Thermal decomposition of oxalates
Part 25. The effect of sample preparation
and environmental atmosphere on the thermal stability
of copper(II) oxalate

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Abstract

The kinetics and thermal stability of copper oxalate prepared under stoichiometric and non-stoichiometric conditions have been studied by isothermal and rising temperature experiments in nitrogen and in air. In addition, a mechanism-independent method and a computer program were used to interpret the isothermal data to give additional information on the stability of the systems. In nitrogen, the presence of excess copper chloride stabilizes the salt whilst the presence of excess oxalic acid reduces the stability. This trend is also observed for silver oxalate.

The interpretations of the stability of the salts based solely on the activation energy were misleading. The use of a computer program shows that a more accurate evaluation requires the consideration of the pre-exponential factor and the reaction mechanism in addition to the activation energy.

INTRODUCTION

In a previous report, the effect of sample preparation and environmental atmosphere on the thermal stability of silver oxalate was studied [1]. It was shown that samples prepared with an excess of oxalate ions were less stable than samples with an excess of nitrate ions. This phenomenon was first reported by MacDonald and Hinshelwood [2]. MacDonald [3], in a further investigation, attributed the increased stability to adsorbed nitrate ions.

Broadbent et al. [4] suggested that non-stoichiometric preparations of copper oxalate tend to reduce the stability of the salt, which is in contrast to the results obtained for silver oxalate. This may be due to the different decomposition route of the two salts. Silver oxalate decomposes to silver metal and CO_2 gas, both in nitrogen and in air. Meanwhile for copper oxalate, copper metal is obtained under an atmosphere of nitrogen, and in air the oxide is formed due to the oxidation of the copper metal. However, no attempt was made to investigate the kinetic aspect of the various preparations of copper oxalate.

In the present study, the kinetics and the thermal stability of copper oxalate prepared using stoichiometric quantities, as well as excess copper chloride and excess oxalic acid were investigated in air and in nitrogen.

EXPERIMENTAL

Sample preparation

In the stoichiometric preparation, 5.0×10^{-3} M aqueous solutions of copper chloride and oxalic acid were mixed. For the excess copper chloride preparation, a 1.5:1 copper chloride to oxalic acid ratio was used and a 1:1.5 ratio was used for the excess oxalic acid preparation. The blue precipitate was filtered without additional washing and air dried.

Thermal analysis

A Dupont 1090 work station coupled to a 951 TG unit was used. All TG experiments were performed under an atmosphere of nitrogen or air at a flow rate of 40 cm^3 min^{-1} using a platinum sample pan. In the isothermal experiments, the sample size was in the range 8.0–11.0 mg. For the rising temperature experiments, a heating rate of 2°C min^{-1} was used with the sample size in the range 10.1–10.6 mg.

RESULTS AND DISCUSSION

A series of isothermal studies were performed under atmospheres of nitrogen and air. The kinetic mechanism that described the decomposition was obtained from the reduced time method [5]. In all cases, an Avrami–Erofeev ($n = 2$) mechanism was found to give the best fit to the experimental data.

Table 1 shows the kinetic data obtained. In both nitrogen and air, the activation energy of the sample prepared with excess oxalic acid is the lowest. This is not surprising as the presence of excess oxalate ions tends to

TABLE 1

Arrhenius parameters of copper oxalate prepared under various conditions obtained by isothermal experiments in nitrogen and in air

Preparation conditions	Nitrogen		Air	
	E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})
Stoichiometric	193	2.83×10^{14}	184	7.14×10^{13}
Excess oxalic acid	141	4.62×10^{9}	164	9.55×10^{11}
Excess copper chloride	178	5.01×10^{12}	274	1.78×10^{22}

reduce the stability of silver oxalate [1]. The activation energy is lower in air for the stoichiometric sample whilst for the non-stoichiometric samples, the activation energy is higher in air than in nitrogen. Since all decompositions obeyed the Avrami–Erofeev (A_2) mechanism and great care was taken to ensure all experimental conditions were kept the same, then the increase in activation energy is attributed to the adsorbed ions.

It would be envisaged that a system with a higher activation energy would be more stable than a system with a lower energy, if the activation energy in solid state kinetics is considered to have the same connotation as the activation energy in homogenous kinetics. From Table 1, the predicted thermal stability in terms of the activation energy in air is excess copper choloride > stoichiometric > excess oxalic acid. This trend is similar to that observed for experiments carried out on silver oxalate. In nitrogen, the predicted stability is stoichiometric > excess copper chloride > excess oxalic acid. This appears to show that the non-stoichiometric preparations reduced the stability of the salt, as suggested by Broadbent et al. [4]. This trend in the activation energy is also reflected in the kinetic parameters calculated from the mechanism-independent method [6].

The integral kinetic equation can be combined with the Arrhenius equation as

$$g(\alpha) = A\, e^{-E/RT} t \tag{1}$$

where $g(\alpha)$ is the integral form of the kinetic equation, A and E are the Arrhenius parameters, R is the gas constant, and T and t are temperature and time in Kelvin and seconds respectively.
Taking natural logarithms and rearranging gives

$$\ln t = \ln g(\alpha) - \ln A - \frac{E}{RT} \tag{2}$$

The activation energy and pre-exponential factor can be obtained from a plot of $\ln t$ against $1/T$ if $\ln g(\alpha)$ is assumed negligible compared to $\ln A$. Tables 2 and 3 show the Arrhenius parameters obtained at $\alpha = 0.1$, 0.3, 0.5, 0.7 and 0.9. The kinetic parameters vary with the extent of decomposition; this has been demonstrated by Krishnan et al. [6]. In spite of this variation, the average Arrhenius parameters gave a close approximation to the values obtained from the conventional "mechanism-dependent" method (Table 1).

A series of rising temperature experiments were also performed to observe the relative stability of copper oxalate based on the temperature at maximum rate of decomposition (T_{max}). Table 4 shows the T_{max} obtained with a $2\,^\circ C\ min^{-1}$ heating rate. In an atmosphere of nitrogen, the presence of excess chloride stabilized the salt, and the oxalate ions reduced its stability. This trend is similar to the trend observed earlier, except that now it is in nitrogen instead of in air. Based on the results obtained for silver

TABLE 2

Arrhenius parameters obtained from the mechanism-independent method in air

α	Stoichiometric ratio		Excess copper chloride		Excess oxalic acid	
	E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})
0.1	163	3.35×10^{12}	262	5.65×10^{21}	165	3.14×10^{12}
0.3	191	5.78×10^{14}	256	7.63×10^{20}	167	2.56×10^{12}
0.5	185	1.14×10^{14}	256	5.49×10^{20}	164	1.13×10^{12}
0.7	183	6.27×10^{13}	260	1.03×10^{21}	163	6.37×10^{11}
0.9	188	1.26×10^{14}	266	2.33×10^{21}	160	2.60×10^{11}
Av.	182	1.89×10^{14}	260	2.06×10^{21}	164	1.55×10^{12}

TABLE 3

Arrhenius parameters obtained from the mechanism-independent method in nitrogen

α	Stoichiometric ratio		Excess copper chloride		Excess oxalic acid	
	E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})
0.1	221	3.19×10^{17}	125	2.51×10^{8}	124	2.86×10^{8}
0.3	225	3.93×10^{17}	146	8.70×10^{9}	143	1.01×10^{10}
0.5	216	4.44×10^{16}	152	2.32×10^{10}	144	1.04×10^{10}
0.7	209	7.28×10^{15}	158	6.57×10^{10}	152	5.34×10^{10}
0.9	200	8.11×10^{14}	167	3.54×10^{11}	151	2.76×10^{10}
Av.	214	1.53×10^{17}	150	9.04×10^{10}	143	2.04×10^{10}

TABLE 4

Temperature at maximum rate (T_{max}) from rising temperature study with a $2\,^{\circ}$C min^{-1} heating rate

Preparation conditions	T_{max} ($^{\circ}$C)	
	Nitrogen	Air
Stoichiometric	332.6	325.9
Excess oxalic acid	326.1	326.8
Excess copper chloride	339.7	314.4

oxalate, it is reasonable for copper oxalate to exhibit this trend in nitrogen as copper metal is the final product of the decomposition. However, in air, the excess chloride ions reduced the stability of copper oxalate. This may be due to a change in the decomposition route where the copper metal formed is now oxidized to copper oxide. When one considers the extent of change in T_{max} when the environment is changed from an inert to an

TABLE 5

Temperature at maximum rate (T_{max}) from theoretical TG curves reconstructed from Arrhenius parameters obtained from isothermal experiments assuming an A_2 mechanism with a $2\,°C\ min^{-1}$ heating rate

Preparation conditions	T_{max} (°C)	
	Nitrogen	Air
Stoichiometric	318.4	308.7
Excess oxalic acid	318.3	310.4
Excess copper chloride	330.9	305.8

oxidizing atmosphere, then from Table 4, the excess oxalic acid sample is the least affected, and the excess copper chloride sample is the most affected with a decrease in T_{max} by approximately 25 °C. T_{max} for the correct ratio sample is moderately decreased by approximately 7 °C.

It is interesting to note that these observations are in contrast to the results obtained based on the magnitude of the activation energy, where the non-stoichiometric preparations seem to stabilize the salts in air and the reverse is true for the stoichiometric preparation. In order to obtain additional stability information from the isothermal data, the Arrhenius parameters obtained from the isothermal experiments are used to simulate the rising temperature experiments using a computer program [7], assuming an A_2 mechanism with a heating rate of 2 °C min^{-1}. Table 5 shows the T_{max} obtained from the theoretical treatment. The relative stability of the salt is now apparent. The results showed that copper oxalate prepared with an excess copper chloride stabilized the salt in nitrogen and reduced its stability in air, presumably due to the excess adsorbed chloride ions. It appears that it is erroneous to assign thermal stability based solely on the activation energy. A more complete interpretation should also include the pre-exponential factor and the mechanism of the reaction.

CONCLUSION

The adsorbed chloride ions tend to stabilize the salt in nitrogen and reduced its stability in air. In nitrogen, the stability trend of copper oxalate is similar to that observed for silver oxalate due to the same reaction occurring in both systems. However, a different trend is observed in air due to an additional reaction occurring in copper oxalate where the copper metal formed is oxidized to copper oxide. Using a computer program, it is shown that an accurate evaluation of the relative stability of various systems requires the consideration of both the activation energy and the pre-exponential factor as well as the reaction mechanism. In this respect, the mechanism-independent method gives a quick approximation of the

Arrhenius parameters from isothermal data but does not give additional stability information.

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