

THERMAL DECOMPOSITION OF OXALATES

Part XXIV. Effect of the sample preparation and environmental atmosphere on the thermal stability of silver oxalate

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(Received 9 July 1990)

ABSTRACT

The thermal decomposition of silver oxalate has been studied using mechanism-dependent and mechanism-independent isothermal kinetics, conventional rising temperature thermogravimetry (TG) and a TG computer program. Studies were carried out on four different preparations of the sample which involved precipitation from stoichiometric and non-stoichiometric conditions. Each sample was studied under atmospheres of nitrogen, air, oxygen, and carbon dioxide as well as under vacuum.

The assignment of stability information based on the magnitude of the Arrhenius parameters is shown to be deceptive. Applying the computer program and the limiting kinetic condition of $\alpha \rightarrow 0$ allows the relative stability of various preparations and the retarding influence of oxygen and carbon dioxide, to be quantitatively evaluated.

INTRODUCTION

In a previous paper [1], we reported kinetic data showing the effect of the environmental atmosphere on the decomposition of silver oxalate. It was also pointed out that the method by which the sample is prepared can effect the decomposition. This phenomenon was first reported by MacDonald and Hinshelwood [2] who used a constant volume vacuum system to show that samples precipitated in the presence of excess oxalic acid produced a more unstable form which decomposed in a highly acceleratory manner, while samples prepared in the presence of excess silver nitrate gave a more stable compound which, on decomposition, followed a feebly acceleratory mechanism.

Further investigation by MacDonald [3] demonstrated that adsorbed nitrate ions were the cause of the increased stability by showing that the more unstable excess oxalic acid preparation could be rendered stable by the addition of a quantity of sodium nitrate solution.

In this paper we have extended the study to include the effect of sample preparation as well as the environmental atmosphere.

Experiments have been conducted under isothermal and rising temperature conditions. Isothermal runs were carried out with the purpose of calculating kinetic parameters using the integral method

$$g(\alpha) = kt \quad (1)$$

where $g(\alpha)$ is the integrated form of the reaction mechanism, k is the specific reaction rate constant, and t is the time. The isothermal data were also treated by the "mechanism independent" method

$$\ln t = \ln g(\alpha) - \ln A + E/RT \quad (2)$$

where T is the temperature, A is the pre-exponential factor, R is the gas constant, and E is the activation energy. Assuming that $\ln g(\alpha)$ is very small in comparison with $\ln A$ allows the calculation of E and A from a plot of $\ln t$ against $1/T$.

Rising temperature curves were produced for additional information on stability and for comparison with the isothermal investigation.

The two methods were also compared using a computer program which generates the rising temperature curve from the activation energy, pre-exponential factor, reaction mechanism, and heating rate.

The isothermal kinetic technique was used on samples prepared using correct, stoichiometric quantities, excess silver nitrate, excess oxalic acid, and also on one prepared in the absence of nitrate ion. Each sample was studied under dynamic atmospheres of nitrogen, air, oxygen, and carbon dioxide as well as under vacuum.

The isothermal TG curves were treated by the integral method to calculate the specific reaction rate constants. The reduced time [4] method was used to identify the reaction mechanism ($f(\alpha)$), with the $\alpha_{\text{experimental}}$ vs. $\alpha_{\text{theoretical}}$ method [5] being used for conformation.

EXPERIMENTAL

Equipment

The thermal analysis was carried out using a DuPont 1090 Thermal Analyzer coupled to a 951 TG unit. Sample size was in the range 5–10 mg, and decomposition was carried out on a platinum sample pan using an atmosphere flow rate of 30 ml min⁻¹. Decompositions in vacuum were carried out in a constant volume Prout-and-Tompkins-type unit [6] using a McCloud gauge as the pressure sensor.

Sample preparation and characterization

The silver oxalate was prepared by combining aqueous solutions of 0.1 M silver nitrate and oxalic acid.

The correct stoichiometric preparation was obtained with a 2:1 silver nitrate to oxalic acid ratio, while the excess oxalic acid preparation used a 1:1 ratio, and the excess silver nitrate preparation a 4:1 ratio. In addition, a fourth sample was prepared from stoichiometric quantities of silver chlorate and oxalic acid to eliminate the effect of the presence of nitrate ion.

The white precipitates were isolated by suction filtration, air dried, and stored in the dark.

Determinations of silver from the TG residue and of oxalate by titration with potassium permanganate for each sample did not deviate significantly from the theoretical values of 71.0% Ag and 29.0% oxalate, based on the formula $\text{Ag}_2\text{C}_2\text{O}_4$.

RESULTS AND DISCUSSION

Isothermal study

Arrhenius parameters and the reaction mechanisms for the various atmospheres and preparations are shown in Table 1.

The authors have previously speculated [7] that the variation in the kinetic results of several studies on a particular compound may be due to the preparative technique. Here it can be seen that the method of preparation not only alters the value of the activation energy and the pre-exponential factor, but also the decomposition mechanism.

The results shown for the correct stoichiometric ratio preparation are taken from our earlier paper [1] and are included here for completeness. The retarding influence of oxygen on the decomposition was first observed by MacDonal and Hinshelwood [2] who also reported the apparent lack of any significant retardation by carbon dioxide, which would appear to contradict Le Chatelier's principle. For the stoichiometric preparation these results can be confirmed by the magnitude of the activation energy; however, the kinetic data for the other preparations do not appear to display a similar trend. Any comparison is complicated by the fact that there is no single mechanism for all the systems and that, in some instances, there is also a mechanism change during the decomposition.

Considering the limiting condition where $\alpha \rightarrow 0$ [8] yields

$$\frac{d\alpha}{dt} = k \quad (3)$$

TABLE 1
Arrhenius parameters and mechanisms for various preparations of silver oxalate

Method of preparation	Decomposition atmosphere			
	Nitrogen	Air	Oxygen	Carbon dioxide
Correct stoichiometric ratio	A ₂ mechanism $E = 124 \text{ kJ mol}^{-1}$ $A = 6.23 \times 10^{10}$	A ₂ mechanism $E = 153 \text{ kJ mol}^{-1}$ $A = 1.07 \times 10^{14}$	A ₂ mechanism $E = 165 \text{ kJ mol}^{-1}$ $A = 1.70 \times 10^{15}$	R ₂ mechanism $E = 128 \text{ kJ mol}^{-1}$ $A = 1.96 \times 10^{10}$
	R ₂ mechanism $E = 132 \text{ kJ mol}^{-1}$ $A = 5.88 \times 10^{11}$	R ₂ mechanism $E = 119 \text{ kJ mol}^{-1}$ $A = 4.46 \times 10^9$	R ₂ mechanism $E = 132 \text{ kJ mol}^{-1}$ $A = 9.72 \times 10^{10}$	A ₂ mechanism ($\alpha = 0-0.5$) $E = 138 \text{ kJ mol}^{-1}$ $A = 8.01 \times 10^{12}$
Excess silver present	A ₃ mechanism ($\alpha = 0.1-0.9$) $E = 165 \text{ kJ mol}^{-1}$ $A = 2.74 \times 10^{14}$	A ₃ mechanism ($\alpha = 0-0.5$) $E = 157 \text{ kJ mol}^{-1}$ $A = 2.30 \times 10^{13}$	A ₂ mechanism ($\alpha = 0-0.4$) $E = 103 \text{ kJ mol}^{-1}$ $A = 1.98 \times 10^7$	R ₂ mechanism ($\alpha = 0.5-1.0$) $E = 101 \text{ kJ mol}^{-1}$ $A = 5.61 \times 10^7$
	A ₂ mechanism ($\alpha = 0.5-1.0$) $E = 140 \text{ kJ mol}^{-1}$ $A = 3.27 \times 10^{11}$	A ₂ mechanism ($\alpha = 0.4-1.0$) $E = 106 \text{ kJ mol}^{-1}$ $A = 2.42 \times 10^7$	A ₂ mechanism $E = 159 \text{ kJ mol}^{-1}$ $A = 1.59 \times 10^{13}$	A ₃ mechanism $E = 128 \text{ kJ mol}^{-1}$ $A = 5.88 \times 10^{11}$
Absence of nitrate ion	A ₃ mechanism $E = 120 \text{ kJ mol}^{-1}$ $A = 9.34 \times 10^9$	A ₃ mechanism $E = 168 \text{ kJ mol}^{-1}$ $A = 1.26 \times 10^{15}$	A ₃ mechanism $E = 128 \text{ kJ mol}^{-1}$ $A = 1.96 \times 10^{10}$	A ₃ mechanism $E = 208 \text{ kJ mol}^{-1}$ $A = 4.53 \times 10^{19}$
	F ₁ mechanism ($\alpha = 0-0.5$) $E = 125 \text{ kJ mol}^{-1}$ $A = 1.95 \times 10^{13}$			

TABLE 2

Specific reaction rates (s^{-1}) calculated from the Arrhenius parameters shown in Table 1, assuming the limiting condition of $\alpha \rightarrow 0$

	Nitrogen	Air	Oxygen	Carbon dioxide	Vacuum
Correct stoichiometric ratio	1.26×10^{-3}	1.36×10^{-3}	1.02×10^{-3}	1.43×10^{-4}	2.37×10^{-3}
Excess oxalate present	1.55×10^{-3}	3.22×10^{-4}	2.57×10^{-4}	4.61×10^{-3} 3.93×10^{-4}	0.305
Excess silver present	1.64×10^{-4}	1.05×10^{-4} 1.13×10^{-4}	8.35×10^{-5} 4.76×10^{-5}	4.38×10^{-5}	4.29×10^{-3}
Absence of nitrate ion	5.22×10^{-4}	3.52×10^{-4}	1.43×10^{-4}	4.84×10^{-4}	—

Calculation of the specific reaction rate constant from the Arrhenius parameters at an arbitrary selected temperature of 200°C allows a clearer comparison to be made. These results are shown in Table 2.

The retarding influence of oxygen, for all preparations, is clearly demonstrated by the slower rates of decomposition, the only anomaly being the correct-ratio preparation in air. Furthermore, the predicted stabilities of the preparations using non-stoichiometric ratios are now apparent. The relatively unstable excess oxalic acid preparation has a faster decomposition rate than the stoichiometric preparation, while the more stable excess silver nitrate preparation has a slower rate. This trend holds true in atmospheres of nitrogen and carbon dioxide; however in air and pure oxygen, the excess oxalic acid preparation is more stable than the correct-ratio preparation. It is assumed that the retarding influence of oxygen is due to poisoning of the nuclei [2]. Thus, the absence of a significant number of adsorbed ions may make it easier for oxygen molecules to reach the surface.

Further consideration of these rates of decomposition also shows that an atmosphere of carbon dioxide does have an effect on the decomposition; however, only in the stoichiometric preparation is the retardation significantly greater than that of oxygen.

The reported highly acceleratory nature of the decomposition in the case of the excess oxalic acid preparation is not apparent. In fact our results show that the deceleratory contracting area mechanism predominates. The acceleratory nature was originally observed under vacuum conditions; however, in this study the results showed the deceleratory first-order mechanism takes place. Similarly, it has been reported that the excess silver nitrate prepara-

TABLE 3

Parameters describing the rising temperature TG curves of various preparations of silver oxalate in the different atmospheres using a heating rate of $1^{\circ}\text{C min}^{-1}$

Preparation	Nitrogen	Air	Oxygen	Carbon dioxide
Correct ratio	Range 176–214 $^{\circ}\text{C}$	Range 188–214 $^{\circ}\text{C}$	Range 180–216 $^{\circ}\text{C}$	^a Range 202–248 $^{\circ}\text{C}$
	α_{max} 0.382	α_{max} 0.487		α_{max} 0.536
	T_{max} 199.0 $^{\circ}\text{C}$	T_{max} 203.2 $^{\circ}\text{C}$		T_{max} 230.8 $^{\circ}\text{C}$
	LoTs 195.2 $^{\circ}\text{C}$	LoTs 197.0 $^{\circ}\text{C}$		LoTs 222.8 $^{\circ}\text{C}$
	HiTs 207.4 $^{\circ}\text{C}$	HiTs 208.5 $^{\circ}\text{C}$		HiTs 238.7 $^{\circ}\text{C}$
	1/2 width 12.2 $^{\circ}\text{C}$	1/2 width 11.5 $^{\circ}\text{C}$		1/2 width 15.9 $^{\circ}\text{C}$
Excess oxalic acid	Range 159–192 $^{\circ}\text{C}$	Range 176–220 $^{\circ}\text{C}$	Range 174–230 $^{\circ}\text{C}$	Range 166–220 $^{\circ}\text{C}$
	α_{max} 0.504	α_{max} 0.561	α_{max} 0.513	α_{max} 0.508
	T_{max} 176.0 $^{\circ}\text{C}$	T_{max} 200.6 $^{\circ}\text{C}$	T_{max} 201.1 $^{\circ}\text{C}$	T_{max} 188.5 $^{\circ}\text{C}$
	LoTs 166.2 $^{\circ}\text{C}$	LoTs 188.6 $^{\circ}\text{C}$	LoTs 193.3 $^{\circ}\text{C}$	LoTs 177.2 $^{\circ}\text{C}$
	HiTs 185.6 $^{\circ}\text{C}$	HiTs 208.9 $^{\circ}\text{C}$	HiTs 207.5 $^{\circ}\text{C}$	HiTs 199.8 $^{\circ}\text{C}$
	1/2 width 19.4 $^{\circ}\text{C}$	1/2 width 20.3 $^{\circ}\text{C}$	1/2 width 14.2 $^{\circ}\text{C}$	1/2 width 22.6 $^{\circ}\text{C}$
Excess silver nitrate	Range 196–250 $^{\circ}\text{C}$	^a Range 190–248 $^{\circ}\text{C}$	^a Range 204–274 $^{\circ}\text{C}$	Range 190–252 $^{\circ}\text{C}$
			α_{max} 0.405	α_{max} 0.466
			T_{max} 248.6 $^{\circ}\text{C}$	T_{max} 230.4 $^{\circ}\text{C}$
			LoTs 241.0 $^{\circ}\text{C}$	LoTs 224.0 $^{\circ}\text{C}$
			HiTs 263.0 $^{\circ}\text{C}$	HiTs 238.0 $^{\circ}\text{C}$
		1/2 width 22.0 $^{\circ}\text{C}$	1/2 width 14.0 $^{\circ}\text{C}$	
Absence of nitrate ion	Range 210–248 $^{\circ}\text{C}$	Range 204–240 $^{\circ}\text{C}$	Range 204–240 $^{\circ}\text{C}$	Range 216–254 $^{\circ}\text{C}$
	α_{max} 0.617	α_{max} 0.692	α_{max} 0.681	α_{max} 0.607
	T_{max} 235.3 $^{\circ}\text{C}$	T_{max} 230.8 $^{\circ}\text{C}$	T_{max} 230.8 $^{\circ}\text{C}$	T_{max} 243.2 $^{\circ}\text{C}$
	LoTs 228.0 $^{\circ}\text{C}$	LoTs 224.3 $^{\circ}\text{C}$	LoTs 223.4 $^{\circ}\text{C}$	LoTs 236.0 $^{\circ}\text{C}$
	HiTs 240.0 $^{\circ}\text{C}$	HiTs 234.0 $^{\circ}\text{C}$	HiTs 235.0 $^{\circ}\text{C}$	HiTs 248.0 $^{\circ}\text{C}$
	1/2 width 12 $^{\circ}\text{C}$	1/2 width 9.7 $^{\circ}\text{C}$	1/2 width 11.6 $^{\circ}\text{C}$	1/2 width 12.0 $^{\circ}\text{C}$

^a Other parameters could not be determined due to the complex shape of the DTG curve.

tion produces a deceleratory decomposition curve, whereas here we see the sigmoidal Avrami–Erofeev mechanisms predominating.

Rising temperature study

Conventional rising temperature thermogravimetric experiments were performed on the various silver oxalate preparations under the different dynamic atmospheres using a heating rate of $1^{\circ}\text{C min}^{-1}$.

The following expressions are used to describe the resulting curves: T_{max} is the temperature at which maximum rate occurs; α_{max} is the value of α at which maximum rate occurs; the 1/2 width is the width of the DTG peak at its half-height; LoTs indicates the low temperature side of the 1/2 width; and HiTs the high temperature side of the 1/2 width.

Table 3 shows the results obtained. It can be seen that the stability information obtained from rising temperature thermogravimetry experi-

ments compares well with the isothermal kinetic results. The observed trends previously discussed, as well as the exceptions, can be seen. The stability of the excess oxalic acid preparation in oxygen-containing atmospheres is again found to be greater than the stoichiometric preparation; in addition, the retarding influence of carbon dioxide is best seen for the correct-ratio preparation.

TG recreation program results

The isothermal Arrhenius parameters and mechanisms previously obtained were used in conjunction with a computer program which produces the rising temperature curve from the activation energy, pre-exponential factor, mechanism, and heating rate. Results are shown in Table 4. A comparison of Table 4 with Tables 1–3 yields some interesting conclusions.

The Arrhenius parameters shown in Table 1 do not apparently show the retarding influence of oxygen except for the stoichiometric preparation. However, using E , A , and $f(\alpha)$ to recreate the TG curves clearly shows the retardation in the form of a higher T_{\max} . Similarly, the apparent non-retardation due to carbon dioxide for the stoichiometric preparation is now apparent in the 21.3°C increase in T_{\max} . As such, the recreation data compliments the approximated rate results shown in Table 2.

By studying the T_{\max} values, the relative retarding influences of oxygen and carbon dioxide become more apparent. Carbon dioxide does have a significant retarding influence, except in the preparation in which silver chlorate was used as the cation source; however, in most cases, the retarding influence of oxygen is comparable with or greater than that of carbon dioxide. These observations are in agreement with the results from the rising temperature data shown in Table 3.

It should be noted that using the isothermal kinetic data in the computer program does not recreate the experimental TG curves. This should not be considered unusual bearing in mind the different conditions under which the nucleation process is forced to proceed.

“Mechanism-independent” isothermal kinetics

Combining the conventional isothermal integral equation and the Arrhenius equation gives

$$g(\alpha) = A e^{-E/RT} t \quad (4)$$

Taking logs and rearranging leads to the straight line equation

$$\ln t = \ln g(\alpha) - \ln A + E/RT \quad (5)$$

If it is assumed that $\ln g(\alpha)$ is very small compared with $\ln A$, then a plot of $\ln t$ against $1/T$ will give a slope of E/R and an intercept of $-\ln A$.

TABLE 4

Parameters describing the theoretical TG plots obtained using the Arrhenius parameters in Table 1 in conjunction with the recreation computer program

Preparation	Nitrogen	Air	Oxygen	Carbon dioxide	Vacuum
Correct ratio	α_{\max} 0.622	α_{\max} 0.624	α_{\max} 0.624	α_{\max} 0.735	α_{\max} 0.635
	T_{\max} 196.4°C	T_{\max} 198.1°C	T_{\max} 201.9°C	T_{\max} 217.7°C	T_{\max} 180.2°C
	LoTs 190°C HiTs 204°C 1/2 width 14°C	LoTs 190°C HiTs 204°C 1/2 width 14°C	LoTs 194°C HiTs 208°C 1/2 width 14°C	LoTs 200°C HiTs 228°C 1/2 width 28°C	LoTs 180°C HiTs 184°C 1/2 width 4.0°C
Excess oxalic acid	α_{\max} 0.736	α_{\max} 0.734	α_{\max} 0.735	$T_{\max 1}$ 181.9°C	α_{\max} 0.613
	T_{\max} 185.4°C	T_{\max} 205.5°C	T_{\max} 209.2°C	$T_{\max 2}$ 200.6°C	T_{\max} 130.3°C
	LoTs 170°C HiTs 194°C 1/2 width 24°C	LoTs 188°C HiTs 216°C 1/2 width 28°C	LoTs 194°C HiTs 218°C 1/2 width 24°C		LoTs 116°C HiTs 142°C 1/2 width 26°C
Excess silver nitrate	α_{\max} 0.629	$T_{\max 1}$ 228.8°C	$T_{\max 1}$ 238.8°C	α_{\max} 0.620	α_{\max} 0.628
	T_{\max} 222.5°C	$T_{\max 2}$ 230.3°C	$T_{\max 2}$ 242.3°C	T_{\max} 239.9°C	T_{\max} 180.6°C
	LoTs 220°C HiTs 228°C 1/2 width 8.0°C			LoTs 232°C HiTs 248°C 1/2 width 16°C	LoTs 180°C HiTs 186°C 1/2 width 6°C
Absence of nitrate ion	α_{\max} 0.627	α_{\max} 0.630	α_{\max} 0.627	α_{\max} 0.631	
	T_{\max} 208.8°C	T_{\max} 213.6°C	T_{\max} 228.2°C	T_{\max} 209.5°C	
	LoTs 202°C HiTs 214°C 1/2 width 12°C	LoTs 210°C HiTs 218°C 1/2 width 8°C	LoTs 222°C HiTs 234°C 1/2 width 12°C	LoTs 208°C HiTs 214°C 1/2 width 6°C	

TABLE 5

Arrhenius parameters shown as a function of the fraction decomposed, calculated using "mechanism-independent" isothermal kinetics

Prep.	α	Nitrogen		Air		Oxygen		Carbon dioxide	
		E (kJ mol ⁻¹)	A (s ⁻¹)	E (kJ mol ⁻¹)	A (s ⁻¹)	E (kJ mol ⁻¹)	A (s ⁻¹)	E (kJ mol ⁻¹)	A (s ⁻¹)
Correct ratio	0.1	97	1.42×10^8	121	6.52×10^{10}	139	6.29×10^{12}	85	3.99×10^6
	0.3	112	4.04×10^9	151	9.91×10^{13}	146	2.05×10^{13}	85	2.33×10^6
	0.5	118	1.45×10^{10}	148	3.84×10^{13}	151	6.34×10^{13}	102	1.10×10^8
	0.7	119	1.36×10^{10}	148	3.02×10^{13}	164	1.37×10^{15}	126	3.69×10^{10}
	0.9	120	1.44×10^{10}	141	3.56×10^{12}	167	1.94×10^{15}	130	6.78×10^{10}
Excess oxalic acid	0.1	129	3.04×10^{12}	140	1.30×10^{13}	68	5.53×10^4	132	4.87×10^{12}
	0.3	115	3.38×10^{10}	147	4.72×10^{13}	104	4.16×10^8	141	2.69×10^{13}
	0.5	124	2.87×10^{11}	149	6.48×10^{13}	109	1.19×10^9	142	2.53×10^{13}
	0.7	119	4.29×10^{10}	151	6.21×10^{13}	129	1.51×10^{11}	153	2.84×10^{14}
	0.9	120	3.98×10^{10}	155	1.01×10^{14}	150	1.85×10^{13}	148	4.37×10^{13}
Excess silver nitrate	0.1	160	2.08×10^{14}	142	2.19×10^{12}	110	6.42×10^8	151	9.54×10^{12}
	0.3	154	3.07×10^{13}	155	3.30×10^{13}	116	1.70×10^9	159	3.50×10^{13}
	0.5	156	3.81×10^{13}	154	2.16×10^{13}	123	6.90×10^9	149	2.31×10^{12}
	0.7	159	6.76×10^{13}	152	7.95×10^{12}	122	3.55×10^9	149	1.49×10^{12}
	0.9	185	3.35×10^{16}	149	2.89×10^{12}	126	5.91×10^9	142	1.99×10^{11}
Absence of nitrate ion	0.1	115	8.72×10^9	205	4.27×10^{19}	143	3.05×10^{12}	215	9.42×10^{20}
	0.3	116	5.97×10^9	188	2.88×10^{17}	134	1.57×10^{11}	203	2.09×10^{19}
	0.5	118	7.20×10^9	180	2.88×10^{16}	128	2.96×10^{10}	202	1.49×10^{19}
	0.7	118	6.94×10^9	180	2.88×10^{16}	128	2.18×10^{10}	200	6.35×10^{18}
	0.9	115	2.30×10^9	177	1.02×10^{16}	131	3.66×10^{10}	201	7.07×10^{18}

The time, t , is usually taken as the time required to reach $\alpha = 0.5$. However, the dependence of the Arrhenius parameters on the value of α selected has been described by Krishnan et al. [9]. Table 5 shows the results obtained by this method with our isothermal data, using degrees of conversion of $\alpha = 0.1, 0.3, 0.5, 0.7,$ and 0.9 .

In general, the Arrhenius parameters do represent a good match to those given in Table 1. The major exception appears to be the excess oxalic acid preparation in an atmosphere of air. Using the contracting area mechanism produced an activation energy of 119 kJ mol^{-1} while here the average activation energy is 148 kJ mol^{-1} .

Thus, the "mechanism-independent" isothermal technique appears to give a quick and close approximation to the Arrhenius parameters. However, the danger in using activation energies as an indication of stability, without considering the mechanism, can be seen by comparing Tables 1 and 4.

CONCLUSION

Using mechanism-dependent and mechanism-independent isothermal kinetics, conventional rising temperature thermogravimetry, and a TG computer program, we have been able to illustrate quantitatively the results of MacDonal and Hinshelwood.

Assigning stability information on the basis of the magnitude of the Arrhenius parameters has been shown to be deceptive. As such, it has been shown that carbon dioxide does significantly retard the decomposition; however, in general, oxygen has an even greater influence.

The non-stoichiometric preparations showed the reported stability trend but not the described acceleratory/deceleratory nature. The trend, however, was not seen in oxygen-containing atmospheres in which the reportedly more unstable excess oxalic acid preparation was seen to be more stable than the correct stoichiometric preparation. This is explained in terms of the oxygen molecules having a freer access to the solid surface due to the presence of fewer adsorbed nitrate ions.

Preparing the silver oxalate from a stoichiometric quantity of silver chlorate and oxalic acid produced a sample which was always more stable than when silver nitrate was used as a cation source. If the nitrate ion is associated with the reason for the preparation dependence, then the conclusion is that the chlorate ion has an even greater stabilizing effect.

Experiments conducted under vacuum conditions can be seen to lead to significantly faster reaction rates than under dynamic atmospheres. This is expected, owing to the ease with which the gaseous products can escape under vacuum conditions.

The use of the TG computer program to give a clearer understanding as to the significance of the activation energy, pre-exponential factor, and

reaction mechanism has been shown to be beneficial. As such, the Arrhenius parameters produced in the mechanism-independent isothermal calculations, despite giving a good approximation, must be carefully considered if being used as an indication of stability.

REFERENCES

- 1 D. Dollimore and T.A. Evans, *Thermochim. Acta* 178 (1991) 263.
- 2 J.Y. MacDonald and C.N. Hinshelwood, *J. Chem. Soc.*, 127 (1925) 2764.
- 3 J.Y. MacDonald, *J. Chem. Soc.*, (1936) 832.
- 4 J.H. Sharp, G.W. Brindley and B.N.N. Achar, *J. Am. Ceram. Soc.*, 49 (1966) 379.
- 5 L.F. Jones, D. Dollimore and T. Nicklin, *Thermochim. Acta*, 13 (1975) 240.
- 6 E.G. Prout and F.C. Tompkins, *Trans. Faraday Soc.*, 40 (1944) 488.
- 7 D. Broadbent, J. Dollimore, D. Dollimore and T.A. Evans, *J. Chem. Soc. Faraday Trans.*, (1990) in press.
- 8 D. Dollimore, G.R. Heal and B.W. Krupay, *Thermochim. Acta*, 24 (1978) 293
- 9 K. Krishnan, K.N. Ninan and P.M. Madhusudan, *Thermochim. Acta*, 79 (1984) 279.