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

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Abstract

The thermal decomposition of copper(II) mellitate proceeds to completion between 470 and 530 K

$C_6(CO_2)_6Cu_3 \rightarrow 5.5CO_2 + 0.03CO + [Cu_3C_{6.5}O_{1.0}]$

by two distinct rate processes. The first is acceleratory and fits the power law ($\alpha^{1/2} = kt$) to fractional reaction (α) = 0.45, during which the copper is extensively reduced ($Cu^{2+} \rightarrow Cu^{+}$); the activation energy is 155 ± 7 kJ mol^{-1}. The second reaction is strongly deceleratory, being expressed by the third order equation; the activation energy is 200 ± 15 kJ mol^{-1}. Textural changes during reactions have been characterized by scanning electron microscope examinations. The salt does not show evidence of melting.

The present work extends a previous investigation of the same reactant. Results here are discussed in the context of similar studies of copper(II) salts of other organic acids; all give evidence of stepwise cation reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) during the two consecutive reactions. It is concluded that, unlike other reactants in this comparison, the second step is not decomposition of copper(I) mellitate but involves a range of condensed aromatic anions. A short comparative survey is given of studies of the thermal decompositions of copper(II) salts of formic, oxalic, malonic, maleic, fumaric, squaric and mellitic acids.

INTRODUCTION

Studies of the thermal decompositions of a range of metal salts of mellitic acid were undertaken to compare kinetic characteristics with the thermal reactions of oxalates containing the same cations [1, 2]. The magnitudes of the calculated activation energies for the anion breakdown reactions of both mellitates and oxalates tended to increase with the enthalpy of formation of the oxide of the constituent metal. From this it was concluded [2] that the activation step in salt breakdown is the rupture of the ionic/covalent link

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between an oxygen of the carboxyl group and the metal ion. Salts of mellitic acid were selected for this comparative investigation because the anhydrous mellitates contain no hydrogen and, therefore, thermal reactions could be studied in the absence of complications arising through the participation of organic radicals in the reactant. It was also thought possible that the excess carbon in the anion $(C_{12}O_{12})^{6-}$ could reduce metal oxides in the product, perhaps inhibit the growth of metallic nuclei and influence the texture of the residual particles.

Recent investigations of the decompositions of copper(II) carboxylates have shown that, under the reducing conditions that apply during these reactions, salt breakdown proceeds through the stepwise reduction of the cation $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$. This common mechanistic feature has been previously demonstrated for the decompositions of copper(II) salts of formic [3], oxalic [4], malonic [5], maleic [6], fumaric [6] and squaric [7] acids. Because this possibility was not considered during the previous study [2] of the decomposition of copper(II) mellitate, we now considered it appropriate to make a more detailed investigation of this reaction. In the report of the earlier work it was noted that, "The characteristic [first order] behaviour observed for the decomposition of this salt was somewhat different from those which have been reported for other salts of this acid". We now find that the decomposition of copper(II) mellitate is not a single rate process, but in common with the other copper(II) salts of organic acids, proceeds with the intermediate formation of monovalent copper (Cu^{+}). We also show by scanning electron micrographs that this decomposition is not accompanied by comprehensive melting. We are aware of no previous study of this reaction, other than that already cited [2].

EXPERIMENTAL

Preparation of the reactant salt

Copper(II) mellitate was prepared, as previously [2], by mixing at 330 K solutions containing appropriate stoichiometric proportions of mellitic acid and basic copper(II) carbonate. The precipitate which formed was filtered and washed with a dilute solution of mellitic acid until the filtrate was acid. The solid product was washed with warm (330 K) water and dried in air. The present work used two similarly prepared samples of reactant.

The compositions of both preparations were virtually identical and agreed with expectation for the pentahydrate (theoretical elemental analysis for composition $Cu_3C_{12}O_{12} \cdot 5H_2O$ is shown in parentheses). C, 23.17% (23.36%); H, 1.61% (1.64%); Cu, 30.0% (30.9%); O (by difference), 30.3% (29.5%); mass loss after 3 h in vacuum at 430 K, 14.87% (14.60% expected for loss of $5H_2O$).

The water of crystallization in these salts is significantly less than that ($9.65H_2O$) of the previous reactant [2]. This is ascribed to the omission here of the exposure of salt to water vapour to complete hydration. The present low water content is not considered important because our work was exclusively concerned with the higher temperatures required to study anion breakdown. Dehydration results in extensive loss of crystal order and is expected to be completed before onset of decomposition.

Kinetic measurements

The kinetics of salt decomposition were studied from measurements of the gas pressure of the principal product, carbon dioxide, evolved in an initially evacuated conventional glass apparatus, previously described [5]. Reactant samples (40–50 mg, weighed ±0.2 mg) were evacuated ($<10^{-4}$ Torr) for 1 h before isolation from the pumps and introduction into the constant temperature (±0.7 K) reaction zone. Pressures of CO_2 evolved in the constant volume were recorded automatically at a prespecified time interval using a Baratron MKS 222B absolute pressure diaphragm gauge (0–10 Torr, read with an accuracy of ±0.001 Torr). A 178 K trap was maintained between heated reactant and gauge to condense evolved water. Pressure, time and temperature readings were stored in the memory of the controlling computer which included the facility of calculating values of the fractional reactions α (equal to p/p_f where p is the pressure at time t and p_f corresponds to completion of reaction) and other appropriate functions of α for testing fit to rate equations.

RESULTS AND DISCUSSION

Reaction stoichiometry

Decomposition of copper(II) mellitate was studied between 470 and 530 K and the gaseous yield was 5.5 ± 0.1 CO_2. Volatile products uncondensed at 78 K were always less than 1% of the CO_2 yield, confirming the absence of appreciable CO formation. The stoichiometric results are satisfactorily represented by

$$Cu_3C_{12}O_{12} \cdot 5H_2O \rightarrow 5H_2O + 5.5CO_2 + 0.03CO + [Cu_3C_{6.5}O_{1.0}]$$

The theoretical weight of the solid residue shown [square brackets] is 46.1%, which is in good agreement with the observations (47%). The carbon content of the residue (24%) is slightly below that expected (27.4%); this could be due to the formation of a small proportion of an unidentified volatile organic product. Oxygen retained in the solid products could be present as cuprous oxide (the ratio $Cu/Cu_2O = 0.85$ was previously reported [2]) or as an oxidized carbonaceous species.

Copper reduction

An important motivation for this work was to characterize the changes in oxidation state of the constituent copper during the progress of reaction.

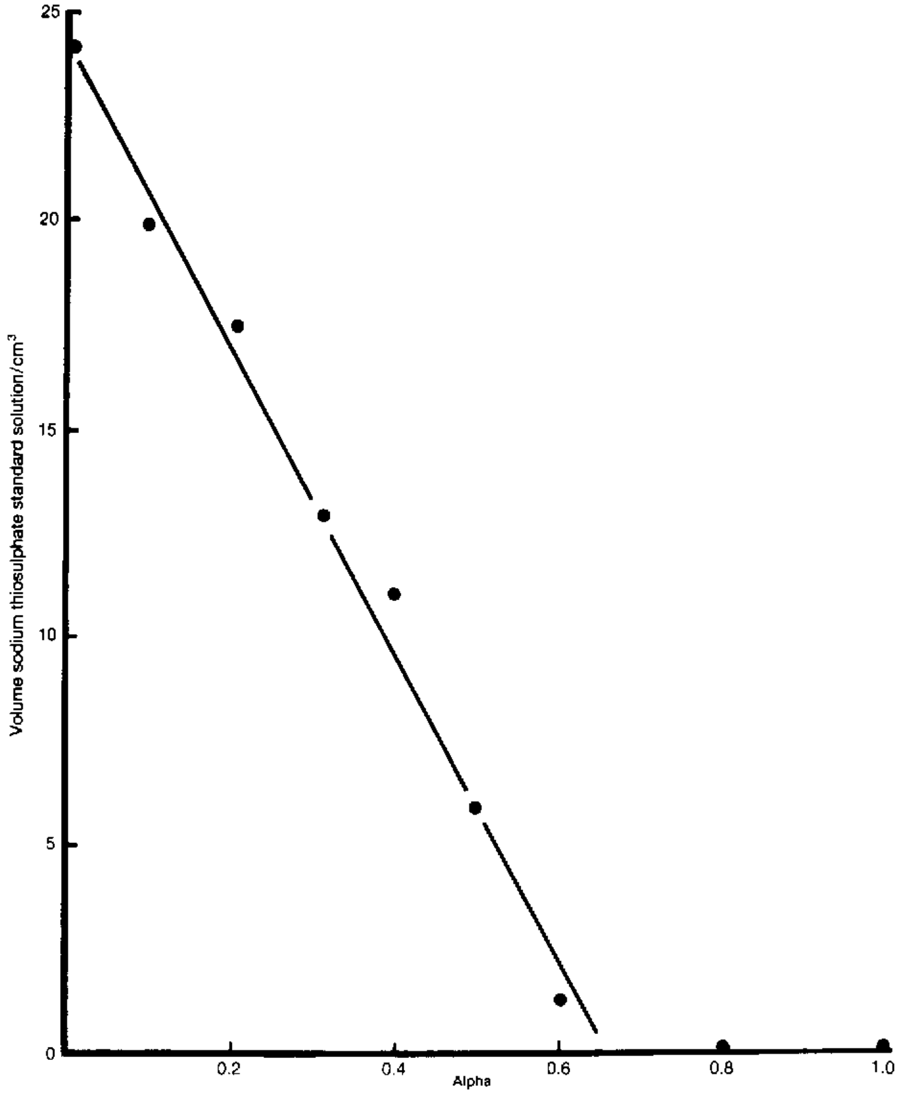


Fig. 1. The amount of Cu^{2+} remaining in partially decomposed samples of copper(II) mellitate diminished more rapidly than α, showing that copper(II) was reduced during the first rate process. The intercept is at $\alpha = 0.65$ due to some overlap with the second process. Amounts of Cu^{2+} were measured from the volume of standard sodium thiosulphate solution required (unit weight of reactant) [1] to titrate the iodine released on dissolving reacted samples to various α values in iodide solutions.

The Cu^{2+} contents of salt samples decomposed partially to various selected α values were measured from the amount of iodine released on dissolution in a solution of iodide by titration with standard sodium thiosulphate. The results shown in Fig. 1 show that the Cu^{2+} content of the salt diminishes more rapidly than α, being complete at $\alpha \approx 0.65$. This pattern was also found in the previous studies [4–7]. These results confirm that copper reduction proceeds in two steps $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$, identified as the intervention of the monovalent state.

Scanning electron microscopic observations

Specimens were examined using a Jeol 35 CF scanning electron microscope; crystals were lightly coated with Au/Pd before observations. Investigations included reactant, product ($\alpha = 1.00$) and salt decomposed to selected known α values and gently crushed after reaction to reveal internal textures. Only features that were both relevant and reproducible were photographed.

The prepared reactant was composed of crystals mainly of diameters 2–10 μm that were rounded, lens-shaped and extensively twinned. The typical appearance of this salt ($\alpha = 0.00$) is shown in Fig. 2. Salt decomposed to $\alpha < 0.20$ and salt only dehydrated were indistinguishable. Samples decomposed to various extents between $0.20 < \alpha < 0.47$ had undergone only slight textural changes that included surface roughening and some cracking that could be a result of crushing, see Fig. 3 ($\alpha = 0.35$).

The second stage of reaction was accompanied by extensive retexturing as shown in Fig. 4(a) and (b) ($\alpha = 0.75$). Textural appearances for salts reacted to $\alpha = 0.75$ and $\alpha = 1.00$ were closely similar. There was no evidence of

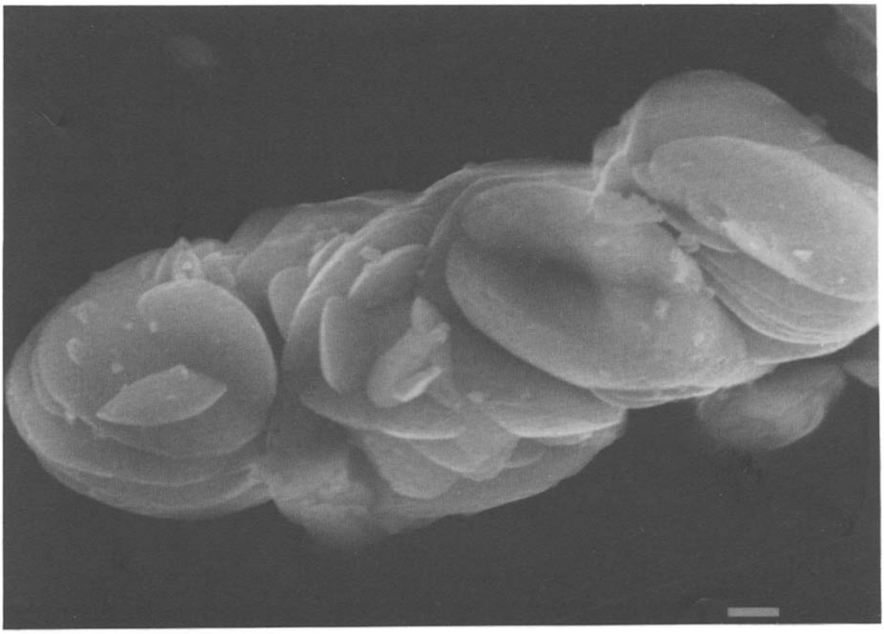


Fig. 2. Scanning electron micrograph (SEM) of prepared reactant crystals. These were lens-shaped, extensively twinned and diameters were mainly 2–10 μm. Scale bar, 1.0 μm.

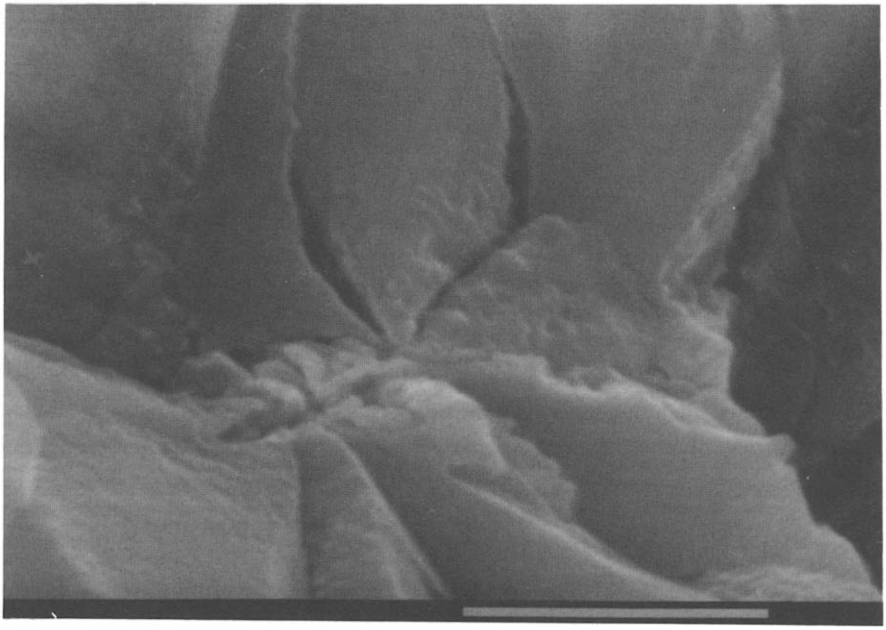
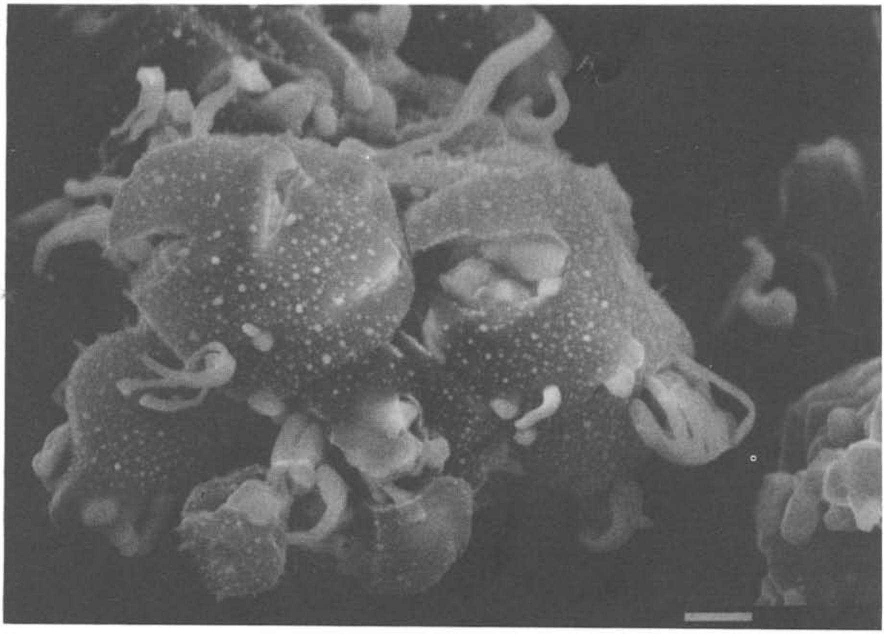


Fig. 3. SEM of copper(II) mellitate partially decomposed to $\alpha = 0.35$. Crystallite sizes and shapes had undergone little change during reaction except for some superficial roughening and cracking. Scale bar, 1.0 μm.

comprehensive or local melting of the reactant [5]. Each aggregate in Fig. 4 is recognized as a residual carbonaceous skeleton that has been derived from a reactant crystallite. The lighter coloured material is identified as copper metal and cuprous oxide. This aggregation of metal to form crystallites on carbon surfaces is similar to the behaviour observed during the decomposition of copper(II) malonate [5].

Reaction kinetics

The present isothermal kinetic studies of the thermal decomposition of copper(II) mellitate were completed between 470 and 530 K, which is significantly below the range of the previous work [2], about 520–558 K. Typical and representative α–time plots are shown in Fig. 5 from which it is seen that reaction proceeds to completion in two distinct rate processes. The first process is acceleratory throughout, to $\alpha = 0.45$–0.50, the extent increasing somewhat with reaction temperature. The rate diminished across a transition interval, during which the first process was completed and the second established. Subsequently this strongly deceleratory second process continued to the completion of reaction. Measurements of the product gas pressure corresponding to completion of decomposition required long intervals for the slower experiments and, sometimes, a final increase in reaction



(a)

(b)

Fig. 4(a) and (b). SEMs showing representative textures of reactant decomposed to $\alpha = 0.75$, the second rate process. Structures are identified, by comparison with copper(II) malonate [5], as copper metal aggregated as elongated crystallites dispersed on carbonaceous residual skeletons of the original reactant particles. Scale bars, 1.0 μm.

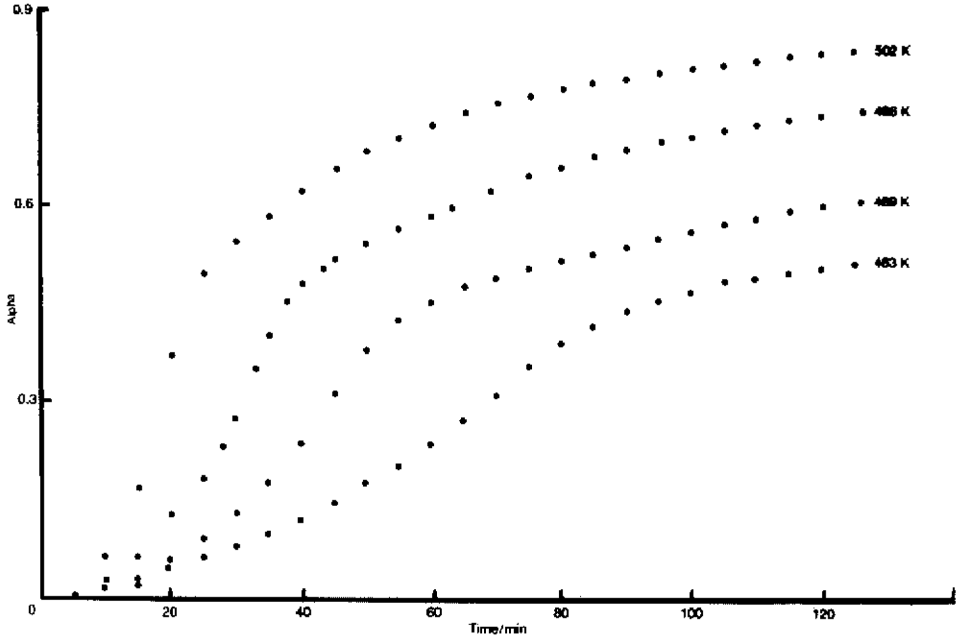


Fig. 5. Representative α–time plots for the isothermal decomposition of copper(II) mellitate. There is a significant diminution of reaction rate between $\alpha = 0.45$ and $\alpha = 0.50$.

temperature was necessary to measure p_f. Reactant predehydration resulted in no detectable change in the kinetic characteristics of the subsequent decomposition.

The first process

The kinetics of this reaction were very satisfactorily described by the square law ($\alpha^{1/2} = kt$ [8]): slopes of plots of $\log \alpha$ against $\log t$ were close to 2.0. This is confirmed by the linear plots of $\alpha^{1/2}$ against time, $0.01 < \alpha < 0.47$, in Fig. 6 for the same experiments as those shown in Fig. 5. There was no reaction induction period; all square law plots intercepted the time axis close to $t = 0$. The calculated activation energy E was 155 ± 7 kJ mol^{-1} and the pre-exponential factor A is given by $\log_{10}(A/\text{min}^{-1}) = 14.61$: these values are in excellent agreement with the Arrhenius parameters reported previously [2]: $E = 160$ kJ mol^{-1} and $\log_{10}(A/\text{min}^{-1}) = 14.57$.

The second process

This reaction was strongly deceleratory and data were well described by the third order equation $0.52 < \alpha < 0.85$. Representative plots, again for the experiments of Fig. 5, are shown in Fig. 7. The upper α limit for the fit to this equation was difficult to establish reliably because, with the strongly deceleratory character, the reaction became very slow during the final

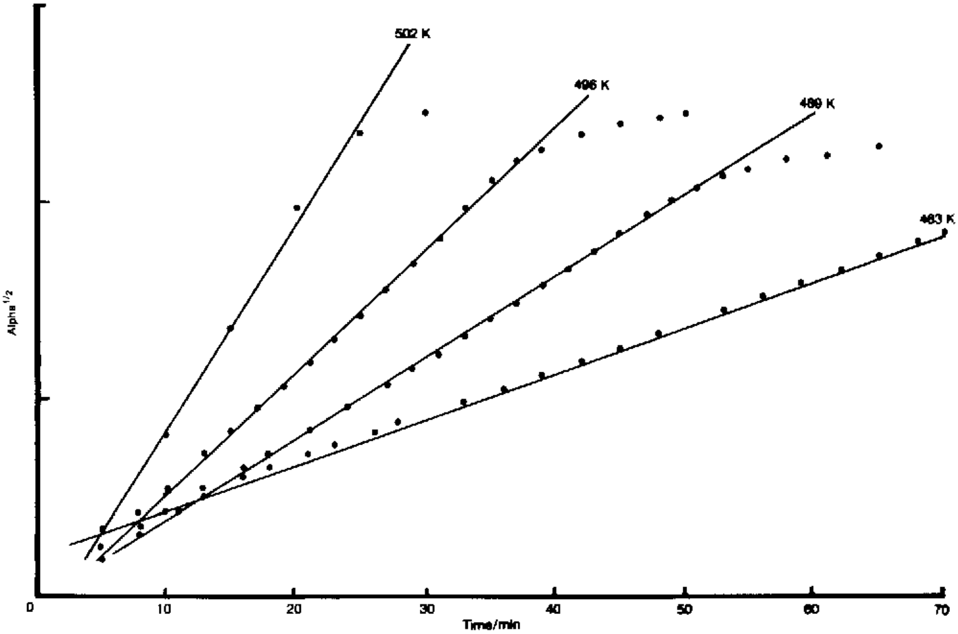


Fig. 6. Power law plots of $\alpha^{1/2}$ against time for the acceleratory first rate process for the same experiments as shown in Fig. 5.

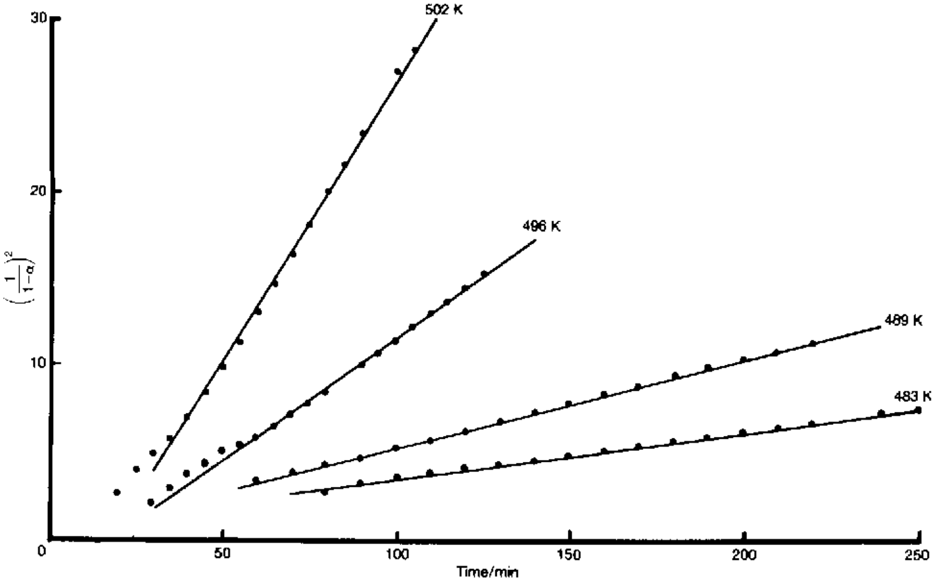


Fig. 7. Third order plots $(1-\alpha)^{-2}$ against time for the strongly deceleratory second rate process for the same experiments as shown in Fig. 5.

stages. The calculated values for the Arrhenius parameters were $E = 200 \pm 15$ kJ mol^{-1} and $\log_{10}(A/\text{min}^{-1}) = 19.50$.

Copper(I) mellitate

Attempts were made to prepare copper(I) mellitate by the reaction of Cu_2O with mellitic acid, following previous successful applications of this method [5, 6]. Rates of CO_2 evolution on heating this mixture under decomposition conditions were slower than the second process for copper(II) mellitate and exhibited different kinetic characteristics. This could be due to incomplete reaction because of acid anhydride formation rather than the metal salt under reaction conditions. Alternatively the product of the first reaction may not be predominantly copper(I) mellitate if decomposition of the copper(II) salt results in condensation between aromatic nuclei of partially decomposed anions. No useful results were obtained from these experiments.

The reaction mechanism

The most important new observation in the present work is the positive analytical evidence that reaction proceeds to completion in two steps, involving stepwise reduction of the cation, $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$. This explains the kinetic characteristics of Fig. 5, from which it is seen that reaction proceeds to completion in two distinct rate processes. The more rapid decomposition of copper(II) mellitate is effectively completed (Fig. 1) before onset of the relatively slower breakdown of the copper(I) salt. The final production of copper metal, distributed on the carbonaceous residue, explains the texture of the final product seen in Fig. 4.

The stepwise cation reduction is consistent with mechanistic conclusions from our studies of other copper(II) salts [3–7]. This feature was, however, missed in the previous work on copper(II) mellitate [2]. This resulted from the use of relatively high reaction temperatures to complete decomposition in a reasonable time and, in consequence, obscured the acceleratory character and, indeed, the separate identity of the first rate process. The present lower temperature experiments, made practicable by the largely automatic collection of kinetic data, permitted the prolonged experiments that are now shown to be capable of resolving the two distinct consecutive rate processes.

The first rate process

The acceleratory character of this reaction, continuing to $\alpha \geqslant 0.45$, is reminiscent of the kinetic behaviour of copper(II) malonate [5]. There were, however, significant differences here in that we were unable to obtain direct evidence of melting from the electron microscopic examinations and we could envisage no intermediate comparable with the acetate. The present rate process resulted in the conversion of about half of the anionic carboxyl groups ($C_6(CO_2^-)_6$) to CO_2 and copper reduction by reactions of the type

$$Ar{-}CO_2{-}Cu{-}CO_2{-}Ar \rightarrow Ar{-}CO_2{-}Cu + Ar^{\bullet} + CO_2$$

The aromatic residues (represented as $Ar^{\bullet}$) are ultimately incorporated into the carbonaceous component of the residue.

The acceleratory behaviour (Figs. 5 and 6) may be ascribed to decomposition within a reactant of increasing disorder in which reactivity is progressively enhanced with greater mobility of the participants. This modification is somewhat less than melting because of maintained bonding between the constituent multivalent anions. The kinetic fit to the square law may be a consequence of growth of decomposition zones expanding within a laminar lattice based on the predominantly planar anions. The magnitude of the activation energy is unchanged from that found previously (see fig. 6 in ref. 2).

The product of this first reaction is probably a polymeric matrix composed of condensed aromatic groups, derived from the anion and retaining a small proportion of the constituent oxygen. This is a stage in the progress towards the amorphous carbon/metallic copper mixture (Fig. 4) that is the final residual product. It is improbable that the intermediate is predominantly copper(I) mellitate. This explains the difference in kinetic characteristics between the present second rate process and the thermal reaction of the Cu_2O–mellitic acid mixture.

The second rate process

The retained carboxyl groups attached to condensed aromatic rings, possibly as a mixture of condensed anions represented as $Ar_{6-n}{-}C_6(CO_2Cu)_n$, are the reactant for the second rate process. The highly deceleratory reaction, third order kinetic behaviour (Figs. 5 and 7), can be ascribed to variations in reactivity within the different reactant group environments. Third order kinetics can be explained by a bimolecular interaction involving two ($-CO_2Cu$) groups within a vitreous phase in which the constituents become progressively less mobile and more widely separated as decomposition advances. The copper atoms released by reaction then aggregate as metal and Cu_2O crystallites dispersed on carbon. Strongly deceleratory reactions have been described for several mellitates [1, 2, 9]. Reactions obeying concentration-controlled rate equations are more familiar from homogeneous rate processes. Here reaction may be proceeding in a disorganized, perhaps vitreous, matrix involving various bonding structures between the multivalent constituent ions. Because the identity of the reactant here has not been characterized, the significance of the magnitude of the activation energy is not discussed [2].

Decompositions of copper(II) salts of selected organic acids

The series of studies of decompositions of copper(II) salts of organic acids [3–7], of which the present report is the latest, identify stepwise cation reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) as one important common mechanistic feature of reactions in this group. It is appropriate, therefore, to consider other features of these reactions to determine whether there are other similarities of behaviour. Interestingly the quantity of kinetic data, for consideration in this comparison, is effectively doubled in this set of two-step reactions. The relevant observations are summarized in Table 1; more detailed accounts of the individual reactions are given in the references cited. We are aware of no other reports for reactions of this type in which the intervention of a copper(I) salt has been described.

The first reaction: copper(II) salts

The acceleratory character of most of the first reactions listed in Table 1 was unexpected. The participation of copper metal in a nucleation and growth process is not possible in the early stages because copper(I) salts were formed and their rates of salt decompositions were relatively slower. It may also be noted that there was no evidence whatsoever that copper metal was catalytically active in promoting carboxyl group breakdown. The most probable explanation for the early rise in reaction rates is, therefore, an increase in reactivity resulting from loss in crystal order which, in the reaction of the malonate [5], results in intracrystalline melting. Thus, the intervention of local and temporary fusion, that cannot always be identified from scanning electron micrographs, is the most convincing explanation of the acceleratory character of these reactions. The decompositions of the most stable of the reactants in the present series, fumarate and squarate (studied from 530 to 600 K), contrasted with the other salts in being deceleratory and zero order respectively.

Reactions of this group showed appreciable variations of kinetic characteristics and of reactivity, as measured by the temperature ranges used for the similar rate studies. This shows that there is a significant influence of the constituent anion in controlling reactivity, although no structural features of the organic constituent could be correlated with the behaviour pattern observed (Table 1). We also note that the magnitudes of the activation energies do not systematically correlate with reaction temperature ranges. The only notable feature discerned was that the lowest values of E were for the anions containing the smallest numbers of carbon atoms (formate and oxalate).

The second reaction: copper(I) salts

The deceleratory character of these reactions contrasts with the predominantly acceleratory behaviour exhibited by the copper(II) salts. Data for several of these reactions (Table 1) fitted the first order equation, often to high α values (>0.95). We conclude, therefore, that reaction does not proceed by the catalytic breakdown of carboxylate groups at the surfaces of active product copper particles. The electron micrographs suggest that the

TABLE 1

Summary of kinetic results for decompositions of copper(II) salts of selected organic acids

Anion	Ref.	First reaction				Second reaction			
		Rate equation	Temp./K	α range	E/kJ mol^{-1}	Reaction order	Temp./K	α range	E/kJ mol^{-1}
Mellitate		$\alpha^{1/2}$	470–530	0.01–0.47	155	3rd	470–530	0.52–0.85	200
Oxalate	4	$\ln \alpha$	515–550	0.04–0.30	140	1st	515–550	0.24–0.91	180
Malonate	5	$\ln \alpha$	486–505	0.07–0.48	200	1st	477–528	0.65–0.97	188
Maleate	6	$\ln(\alpha/(1-\alpha))$	473–508	0.07–0.61	225	1st	509–528	>0.65	139
Fumarate	6	$\ln(1-\alpha)$	533–597	0.12–0.40	167	1st	576–620	0.54–0.96	205
Squarate	7	Zero order	530–590	0.04–0.32	150	1st	593–670	0.75–0.96	210
Formate	3	$\alpha^{1/n}$	440–480	0.02–0.30	115	$(1-\alpha)^{1/n}$	440–480	0.4–0.9	130

product metal aggregates as crystallites distributed across the residual carbonaceous material. The first order behaviour may be ascribed to reactant concentration, involving the breakdown of the individual (–CO_2Cu) groups distributed within the reactant matrix. This is consistent with the small range of activation energy values (most were between 180 and 210 kJ mol^{-1}). Exceptions to this pattern are as follows. (i) The maleate ion isomerizes to fumarate at reaction temperature, see ref. 6 for a discussion of these reactions. (ii) Decomposition of the formate involved volatilization of copper(I) salt. (iii) The mellitate, where the third order equation was obeyed.

Copper mellitate, second reaction

This unique (Table 1) third order behaviour is ascribed to a mechanism of mellitate ion breakdown that contrasts with the formation of copper(I) salts believed to occur with most of the other anions. It seems more probable that decomposition here will result in a range of condensed aromatic anions that contain, on average, about 3(–CO_2Cu). The overall strongly deceleratory character of the reaction may, therefore, be a consequence of the concurrent decompositions of different salts of a range of different reactivities within this composite reactant mixture. An alternative explanation of the third order behaviour is that decomposition follows bimolecular interaction of two (–CO_2Cu) groups in a matrix that permits some mobility of the constituents. It is clear that the second reaction in copper(II) mellitate decomposition differs in at least one important respect from the reactions of these (Table 1) other copper(II) salts.

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