

A kinetic and mechanistic study of the thermal decomposition of copper(II) oxalate

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Abstract

A kinetic and mechanistic study of the thermal decomposition of copper(II) oxalate has been completed. The reaction stoichiometry was well represented as $\text{CuC}_2\text{O}_4 \cdot 0.25\text{H}_2\text{O} \rightarrow 1.92\text{CO}_2 + 0.06\text{CO} + 0.25\text{H}_2\text{O} + [\text{Cu} + 0.01\text{C}]$. Reactant crystallites were below the minimum size required for resolution of surface textural detail by scanning electron microscopy. It was shown that the crystallites formed adherent aggregates and there was significant particle re-texturing during the latter half of the reaction.

Analytical measurements confirmed that decomposition proceeded with stepwise cation reduction ($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$). Fractional reaction (α)-time curves were sigmoid in shape. The acceleratory stage in the reaction obeyed the exponential law in the range $0.04 < \alpha < 0.3$ and the activation energy was $140 \pm 7 \text{ kJ mol}^{-1}$ (515–550 K). The first-order reaction was obeyed in the range $0.24 < \alpha < 0.91$ and the activation energy was somewhat larger at $180 \pm 7 \text{ kJ mol}^{-1}$ (515–550 K). The reaction was significantly reduced in crushed mixtures of the salt with either Cu_2O or CuCl .

It is concluded that reaction proceeded with intracrystalline but not comprehensive melting; perhaps local and temporary fusion within the particles took place. The decomposition of copper(II) oxalate, dominant when $\alpha < 0.5$, proceeded somewhat more rapidly than the subsequent ($\alpha > 0.5$) decomposition of copper(I) oxalate. These conclusions are supported by comparative kinetic studies of the thermal decompositions of equimolar mixtures of oxalic acid with either Cu_2O or CuO . There was some evidence that the rate-limiting step was electron transfer from anion to cation.

INTRODUCTION

Kinetic investigations concerned with the characterization of the mechanisms of solid state decompositions have included many studies of the thermal reactions of oxalates, some of which have been the subject of multiple independent examinations by different groups of workers [1, 2]. Boldyrev et al. [3] have classified these reactions on the basis of the principal residual product (carbonate, oxide or metal) which depends on

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the electropositivity of the cation. These workers identify the initial step in all oxalate decompositions as the rupture of the C–C bond in the anion. The literature on this group of decompositions is extensive and several salts, notably nickel oxalate and silver oxalate, have been examined in particular detail [2].

Much less attention has been directed to the decomposition of copper(II) oxalate, though a recent report [4] was concerned with the influence of sample preparation and environmental atmosphere on the thermal stability of this salt. Our present study was undertaken primarily to determine whether the decomposition of copper(II) oxalate proceeded through the intervention of the copper(I) salt. It has been shown [5] that the decomposition of copper(II) malonate proceeds to completion through two distinct rate processes. The second of these reactions was the decomposition of copper(I) malonate, and the reaction also involved melt formation together with acetate formation. Similarly, copper(II) fumarate and copper(II) maleate [6], and copper(II) squarate [7] decomposed with the intervention of copper(I) salts. Earlier, copper(I) formate [8] was inferred as a participant in the decomposition of copper(II) formate. Thus the decompositions of these several copper(II) carboxylates proceed with stepwise cation reduction, $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$, a common chemical characteristic within a field where behavioural similarities between related reactants are unusual [2]. It was, therefore, of interest to compare the thermal behaviour of copper(II) oxalate with the results already obtained for the other copper(II) salts and to discuss the reaction mechanism in the context of the data available.

EXPERIMENTAL

Copper(II) oxalate

The sample of copper oxalate powder used throughout the present work was prepared as follows. Basic copper carbonate, 10.5 g, approximate composition $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$, was added in small amounts to a solution of 12.6 g oxalic acid in 500 ml distilled water, maintained at 330 K throughout the addition and for 1 h afterwards. The solution was filtered, washed with water at 330 K and dried in air.

The mean results from three combustion analyses for carbon and hydrogen, and from the copper analysis by atomic absorption are given in Table 1. The composition of the salt gives evidence that it contains a small proportion of water. The weight loss in vacuum at 400 K, well below decomposition temperature, corresponded to approx. $0.25\text{H}_2\text{O}$ and no other gas was evolved concurrently.

TABLE 1
Analysis of copper(II) oxalate

| | %Cu | %C | %H | %O (by difference) |
|---|------|-------|------|-----------------------|
| Prepared salt | 40.4 | 15.38 | 0.29 | 43.9 |
| Theoretical for $\text{CuC}_2\text{O}_4 \cdot 0.25\text{H}_2\text{O}$ | 40.3 | 15.39 | 0.32 | 44.0 |

Apparatus

The kinetics of the decomposition of copper(II) oxalate, and related reactions, were studied in a conventional glass apparatus that was initially evacuated prior to heating the reactant sample to the constant reaction temperature (± 1 K) after isolation from the pumps. Extents of reaction were measured from the pressure of gas present in the apparatus at known times using either a McLeod gauge or a Baratron (222B) diaphragm gauge. A 178 K trap was maintained between the heated salt and the gauge to remove water and other condensible products. The apparatus using the Baratron gauge collected and stored the pressure, time and temperature values automatically, and also included facilities for data processing. The method has been described by Carr and Galvey [5].

Electron microscopy

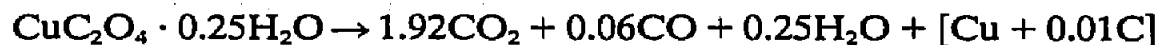
Samples of salt, of product and of salt decomposed to various known extents were examined in a Jeol 35CF scanning electron microscope to characterize the textural changes that occurred during reaction. Before examination, each sample was rendered conducting by pre-coating with a thin film of Au/Pd.

RESULTS AND DISCUSSION

Reaction stoichiometry

The carbon dioxide yield from the completed salt decomposition was 1.92 ± 0.05 mol CO_2 per mol reactant, measured from the pressure of gas evolved in the calibrated volume of the vacuum apparatus. The amount of

permanent gaseous products was 0.060 mol CO per mole reactant, similarly measured but with a 78 K trap. Mass spectrometric analyses of the gaseous reaction products detected species only at masses 44 (CO₂) and 28 (CO) confirming the above identifications. The mean weight of the residual decomposition products was 40.8% which is close to the copper content of the reactant (40.4%) and only 0.22% carbon was detected by combustion analysis of this residue. The stoichiometry of the decomposition of copper(II) oxalate can be expressed, from the above data and showing the residual products in brackets, by



Copper(II) ion reduction

As in our previous studies [5–7], progressive changes in the proportion of Cu²⁺ remaining in the reactant as decomposition proceeded were measured by iodometric titration. Weighed reactant samples were decomposed, under conditions identical to those used in kinetic studies, to known extents (fractional reaction, α) and each sample was dissolved at once in acid iodide solution followed by titration of the iodine released with standard sodium thiosulphate.

The present results are summarized in Fig. 1. The amount of Cu²⁺ diminishes approximately linearly with α during the first half of the reaction

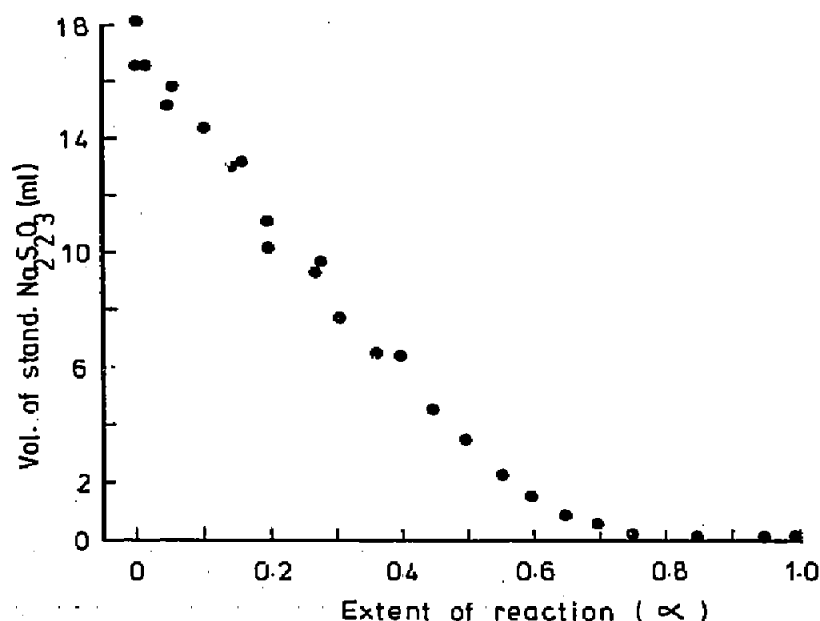


Fig. 1. Reduction in amount of copper(II) present with extent of decomposition of copper(II) oxalate. The Cu²⁺ content approaches zero when $\alpha \approx 0.65$. Cu²⁺ contents were measured, for equal weights of salt decomposed to an appropriate range of α values, by titration with standard sodium thiosulphate solution. The composition of the unreacted samples ($\alpha = 0.00$) corresponds with expectation for copper(II) oxalate.

and relatively more slowly towards zero in the subsequent interval, $0.5 < \alpha < 0.7$. This shows that copper reduction is again [5–7] stepwise, $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$. About 80% of the copper is reduced during the 1st half of the reaction (to $\alpha = 0.5$) and that remaining soon follows, but there is some overlap of the decomposition of copper(II) oxalate with the subsequent breakdown of copper(I) oxalate.

Electron microscopy

Scanning electron micrographs for copper(II) oxalate are not reproduced here because the individual crystallites of the reactant were too small ($< 0.5 \mu\text{m}$) to permit satisfactory resolution of textural features. Picture quality was often poor due to charge retention arising from the low electrical conductivity of the porous aggregates that constituted the particle assemblages. Nevertheless, some 120 photographs were obtained for reactant, product and salt decomposed to various intermediate α values. From our comparative examinations, the following conclusions were reached.

The reactant was composed of aggregates, up to $50 \mu\text{m}$ in diameter, and irregular shapes of large numbers of small rounded particles with diameters up to $0.5 \mu\text{m}$, though many were smaller. No surface detail of these apparently smooth surfaced particles could be resolved. No textural changes could be detected during the early stages of reaction ($\alpha \leq 0.3$). Small crystals remained in the form of large aggregates but comprehensive melting did not occur. At $\alpha = 0.5$ the same macrotecture was maintained but the individual crystallites ($< 0.5 \mu\text{m}$) became pitted and generated protuberances ($0.05 \mu\text{m}$ diameter). Surfaces were modified by roughening through the development of these features at the limits of microscope resolution. On completion of decomposition ($\alpha = 1.0$), the product consisted of large coherent but irregular aggregates, up to $100 \mu\text{m}$ in diameter, composed of small rounded particles that were too small (approx. $0.05 \mu\text{m}$) to permit textures to be characterized.

Textural modifications within the small reactant particles could not be resolved or characterized in detail by the microscopic techniques available; thus the observations are not useful for the interpretation of kinetic data. There was no evidence that the salt underwent comprehensive fusion and, in this respect, the present reactant resembled copper(II) malonate, where melting was intracrystalline [5]. There are indications, however, that copper(II) oxalate underwent significant re-texturing during reaction, requiring appreciable movement of material: this could be regarded as local and/or temporary fusion. The microscopic evidence here is inconclusive, although the rounded surfaces of particles and the coherence of the particles in aggregates are consistent with some local sintering or superficial fusion.

Kinetics of the decomposition of copper(II) oxalate

Isothermal α -time curves for the decomposition of copper(II) oxalate in the range 515–550 K were sigmoid shaped; representative plots for five typical experiments are shown in Fig. 2. Following reactant heating, there was evolution of approx. 3% product gas, identified as an initial rapid reaction ($\alpha_1 = 0.03$). This contribution was subtracted from the yield-time data in subsequent kinetic analyses. The main decomposition was completed in three distinguishable rate processes. The acceleratory phase was completed by approx. $\alpha = 0.25$; the subsequent median stage proceeded at an approximately constant rate, $0.2 < \alpha < 0.6$, before the deceleratory approach to completion (when $\alpha > 0.6$).

None of the rate equations applicable to nucleation and growth reactions [1], processes that characteristically exhibit sigmoid shaped α -time curves, satisfactorily represented the present yield-time data across the overall reaction.

The best fit for the acceleratory phase was provided by the exponential rate law. Plots of $\ln(\alpha - 0.03)$ against time were linear, see Fig. 3, between $\alpha = 0.04$ and an upper limit that was somewhat variable, $\alpha = 0.30 \pm 0.06$, though such values did not vary systematically with temperature. (Values of α were corrected by subtraction of $\alpha_1 = 0.03$ for the initial process.) The activation energy, calculated from 17 measured rate constants for isothermal decompositions between 515 and 550 K, was $140 \pm 7 \text{ kJ mol}^{-1}$.

Data measured during the acceleratory phase were also tested for accuracy of fit to the power law $\alpha^{1/n} = kt$ [1]. Plots of $\ln(\alpha - 0.03)$ against $\ln t$ indicated values for $n = 5-6$, which is larger than the range most usually found applicable to nucleation and growth reactions.

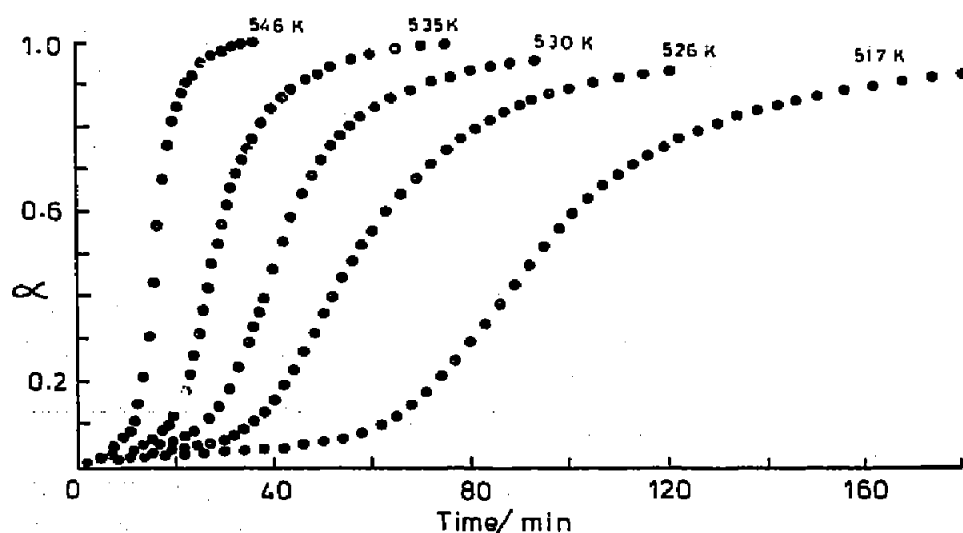


Fig. 2. Typical isothermal fractional reaction α -time curves for the thermal decomposition of copper(II) oxalate at representative temperatures within the range investigated.

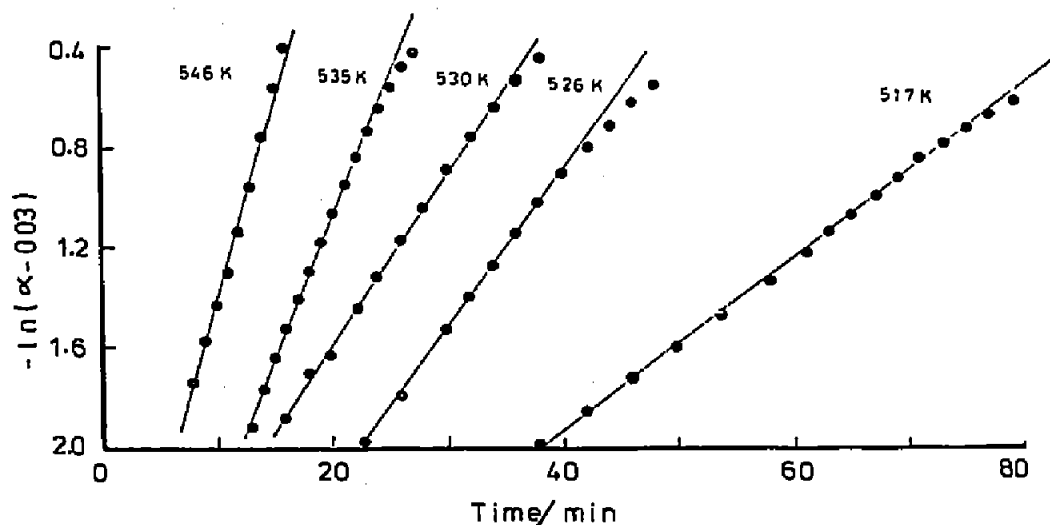


Fig. 3. Fit of data to the exponential equation $\ln(\alpha-0.03) = kt$ for the acceleratory stage of the experiments in Fig. 2. The contribution from the initial rapid reaction, $\alpha_1 = 0.03$, has been subtracted from each value.

The first-order rate equation was applicable across the widest α -time interval, $0.24 \pm 0.02 < \alpha < 0.91 + 0.02$, of all the expressions tested, see Fig. 4. Data were satisfactorily represented by this relation from the completion of the acceleratory process, but in the final stages ($\alpha > 0.91$) rates were more deceleratory than expected for first-order behaviour. It is considered to be significant that reaction did not proceed to the relatively rapid completion that is the kinetic characteristic of many interface-advance processes. The activation energy, calculated from the same 17 experiments mentioned for the acceleratory stage analysis, was $180 \pm 7 \text{ kJ mol}^{-1}$.

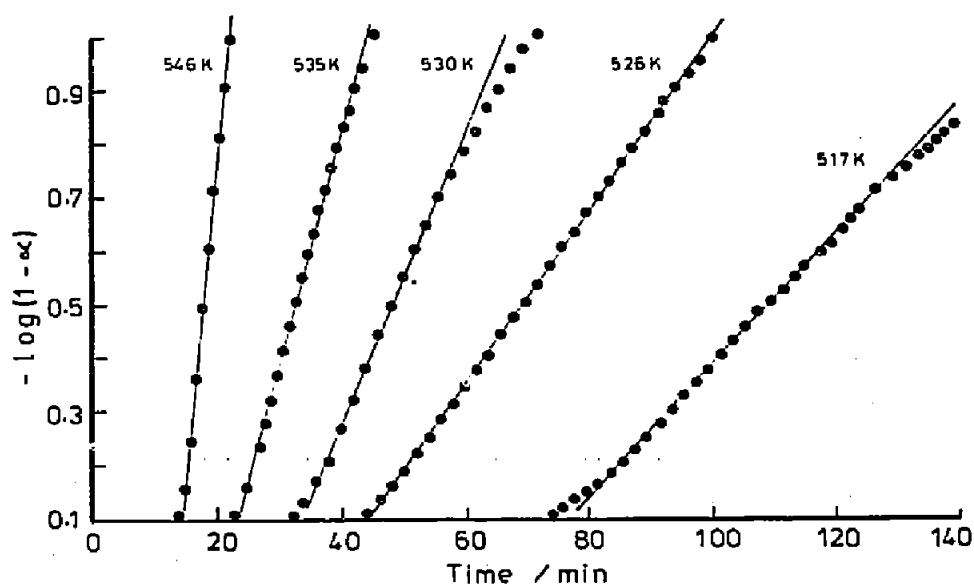


Fig. 4. First-order obedience during the median and deceleratory stages of the experiments shown in Fig. 2.

It was also noted that data obeyed the Prout–Tompkins equation [1], $\ln(\alpha/(1 - \alpha)) = kt$, over the restricted α range 0.10–0.52 and again the rate was relatively more deceleratory after the half-way stage, when $\alpha > 0.5$. Alternatively (again) reaction proceeded at an approximately constant rate between $0.2 < \alpha < 0.7$ (zero-order kinetics). Arrhenius activation energy values calculated for both these rate expressions applicable to the median range gave activation energies, $160 \pm 10 \text{ kJ mol}^{-1}$, intermediate between the values cited above for equations obeyed during the acceleratory and the deceleratory stages of reaction.

Crushing

Crushing of the reactant in a pestle and mortar resulted in no detectable change in the rate or kinetic characteristics of subsequent decomposition. Plots of α -time for the prepared and for pre-crushed copper(II) oxalate coincided within the limits of experimental error.

Added metal

Copper(II) oxalate crushed with an equimolar amount of copper metal powder exhibited decomposition kinetics that were indistinguishable from those of the pure reactant. Plots of α -time for a similar mixture with platinum were similarly identical with results for the pure salt when $\alpha > 0.15$. However, during the onset of decomposition, the acceleratory process characteristic of the pure salt was replaced by an approximately constant reaction rate that, after 15% reaction, coincided with results from the pure salt and proceeded unchanged thereafter.

DISCUSSION

The reaction mechanism must be discussed in the context of analytical data that demonstrate conclusively that cation reduction proceeds in two steps: decomposition of copper(II) oxalate followed by, and overlapping with, copper(I) oxalate. When $\alpha < 0.5$, copper is reduced, $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, and in the latter stages this overlaps with cation reduction to the metal, $\text{Cu}^+ \rightarrow \text{Cu}^0$. Although α -time curves are sigmoid shaped, data did not fit a single (solid state) rate equation and this is consistent with the occurrence of two consecutive and different chemical steps in the overall reaction. Activation energy values for the two steps are significantly different: the value of E for the decomposition of copper(II) oxalate (140 kJ mol^{-1}) when $\alpha < 0.5$, was appreciably less than that for the copper(I) salt (180 kJ mol^{-1}), when $\alpha > 0.5$.

Obedience of the reaction acceleratory stage to the exponential law closely resembles behaviour of copper(II) malonate [5] where reaction is identified as proceeding increasingly rapidly in a progressively rising amount of molten material. The stoichiometric observations here provide

evidence that copper(I) oxalate is formed (there is no analogue to the copper acetate formed during decomposition of copper(II) malonate [5]). If copper(I) oxalate or a eutectic with the copper(II) salt melts within the reactant crystallites, the exponential obedience is explained; reaction accelerates in proportion to the amount of product formed and the exponential law is obeyed, $d\alpha/dt = k\alpha$ [5].

Although comprehensive melting was not observed microscopically, the apparent absence of crystallite textural changes during decomposition is identical with the behaviour of copper(II) malonate. The rapid initial decomposition of a superficial reactant crystallite layer is believed to preserve particle identity through the generation of a durable "skin" [5]. Thereafter reaction proceeded within the molten zones of the intraparticulate reactant. These particles tended to remain coherent in aggregates.

Copper metal did not promote anion breakdown. Addition during the early stages did not accelerate the onset of decomposition and its appearance as a product ($\alpha > 0.4$) was not associated with any acceleration of reaction or rapid completion during the first-order deceleratory process. The second reaction was somewhat slower than the first. Platinum metal apparently did catalyse the onset of reaction but the promotional effect was small and temporary. Intracrystalline decomposition with local melting is consistent with the absence of influence of reactant crushing on decomposition kinetics. Particle size usually exerts an important control on solid state reaction rates [1] and the destruction of the crystal structure on melting means that kinetic characteristics are determined by homogeneous controls. Microscopy gave no evidence of nucleation and growth processes. The present observations demonstrate conclusively that the sigmoid shaped α -time curve is not the copper-catalysed decomposition of oxalate ions at an advancing metal-salt interface. In contrast, reaction is identified as an intracrystalline homogeneous decomposition proceeding preferentially within progressively increasing zones of molten salt.

KINETICS OF DECOMPOSITION OF OXALIC ACID + COPPER OXIDE MIXTURES

Copper(I) salts of organic acids are not usually prepared from aqueous solutions because the copper(I) ion readily disproportionates, $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0$. The present studies, therefore, followed the previously applied procedures [5–7] in which crushed mixtures of oxalic acid with the appropriate metal oxide were heated rapidly to decomposition temperature. We here complete kinetic measurements of the reactions of the crushed mixtures ($\text{C}_2\text{O}_4\text{H}_2 + \text{Cu}_2\text{O}$ and $\text{C}_2\text{O}_4\text{H}_2 + \text{CuO}$), both in equimolar proportions. The product yields corresponded to the CO_2 yields expected from breakdown of the constituent oxalic acid of the reactant mixture, and no appreciable acid sublimates were observed.

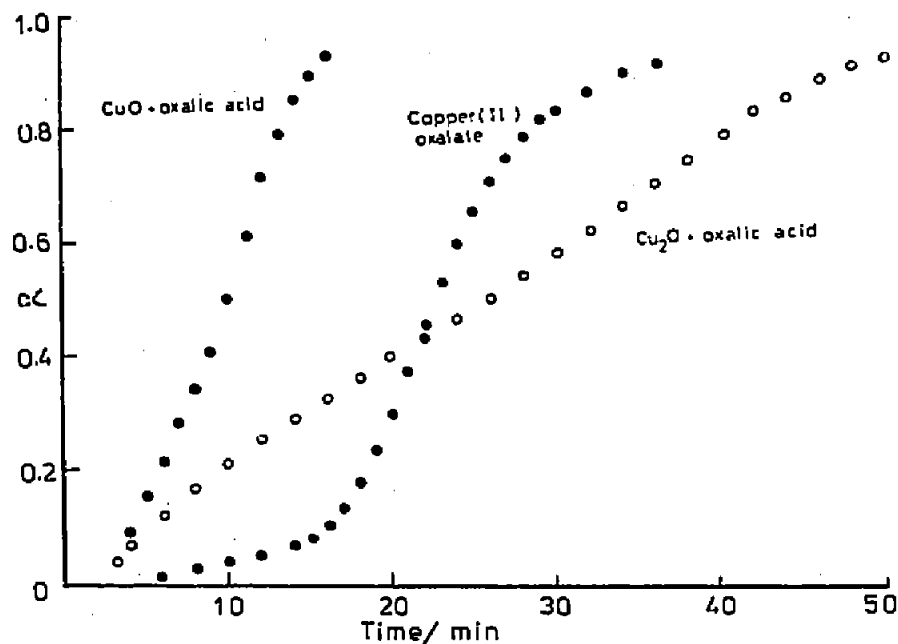


Fig. 5. Plots of α -time for the decomposition at 540 K of equimolar mixtures of ($\text{C}_2\text{O}_4\text{H}_2 + \text{CuO}$) and of ($\text{C}_2\text{O}_4\text{H}_2 + \text{Cu}_2\text{O}$) together with a reaction of copper(II) oxalate at the same temperature. The significance of these relative rates is discussed in the text.

Comparative α -time plots, representative of the kinetic behaviour of CO_2 evolution at 540 K for ($\text{Cu}_2\text{O} + \text{C}_2\text{O}_4\text{H}_2$) and for ($\text{CuO} + \text{C}_2\text{O}_4\text{H}_2$) mixtures, together with a comparative curve for copper(II) oxalate decomposition are shown in Fig. 5. These characteristically exhibited linear reaction-rate intervals and slopes in the median region were 0.0195 ($\text{Cu}_2\text{O} + \text{C}_2\text{O}_4\text{H}_2$), 0.080 ($\text{CuO} + \text{C}_2\text{O}_4\text{H}_2$) and 0.069 min^{-1} (copper(II) oxalate).

Reactions of both of the oxide-containing mixtures differ significantly from the behaviour of the prepared salt in that there was no induction period. Reactions of the mixtures started at a maximum rate and subsequently decelerated during the approach to completion. We have identified (above) the acceleratory stage in the reaction of copper(II) oxalate with the onset of melting in the solid reactant. The rapid heating of the present reactant (oxide + acid) mixtures can be expected to result in acid melting (m.p. of oxalic acid 462 K) accompanied by onset of breakdown of any copper salt formed. This fused material is probably similar to the molten phase in copper(II) oxalate decomposition. Thus the absence of solidification of any salt formed in the ($\text{CuO} + \text{C}_2\text{O}_4\text{H}_2$) mixture explains the rapid onset of reaction that proceeds at a rate (0.080 min^{-1}) that is only slightly greater than that of copper(II) oxalate at the same temperature (0.069 min^{-1}). This agreement is sufficiently close at this, and also at other temperatures, to conclude that the same mechanism of anion breakdown occurs in both reactant mixtures. Reaction in mixtures

($\text{Cu}_2\text{O} + \text{C}_2\text{O}_4\text{H}_2$) were significantly slower (0.0195 min^{-1}) and this is entirely consistent with the behaviour of the salt where the slower reaction occurred later with copper(I) oxalate. We conclude, therefore, that these data provide further direct evidence that the decomposition of copper(II) oxalate proceeds with stepwise cation reduction within a reactant that undergoes progressive melting.

KINETICS OF DECOMPOSITION OF COPPER(II) OXALATE + COPPER(I) OXIDE AND COPPER(II) OXALATE + COPPER(I) CHLORIDE MIXTURES

Plots of α -time for the isothermal decomposition of copper(II) oxalate at 540 K alone and in equimolar crushed mixtures ($\text{CuC}_2\text{O}_4 + \text{Cu}_2\text{O}$) and ($\text{CuC}_2\text{O}_4 + \text{CuCl}$) are shown in Fig. 6. Both additives markedly reduce decomposition rates; zero-order rate constants for the approximately linear median region of the reactions were 0.069 , 0.0074 and 0.0038 min^{-1} for the pure salt and with Cu_2O and CuCl , respectively. The addition of CuBr similarly slowed copper(II) oxalate decompositions.

Comparative α -time curves for the decomposition of crushed mixtures of copper(II) oxalate with various proportions (x , added wt.%) of Cu_2O are shown in Fig. 7. There is a dominant trend of reduction in rate as x is progressively increased. For all mixtures studied, behaviour resembled that of the pure salt in that α -time curves were sigmoid shaped. The initially acceleratory process was completed by $\alpha = \text{approx. } 0.2$. This was followed by an approximately zero-order process and the final deceleratory reaction

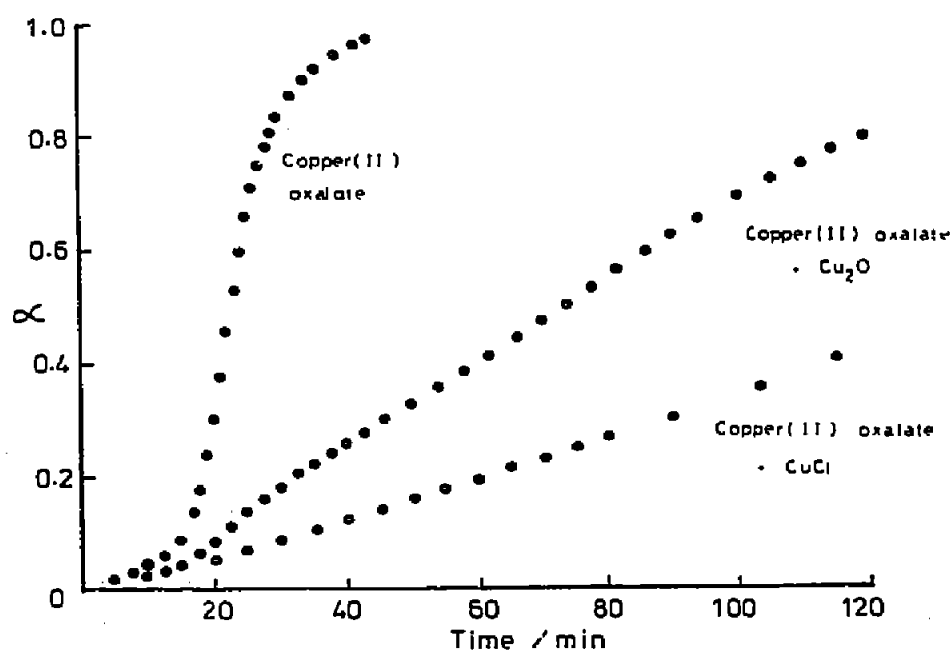


Fig. 6. The rate of decomposition of copper(II) oxalate at 540 K is significantly reduced by crushing in equimolar mixtures with Cu_2O or with CuCl .

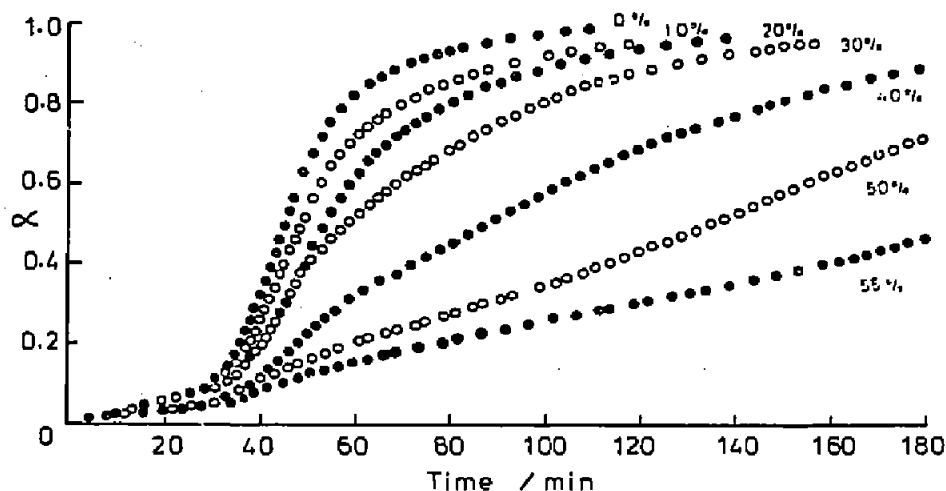


Fig. 7. Plots of α -time for the decomposition of copper(II) oxalate at 527 K mixed and crushed with the various added weights of Cu_2O ($\text{CuC}_2\text{O}_4 + (x \text{ wt.}\%) \text{Cu}_2\text{O}$). Progressive addition of oxide leads to a systematic reduction of decomposition rate.

obeyed the first-order equation. The changing pattern of kinetic behaviour with composition is usefully expressed through the variation in magnitudes of zero-order rate constants with composition shown in Fig. 8. The shapes of α -time curves when $x < 20\%$ resemble those of the pure salt, though rates reduce in direct proportion to the amount of additive present. When $20\% < x < 30\%$, there is a significant relative diminution of rate in the later stages and two rate processes can be distinguished. When $x > 30\%$, a single

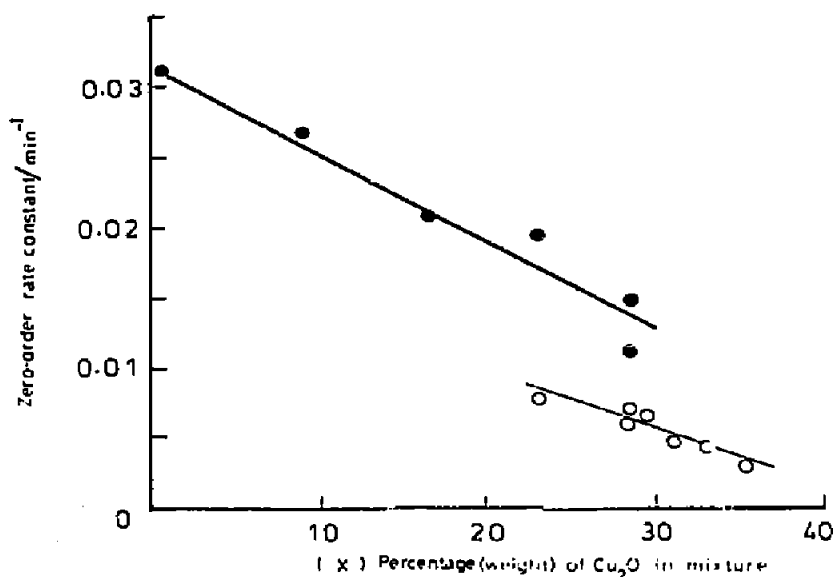


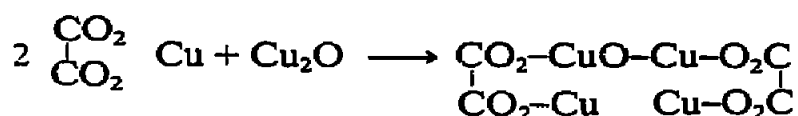
Fig. 8. Approximate zero-order rate constants for the median regions of copper(II) oxalate α -time curves at 527 K in Fig. 7, plotted against wt.% of added Cu_2O . Rates diminished progressively with proportion of oxide added and there was a discontinuous decrease close to the stoichiometric proportion ($x = 31\%$), though two values could be distinguished in the vicinity of this value.

slower reaction is identified: the stoichiometric mixture $\text{Cu}_2\text{O}:\text{CuC}_2\text{O}_4$ occurs at $x = 31\%$. In contrast, the incorporation of copper(II) oxide in crushed mixtures resulted in no appreciable change in the rate of copper(II) oxalate decomposition.

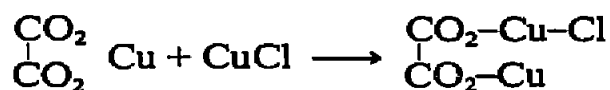
DISCUSSION

The marked reduction in rate of copper(II) oxalate decomposition when crushed with relatively large proportions of Cu_2O or CuCl suggests the facile completion of a chemical reaction between the components of the mixture. This change in reactivity is also consistent with the above conclusion that copper(II) oxalate undergoes breakdown involving at least partial fusion. Extensive reorganization of the components of the mixture is an essential prerequisite to the modifications required to generate substances that are somewhat more stable than the original reactant, CuC_2O_4 .

The systematic experiments with $(\text{CuC}_2\text{O}_4 + x\text{Cu}_2\text{O})$ mixtures, Fig. 7, show that there is some diminution in the decomposition rate at low values of x which can be attributed to an increase in the availability of Cu^+ in the mixture (Fig. 8, ●). At higher proportions of Cu_2O , however, the effective reduction in rate is appreciably greater (Fig. 8, ○). This may be ascribed to the formation of a more stable molecular grouping, one possibility is



Linkage of the Cu^{2+} ion to oxygen would reduce the ease of electron transfer and thus stabilize the salt. An analogous structure may be envisaged for reactions with CuCl



CONCLUSIONS

Probably the most significant mechanistic observation of the present study was the confirmation that copper(II) oxalate decomposition proceeds with stepwise cation reduction ($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$), as with other copper salts of carboxylic acids [5–8]. As previously observed, the second reaction was somewhat slower than the first [5].

Scanning electron microscopic observations were unable either to confirm or alternatively to exclude the possibility of melting during

reaction. There was, however, evidence of textural changes, at the limits of resolution, indicative of some mobility within the reacting material. The kinetic evidence provides support for the participation of fusion, through the observed obedience of data to the exponential law, confirmed more positively previously by the observations for copper(II) malonate decomposition [5]. The absence of any change in decomposition rate on salt crushing is again evidence that crystal size and perfection are not dominant features in controlling the breakdown rate of the present salt. Further observations supporting the intervention of melts, already discussed above, are the absence of an induction period in the reactions of oxalic acid with the copper oxides, the rates of established reactions being comparable with those for copper(II) oxalate. Copper(II) oxalate also reacted very readily on heating with Cu_2O or CuCl , leading to a reduction in the decomposition rate of the mixture.

The activation energy for the decomposition of copper(II) oxalate, $140 \pm 7 \text{ kJ mol}^{-1}$, gives a point that is on the line (dotted) for decompositions of divalent oxalates (see Fig. 6 of ref. 9). This relationship is based on the identification of the rate-limiting step as electron transfer [9]. The value for the decomposition of copper(I) oxalate is appreciably above this line.

There is a point of similarity between the decomposition of copper(II) oxalate and that of ferric oxalate, which we have recently studied [10], in that decomposition of ferric oxalate was also found to proceed through a cation reduction process ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$).

REFERENCES

- 1 M.E. Brown, D. Dollimore and A.K. Galway, *Comprehensive Chemical Kinetics*, Vol. 22, Elsevier, Amsterdam, 1980.
- 2 D. Dollimore and D.L. Griffiths, *J. Thermal Anal.*, 2 (1970) 229.
- 3 V.V. Boldyrev, I.S. Nev'Yantsev, Y.I. Mikhailov and E.F. Khairtdinov, *Kinet. Katal.*, 11 (1970) 367.
- 4 D. Dollimore, T.A. Evans and Y.F. Lee, *Thermochim Acta*, 194 (1992) 215.
- 5 N.J. Carr and A.K. Galway, *Proc. R. Soc. London Ser. A*, 404 (1986) 101.
- 6 N.J. Carr and A.K. Galway, *J. Chem. Soc., Faraday Trans 1*, 84 (1988) 1357.
- 7 A.K. Galway, M.A. Mohamed, S. Rajam and M.E. Brown, *J. Chem. Soc., Faraday Trans. 1*, 84 (1988) 1349.
- 8 A.K. Galway, D.M. Jamieson and M.E. Brown, *J. Phys. Chem.*, 78 (1974) 2664.
- 9 R.J. Acheson and A.K. Galway, *J. Chem. Soc. A*, (1967) 1167.
- 10 A.K. Galway and M.A. Mohamed, *Thermochim. Acta*, 213 (1993) 279.