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# THERMAL DECOMPOSITION KINETICS OF ZINC(II) BIS(OXALATO)ZINCATE(II) TETRAHYDRATE

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## ABSTRACT

Zinc(II) bis(oxalato)zincate(II) tetrahydrate, $Zn[Zn(C_2O_4)_2]\cdot 4H_2O$, was prepared and characterized by elemental analysis and reflectance and IR spectral studies. From thermal decomposition studies (DTA, TGA, DTG and DSC) in air and nitrogen, the kinetic parameters, e.g. activation energies and entropies of activation, were evaluated by Freeman and Carroll, Flynn and Wall and modified Freeman and Carroll methods. The kinetic parameters evaluated from the TG data differed considerably from those evaluated from DSC, which showed a dependence of the decomposition temperature on the heating rate. The X-ray powder diffraction and IR spectral data were used to identify the final product. A tentative mechanism for the thermal decomposition of the complex in air has been proposed.

## INTRODUCTION

Oxalato complexes of transition and non-transition metals have been studied extensively by various workers [1–9]. Several qualitative and quantitative thermal decomposition studies relating kinetic parameters to experimental variables have been reported [10–15] for isothermal and dynamic conditions. Ninan and coworkers [16,17] investigated the effect of the simultaneous variation of sample mass and heating rate on the dehydration kinetics of $ZnC_2O_4\cdot 2H_2O$. The influence of sample mass on the kinetic parameters of the isothermal dehydration reaction of zinc oxalate dihydrate and a mathematical correlation between activation energy, pre-exponential factor and sample mass have been reported [18]. However, studies on compounds of the type $M_1[M_2(C_2O_4)_2]\cdot XH_2O$ (where $M_1$ and $M_2$ are the same metal) are scarce [19]. This paper describes the synthesis of the hitherto unknown zinc(II) bis(oxalato)zincate(II) tetrahydrate, $Zn[Zn(C_2O_4)_2]\cdot 4H_2O$, and its characterization by elemental analysis and spectroscopic methods. The kinetic parameters of the dehydration and decomposition path

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are also evaluated by three different methods. DSC studies reveal a dependence of the decomposition temperature on the heating rate.

## EXPERIMENTAL

### *Preparation of the complex*

Zinc hydroxide, prepared from zinc chloride, was made free from chloride. It was dissolved in glacial acetic acid and heated on a steam bath. A white compound was precipitated by dropwise addition of a saturated solution of oxalic acid in glacial acetic acid. The compound was filtered off and purified by a standard procedure [19]. The water content was determined gravimetrically and the zinc content was estimated gravimetrically by precipitating as pyridine thiocyanate. Carbon and hydrogen were analysed on a Thomas CH analyser. Calculated for $Zn[Zn(C_2O_4)_2] \cdot 4H_2O$: Zn, 34.52%; C, 12.68%; H, 2.13%; $H_2O$, 19.02%; found: Zn, 34.43%; C, 13.11%; H, 2.16%; $H_2O$, 19%.

IR spectra (4000–600 $cm^{-1}$) were recorded as nujol mulls using a Perkin–Elmer 781 spectrophotometer. Far IR spectra were obtained using a Polytec FIR-30 instrument. Diffuse reflectance spectra were recorded with a Shimadzu UV-240 spectrophotometer using $BaSO_4$ as the reference material.

TG and DTG were carried out at a heating rate of 10 °C $min^{-1}$ in dynamic air and nitrogen with a flow rate of 40 $cm^3$ $s^{-1}$ (approximate) using a Perkin–Elmer thermal analyser. DTA was performed up to 500 °C using an instrument described elsewhere [19], operating at a heating rate of 10 °C $min^{-1}$. DSC was carried out using a standard cell of a Mettler DSC-20 instrument with a TA processor of a Mettler TC10. Air was used as the furnace atmosphere which was purged at a rate of 30 $cm^3$ $min^{-1}$. Heating rates of 10 °C $min^{-1}$ and 5 °C $min^{-1}$, were used.

X-ray powder diffraction photographs were taken using a Debye–Scherrer camera and Cu K$\alpha$ radiation. The time of exposure was 4 h. The IR spectra of the gases evolved during decomposition were recorded as described previously [19].

## THEORETICAL

Three different methods were used to evaluate the kinetic data from the TG curves. The general form of the kinetic equation for the thermal decomposition of solids is given by Flynn and Wall [20] and is called the "simple differential method"

$$\log \frac{\mathrm{d}w_t/\mathrm{d}T}{(W_0 - W_t)^n} = \log(A/B) - E/2.3RT \qquad (1)$$

The terms used have their usual meaning. The trial values of $n$ were substituted into an Arrhenius-type plot of $\log(\mathrm{d}w_t/\mathrm{d}T)/(W_0 - W_t)^n$ vs. $T^{-1}$ until a straight line was obtained. The slope of the line gives $-E/2.3R$ and thus, the activation energy $E$ can be calculated.

The second method is also of the differential type, developed by Freeman and Carroll [21]

$$\frac{(-E/2.3R)\ \Delta T^{-1}}{\Delta \log W_\mathrm{r}} = -X + \frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log W_\mathrm{r}} \tag{2}$$

A plot of $\Delta \log(\mathrm{d}w/\mathrm{d}t)/\Delta \log W_\mathrm{r}$ against $\Delta T^{-1}/\Delta \log W_\mathrm{r}$ gives a line whose slope is $-E/2.3R$ and the activation energy can be calculated.

The third technique [22] is the modified Freeman and Carroll method. When the order of reaction is close to unity, the energy of activation, and hence the entropy of activation $\Delta S^\star$, can be calculated using the equations

$$\log[(\mathrm{d}w/\mathrm{d}t)/W_\mathrm{r}] = -E/2.3RT + \log Z \tag{3}$$

and

$$Z = \frac{KTs}{h}\exp\left(\frac{\Delta S^\star}{R}\right) \tag{4}$$

where the terms have their usual meaning.

## RESULTS AND DISCUSSION

The white crystalline compound is insoluble in water and common organic solvents. However, it decomposes in the presence of strong acid or alkali.

The analytical results show good agreement with the calculated values of metal, carbon and hydrogen content for the proposed formula $\mathrm{Zn[Zn(C_2O_4)_2]\cdot 4H_2O}$. The analysis of the water content reveals that the compound should contain four molecules of water of crystallization per molecule of the compound. The IR spectrum (Table 1) was assigned on the basis of earlier studies [23,24]. Most of the bands indicate the presence of coordinated oxalato groups. However, the possibility of the association of some of the water molecules with coordinated oxalato groups through hydrogen bonding cannot be ruled out as shown by the presence of a broad band between 3200 and 3600 $\mathrm{cm}^{-1}$ in the IR spectrum. This would explain the removal of the water molecules at a much higher temperature than expected in the TG curve. In the far IR region a medium sharp band around 190 $\mathrm{cm}^{-1}$ suggests the presence of a metal–metal bond [25]. The extreme insolubility of the compound may partially give credence to this view. The intense bands observed in the UV region of the diffuse reflectance spectrum of the complex are due to intraligand $\pi \rightarrow \pi^*$ transitions.

TABLE 1

Selected bands in the IR spectrum of the complex $Zn[Zn(C_2O_4)_2]\cdot 4H_2O$

| IR band ($cm^{-1}$) | Assignment |
|---|---|
| 3200–3600b | $\nu_{sy}$(O–H) + $\nu_{asy}$(O–H) or hydrogen bonding |
| 1610s | $\delta_{sy}$(H–O–H) |
| 1500–1700b | $\nu_{asy}$(C=O) |
| 1350m | $\nu_{sy}$(C–O) and/or $\nu$(C–C) |
| 1300s | $\nu_{sy}$(C–O) and/or $\delta$(O–C=O) |
| 810s | $\nu$(Zn–O) and/or $\delta$(O–C=O) |
| 750b | Coordinated water |
| 600m | Water of crystallization |
| 490s | $\nu$(C–C) and/or ring deformation |
| 455m | $\nu$(Zn–O) and/or ring deformation |
| 370m | $\delta$(O–C=O) |
| 340–215b (split into 285) | Out-of-plane bending |
| 190ms | $\nu$(Zn–Zn) |

b, broad; s, strong; m, medium.

The thermal analysis results are summarized in Tables 2, 3 and 4. The compositions of the intermediate products were determined using the observed weight loss in TG, intermittent chemical analysis, IR spectra and X-ray powder diffraction patterns. The thermogravimetric results are in agreement with the DTA data, but not with the DSC results. The well-defined DTG peaks at 137 °C in air and at 160 °C in nitrogen with a weight loss over the temperature range 90–180 °C in the TG curve correspond to the dehydration process. The loss of mass at the end of this stage (Table 2) is in good agreement with the formation of the anhydrous compound. The endothermic dehydration is also indicated by the presence of a DTA peak around 180 °C. The weight loss observed during independent pyrolysis in air up to this temperature is in good agreement with the calculated value. The temperature arrest technique was used to isolate the anhydrous compound. The chelating character of the oxalato group is retained as shown by the IR spectrum. On exposure to a humid atmosphere the anhydrous compound absorbs moisture immediately; this is shown by the presence of a broad band around 3000–3650 $cm^{-1}$ in the rehydrated complex. For the dehydration step the relevant portion of the TG curve was chosen for kinetic study both in air and in nitrogen using the three methods described earlier, and the values are tabulated in Table 4. It can be seen that comparable values of $E$ are obtained using the three methods with a slight increase on going from methods (a) to (c) in the table. The order of reaction is close to unity. Thus similar values of $\Delta S^{\star}$ are obtained in air and nitrogen using eqn. (4). The negative values indicate that the reactions are slower than normal [26].

The anhydrous compound formed is fairly stable up to 318 °C in air and 331 °C in nitrogen in the TG curve. Beyond these temperatures it starts to

TABLE 2

TG, DTG and DTA data of $Zn[Zn(C_2O_4)_2]\cdot 4H_2O$

| Medium | Step | TG temperature range (°C) | Weight loss (%) | | | DTG temperature range (°C) | DTG peak temperature (°C) | DTA peak temperature (°C) | Reaction |
|---|---|---|---|---|---|---|---|---|---|
| | | | Found | Calcd. | From independent pyrolysis | | | | |
| Air | 1 | 91.78–180 | 18.6 | 19.01 | 18.8 | 90–180 | 137 | 180 (endo) | Dehydration |
| | 2 | 318–436 | 57.33 | 57.03 | 57 | 322–430 | 408 | 390 (exo) | Decomposition |
| Nitrogen | 1 | 91.76–181.64 | 18.2 | 19.01 | – | 100–188 | 160 | 183 (endo) | Dehydration |
| | 2 | 331–438.85 | 55.73 | 57.03 | | 328–444 | 405 | 404 (exo) | Decomposition |

TABLE 3

DSC data of $Zn[Zn(C_2O_4)_2]\cdot 4H_2O$ in air

| Heating rate (°C min$^{-1}$) | Step | Temperature range (°C) | Peak temperature (°C) | Weight loss (%) | | ln $k_0$ | $E$ (kcal mol$^{-1}$) | $\Delta H$ (kcal mol$^{-1}$) | Order of reaction | Reaction |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Found | Calcd. | | | | | |
| 5 | 1 | 120.7–179.3 | 163 | 19 | 19.02 | 32.35±0.24 | 32.27±0.2 | $5.1\times10^4$ | 0.37±0.01 | Dehydration |
| | 2 | 347–412 | 389.5 | 57.96 | 57.03 | 58.33±2.01 | 83.17±1 | $2.04\times10^4$ | 0.96±0.05 | Decomposition |
| 10 | 1 | 121.3–189.3 | 165.2 | 19.2 | 19.02 | 35.43±0.55 | 34.5 ±0.46 | $5.4\times10^4$ | 0.62±0.02 | Dehydration |
| | 2 | 360–425 | 400.1 | 56.95 | 57.03 | 69.23±1.15 | 97.85±1.5 | $2.5\times10^4$ | 1.14±0.03 | Decomposition |

TABLE 4

Kinetic data evaluated by the methods: (a) Freeman and Carroll, (b) Flynn and Wall and (c) modified Freeman and Carroll

| Medium | Step | Method | $E$ (kcal $mol^{-1}$) | log $Z$ | $\Delta S^{\star}$ (e.u.) | Order of reaction | Reaction |
|---|---|---|---|---|---|---|---|
| Air | 1 | (a) | 13.06 | | | 0.74 | Dehydration |
| | | (b) | 13.33 | | | 1.5 | |
| | | (c) | 15.99 | 0.25 | −24.27 | | |
| | 2 | (a) | 54.84 | | | 0.35 | Decomposition |
| | | (b) | 58.13 | | | 1 | |
| | | (c) | | | | | |
| Nitrogen | 1 | (a) | 14.85 | | | 0.8 | Dehydration |
| | | (b) | 15.23 | | | | |
| | | (c) | 17.13 | 0.2 | −24.49 | | |
| | 2 | (a) | 68.55 | | | 0.85 | Decomposition |
| | | (b) | 68.55 | | | 1 | |
| | | (c) | 70.3 | 0.85 | −24 | | |

lose weight up to 436 °C in air and 439 °C in nitrogen. Very strong DTG peaks are observed at 408 °C and 405 °C, which are well defined and non-overlapping. The mass loss at the end of this stage indicates the formation of the stable compound 2ZnO in good agreement with the calculated value (Table 2). Independent pyrolysis in air also confirms that the compound is ZnO (Zn: found, 80.1%; calculated, 80.34%). The X-ray powder diffraction pattern and the very broad band at 450 $cm^{-1}$ in the IR spectrum are similar to those obtained for pure ZnO [27,28]. This further substantiates that the residue is ZnO as does the observation of its inherent peculiarities (yellow while hot and white on cooling).

The kinetic parameters for the decomposition stage are tabulated in Table 4. Methods (a) and (b) yield exactly the same values of $E$ in nitrogen, but there is a slight increase in the value of $E$ obtained using method (c). In air, methods (a) and (b) yield slightly different values of $E$. Negative values of $\Delta S^{\star}$ are obtained for the decomposition step as in the dehydration step.

The water vapour, carbon dioxide and carbon monoxide evolved during the complete decomposition were identified by IR spectroscopy as described earlier [23].

The DSC traces (Table 3) in air at heating rates of 5 and 10 °C $min^{-1}$ show two distinct endothermic processes corresponding to the dehydration and decomposition stages (good agreement in weight loss after isolation by temperature arrest technique). For the dehydration step the peaks occur at 163° C (onset at 120.7 °C) and 165.2° C (onset at 121.3° C) for heating rates of 5 and 10 °C $min^{-1}$ respectively. Similarly for the decomposition step the corresponding peak maxima occur at 389.5 °C (onset at 347 °C) and at

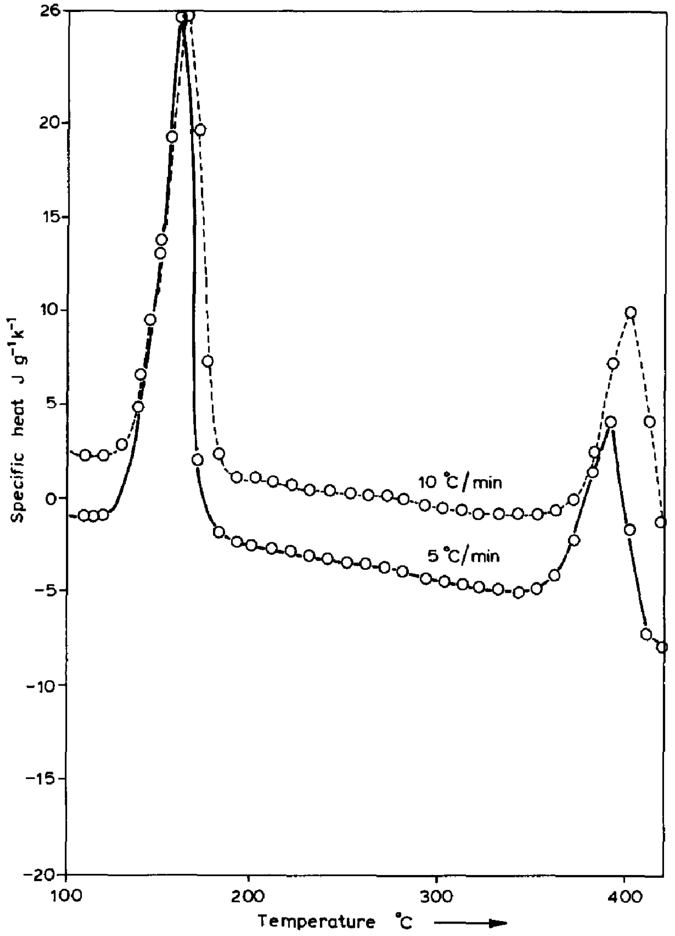

Fig. 1. Plot of specific heat vs. temperature at heating rates of 5 and 10 ° C $\min^{-1}$.

400.1 ° C (onset at 360 ° C). It can be inferred from the table that with the higher heating rate the temperature of decomposition increases. Similarly the kinetic parameters $E$ and $\Delta H$ increase with increasing heating rate as do ln $k_0$ (from the Arrhenius plot) and the order of reaction. A slight difference is also observed in the $E$ values calculated using the TG and DSC data. A plot of specific heat vs. temperature (Fig. 1) also shows transitions over similar temperature ranges as in the corresponding DSC traces.

## *Stoichiometry of the reaction*

The inclined nature of the TG curve in the temperature range 90–180 ° C indicates that the complex is not dehydrated in a single step. From the weight loss in TG it can be inferred that the successive removal of water molecules occurs at 140, 152, 162 and around 180 ° C. It has been reported

[29] that removal of water below 150 °C is indicative of water of crystallization and that water removed above 150 °C is coordinated water. From this, and on the basis of the TG pattern described above, it can be concluded that one water molecule is bound as water of crystallization and the other three are coordinated to the metal and may be linked to the chelated oxalato group through hydrogen bonding.

On the basis of the above results a tentative scheme of the thermal decomposition in air may be summarized as

$$Zn[Zn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{140\,^\circ C} Zn[Zn(C_2O_4)_2]\cdot 3H_2O + H_2O(v)$$

$$\xrightarrow{150-162\,^\circ C} Zn[Zn(C_2O_4)_2]\cdot H_2O + 2H_2O(v)$$

$$\xrightarrow{\approx 180\,^\circ C} Zn[Zn(C_2O_4)_2] + H_2O(v)$$

$$\xrightarrow{\text{above } 430\,^\circ C} 2ZnO(s) + 2CO(g) + 2CO_2(g)$$

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