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THE THERMAL DECOMPOSITION OF OXALATES

Part 23. An isothermal kinetic study into the effect of the environmental atmosphere on the thermal decomposition of silver oxalate

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ABSTRACT

The thermal decomposition of silver oxalate has been carried out under isothermal conditions using atmospheres of nitrogen, air, oxygen and carbon dioxide, as well as under vacuum. The decomposition results obtained are treated by conventional methods to obtain the reaction mechanisms, $f(\alpha)$, and by the integral method to obtain the rate constants and hence the Arrhenius parameters. Differential scanning calorimetry (DSC) has been used to follow the energy profile of the decomposition and in each case the decomposition has been found to be exothermic and the final product to be silver metal. The exothermic nature can be explained on the basis of conventional thermodynamics, although a release of the strain set up in the solid during the decomposition is proposed to account for the unsymmetrical energy profiles obtained.

INTRODUCTION

The first reported investigation into the thermal decomposition of silver oxalate was carried out by MacDonald and Hinshelwood [1] in 1925, who showed that under vacuum the decomposition produced silver metal and carbon dioxide in an autocatalytic reaction. However the decomposition could be drastically altered by the preparation of the sample. Compared with the behavior of silver oxalate prepared from solutions containing stoichiometric proportions of silver and oxalate ions, samples prepared from solutions containing excess oxalate were more unstable and acceleratory, whilst samples prepared from solutions containing excess silver ions were more stable and only feebly acceleratory.

However subsequent investigations into the thermal decomposition of silver oxalate [2–5] gave markedly different results and consequently different interpretations of the kinetics.

The light sensitivity of silver oxalate has been extensively studied including the effect of pre-irradiation with UV [2,5,6] upon the decomposition. However, satisfactory conclusions have yet to be obtained.

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The presence of finely divided silver metal as a decomposition product has industrial applications in the catalyst industry, and silver oxalate can be found being used as a precursor for silver metal to be used in the production of a catalyst for the attempted epoxidization of ethene to ethylene oxide [7,8].

In this investigation we report fresh work on the thermal decomposition of silver oxalate by considering the effect of the decomposition atmosphere on the decomposition kinetics.

The investigation reported here is confined to the correct stoichiometric ratio preparation; however, in subsequent publications the effect of sample preparation will be reported in detail.

EXPERIMENTAL

Equipment

The thermal analysis was carried out using a DuPont 1090 Thermal Analyzer coupled to a 910 DSC module and a 951 TG unit.

The sample size in the TG experiments was between 5–10 mg, and decomposition was carried out on a platinum sample pan using an atmosphere flow rate of 30 ml min^{-1}. The heating rate in the DSC experiment was 1°C min^{-1}, and sample size was 12–25 mg.

Decompositions in vacuum were carried out on a Prout and Tompkins type unit, using a McCloud gauge as the pressure sensor [9].

X-Ray powder diffraction utilized a Philips PW 1024 Debye Scherrer camera and a PW 1012 camera bracket.

Sample preparation and characterization

The silver oxalate was prepared by combining aqueous solutions of silver nitrate and oxalic acid in proportions necessary to give a stoichiometric precipitate. The white precipitate was subjected to suction filtration, dried in air and stored in the dark. Silver was determined from the residue in a TG experiment. The oxalate content was determined from a potassium permanganate titration. The results agreed with the theoretical values of 71.0% Ag and 29.0% oxalate based on the formula $Ag_2C_2O_4$. X-Ray powder diffraction identified the product as silver metal.

RESULTS AND DISCUSSION

Initial rising temperature experiments showed that silver oxalate decomposed to silver metal in all atmospheres. However using heating rates of

$> 1°\mathrm{C\ min^{-1}}$ in atmospheres of air and oxygen resulted in the decomposition being accompanied by severe decrepitation. Carrying out the decomposition under vacuum with a liquid nitrogen cold trap positioned in front of the pressure sensor confirmed that no carbon monoxide was produced and that carbon dioxide is the only gaseous product.

In each atmosphere DSC was used to record the energy profile of the decomposition. Results are shown in Fig. 1, and it can be seen that in each atmosphere the decomposition is exothermic in nature.

The decomposition sequence of

$$Ag_2C_2O_4 \xrightarrow{\text{exo}} 2\ Ag + 2\ CO_2$$

is initially of interest as it does not fit into any of the four known decomposition routes for oxalates [10]. The exothermic nature of a decomposition is usually associated with an interaction of one or more of the decomposition products with the environmental atmosphere; however here it appears to be purely thermodynamic in nature.

Considering enthalpies of formation of reactants and products [11] we have

$$\Delta H_\mathrm{f}(Ag_2C_2O_4) = -668\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_\mathrm{f}(Ag) = 0\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_\mathrm{f}(CO_2) = -395.0\ \mathrm{kJ\ mol^{-1}}$$

so using

$$\Delta H_\mathrm{reaction} = \Sigma\ \Delta H_\mathrm{products} - \Sigma\ \Delta H_\mathrm{reactants}$$

we have

$$\Delta H_\mathrm{reaction} = 2 \times (-395.0) - (-668)\ \mathrm{kJ\ mol^{-1}} = -122\ \mathrm{kJ\ mol^{-1}}$$

The differential scanning calorimeter (DSC) was calibrated using an indium standard and the enthalpy of decomposition under each atmosphere is shown in Table 1.

The production of silver metal as a decomposition product in all atmospheres is also unique, and is unusual as it would seem that decomposition in air and oxygen spans a temperature range in which silver oxide can be found.

$$4\ Ag + O_2 \rightarrow 2\ Ag_2O$$

Further TG experiments showed the dissociation temperature of the oxide to be 380°C.

The non-symmetrical shape of the DSC traces in air and oxygen may suggest the presence of an intermediate, possibly the oxide or even the carbonate.

An isothermal calcination series was prepared by decomposing silver oxalate to various stages of the overall decomposition in an oven set at

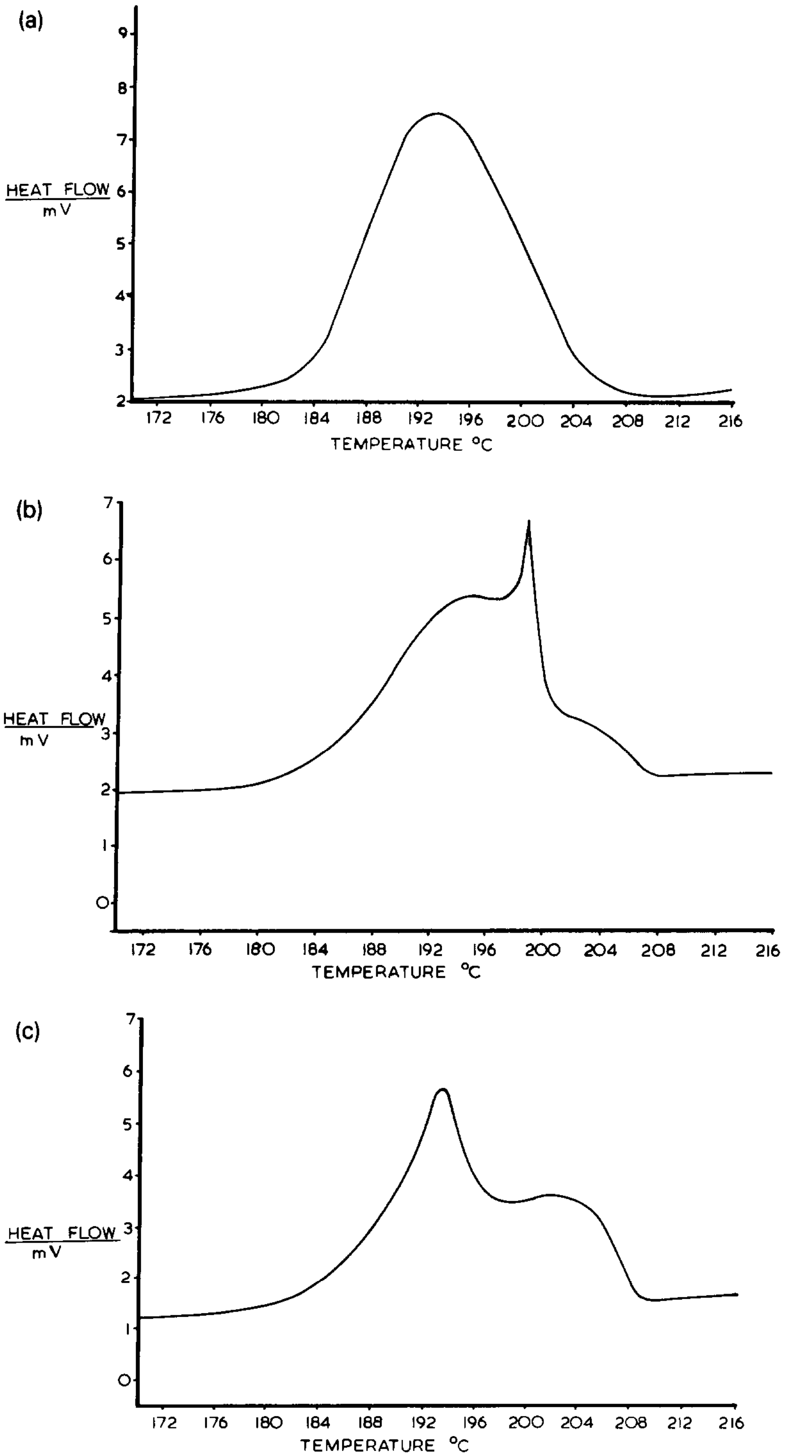

Fig. 1. DSC data for the decomposition of silver oxalate in (a) nitrogen, (b) air, (c) oxygen, (d) carbon dioxide.

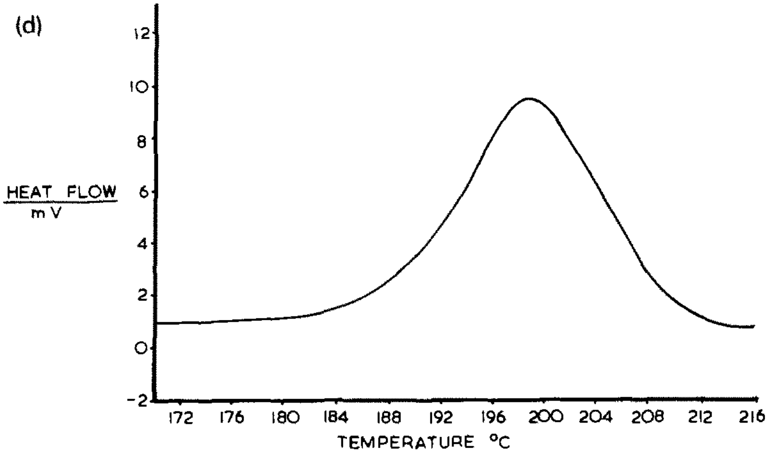

Fig. 1. (continued).

180°C. These freshly prepared samples were then used to obtain X-ray powder diffraction patterns in order to show the composition of the solid throughout the decomposition.

Results showed the overall picture of the oxalate decomposing to the metal, with the lines associated with the silver oxalate becoming fainter throughout the decomposition whilst the lines associated with the silver metal became more intense.

At each stage of the decomposition all the lines are accounted for by the oxalate or metal patterns and hence no oxide or carbonate was found.

An interesting observation was the apparent drop-off of line intensities for the $\alpha = 0.9$ stage of the decomposition. The experiment was repeated with the same sample after it had been allowed to age for around 1 month and strong intensity lines were then obtained. This indicates the formation of an amorphous form of the silver metal during the decomposition, which on ageing converts to a crystalline form.

As it appears that the shapes of the DSC peaks in air and oxygen cannot be attributed to any interaction with the atmosphere an alternative explanation must be found. In both atmospheres decomposition at high isothermal

TABLE 1

Enthalpy data for decomposition of silver oxalate

Atmosphere	$\Delta H_{\text{decomposition}}$ (kJ mol^{-1})
N_2	-76 ± 4
Air	-76 ± 2
O_2	-81 ± 2
CO_2	-72 ± 1

temperatures and higher heating rates resulted in decrepitation which is attributed to the "spike" in the DSC plot. The density of silver oxalate is 5.029 g cm^{-3} whilst the density of silver is 10.5 g cm^{-3}. Hence, in the decomposition of 1 mol of silver oxalate a volume change occurs from 60.39 cm^3 to 20.53 cm^3 in the solid state. It has been shown that when changes of this nature occur in solids, there is a sudden generation of smaller fragments formed by the release of the extra strain imposed on the system [12]. These changes do not necessarily occur upon completion of the chemical reaction as they represent factors caused solely by changes in the volume of a solid. The "spike" in the DTA traces is attributed to this effect and represents a sudden release of energy. The particle size is now smaller, possibly leading to a different kinetic mechanism for the remainder of the decomposition. This theory is supported by the decrease in line intensity in the X-ray powder diffraction pattern at $\alpha = 0.9$.

Why this phenomenon only occurs in air and oxygens has still to be explained; however it has been shown that decomposition of silver oxalate in an inert medium of glycerol produces a very fine silver micropowder of particle size range 0.1–0.5 μm [13]. Therefore, it does appear that the extent to which decrepitation occurs depends on the decomposition medium.

Kinetic determination

Isothermal decomposition of silver oxalate was carried out under atmospheres of nitrogen, air, oxygen and carbon dioxide as well as under vacuum. Figure 2 shows the isothermal decomposition curves for silver oxalate in a nitrogen atmosphere.

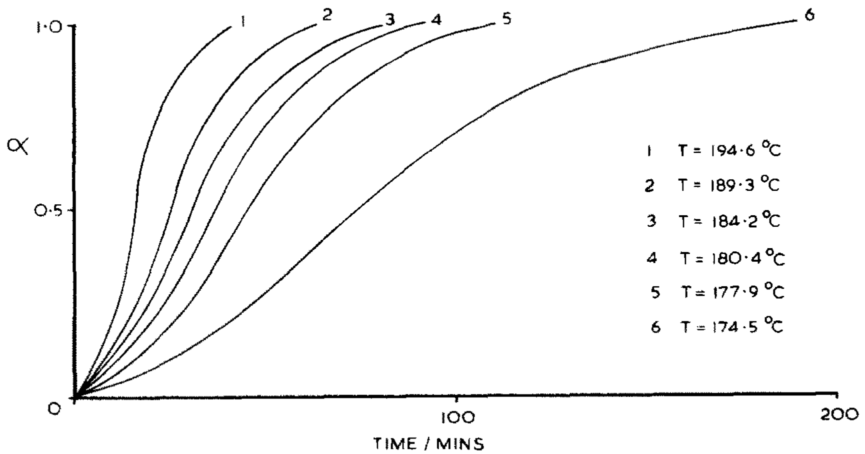

Fig. 2. Isothermal curves for silver oxalate decomposition in nitrogen.

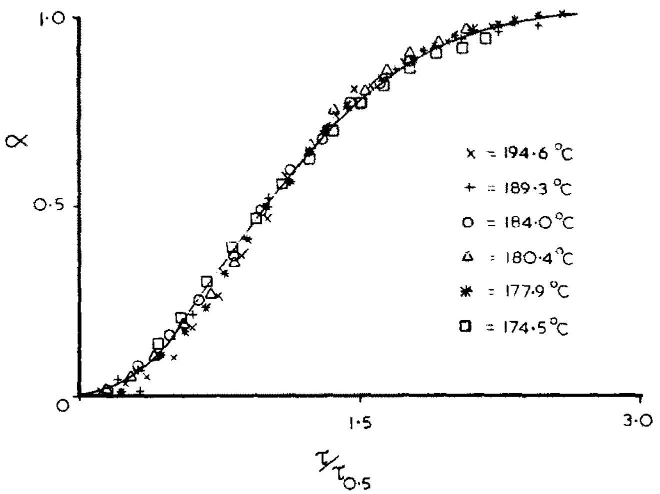

Fig. 3. Normalized data at $\alpha = 0.5$ for silver oxalate decomposition in nitrogen.

These curves were then treated by the reduced time method normalizing at the half decomposition time and for confirmation by the $\alpha_{\text{experimental}}$ versus $\alpha_{\text{theoretical}}$ method to identify the reaction mechanism, $f(\alpha)$. Figure 3 shows the reduced time plot for the isothermal data in a nitrogen atmosphere along with the superimposed theoretical curve for the Avrami–Erofeev equation with $n = 2$.

Using the integral method equation

$$g(\alpha) = kt$$

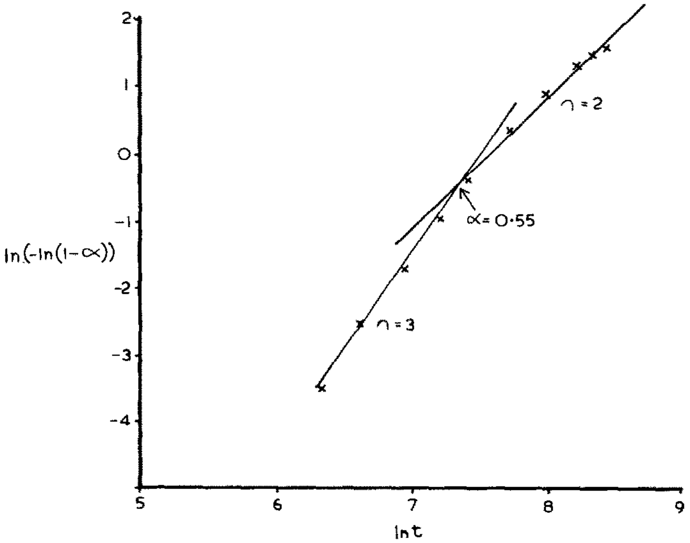

Fig. 4. Plots of $\ln(-\ln(1-\alpha))$ vs. $\ln t$ for silver oxalate in oxygen at 190.9°C.

TABLE 2

Kinetic data for thermal decomposition of silver oxalate

Atmosphere	Mechanism [a]	E (kJ mol^{-1})	A
N_2	A_2	124	6.23×10^{10}
Air	A_2	153	1.07×10^{14}
O_2	A_2	165	1.70×10^{15}
CO_2	R_2	128	1.96×10^{10}
Vacuum	A_5	97.7	1.46×10^{8}

[a] A_2 and A_5 represent the Avrami–Erofeev equation with $n = 2$ and 5 respectively; R_2 represents the contracting area expression.

the specific reaction rate constants were determined and subsequently the Arrhenius parameters.

Table 2 shows the mechanism of decomposition and the Arrhenius parameters for decompositions in the various atmospheres. Perhaps the most significant observation from Table 2 is the retarding influence of oxygen on the decomposition which is greater than the retarding influence of carbon dioxide. Although by Le Chatelier's principle we would expect the activation energy to be raised quite considerably in an atmosphere of carbon dioxide, the increase is only slight. This was observed in the original paper by MacDonald and Hinshelwood [1] and also by Osinovik and Zhoglo [14].

The fact that the decomposition has been reported to be explosive in air and oxygen would suggest a lower activation energy in these atmospheres. Our assumption, that the explosive nature is due to the decrepitation caused by the release of strain set up by the volume change in the solid state, explains this abnormality. Why the presence of oxygen causes such a retarding influence is still unclear, and we can put forward no other explanation except to agree with MacDonald and Hinshelwood's theory [1] that oxygen poisons the nuclei.

Whilst A_2 is the best fitting mechanism for the decomposition in oxygen, in fact the decomposition is best described by a mechanism change from A_3 to A_2 at a point in the decomposition that corresponds to $\alpha = 0.55$ (Fig. 4).

Relating this to the DSC curves shows that this value corresponds to a point close to the minima between the two peaks, again adding further evidence to the hypothesis regarding release of strain. Arrhenius parameters for the two stages of decomposition are shown in Table 3.

TABLE 3

Details of kinetic mechanism change in thermal decomposition of silver oxalate in oxygen

α	Mechanism	E (kJ mol^{-1})	A
0–0.55	A_3	145	9.67×10^{12}
0.55–1.00	A_2	163	9.62×10^{14}

Under vacuum, as expected, a lower activation energy is obtained which can be related to the ease with which the gaseous species are liberated in the absence of an external pressure.

The mechanism A_5 for the vacuum decomposition, although unusual, is not unknown. The usual explanation is to say that the exponent $n = 5$ represents a combination of factors given by $n = \beta + \lambda$ where β is the number of steps involved in nucleus formation and λ is the number of dimensions involved in nuclei growth. On the assumption of the maximum dimensions of 3 being involved this would involve a two-stage nucleation process. Speculatively, such a model is possible involving, say, first the production of single silver atoms followed by migration and aggregation to form suitably sized nuclei from which growth can proceed.

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