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A MECHANISTIC INVESTIGATION OF THE REACTION BETWEEN COPPER(II) MALONATE AND COPPER(II) BROMIDE

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ABSTRACT

The temperature at which copper(II) malonate decomposes is significantly reduced in crushed mixtures containing excess $CuBr_2$. From kinetic and stoichiometric comparisons it was shown that in this process each mole of copper(II) malonate reacted required 3.5 ∓ 0.5 moles $CuBr_2$. Decomposition of any excess carboxylate, remaining in such mixtures, was not influenced by the relatively rapid initial reaction.

The present reaction can be partially represented as follows

$$CH_2(COO)_2Cu + 4CuBr_2 \rightarrow 5CuBr + 1.5CO_2 + Br_2 + HBr$$

together with a (probably polymeric) carbonaceous constituent of the residue. Isothermal CO_2 evolution exhibited a sigmoid shaped CO_2 yield–time curve. This is ascribed to increasing ease of reaction in a reactant phase of increasing mobility, perhaps with local or temporary melting or the generation of a relatively reactive intermediate. The rate subsequently diminishes as the amount of reactant remaining diminishes. A reaction mechanism is proposed in which an essential step is

$$CH_2(COO)_2Cu + CuBr_2 \rightarrow CH_2(COOCuBr)_2$$

followed by decomposition of the relatively more reactive bromo salt. This constituent bromide is identified as facilitating the electron transfer steps culminating in carboxylate group breakdown, a role similar to, but more effective than, that of acetate in the autocatalytic decomposition of pure copper(II) malonate.

INTRODUCTION

In a recent mechanistic study [1] of the thermal decomposition of copper(II) malonate, kinetic data were interpreted in the context of complementary microscopic and analytical observations. It was concluded that the distorted sigmoid shape of the isothermal fractional reaction α–time curve was due to a two-process overall reaction proceeding through stepwise cation reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$). The proposed mechanism is discussed in detail elsewhere [1]. The following abbreviated account is given to

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provide the background information necessary to introduce the present study of the reaction of copper(II) malonate in binary mixtures with copper(II) halides, and in particular copper(II) bromide.

The distorted sigmoid shaped α–time curve for the reaction of copper(II) malonate could not be satisfactorily correlated quantitatively with rate equations applicable to solid decompositions, often identified [2,3] with this pattern of kinetic behaviour. Moreover, microscopic observations gave no evidence that this was a nucleation and growth process [2,3]. The progressive froth-like development during the first reaction, however, was entirely consistent with gas evolution within a viscous melt in which bubble shape was controlled by surface tension. The acceleratory period, during this first reaction, was identified as an autocatalytic process in which acetate product promoted copper(II) malonate decomposition and this was accompanied by local melt formation. On completion of the first reaction, at $\alpha = 0.55$, the reactant contained no Cu^{2+}, and the slower and deceleratory second reaction is identified as the first order breakdown of copper(I) malonate. These conclusions were based on a consideration of the kinetic observations in the context of microscopic investigations of the concurrent textural changes together with analytical measurements of concentrations of intermediates participating in the chemical changes occurring.

A similar experimental approach was used in the present study, which was principally concerned with an investigation of the strong promotional effect exerted by copper(II) bromide and, to a lesser extent, by copper(II) chloride [4] on the decomposition of copper(II) malonate. Kinetic data were interpreted with a due regard for the chemistry of the possible intermediate but the microscopic investigations were less effective than in the study [1] of the pure salt.

EXPERIMENTAL

Experimental techniques were identical with those already described [1], since the present study effectively constitutes a continuation of the earlier work. All kinetic data were obtained from isothermal experiments during which the reactant temperature was maintained constant ∓ 1 K, and samples were evacuated to ca. 10^{-5} Torr for 2 h before reaction. All rate studies were obtained from pressure measurements in the glass apparatus using a 175 K refrigerant trap between the heated reactant and gauge. (The automatic data-recording equipment [1] was not used here because of the risk that evolved halogen could damage the metal diaphragm.)

Reactants

The previous study showed [1] that the kinetic characteristics of the decompositions of several preparations of copper(II) malonate were effectively identical. In the present work the same preparations were again used so that quantitative comparisons could be made between the rates of reaction of the prepared salt and in mixtures with copper(II) bromide. Reactant mixtures were prepared from known weights of each salt; $CuBr_2$ was dried and copper(II) malonate was usually dehydrated, and these were crushed together in a pestle and mortar.

Comparisons specified below refer to molar ratios of the anhydrous salts, $CH_2(COO)_2Cu:CuBr_2$. Comparative kinetic studies were always based on data obtained for reactants from a single batch, stored in a desiccator. Slight differences in reactivity were found between mixtures apparently prepared identically, which presumably result from variations in the effectiveness of the crushing and/or mixing procedure.

Other reactants investigated are described at appropriate places in the text below.

RESULTS AND DISCUSSION

The decomposition of copper(II) malonate + copper(II) bromide mixtures

Reaction stoichiometry

The addition of $CuBr_2$ to copper(II) malonate resulted in a much enhanced rate of decomposition. The extent of this rapid reaction was, however, much less than the molar proportion of halide added. Each mole of anhydrous $CH_2(COO)_2Cu$ decomposed required 3.5 ∓ 0.5 moles of $CuBr_2$. The addition of $CuBr_2$ did not, however, significantly change the yield of CO_2 from copper(II) malonate decomposition and the relative proportion of CO in the volatile products remained small (ca. 2%).

NMR analyses of solutions of anions derived from partially decomposed $CH_2(COO)_2Cu:CuBr_2$ mixtures (after removal [1] of dissolved copper and residuals) detected unreacted malonate but there was never any evidence that bromoacetate was produced. Acetate was detected during the decomposition of mixtures that contained smaller proportions of $CuBr_2$ and was an intermediate in copper(II) malonate decomposition [1].

Chemical analysis of the residual mixtures remaining after completion of the initial rapid reaction showed that only about half of the bromide originally present was retained in the solid. This suggests $CuBr_2$ reduction to CuBr. Bromine release during reaction was indicated by the formation of a red-brown condensate in the cold trap. Dissolution of the volatilized products of decomposition from mixtures containing excess $CuBr_2$ (1 : 5 molar ratio) in KI solution, followed by $Na_2S_2O_3$ titration, showed that 20–25% of the bromide originally present was oxidized to Br_2 during reaction. Titrations of aqueous solutions of the acid released during reaction showed that a smaller proportion of the bromide, ca. 10%, was converted to HBr. This was confirmed by the appearance of the characteristic cream-like precipitate on addition of $AgNO_3$ to these solutions.

These determinations of Br_2 and HBr yields were somewhat variable so that a precise determination of the reaction stoichiometry could not be achieved. However, the available data, together with the confirmation by mass spectrometry that Br_2, HBr and CO_2 were the principal volatile products, demonstrate that the overall reaction can be approximately represented as follows

$$CH_2(COO)_2Cu + 4CuBr_2 \rightarrow 5CuBr + 1.5CO_2 + Br_2 + HBr$$
$$+ [C_{1.5}, H_{1.0}, O_{1.0}]$$

where the elements in square brackets are probably a polymeric material retained in the residue [1].

Electron microscopy

Several reactant samples, decomposed to various known extents, and portions of which were lightly crushed to expose internal structures, were examined under a scanning electron microscope. The procedure was similar to that used previously [1]. However, after careful examination of many samples, we were unable to discern any recognizable pattern of textural change attributable to the occurrence of decomposition. Features characteristic of dehydrated copper(II) malonate and of unreacted $CuBr_2$ were identified. External crystal surfaces and faces exposed by fracture during crushing of the various reacted materials showed some variations of structure within each specimen but the differences between mixtures, reacted to different extents, were not sufficient to provide evidence of systematic textural changes during the course of reaction. Thus, from the microscopic work we were unable to obtain observational evidence that could be used to elucidate the mechanism of this reaction.

Kinetic measurements

The addition of $CuBr_2$ to copper(II) malonate resulted in the occurrence of a rapid initial reaction that was not observed during the decomposition of the pure salt. This was not a catalytic process since both participants underwent chemical change. Moreover a large excess of the additive was required to result in complete decomposition of the carboxylate, through the alternative reaction. To obtain satisfactory kinetic data for this different rate process, studies were undertaken in a lower temperature range, 383–433 K, than that investigated for the pure salt, ca. > 460 K. When mixtures contained insufficient $CuBr_2$ to result in complete reaction, this rapid rate process was followed by the slower decomposition characteristic of pure copper(II) malonate. The following paragraphs report the observed kinetic characteristics for the decompositions of various crushed powder mixtures, expressed as molar proportions. (Salt A was dehydrated copper(II) malonate, $CH_2(COO)_2Cu$.)

Salt A: $CuBr_2$ (1.00:0.085). This mixture was used to investigate the influence of the initially rapid, but limited (completed at ca. $\alpha = 0.03$), rate process on the subsequent decomposition of salt A at 473 and 483 K. Following the reaction with $CuBr_2$, completed in < 5 min, there followed a slow, linear evolution of gas, identical in rate and extent to the initial reaction of the pure salt. Thereafter, the acceleratory process was indistinguishable from that characteristic [1] of the decomposition of pure salt A, except that subtraction of a proportionally larger value of α_1 was required to obtain correlation with the exponential equation. Rate constants, and range of fit of kinetic expressions were, within experimental error, in excellent agreement with observations [1] for pure copper(II) malonate. Identical behaviour was observed for reactions of several other prepared mixtures containing low proportions of $CuBr_2$. It is concluded, therefore, that the reaction between salt A and $CuBr_2$, and the presence of products from this reaction, exerted no perceptible influence on the subsequent decomposition of copper(II) malonate.

Salt A: $CuBr_2$ (1.00:0.152). The initial reaction of this mixture was (again) of limited extent, being completed at ca. $\alpha = 0.04$. The difficulties encountered in obtaining sufficiently effective mixing to give satisfactorily reproducible kinetic data are exemplified in Fig. 1 which shows the sigmoid-shaped α–time curves for decompositions at different temperatures using samples from a single preparation. Since data did not fit rate expressions characteristic [2] of solid decompositions, it is considered probable that the initial acceleratory phase of this reaction may be due to diffusive mixing of the reactants. The apparent activation energy ($\alpha < 0.04$) was 105 ∓ 8 kJ mol^{-1}, between 383–440 K. The subsequent linear phase of the continued decomposition ($0.04 < \alpha < 0.08$) gave rate constants which were identical with those measured [1] for the initial reaction of the pure salt. Again it was evident that decomposition, after the rapid reaction characteristic of the mixture, is entirely independent of the additive and indistinguishable from that of pure copper(II) malonate.

Salt A: $CuBr_2$(1.00:2.00). Two representative α–time curves for reactions of the same mixture at different temperatures are shown in Fig. 2. These data did not fit any rate equation characteristic [2] of solid state reactions and kinetic behaviour appeared to consist of two distinct processes. The initial, slightly acceleratory, evolution of gas obeyed the power law, $\alpha = (kt)^2$, and can be ascribed to a reaction following the increasingly facile mixing of the two reactants during the initial onset of the chemical change. This process is terminated, or overtaken, by the onset of rapid (bromide–malonate) decomposition that was completed at ca. $\alpha = 0.55$. This reaction was linear in the median region and subsequently became deceleratory.

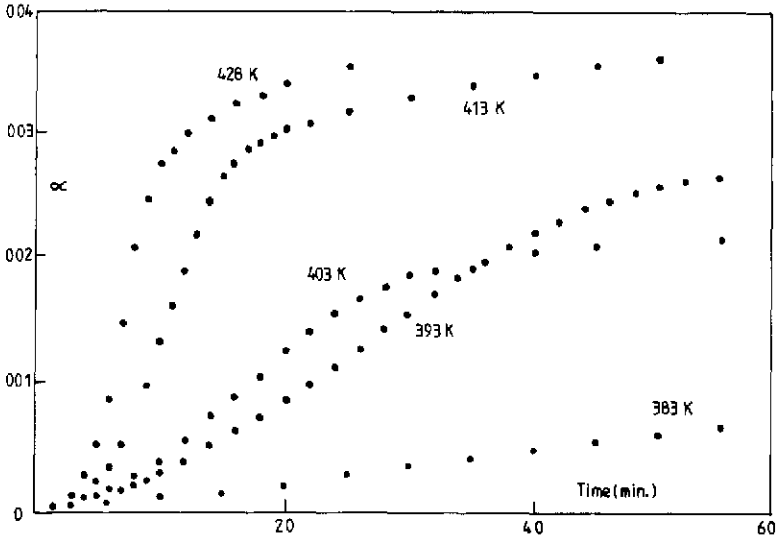


Fig. 1. Typical sigmoid shaped curves for the initial, limited stage of rapid reaction during decomposition of a salt A:$CuBr_2$ (mole ratio 1.00:0.152) crushed mixture at various temperatures. Although samples were from a single preparation, different experiments showed variations in the final yield which accounted for only a small proportion of the total reaction.

Salt A: $CuBr_2$ (1.00:6.45). Decomposition of this additive-rich mixture proceeded almost to completion ($\alpha > 0.90$) by a single sigmoid-shaped α–time curve that approximately obeyed the Prout–Tompkins expression [2]. This obedience was not, however, entirely satisfactory and behaviour was interpreted as arising from progressively increasing ease of diffusive mixing during the early stages leading, after a period of an approximately constant reaction rate, to first order behaviour as the amount of reactant

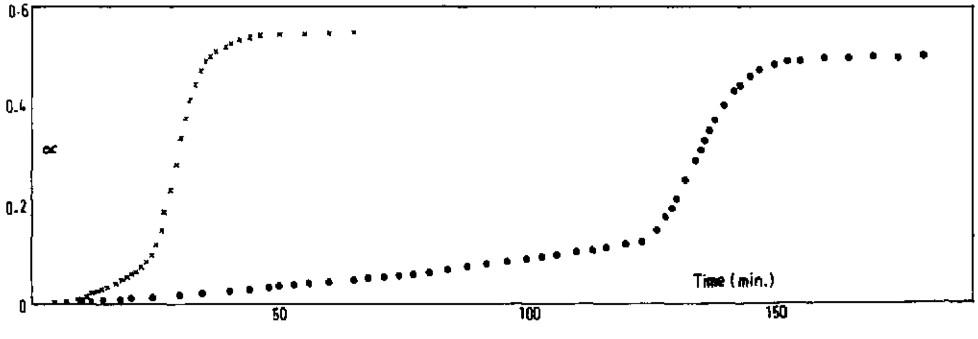


Fig. 2. Representative α–time curves for the decomposition of two samples from the same salt A:$CuBr_2$ (mole ratio 1.00:2.00) crushed mixture at 398 and 413 K. The marked difference in induction period is identified with the onset of reactant mixing followed by more rapid reaction once precursor mobility has been achieved.

remaining was reduced. Rates during the approximately linear intermediate region, $0.15 < \alpha < 0.6$, were in good agreement with those measured for mixtures containing smaller proportions of $CuBr_2$.

This rate process did not include a marked diminution in rate at about the half-way stage, an important feature of the decomposition of pure copper(II) malonate [1]. This confirms the conclusion that participation by $CuBr_2$ modifies the overall reaction mechanism. This is also evidence that the availability of excess Cu^{2+} in these mixtures ensures that, during the later stages of decomposition, malonate ion breakdown does not require the intervention of the less reactive Cu^+ salt and this ion accumulates in the product CuBr.

Salt A: copper(I) bromide. Decomposition of copper(II) malonate + copper(I) bromide (1.00:0.70) crushed mixtures between 473–493 K gave no detectable initial rapid reaction, indeed, kinetic characteristics were indistinguishable from those of pure salt A. (A similar proportion of $CuBr_2$ resulted in a rapid reaction to ca. $\alpha = 0.2$.) This confirms that CuBr does not participate in the alternative reaction and that its presence, as a product from the reaction in mixtures containing $CuBr_2$, does not influence the subsequent decomposition of pure copper(II) malonate.

Malonic acid + copper(II) bromide. On heating mixtures of malonic acid and copper(II) bromide (1.00:1.00) at 398 K, the rate of CO_2 evolution was similar to that characteristic of salt A + $CuBr_2$ mixtures. The principal difference was the absence of the prolonged initial slow process, characteristic of the salt A-containing mixture (120 min at 398 K, see Fig. 2). Thereafter, the rates of decomposition of both mixtures were comparable, from $\alpha = 0.1$ to $\alpha = 0.4$ in 10–15 min at 398 K, with the acid-containing mixtures reacting slightly more rapidly. About half of the total product yield of CO_2 was released in this low temperature process, a further, equal volume was evolved on heating within the copper(II) malonate decomposition range.

From the close similarity of decomposition rates of both mixtures (salt A or $CuBr_2$ crushed with malonic acid) it was concluded that both reactions proceed through breakdown of the same reactive participant. The formation of this intermediate is initially slower in the salt A-containing reactant where the solid reactants may require diffusive mixing. In contrast, malonic acid melts at ca. 400 K and may interact more readily with $CuBr_2$ to yield the same reactive (and perhaps molten) intermediate, which is probably $CH_2(COOCuBr)_2$, which subsequently decomposes.

Reactions of these malonic acid : $CuBr_2$ mixtures resulted in the volatilization of about 40% of the acid component, measured by titration of the white deposit formed at the edge of the heated zone during decomposition. A proportion of the residual product ($\alpha = 1.0$) was insoluble and was identified as CuBr from the measured (volatile products and deposit) weight loss during reaction and consideration of the stoichiometry of the products characterized.

Reactivities of possible reaction intermediates

A possible mechanism whereby carboxylate breakdown in the presence of added bromide could proceed more rapidly than that of the pure salt alone is through incorporation of bromine into the anion, thereby producing a more reactive intermediate. To determine the reactivity of appropriate copper salts, copper(II) bromomalonate and copper(II) bromoacetate were prepared and their decomposition characteristics compared with those of the pure copper(II) malonate and its mixtures with $CuBr_2$.

Copper(II) monobromomalonate. Monobromomalonic acid was prepared by adding the calculated amount of bromine to a solution of malonic acid in ether [5]. The solvent was evaporated and the product dried in a vacuum. This acid was then dissolved in water at 320 K and the appropriate amount of basic copper(II) carbonate added slowly with stirring. No precipitate formed, but a solid crystalline substance separated as water was removed in a stream of air at ambient temperature. Elemental analysis of this product agreed well with theoretical expectation for $BrCH(COO)_2Cu \cdot 2H_2O$.

The thermal decomposition of this salt was a strongly deceleratory process at 490 K. There was no induction period, reaction was relatively rapid to ca. $\alpha = 0.15$ and thereafter the rate progressively diminished. There was no discontinuous diminution in rate at the half-way stage. The kinetics of the initial reaction were studied in the lower temperature interval, 410–430 K, and it was found that the onset of strongly deceleratory behaviour occurred at progressively lower α values as the reaction temperature was reduced, being $\alpha = 0.1$ at 410 K.

Mass spectrometric analyses of the volatile reaction products gave the largest response for CO_2, with smaller amounts of CO and many larger mass fragments were detected. No acetate, nor indeed any other anion was identified by NMR analyses of copper-free [1] solutions of partially reacted salt.

This pattern of behaviour is, therefore, quite different from the decomposition of copper(II) malonate + copper(II) bromide mixtures and monobromomalonate anion intervention cannot be regarded as an acceptable reaction intermediate.

Copper(II) monobromoacetate. This salt was prepared by the slow addition, with constant stirring, of the calculated quantity of basic copper(II) carbonate to an aqueous solution of monobromoacetic acid. The filtered solution was evaporated to dryness and the composition of the residual product agreed well with theoretical expectation for $(BrCH_2COO)_2Cu \cdot H_2O$

Kinetic studies showed that the rate of decomposition became appreciable above 480 K and that this was accompanied by sublimation. Kinetic data were unsatisfactory because the CO_2 yield was well below that expected from the breakdown of the constituent carboxyl groups of the reactant. It was also shown that this compound did not promote the breakdown of pure copper(II) malonate below 480 K.

The mass spectrum of the volatile products of reaction of this salt was very similar to that of the acid, $BrCH_2COOH$. The yield of CO_2 was low and responses were found at the *m/e* ratios characteristic of the acid, $BrCH_3$, HBr, Br etc. The DSC response trace for the decomposition of copper(II) monobromoacetate included an endotherm at 445–458 K, attributable to dehydration, and a decomposition exotherm above 515 K.

This pattern of behaviour is quite different from that observed for salt $A + CuBr_2$ mixtures and, therefore, we conclude that $(BrCH_2COO)_2Cu$ is not an intermediate in this reaction.

The decomposition of copper(II) malonate and copper(II) chloride mixtures

Copper(II) malonate decomposed more readily in crushed mixtures with $CuCl_2$, than in the reaction of the pure salt, but the effect of this additive was very much less than that of $CuBr_2$. The magnitude of the promotional effect here was, however, difficult to express quantitatively, since kinetic behaviour was different from that of the pure salt. The best estimate indicated that the rate was increased by about fourfold for a salt $A : CuCl_2$ (1.0:1.0) mixture, compared with the reaction of pure salt A. α–Time curves

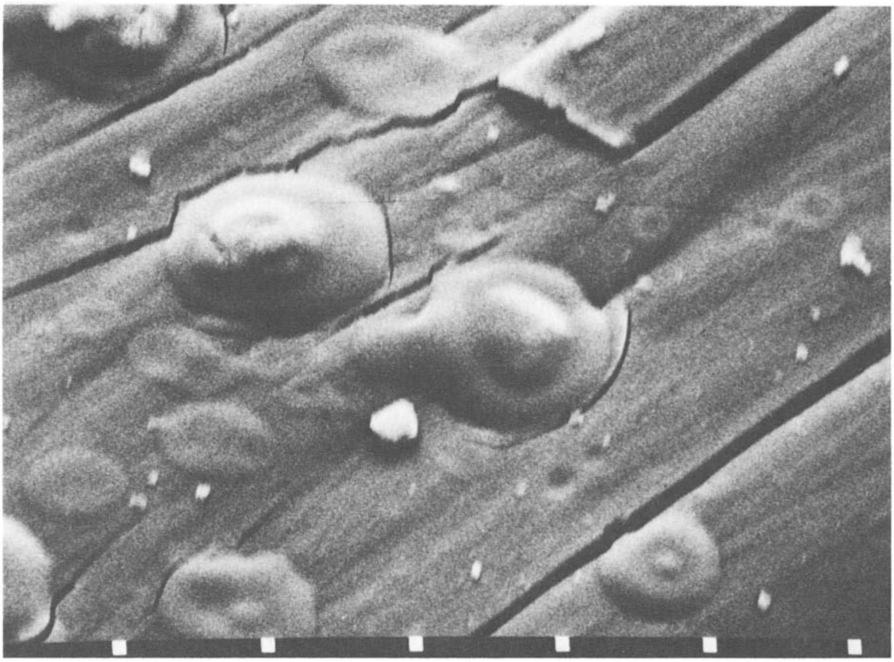


Fig. 3. After heating for 25 min at 400 K, somewhat below reaction temperature, copper(II) chloride particles had evidently fused into the surfaces of the larger copper(II) malonate crystals in this mixture. Scanning electron micrograph: spacing between scale units at lower edge of photograph 10 μm (see also Plate 5, ref. 4).

were sigmoid shaped, extending to $\alpha = 0.90$. The acceleratory behaviour was less pronounced than that of the pure salt and in the median region, the reaction rate was approximately constant. The extension of the first reaction is ascribed to the increased availability of Cu^{2+} in these reactant mixtures [1].

Scanning electron microscopic examinations of the surfaces of crystals soon after the initiation of reaction gave strong evidence, as in Fig. 3 (see also Plate 5 in ref. 4) that small crystals of $CuCl_2$ fused into the surfaces of larger copper(II) malonate crystals. The latter exhibit the parallel crack development characteristic of the dehydrated reactant [1]. These rounded features were not present during the decomposition of copper(II) malonate, nor in partly reacted salt A + $CuBr_2$ mixtures, and are attributed to mixed melt formation along the salt A/$CuCl_2$ contacts.

Other reactions

Qualitative experiments (undertaken for reasons discussed below) showed that $CuBr_2$ reacted with dibromomethane at 400 K with the evolution of bromine gas. Thus it is concluded that a residual bromo-hydrocarbon product, or the component brominated methylene group of the anion in copper(II) malonate may interact with $CuBr_2$ under reaction conditions to yield the bromine and/or hydrogen bromide found in the products.

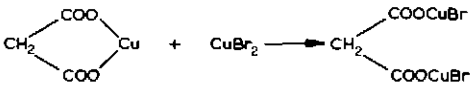
A parallel experiment showed that $CHCl_3$ did not release Cl_2 on contact with $CuCl_2$ at 490 K. This is consistent with the lower reactivity of $CuCl_2$ in promoting copper(II) malonate decomposition.

Reaction mechanism

The principal observations of the present study were that $CuBr_2$ reacts with copper(II) malonate at a temperature significantly below that of the decomposition of the pure salt and that kinetic characteristics of both reactions were different. The present observations are explained by the following reaction mechanism which, unfortunately, did not include microscopic characterization of the textural changes that accompanied the reaction.

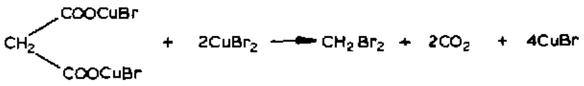
On heating, the initially solid reactants undergo slow diffusive mixing at temperatures above ca. 390 K, accompanied by some CO_2 release, attributable to carboxylate group breakdown. This slow stage was absent from reactions of $CuBr_2$ with malonic acid, which is molten at the reaction temperature. The rapid reaction may therefore be attributed to salt breakdown in a more mobile reactant matrix, perhaps including retained products. This behaviour is indicated by the approximate obedience to the Prout–Tompkins equation [2] by the reaction of the salt A : $CuBr_2$ mixture.

This enhanced mobility within the reaction matrix may be due to progressive mixing of the reactants but may also include intermediates and products. It has been shown above that CH_2Br_2 reacts with $CuBr_2$ under the reaction conditions and the increasing involvement of fluids must be considered probable as the reaction progresses. The effective participation of bromine-containing organic compounds, derived from the methylene group of the anion, contributing to the mobile reaction medium and undergoing secondary reactions explains two important aspects of the observed behaviour. Firstly, CH_2Br_2 was shown to react with $CuBr_2$ at a decomposition temperature well below the temperature that the interaction between $CHCl_3$ and $CuCl_2$ could be detected. This parallels the activities of both copper halides in promoting copper(II) malonate breakdown. Secondly, the formation of bromine-containing organic compounds accounts for the relatively large stoichiometric proportion of $CuBr_2$ required in the reaction. Condensed organic products possibly contribute to a fluid, even including condensed liquid, reaction medium in which the chemical changes proceeded. The long induction period could reflect the time necessary for this to develop. Possible steps in the reaction may then be represented [6]



(a)

this intermediate reacts further with $CuBr_2$ as follows



$CH_2(COOCuBr)_2 + 2CuBr_2 \rightarrow CH_2Br_2 + 2CO_2 + 4CuBr$

(b)

CH_2Br_2 (and/or related compounds) reacts with $CuBr_2$ to yield Br_2 and HBr, both of which we have shown to be present as reaction products as well as other unidentified products. CuBr does not participate further in the reaction nor, indeed, does it influence the decomposition of copper(II) malonate. Alternative mechanisms, involving the intermediates $BrCH(COO)_2Cu$ or $(BrCH_2COO)_2Cu$ were discounted. These intermediates were not detected in the partially reacted salt and their reactivities and decomposition characteristics were shown to be insufficient to explain the rapid salt A : $CuBr_2$ reaction.

The mechanism described above assumes that the reactivity of copper bromomalonate, $CH_2(COOCuBr)_2$, is greater than the malonate. Two possible reasons may be advanced to explain this increased lability, both of which are consistent with the proposed [1] role of acetate in decomposition of pure copper(II) malonate. Firstly, the enhancement of mobility, perhaps extending to local melting, permits freedom for the reactant to adopt the configuration most favourable to decomposition and relaxes the constraints resulting from the structure of the solid carboxylate. Secondly, we identify the bromine or $[CuBr]^+$ group as a more effective electron donor than the acetate, so facilitating the electron redistribution steps discussed previously [1]. The present proposals are entirely consistent with the conclusions concerning the mechanism of decomposition of copper(II) malonate and, indeed, extend the scope of this work.

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REFERENCES

1 N.J. Carr and A.K. Galwey, Proc. R. Soc. (London), Ser. A, 404 (1986) 101.
2 M.E. Brown, D. Dollimore and A.K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
3 A.K. Galwey, Proc. 7th Int. Conf. Therm. Anal., Wiley, New York, 1982, p. 38.
4 N.J. Carr, A.K. Galwey and W.J. Swindall, Proc. 7th Int. Conf. Therm. Anal., Wiley, New York, 1982, p. 443.
5 P.E. Yankwich and E.C. Stivers, J. Chem. Phys., 21 (1953) 62.
6 A.K. Galwey and L. Pöppl, Phil. Trans. R. Soc. (London), Ser. A, 311 (1984) 159.