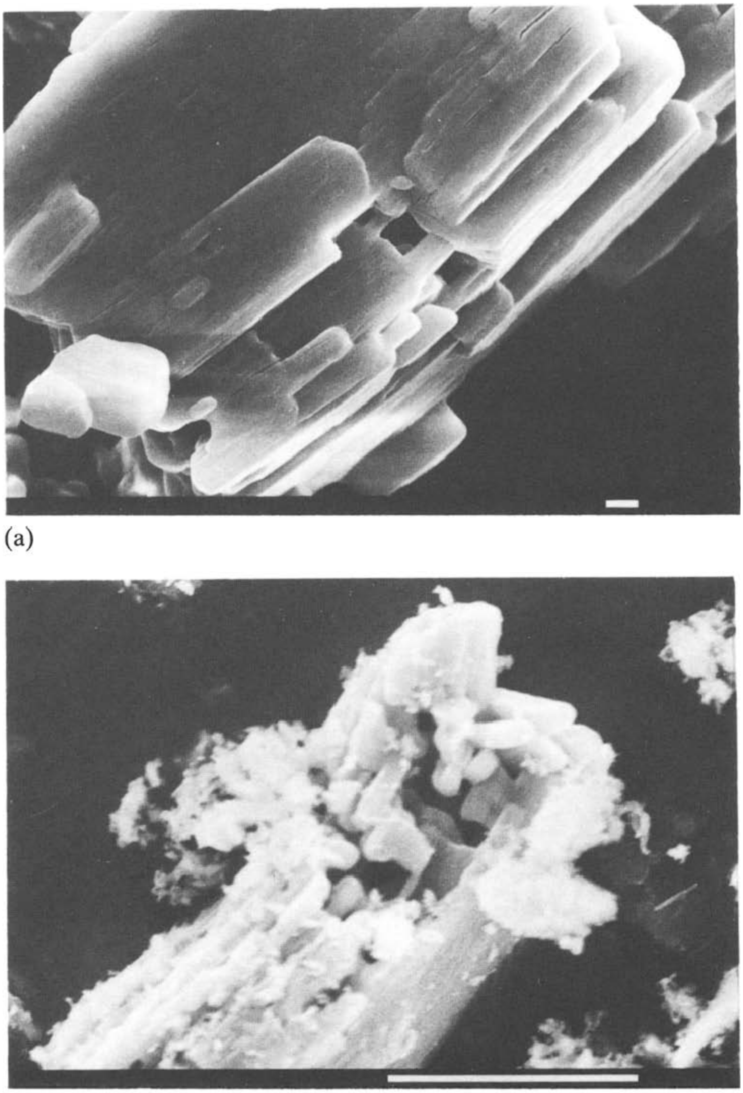
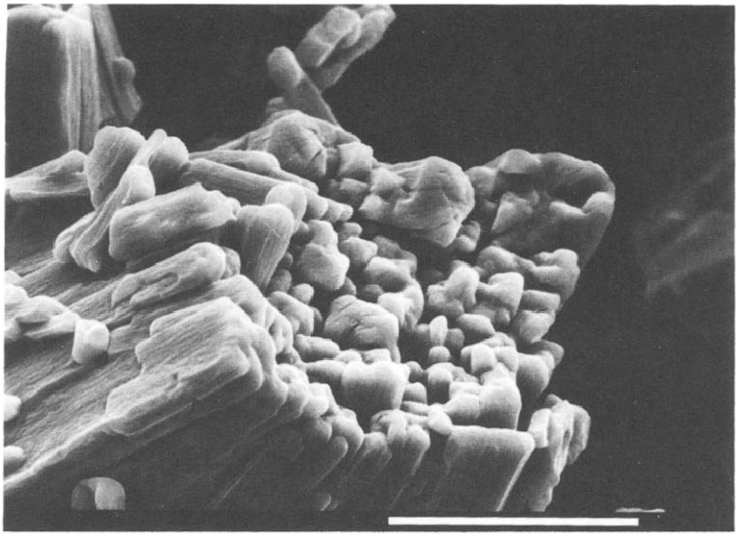


Fig. 4. Three representative scanning electron micrographs for ferrous oxalate: (a) the dehydrated reactant (scale bar, 1.0 μm), (b) partially decomposed reactant, $\alpha = 0.5$, then lightly crushed (scale bar, 10 μm) and (c) salt completely decomposed, $\alpha = 1.00$ (scale bar, 10 μm).



(c)

Fig. 4 (continued).

the scanning electron microscope. No textural evidence of melting was obtained; reactant crystallites remained discrete and product particles were pseudo-morphic with those of the reactant. We conclude, therefore, that decomposition proceeded in the solid state.

The reactant was composed of approximately rectangular crystallites, most of which were 10–30 μm edge length. Representative crystals of the dehydrated salt are shown in Fig. 4(a), in which the superficial cracking is ascribed to water loss. The crystallite in Fig. 4(b) is salt decomposed to $\alpha = 0.5$, lightly crushed, which reveals that extensive decomposition has occurred in the crystal interior. Figure 4(c) shows a product crystallite ($\alpha = 1.0$), pseudo-morphic with the reactant, showing that the original particle shape and size has been retained throughout decomposition.

Reaction mechanism

The proportion of carbon dioxide in the gaseous products evolved (CO_2:CO 3:2), together with the observed retention of carbon in the solid products, showed that salt decomposition is more complicated than the disintegration of individual anions ($FeC_2O_4 \rightarrow FeO + CO + CO_2$). It is also known that FeO disproportionates at reaction temperature: Halsey and Pritchard [17] using Mössbauer spectroscopic measurements found no evidence of FeO in the products. We conclude, therefore, that the primary products of reaction (FeO and $CO + CO_2$) undergo heterogeneous reactions during disproportionation of 4FeO ($\rightarrow Fe_3O_4 + Fe$) to yield the products detected here. Identification of the individual contributory steps on the surfaces of the finely divided product solids [23] is not practicable. The possible participation of ferric ions in oxalate ion breakdown must also be considered here: ferric oxalate decomposition was studied between 410 and 450 K, well below the temperature of the present studies (>596 K). We considered this possibility because it was shown above that CO production was relatively more rapid (×1.3) than ($CO + CO_2$) formation, providing evidence that the residual cations are more highly oxidized during the early stages of reaction.

Addition of solid ferric oxalate (10%) to the present reactant resulted in an enhanced initial decomposition rate but this rapid process was not sustained. We conclude that the individual components (Fe^{3+} and Fe^{2+} salts) of the mixture react separately. The residue from ferric oxalate decomposition, ferrous oxalate containing probably 10% of the ferric salt (see Fig. 5, in ref. 22) reacts at twice the rate of the pure ferrous salt. We conclude that in this mixture, the Fe^{3+} ions present are more efficiently dispersed within the ferrous oxalate and reaction is promoted significantly, perhaps through its early establishment at a relatively larger number of reactive sites.

The initiation of ferrous oxalate decomposition was rapid, instantaneous nucleation [1], and the α–time curves were sigmoid shaped (Fig. 2). We conclude that the reaction proceeded at advancing interfaces and this is consistent with the above mechanistic discussion where several interrelated reactions are regarded as contributing together to the overall chemical change. This model explains the observed satisfactory obedience to the Avrami–Erofe'ev equation [1]. It was not found possible, however, to provide direct observational support for this nucleation and growth reaction model because no textural modifications of the solid, capable of distinguishing between the reactant and product phases, could be recognized in microscopic observations. Reaction did result in the local disintegration of parts of the central regions of crystallite assemblages, Fig. 4(b). The boundaries of reacted zones within individual crystallite assemblages could not, however, be identified and delimited by observation.

The activation energy for salt decomposition, $175 \pm 7\,\mathrm{kJ\,mol^{-1}}$, is significantly larger than that for the ferric salt [22], $115 \pm 10\,\mathrm{kJ\,mol^{-1}}$, and is comparable with values reported for other divalent oxalates [1, 10]. We conclude that the reaction mechanism differs from that of ferric oxalate where a proportion, only, of the anion present reacts and there is cation reduction ($Fe^{3+} \rightarrow Fe^{2+}$) to give the present reactant. The value of E for FeC_2O_4 decomposition ($E = 42\,\mathrm{kcal\,mol^{-1}}$ and $\Delta H(\mathrm{FeO}) = -64\,\mathrm{kcal\,mol^{-1}}$) is close to midway between the two lines in Fig. 6 of ref. 10. We conclude, therefore, that the factors controlling the decomposition rate of ferrous oxalate are probably the same as those in other divalent oxalates and that the energy barrier to anion breakdown is the strength of the bond between the ferrous iron and carboxyl oxygen.

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