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A THERMOANALYTICAL STUDY OF THE THERMAL DECOMPOSITION OF SILVER SQUARATE

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ABSTRACT

The solid-state decompositions in nitrogen of two silver(I) salts of squaric acid, $AgHC_4O_4$ H_2O and $Ag_2C_4O_4$, have been studied using differential scanning calorimetry (DSC) The acid salt dehydrates above 370 K and the anion in both salts undergoes strongly exothermic decomposition above 500 K Decomposition of solid squaric acid occurs above 570 K and is also strongly exothermic The enthalpies of decomposition in kJ per mol of squarate are -89 ± 6 for the acid, -140 ± 8 for the acid salt and -160 ± 10 for the disilver salt

The reactions of these compounds on heating separately in oxygen and in carbon monoxide have also been examined, and suitable combination of the DSC results has enabled the enthalpies of formation of $Ag_2C_4O_4(s)$ to be estimated as -665 ± 20 kJ mol^{-1} and of $H_2C_4O_4(s)$ as -580 ± 10 kJ mol^{-1}

Kinetic parameters, determined from isothermal DSC experiments, were in reasonable agreement with results from a complementary low-pressure kinetic study The DSC curves obtained were compared to those expected for sigmoid expressions and apparent activation energies were derived as 203 ± 46 kJ mol^{-1} for decomposition of the acid salt and 178 ± 22 kJ mol^{-1} for the disilver salt

A mechanism for decomposition is suggested in which silver(I) oxide is formed as an intermediate in a two-stage consecutive reaction and reacts further with some of the product CO to give the CO_2 observed in the evolved gases, as well as the solid residue of silver particles in a carbonaceous pseudomorph of the reactant crystallites

These results are compared with those obtained for the decompositions of copper(II) and nickel(II) squarates

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INTRODUCTION

There is now considerable literature [1] devoted to the thermal decompositions of initially crystalline reactants The mechanisms of the decompositions of a wide variety of individual substances have been determined, but the patterns of behaviour observed have not been able to be related systematically to the compositions, or to the constituent components, of the salts concerned Comparative investigations of the reactions of series of salts containing common atomic groupings have shown that the presence of a constant cation or anion does not necessarily result in comparable rate characteristics during thermally induced breakdown There is, at present, no generally accepted comprehensive theoretical framework that enables the rate-limiting step in these reactions to be characterized and correlated within groups of similar substances or to be predicted in hitherto untested systems

One group of substances that has attracted considerable interest in the field of decomposition of solids is the metal carboxylates [1], particularly the salts of oxalic acid, but also metal formates, acetates, malonates and mellitates The factors controlling reactivity have been identified for only a limited number of these substances Accordingly, we considered it appropriate to undertake a systematic study of the decompositions of metal salts of squaric acid, $H_2C_4O_4$, because these salts contain carbon–oxygen–cation linkages that are different from those in the more extensively investigated carboxylates The ultimate objective of these continuing studies is to provide a complementary series of investigations in which the behaviour of both the carboxylates and the squarates may be compared, to provide evidence towards unravelling the mechanisms of breakdown of salts of both anions

We have already published [2–4] stoichiometric, kinetic, microscopic and thermochemical investigations for the dehydration and thermal decompositions of nickel(II) squarate and of copper(II) squarate The present thermochemical study extends and complements a similar stoichiometric, kinetic and microscopic study [5] of the breakdown of silver squarate We are aware of no other previous study of the decomposition of this reactant, although thermoanalytical measurements for several divalent metal squarates have been reported [6]

EXPERIMENTAL

Preparation of silver squarate

The several samples of silver squarate reactant used in the present work were prepared by a method based on that given by West and Niu [7] Two solutions were prepared 0 02 mol of squaric acid, $H_2C_4O_4$ (Aldrich Chem-

TABLE 1

Analytical and thermochemical results

Salt	Silver content (%)	Overall mass loss N_2 (%)	ΔH (kJ per mol squarate) Endotherm N_2	Exotherm N_2	Exotherm O_2	Exotherm CO
1	45 2		53 ± 2	-113 ± 1		
2	46 2	38 6	56 ± 2	-107 ± 5		
3	50 5		50 ± 3	-137 ± 7		
4	52 4	39 9	55 ± 4	-141 ± 8		
3T	70 0	23 9	–	-154 ± 4		
4T	70 7	23 6	–	-167 ± 8	-525 ± 25	-156 ± 5
5T	69 2	31 5	24 ± 2	-177 ± 4		-168 ± 5
$H_2C_4O_4$	–		–	-89 ± 6	-134 ± 10	

Salt	Molecular mass	Ag (%)	C (%)	H (%)	H_2O (%)
$Ag_2C_4O_4$	327 8	65 8	14 6		
$AgHC_4O_4$ H_2O	238 9	45 1	20 1	1 26	7 5
Prep 2 found		46 2	20 1	1 18	$7\,0 \pm 0\,5$

icals) in 60 cm^3 of deionized water at 333 K, and 0 04 mol of silver nitrate in 50 cm^3 of water, also at 333 K The $AgNO_3$ solution was poured into the squaric acid solution, with stirring A yellowish-green precipitate formed immediately, the colour of which changed rapidly to white The hot solution was filtered through sintered glass, and the precipitate was washed with water and dried in air at 350 K

Samples of silver squarate (salts 1–5T, Table 1) were prepared in this way, with slight differences in temperature and the time that elapsed before filtering the precipitate and, for salt 5, in the concentrations of the solutions used [5] Product compositions of salts 1–4 varied somewhat but corresponded approximately to $AgHC_4O_4$ H_2O This is evident from the silver analyses (atomic absorption spectroscopy) included in Table 1. After these prepared salts were heated for 3 h with excess ethanol at 323 K, and filtered and dried, a yellow-green solid was obtained in which the increased silver content corresponded more closely with theoretical expectation for the anhydrous disilver salt $Ag_2C_4O_4$ (Table 1, salts 3T, 4T and 5T)

Apparatus

A Perkin–Elmer DSC-2 differential scanning calorimeter (DSC), with the differential power output coupled via a 12-bit A/D converter to an Apple II Plus microcomputer, was used for data capture and analysis Software was in Applesoft BASIC

Samples were contained in aluminium pans which were covered with aluminium lids but not crimped The overall mass losses after DSC experiments were recorded The atmosphere, unless otherwise specified, was nitrogen at an inlet pressure of 207 kPa Other carrier gases used in a few experiments were oxygen and carbon monoxide In each isothermal DSC experiment the sample was initially heated at 320 K min^{-1} to the required constant reaction temperature The DSC response was then recorded as a function of time. Switching disturbances were corrected for by subtraction of the DSC response recorded during an otherwise identical blank experiment

Evolved gas analysis (EGA)

Samples of the gases evolved during DSC scans could be introduced into a Taylor Servomex gas chromatograph with a thermal conductivity detector A stainless steel column packed with Porapak Q was used either at 373 K for observing the water evolved, or at 303 K for separation of the CO and CO_2 products The carrier gas was nitrogen at pressures slightly above the DSC inlet pressure of 207 kPa Sampling intervals and flushing times were controlled by an adjustable programmer

RESULTS AND DISCUSSION

Structure of prepared salts infrared spectra

Infrared spectra of the silver squarate salts, as prepared and after ethanol treatment, and of squaric acid, incorporated in KBr disks, were recorded by standard methods.

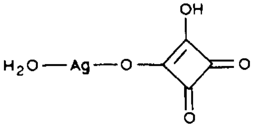
Infrared spectra [7] of most of the divalent metal squarates are dominated by a broad and strong band at 1700–1400 cm^{-1} (mixture of C–C and C–O stretching) with other bands at 1150 and 1105 cm^{-1} and a weak overtone at 2210 cm^{-1} The absence of a sharp band above 1600 cm^{-1} suggests [7] that all the C–O groups are coordinated to metal ions and the D_{4h} symmetry of the ion is maintained Copper(II) squarate has additional bands at 1360, 1320, 985 and 900 cm^{-1} indicating a less symmetrical structure, as confirmed by X-ray diffraction [7]

The infrared spectrum of squaric acid is composed of bands at 3400(s), 2400(s and broad), 1800(m and sharp), 1640(m), 1520(s), 1350(s and broad), 910(m), 850(m) and 710(m) cm^{-1} (s = strong, m = medium)

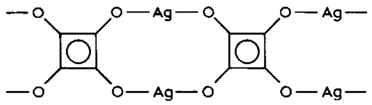
The original precipitate of silver squarate gave a spectrum having bands at 3400(s and broad), 1820(m and sharp), 1650(s), 1500(weak) and 1080(m and sharp) cm^{-1} After treatment in ethanol, the spectrum changed to bands at 3400(broad), 1500(s and broad), 1000(m) and 700(m) cm^{-1}

Thus the ethanol treated material gives a spectrum characteristic of a very symmetrical coordination structure [7], while the original (untreated) pre-

cipitate is a compound of lower symmetry From these spectral data and the analytically determined differences in composition we schematically represent the two materials as follows
The original precipitate is identified as the acid salt monohydrate



Ethanol treatment at 323 K results in polymerization, dehydration and acid elimination



The low-temperature (370–420 K) endothermic (dehydration) reaction

DSC traces for the untreated preparations, heated at 20 K min^{-1} in nitrogen, included an endothermic response between 370 and 420 K, a process that was completed well below the temperature range of the exothermic peak identified as anion breakdown (500 K) This low-temperature response is ascribed to dehydration since water vapour was the only volatile product identified by evolved gas analyses Measured mass losses (6 5–7 4%) were consistent with the calculated water content (7 5%) for the acid salt monohydrate (Table 1) Moreover, salt heated to 460 K, and cooled to ambient temperature in the absence of water vapour, exhibited no endotherm when reheated in the DSC to 460 K. If, however, a cooled sample was exposed to water vapour for several hours, the mass increased to its original value and on rescan the endotherm reappeared The enthalpy change was virtually unchanged although the peak shape changed slightly

Treated salt, identified from analytical data as anhydrous, exhibited no endothermic response either originally or after lengthy exposure to water vapour

The 370–420 K endotherm, characteristic of the acid salt is, therefore, identified as dehydration and is reversible The measured enthalpy of dehydration is 225 ± 25 J (g of salt)$^{-1}$ (or 3 00 ± 0 33 kJ (g H_2O)$^{-1}$ or 54 0 ± 6 0 kJ (mol H_2O)$^{-1}$) Both the temperature interval and the ΔH values are lower than those reported [4] for the dehydration of copper(II) squarate dihydrate, which were 440–470 K and 70 ± 6 kJ (mol H_2O)$^{-1}$, respectively Values for the dehydration of nickel(II) squarate dihydrate could not be obtained since [2] this process overlaps with decomposition

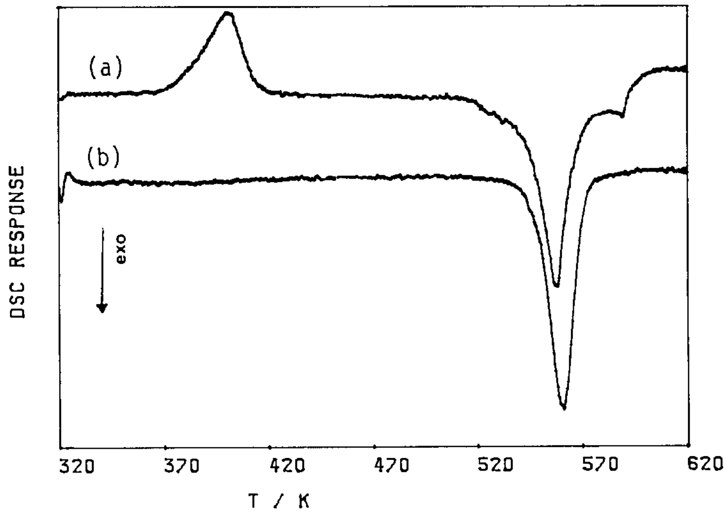


Fig 1 DSC trace (320–620 K) for silver squarate salts heated at 20 K min^{-1} in nitrogen (a) silver hydrogen squarate monohydrate (salt 4, 1 03 mg), (b) disilver squarate (salt 4T, 0 96 mg)

The higher-temperature (500 K) reactions (decompositions) in nitrogen

Standard conditions adopted throughout this series of measurements were the use of approximately 1 mg of reactant (weighed to $\pm 1\%$) heated at 20 K min^{-1} in a nitrogen flow Thermochemical data obtained are summarized in Table 1 Measured values showed some variations amongst the several preparations These are attributed to compositional differences, notably in the proportions of hydrate present in the various samples

(a) *The acid hydrate* All the untreated preparations (salts 1–4) gave scans which included generally similar features, although there were slight differences in detail A representative trace is shown in Fig 1, curve (a) The first endothermic reaction (onset 370 K, maximum at 400 K) was identified as dehydration (see above) The subsequent exothermic reaction is ascribed to anion breakdown (onset 510 K, maximum at 555 K and followed by a small subsidiary maximum) The shape of this exotherm varied slightly from one preparation to another and, for a given preparation, to some extent with sample mass

(b) *The disilver salt* Ethanol-pretreated preparations exhibited no initial endotherm, with the exception of salt 5T, where the characteristic response was substantially reduced ($\times 0$ 5) The subsequent exothermic peak is again ascribed to anion breakdown and the peak maximum (560 K) is close to that found for untreated samples Peak shape, however, varied appreciably amongst the different preparations The subsidiary maximum on the higher temperature side of the response was absent and in some traces it was

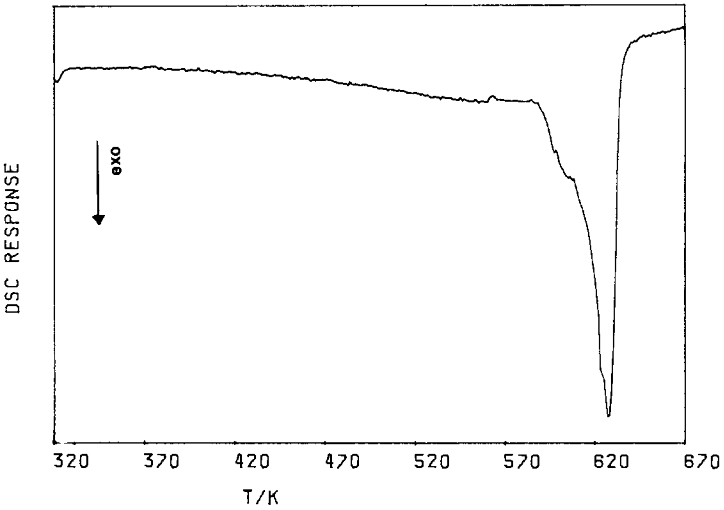


Fig 2 DSC trace (320–670 K) for squaric acid (2 04 mg) heated at 20 K min^{-1} in nitrogen

replaced by a small endotherm A representative scan (salt 4T) is shown in Fig 1, curve (b)

(c) *Squaric acid* The DSC response for squaric acid (Fig 2) shows onset of a sharp but complex exotherm at 580 K, with the peak maximum at 630 K These temperatures are significantly greater than those for silver squarate decomposition under identical conditions There was no evidence on the DSC trace of the first-order phase transition reported [8] for squaric acid at 373 K Evolved gas analysis showed that decomposition yielded CO, CO_2 and H_2O The mass loss measured was 84 0 ± 0 5% There was evidence of some sublimation, but the appearance of the black carbonaceous residue after decomposition gave no indication that melting had occurred The enthalpy change for the decomposition of squaric acid was -780 ± 50 J g^{-1} or -89 ± 6 kJ mol^{-1} The occurrence of sublimation makes accurate determination of the baseline for integration difficult, and hence increases the uncertainty in the enthalpy values

The residual solid product of decomposition of the silver salt was shown, by X-ray diffraction and by chemical analysis, to contain silver metal together with a polymeric carbonaceous residue comprising some 6 0% of the reactant mass for the treated samples, and up to 14% of the acid hydrate The volatile products were CO and CO_2, confirmed by EGA, and the overall stoichiometry was expressed [5] by the equation

$$Ag_2C_4O_4(s) \rightarrow 2Ag(s) + CO_2(g) + 1\ 5CO(g) + (C_{1\ 5}O_{0\ 5})_n(s)$$

The mass losses of 28 ± 4%, measured for decomposition of the disilver salt, are consistent with the value of 26 2% expected for the above stoichiometry The measured enthalpy of decomposition of the dehydrated acid hydrate (salt 4, Table 1) was -141 ± 8 kJ (mol squarate ion)$^{-1}$, which is lower than the value for the disilver salt (salt 4T, -167 ± 8 kJ (mol squarate ion)$^{-1}$) The enthalpy value for salt 4 was calculated from the total peak area including the initial shoulder and the subsidiary maximum on the high-temperature side of the main peak (Fig 1, curve (a)) If the reaction

$$2AgHC_4O_4(s) \rightarrow Ag_2C_4O_4(s) + H_2C_4O_4(s)$$

had occurred, the DSC traces for the acid salt would be expected to show the separate contributions from the subsequent decomposition of the disilver salt and the higher temperature decomposition of squaric acid. Other than the dehydration endotherm, only the main exotherm, shown in Fig 1, curve (a), was found, however This exotherm is qualitatively similar to that for the disilver salt, Fig 1, curve (b), and the differences in the enthalpy values for decomposition of the acid and the disilver salts, Table 1, must arise from differences between the environment of the squarate ion in the two salts during the decomposition

Reactions in oxygen

The conditions used were closely similar to those above, except that oxygen was used as the carrier gas in the DSC

The disilver salt Decomposition of silver squarate in oxygen gives a sharp exothermic response, superimposed on the usual broader decomposition exotherm (Fig 3, salts 4T and 5T) The enthalpy of the overall reaction in oxygen is -525 ± 25 kJ (mol squarate ion)$^{-1}$

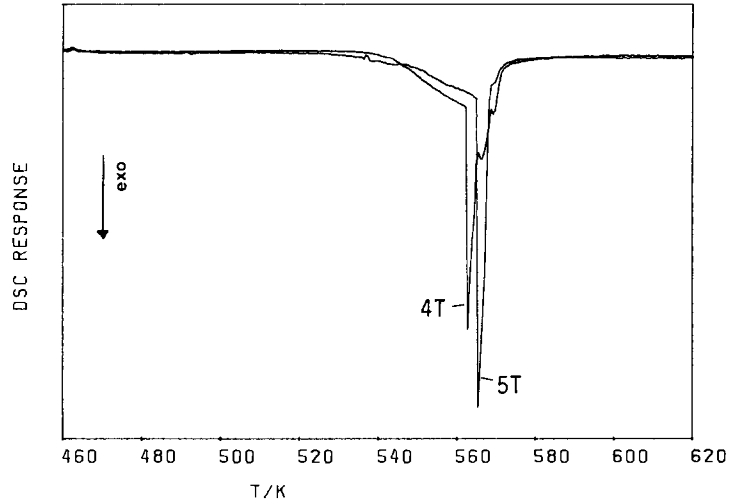


Fig 3 DSC traces (320–620 K) for disilver squarate (salt 4T, 0 24 mg and salt 5T, 0 19 mg) heated at 20 K min^{-1} in oxygen

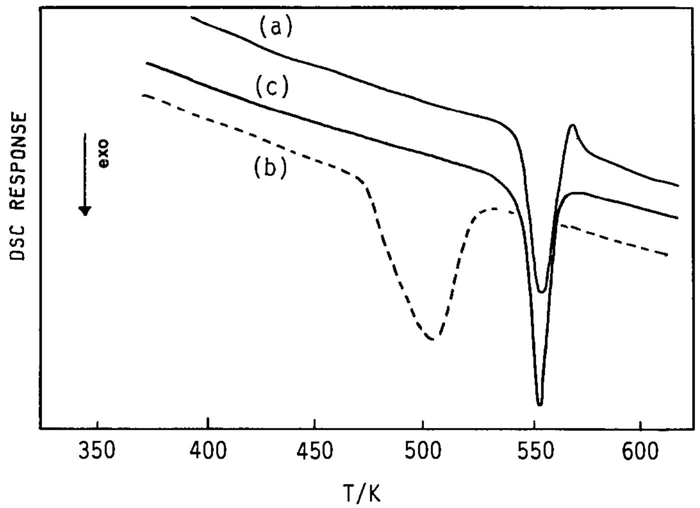


Fig 4 DSC traces (320–620 K) for (a) disilver squarate (salt 4T) heated at 20 K min^{-1} in nitrogen, (b) the product of run (a) heated at 20 K min^{-1} in oxygen and (c) disilver squarate (salt 4T) heated at 20 K min^{-1} in carbon monoxide

The solid product of decomposition of the disilver salt in nitrogen When the residue from decomposition of disilver squarate in nitrogen was reheated at 20 K min^{-1} in oxygen, an exothermic process was recorded (-328 ± 10 kJ (mol squarate ion)$^{-1}$) with onset temperature of ~ 450 K for salt 4T (Fig. 4) and ~ 500 K (Fig 5) for salt 5T The mass losses measured were 10 4 ± 0 4% of the residue of the 4T salt and 12 5 ± 0 4% of the residue of the 5T salt

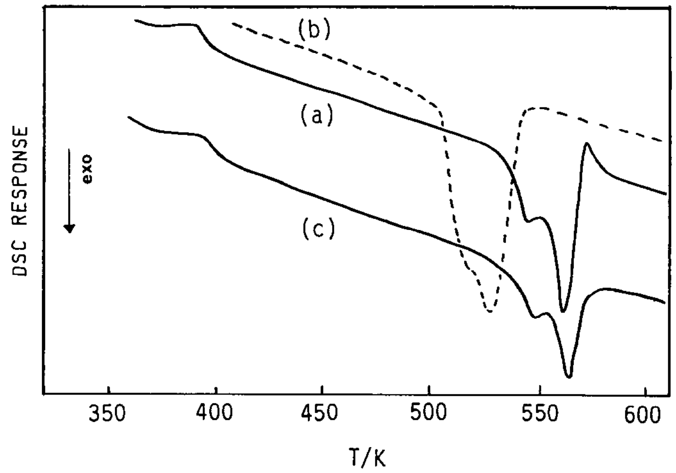


Fig 5 DSC traces (320–620 K) for (a) disilver squarate (salt 5T) heated at 20 K min^{-1} in nitrogen, (b) the product of run (a) heated at 20 K min^{-1} in oxygen and (c) disilver squarate (salt 5T) heated at 20 K min^{-1} in carbon monoxide

These results suggest that this reaction does not result in oxidation of the silver because the mass loss calculated for

$$(2Ag + C_{1\,5}O_{0\,5})(s) \xrightarrow{O_2} 2Ag(s) + 1\,5CO_2(g)$$

is 10 7%, while the calculated mass loss, assuming the formation of $Ag_2O(s)$ instead of Ag(s), is only 4 1% The absence of Ag_2O in the product of this reaction in oxygen was confirmed, see below, by further experiments in a CO atmosphere

Squaric acid When squaric acid was heated in oxygen at 20 K min^{-1}, a complex exothermic process was observed (onset ~ 590 K) The mass loss observed was 92% and the enthalpy change was -134 kJ mol^{-1} This retention of some carbonaceous residue, following reaction in oxygen, contrasts with the behaviour of the silver salt

The solid residue from decomposition of squaric acid in nitrogen When this residue was heated in oxygen, a broad exotherm (onset ~ 520 K) was observed This mass loss corresponded to only a further 6 0% of the original sample, representing a total mass loss of 90 5 ± 0 5% The enthalpy change for this oxidation step was -41 ± 1 kJ (mol squaric $acid)^{-1}$ This may be compared with the reaction of squaric acid in oxygen, where 8% of the original sample mass is a carbonaceous residue which is resistant to oxidation under these conditions (< 670 K)

Reactions in carbon monoxide

Conditions used were again similar to those above, except that for safety reasons, while using carbon monoxide as the carrier gas, the DSC response was only recorded on a chart recorder without correction for baseline slope

The disilver salt Disilver squarate decomposes in a carbon monoxide atmosphere over the same temperature range as in nitrogen The DSC responses for the 4T and 5T salts (Figs 4 and 5) are, however, exothermic throughout, without the slight endothermic contribution on the high-temperature side of the main exotherm in nitrogen The measured enthalpy changes for reaction in CO (-156 ± 5 kJ (mol $squarate)^{-1}$ for the 4T salt and -168 ± 5 kJ (mol $squarate)^{-1}$ for the 5T salt) were only slightly lower than the values in nitrogen (-175 ± 4 kJ (mol $squarate)^{-1}$ for salt 4T and -173 ± 13 kJ (mol $squarate)^{-1}$ for salt 5T), measured under closely similar conditions

Silver(I) oxide Silver oxide, Ag_2O, is readily reduced [9] in a CO atmosphere (Fig 6) The onset of reaction was at or below the start of the scan at 320 K and reaction was complete by 420 K The enthalpy of reaction measured for the Ag_2O sample used (Johnson Matthey Ltd) was -263 ± 5 kJ mol^{-1}, compared with the standard enthalpy of reaction of -254 kJ for

$$Ag_2O(s) + CO(g) \rightarrow 2Ag(s) + CO_2(g)$$

The ease with which this reaction occurs made the reaction a useful test for

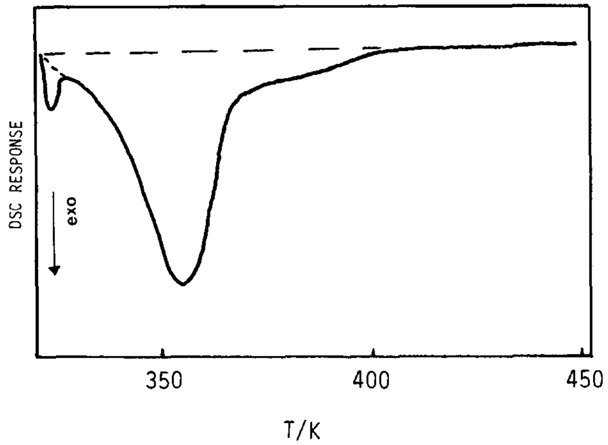


Fig 6 DSC trace (320–450 K) for silver(I) oxide heated at 20 K min^{-1} in carbon monoxide

the presence of Ag_2O in the solid products of reaction of silver squarate in oxygen In several experiments, salt was successively heated in the sequence of carrier gases N_2, then O_2, followed by CO No thermal events were observed during such scans in CO, so it was concluded that the exothermic process observed for reaction in O_2 of the decomposition product in N_2 was due to oxidation of the carbonaceous residue only, and that the solid residue from reaction of silver squarate in O_2 was silver metal only

Thermochemistry

Silver squarate The enthalpy changes for the following three reactions have been measured

$$Ag_2C_4O_4(s) \xrightarrow{N_2} 2Ag(s) + (C_{1\,5}O_{0\,5})(s) + 1\,5CO(g) + CO_2(g) \qquad (1)$$

$\Delta H_1 = -164 \pm 8$ kJ

$$(C_{1\,5}O_{0\,5})(s) \xrightarrow{O_2} 1\,5CO_2(g) \qquad \Delta H_2 = -328 \pm 10 \text{ kJ} \qquad (2)$$

$$Ag_2C_4O_4(s) \xrightarrow{O_2} 2Ag(s) + aCO(g) + (4 - a)CO_2(g) \qquad (3)$$

$\Delta H_3 = -525 \pm 25$kJ

From reaction (2), the standard enthalpy of formation of $(C_{1\,5}O_{0\,5})(s)$ is estimated as -266 ± 10 kJ mol^{-1} Using this value in reaction (1), the standard enthalpy of formation of $Ag_2C_4O_4(s)$ is estimated as -665 ± 20 kJ mol^{-1} This value, when used in turn in reaction (3), leads to a value of $a = 1\,4$ which is approximately the stoichiometry of reaction (1) and suggests, on thermochemical grounds, that the CO evolved in the decomposition of the squarate salt is not oxidised in the vicinity of the solid sample, although it may be oxidised in secondary gas reactions EGA could not be done in oxygen atmospheres without damaging the thermal conductivity detector

The enthalpy of formation of $Ag_2C_4O_4(s)$ of -665 ± 20 kJ mol^{-1} is higher than the value of -472 kJ mol^{-1} estimated [4] for $CuC_4O_4(s)$

Squaric acid If the solid residue from the decomposition of squaric acid in N_2 is assumed to be carbon only, the mass loss of $84\ 0 \pm 0\ 5\%$ measured suggests the stoichiometry

$$H_2C_4O_4(s) \xrightarrow{N_2} 1\ 5C(s) + H_2O(g) + 2CO(g) + 0\ 5CO_2(g) \qquad (4)$$

The enthalpy change for this reaction, ΔH_4, was measured as -89 ± 6 kJ EGA showed the presence of all three of the above gaseous products

When this solid product of decomposition in N_2 was reheated in O_2, the overall mass loss ($90\ 5 \pm 0\ 5\%$) and the enthalpy change (-41 ± 1 kJ (mol squaric acid)$^{-1}$) corresponded approximately to

$$1\ 5C(s) \xrightarrow{O_2} C(s) + 0\ 5CO(g)$$

(calculated $\Delta H = -55$ kJ)

The mass loss for the reaction of squaric acid in O_2 suggests that the final products of reactions proceeding through the two paths are the same

$$\begin{tikzcd}
H_2C_4O_4(s) \arrow[r, "N_2"] \arrow[dr, "O_2"'] & 1\ 5C(s) + H_2O(g) + 2CO(g) + 0\ 5CO_2(g) \arrow[d, "O_2"] \\
& C(s) \quad + H_2O(g) + 2\ 5CO(g) + 0\ 5CO_2(g)
\end{tikzcd}$$

Assuming that the enthalpy of formation of the carbon residue is approximately zero, the enthalpy of formation of $H_2C_4O_4(s)$ is estimated as -580 ± 10 kJ mol^{-1}

The silver oxide/squaric acid reaction The enthalpy of the reaction

$$Ag_2O(s) + H_2C_4O_4(s) \rightarrow Ag_2C_4O_4(s) + H_2O(g)$$

is estimated from the enthalpies of formation of silver oxide, disilver squarate and squaric acid to be -296 ± 30 kJ This reaction and the reaction of other metal oxides with squaric acid are being studied further [10]

DSC measurements of the isothermal decomposition of silver squarate in nitrogen

Where necessary, samples were preheated at 20 K min^{-1} in nitrogen between 320 and 460 K to complete the endotherm Typical traces for the isothermal decomposition at 525 K are shown in Fig 7(a) (untreated

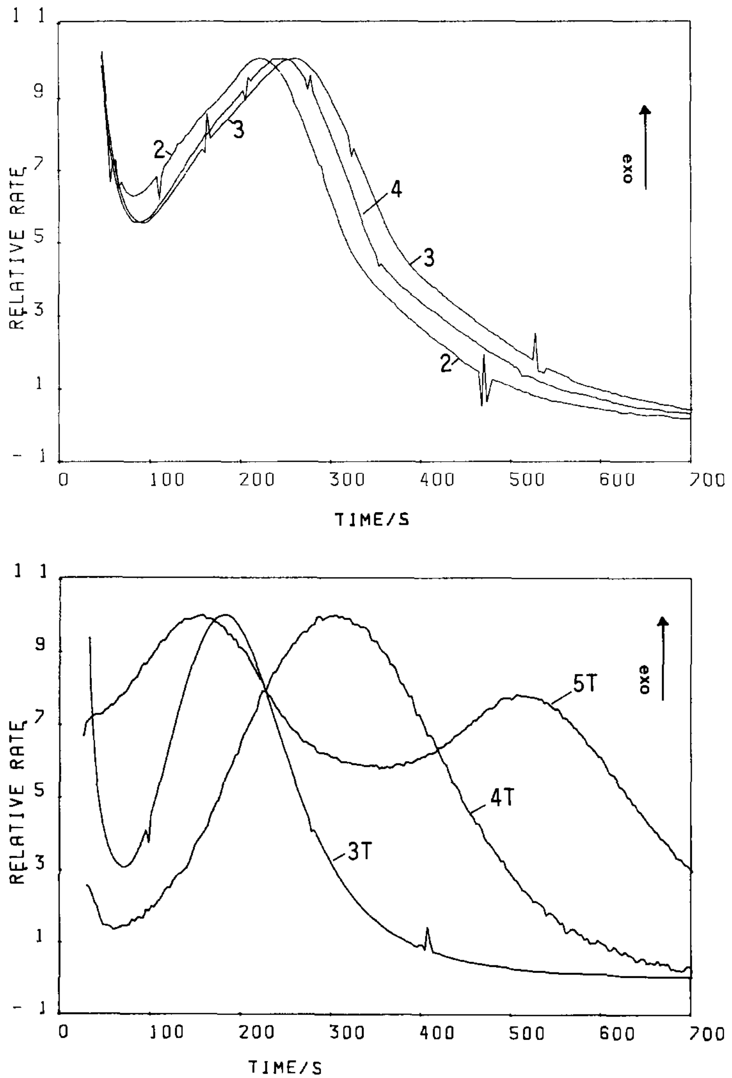


Fig 7 Isothermal DSC runs on silver squarate at 525 K in nitrogen, scaled to a response of 1 00 at the peak maximum (a) untreated preparations 2, 3 and 4, (b) treated preparations 3T, 4T and 5T

preparations) and Fig 7(b) (treated preparations) For this comparison the traces have been inverted and normalized to a common value of 1 00 for the DSC response at the maximum of the exotherm in each experiment

It is evident that reproducibility from one preparation to another is better amongst the untreated salts than amongst the treated salts This suggests that the structural reorganisation that occurs during the treatment with ethanol does not yield completely identical products

Isothermal experiments were completed for each of the preparations at selected temperatures between 515 and 535 K Results were scaled to give relative-rate reduced-time (RRRT) curves [11] with both the DSC response (taken as a measure of reaction rate) and the time scaled to 1 00 at the peak maximum of each run The scaling factors calculated are recorded in Table 2, which also reports the Arrhenius parameters derived from these data Results for three preparations (salts 2, 4T and 5T) are shown in Fig 8(a)–(c), respectively The behaviour of salt 5T differed from those of the other preparations since two peaks were observed and there was a change of shape with temperature

Isothermal DSC measurements may be used [11] to analyse the kinetic characteristics of solid-state decompositions The RRRT curves recorded here were of similar shapes, so that the traces could be superimposed with acceptable accuracy for the acid salt (salt 2) and the disilver salt (salt 4T) as separate groups, Fig 8(a) and (b), respectively This is evidence that the kinetic obedience does not change with temperature The curves for salt 5T (Fig 8(c)) were, however, more complicated, being composed of two overlapping exotherms, the relative areas of which varied systematically with temperature

The characteristic "bell" shape of the RRRT curves in Fig 8(a) and (b) and the components of the complex curve in Fig 8(c), indicate that the α–time curves are sigmoid, usually identified with obedience to nucleation-and-growth models The theoretical RRRT curves for the Avrami–Erofe'ev group of rate equations [11,12] with n ranging from 1 5 to 4 0 are shown in Fig 8(d) Comparison of the composite curve for salt 2 with the curves for the Avrami–Erofe'ev expressions (Fig 8(d)) shows that coincidence is not good in the regions where discrimination is best A similar comparison of the composite curve for salt 4T shows reasonable coincidence with the curve for $n = 3\ 5$ before the peak maximum, changing to $n = 3\ 0$ beyond the peak

It has been shown [11] that for the Avrami–Erofe'ev model, the time to the peak maximum, t_m, is inversely proportional to the rate coefficient, k, for the reaction ($t_m = ((n-1)/n)^{1/n}/k$) Values of t_m for the acid salt (salt 2) and the disilver salt (salt 4T) are given in Table 2 together with values of E_a and $\ln(A)$ obtained from Arrhenius plots of $1/t_m$ against $1/T$ A less acceptable, but nevertheless often used, approximation in kinetic analysis assumes first-order behaviour, for which the heights, h, of the DSC peaks at the maxima, corrected for sample mass, m, may be used as first-order rate coefficients The Arrhenius parameters derived in this way have also been included in Table 2 The values for E_a obtained by the two procedures are comparable, as may be expected because the temperature coefficient of reaction is often found to be fairly insensitive to the kinetic model chosen for analysis [13,14] The apparent activation energy for decomposition of the acid salt is slightly greater than that for the disilver salt

Applying similar procedures to the results for salt 5T, omitting all

TABLE 2

Kinetic parameters for the decomposition in nitrogen of various preparations of silver squarate

T (K)	Salt 2		Salt 4T		Salt 5T			
	t_m (s)	h/m (mm mg^{-1})	t_m (s)	h/m (mm mg^{-1})	t_1 (s)	h_1/m (mm mg^{-1})	t_2 (s)	h_2/m (mm mg^{-1})
515	443	79 1	670	74 0	324	52 4	1316	27 3
520	298	110	454	126	208	81 1	793	61 4
525	187	123	303	187	155	127	509	99 0
	196	267						
530	124	252	227	263	112	172	380	125
535	76	458	150	386	76	286	250	191
E_a (kJ mol^{-1})	207 ±6	198 ±46	169 ±5	180 ±7	161 ±6	192 ±9	179 ±15	189 ±22
ln(A) (s^{-1})	42 1±1 3	50 7± 9 5	33 0±1 0	46 4±1 6	31 9±1 3	48 9±2 0	34 8± 3 4	47 8± 5 0
r	0 9985	0 9221	0 9984	0 9978	0 9982	0 9967	0 9895	0 9804

allowance for overlapping processes, gives apparent activation energies not significantly different from those of salt 4T (see Table 2) and close to the value reported [5] for salt 5T decomposed in vacuum ($\alpha < 0.5$, 483–508 K) of 190 ± 8 kJ mol^{-1}

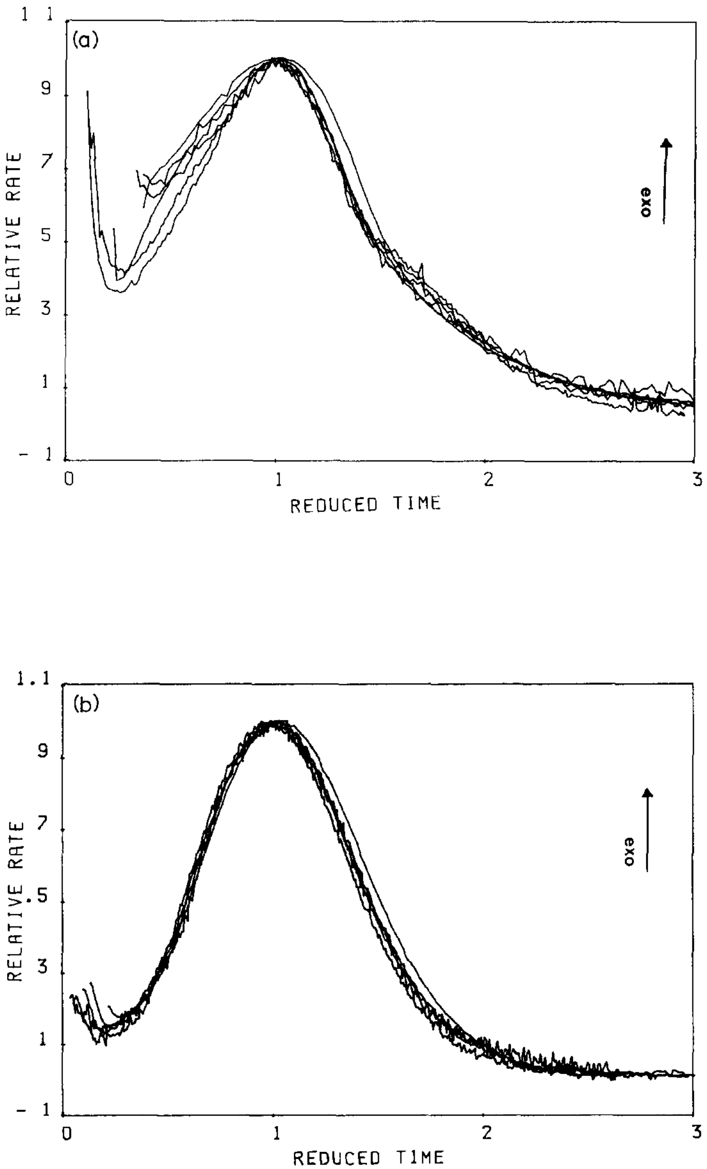


Fig 8 Relative-rate reduced-time (RRRT) curves for silver squarate from isothermal DSC runs in nitrogen carried out at a series of different but constant temperatures (a) salt 2, (b) salt 4T, (c) salt 5T, (d) Avrami–Erofe'ev models

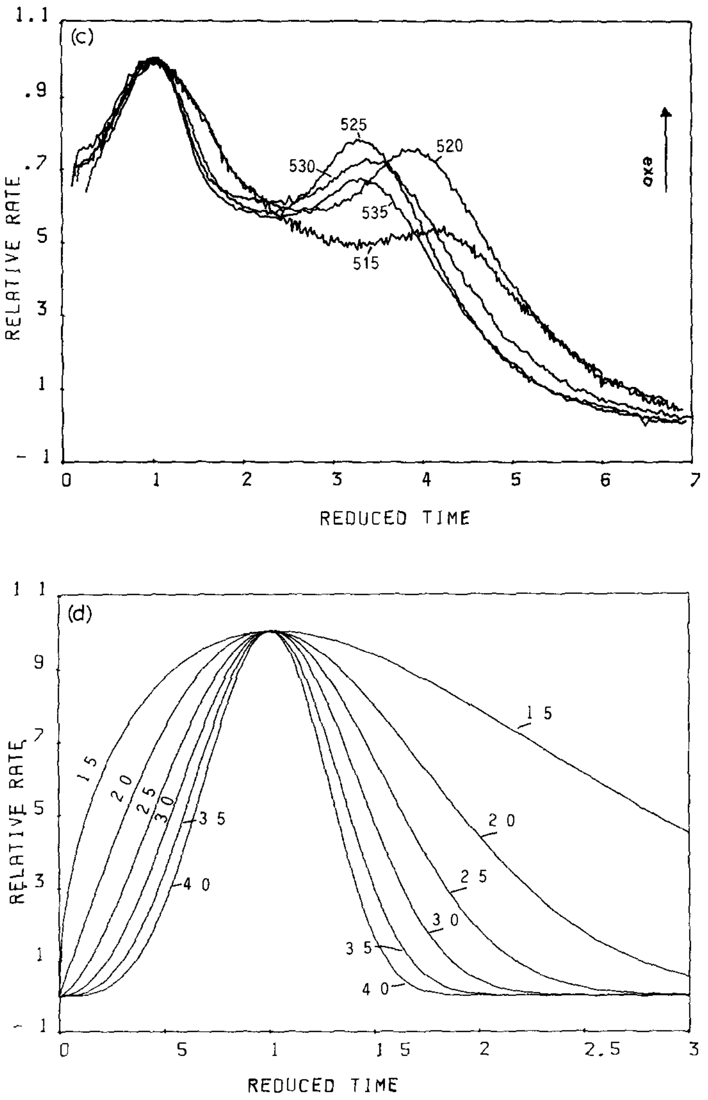


Fig 8 (continued)

CONCLUSIONS

We have prepared two silver(I) salts of squaric acid an acid salt hydrate with composition approximating to $AgHC_4O_4$ H_2O and the anhydrous disilver salt $Ag_2C_4O_4$ The disilver salt was formed by treatment of the acid salt with ethanol and its formation involves considerable structural rearrangement, evident from comparisons between the infrared spectra, and consequently these treated salts show some variations in individual behaviour On heating, the acid salt hydrate was dehydrated in an endothermic process (onset ~ 370 K), that was completed before further decomposition of the salt This behaviour is qualitatively similar to that of the copper(II) salt [4], but both differ from the nickel(II) salt [2] in which dehydration overlaps with the onset of decomposition of the anion

Both in the acid salt and in the disilver salt, decomposition of the anion in nitrogen proceeds in the solid state by strongly exothermic processes Both these exotherms have onset temperatures at approximately 500 K and are similar in general shape The decomposition of squaric acid in nitrogen is also a strongly exothermic reaction, becoming evident above 570 K, which is greater than the temperature of onset of decomposition of the salts discussed here There was no evidence of any preliminary dehydration step or of melting in the reaction of the acid The enthalpy of reaction, measured per mole of squarate, increases from -89 ± 6 kJ for squaric acid, to -140 ± 8 kJ for the acid salt, and -160 ± 10 kJ for the disilver salt

The gaseous products of all of the decompositions referred to here contained some CO_2 and the solid products contained some carbonaceous residue, and it is suggested that CO_2 is formed through the intervention of $Ag_2O(s)$

$$Ag_2O(s) + CO(g) \rightarrow 2Ag(s) + CO_2(g)$$

with the Ag_2O being formed, momentarily at least, by the reaction

$$Ag_2C_4O_4(s) \rightarrow [Ag_2O] + [C_4O_3]$$

The carbonaceous residue of decomposition of the salts, formed in further reaction of the intermediate

$$[C_4O_3] \rightarrow 2\ 5CO(g) + (C_{1\ 5}O_{0\ 5})(s)$$

can be oxidized by reheating in oxygen, but the residue from decomposition of squaric acid is more resistant to oxidation, which suggests that the silver plays an active catalytic role in the oxidation

Experiments in a carbon monoxide atmosphere showed that reaction between Ag_2O and CO occurs very readily Decomposition of the disilver salt in carbon monoxide showed only slight differences compared to decomposition in nitrogen Direct reaction with the undecomposed salt

$$Ag_2C_4O_4(s) + CO(g) \rightarrow 2Ag(s) + CO_2 + [C_4O_3]$$

has been suggested [5] In a nitrogen atmosphere the removal of product CO may be hindered

In contrast to the strongly exothermic decompositions of squaric acid and the silver squarates, the decompositions of the copper(II) and nickel(II) salts are endothermic (30 ± 2 kJ mol^{-1} for the copper salt and 185 kJ mol^{-1} for the nickel salt, this value incorporates a contribution from concurrent dehydration) These latter two salts did not yield significant amounts of CO_2 in the gaseous products

TABLE 3

Activation energies for the decomposition of metal squarates in nitrogen

Salt	E_a (kJ mol^{-1})	Reaction temperature (K)
$AgHC_4O_4$	203 ± 46	515–535
$Ag_2C_4O_4$	178 ± 22	515–535
CuC_4O_4	150 ± 17	590–615
NiC_4O_4	146 ± 6	560–600

The results obtained for isothermal DSC experiments on the disilver salt, 5T, (Fig 8(c)), are basically similar to the isothermal differential gas accumulation curves (fig 3 of ref 5) Kinetic studies using isothermal DSC are somewhat limited in the temperature interval that can be used by the need for a measurable DSC signal, dq/dt These restrictions do not apply to integral methods, such as measurements of total gas accumulated [5], so that the range of temperatures was able to be extended at the lower end in the parallel study [5] Because of the above restrictions, the kinetics of the earlier stages of the reaction are probably better seen in the accumulatory system [5] The accelerative processes observed to varying degrees in the salts under different conditions, and, for salt 4T, even approximating to the Avrami–Erofe'ev model, are suggested [5] to arise from changes in the chemical steps involved rather than from geometrical considerations such as the formation and growth of nuclei or the movement of a reactant–product interface No definite reactant–product interface could be identified in electron micrographs of partially-decomposed salt [5]

Apparent activation energies for the disilver salt 5T determined in the two studies under different conditions are in reasonable agreement The E_a value for the acid salt is slightly higher than for the disilver salt Values for the squarates studied are summarised in Table 3 The copper and nickel salts decompose in higher temperature ranges and with lower apparent activation energies than the silver salts The two-stage consecutive reaction involving Ag_2O as intermediate which reacts further with product CO to give CO_2 in the final products may account for these differences

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