# Kinetic Studies on Thermal Decomposition of Oxalates Doped with Malonate

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Thermal decomposition of metal oxalates is one of the important methods of preparation of pure or mixed metal oxides having special properties. Cationic or anionic doping may affect their decomposition. Here, the effect of doping by malonate ion on the thermal decomposition of oxalates of lead, zinc, manganese, nickel and cobalt was studied. The pure oxalates were prepared by treating a hot solution of salt of the metal with a hot solution of sodium oxalate. The doped samples of the above oxalates were prepared by taking a mixture of sodium oxalate and sodium malonate for precipitation. The decomposition was followed by thermogravimetric method The kinetic parameters like energy of activation (E), frequency factor (Z) and entropy of activation ($\Delta S^*$) of cobalt oxalate and nickel oxalate decreased considerably whereas the values for oxalates of lead, zinc and manganese increased on doping. The temperature at which the decomposition began ($T_i$) and temperature of completion ($T_f$) decreased whereas temperature of maximum decomposition ($T_s$) increased for cobalt oxalate and remained constant for nickel oxalate. In the case of lead oxalate doping with malonate ion increased $T_i$, but no appreciable change was observed for $T_f$ and $T_s$. For zinc oxalate and manganese oxalate $T_i$, $T_f$ and $T_s$ remained practically constant.

Key Words: Thermal decomposition, Oxalates, Malonate, Kinetic parameters.

## INTRODUCTION

The thermal decomposition of solids is influenced by many factors like irradiation by high-energy radiation, doping, etc. Considerable volume of work has been done on the thermal decomposition of pure and mixed oxalates. The effect of doping in this process is also a subject matter of study[1–4]. The decomposition of metal oxalates, coprecipitated oxalates, oxalato complexes assumes importance because this is a common method for the preparation of oxides, pure or mixed, which are having special properties like magnetic, piezoelectric and ceramic properties. Here the effect of doping with malonate ion on kinetics of thermal decomposition of oxalates of lead, zinc, manganese, nickel and cobalt was studied.
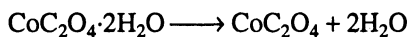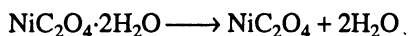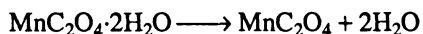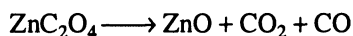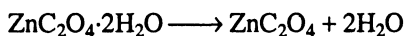
## EXPERIMENTAL

The pure oxalates were prepared by treating a hot solution of lead nitrate, zinc sulphate, manganese sulphate, nickel sulphate or cobalt nitrate with a hot solution of sodium oxalate. The precipitated oxalates were filtered, washed with water and dried. The doped samples of the above oxalates were prepared by taking a mixture of sodium oxalate and sodium malonate for precipitation[5]. The dopant concentration was fixed as 1%.

The oxalates were sieved and samples in the range of 90–106 micron were collected. Non-isothermal TGs were taken by using Shimadzu thermal analyzer in nitrogen atmosphere with heating rate 5 K min$^{-1}$. In each case 10 mg of the sample was taken. The composition and purity were established by chemical analysis and from the mass loss noted in the TG.

## RESULTS AND DISCUSSION

Lead oxalate decomposes in a single stage and all others, being hydrated, in two stages as given below:

$$PbC_2O_4 \longrightarrow PbO + CO_2 + CO$$

$$ZnC_2O_4 \cdot 2H_2O \longrightarrow ZnC_2O_4 + 2H_2O$$

$$ZnC_2O_4 \longrightarrow ZnO + CO_2 + CO$$

$$MnC_2O_4 \cdot 2H_2O \longrightarrow MnC_2O_4 + 2H_2O$$

$$MnC_2O_4 \longrightarrow MnO + CO_2 + CO$$

$$NiC_2O_4 \cdot 2H_2O \longrightarrow NiC_2O_4 + 2H_2O$$

$$NiC_2O_4 \longrightarrow NiO + CO_2 + CO$$

$$CoC_2O_4 \cdot 2H_2O \longrightarrow CoC_2O_4 + 2H_2O$$

$$CoC_2O_4 \longrightarrow CoO + CO_2 + CO$$

The kinetics of decomposition of oxalates to metal oxide, $CO_2$ and CO was studied here. The kinetic parameters like energy of activation (E), frequency factor (Z) and entropy of activation ($\Delta S^*$) were calculated by using Coats-Redfern[6] and Freeman-Carroll[7] methods.

### The Coats-Redfern method

According to this method,

$$\log [\{1 - (1 - \alpha)^{1-n}\}/\{(1 - n)T^2\}] = \log [\{ZR/\phi E\}\{(1 - 2RT/E)\}] - E/2.303RT$$
$$\text{for } n \neq 1$$

and

$$\log [-\{\log(1 - \alpha)\}/T^2] = \log [\{ZR/\phi E\}\{(1 - 2RT/E)\}] - E/2.303RT \quad \text{for } n = 1$$

Here, $\alpha$ is the fraction of reactant decomposed, T temperature in Kelvin, Z frequency factor, E energy of activation, R gas constant $\phi$ heating rate and n the

order of the reaction. The quantity $\log [\{ZR/\phi E\}\{(1 - 2RT/E)\}]$ is practically a constant. Therefore, plots of

$$\log [\{1 - (1 - \alpha)^{1-n}\}/\{(1 - n)T^2\}] \ vs. \ 1/T \qquad \text{for } n \neq 1$$

and

$$\log [-\log (1 - \alpha)/T^2] \ vs. \ 1/T \qquad \text{for } n = 1$$

results in a straight line for correctly chosen values of n. Least square linear regression method was used. The order of the reaction is found to be one. The E and Z were calculated from the slope and intercept respectively.

The entropy of activation $\Delta S^*$ is given by

$$\Delta S^* = [\log Z - \log (kT_s/h)]2.303R$$

where $T_s$ is the temperature of maximum decomposition. The values obtained are given in Table-1.

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TABLE-1
COATS-REDFERN METHOD
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| Sample | $T_i$ | $T_f$ | $T_s$ | $E$ (kJ mol$^{-1}$) | $Z$ (min$^{-1}$) | $\Delta S^*$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Lead oxalate | 565 | 653 | 644 | 309.8 | $2.9 \times 10^{40}$ | 523.4 |
| Lead oxalate + M | 583 | 653 | 641 | 335.2 | $1.9 \times 10^{45}$ | 615.6 |
| Zinc oxalate | 442 | 680 | 668 | 256.8 | $2.2 \times 10^{30}$ | 329.2 |
| Zinc oxalate + M | 445 | 680 | 668 | 282.4 | $3.0 \times 10^{34}$ | 408.4 |
| Manganese oxalate | 427 | 590 | 559 | 161.0 | $7.8 \times 10^{19}$ | 130.6 |
| Manganese oxalate + M | 427 | 593 | 577 | 177.3 | $2.0 \times 10^{22}$ | 176.6 |
| Nickel oxalate | 563 | 632 | 614 | 307.0 | $1.0 \times 10^{42}$ | 553.5 |
| Nickel oxalate + M | 536 | 623 | 614 | 209.8 | $1.8 \times 10^{25}$ | 232.5 |
| Cobalt oxalate | 481 | 562 | 544 | 233.8 | $8.9 \times 10^{34}$ | 419.2 |
| Cobalt oxalate + M | 478 | 559 | 553 | 188.3 | $3.2 \times 10^{25}$ | 238.1 |

**The Freeman-Carroll method**

This method, for first order reaction, gives the relation

$$\log [(dw/dt)/W_r] = -E/2.303RT + \log Z$$

Here, $W_r = (W_\alpha - W) \cdot W_\alpha$ is the mass loss at the completion of the reaction and W the mass loss up to time t. The temperature slope dw/dT is converted into time slope dw/dt by using the relation

$$dw/dt = (dw/dT)(dT/dt) = (dw/dT)\phi$$

where $\phi$ is the heating rate.

Thus, a plot of $\log [(dw/dt)/W_r] \ vs. \ 1/T$ is a straight line with slope $-E/2.303R$ and intercept $\log Z \cdot \Delta S^*$ is calculated by the relation,

$$\Delta S^* = [\log Z - \log (kT_s/h)]2.303R$$

The E, Z and $\Delta S^*$ obtained by this method are given in Table-2.

TABLE-2
FREEMAN-CAROLL METHOD

| Sample | $T_i$ | $T_f$ | $T_s$ | E (kJ mol$^{-1}$) | Z (min$^{-1}$) | $\Delta S^*$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Lead oxalate | 565 | 653 | 644 | 401.8 | $2.4 \times 10^{32}$ | 368.7 |
| Lead oxalate + M | 583 | 653 | 641 | 462.4 | $6.8 \times 10^{37}$ | 473.1 |
| Zinc oxalate | 442 | 680 | 668 | 297.4 | $5.2 \times 10^{22}$ | 183.2 |
| Zinc oxalate + M | 445 | 680 | 668 | 299.4 | $7.5 \times 10^{22}$ | 186.3 |
| Manganese oxalate | 427 | 590 | 559 | 232.1 | $1.2 \times 10^{21}$ | 153.1 |
| Manganese oxalate + M | 427 | 593 | 577 | 256.8 | $1.1 \times 10^{23}$ | 191.0 |
| Nickel oxalate | 563 | 632 | 614 | 398.3 | $2.1 \times 10^{33}$ | 386.9 |
| Nickel oxalate + M | 536 | 623 | 614 | 321.5 | $4.9 \times 10^{26}$ | 260.1 |
| Cobalt oxalate | 481 | 562 | 544 | 270.2 | $2.4 \times 10^{25}$ | 235.8 |
| Cobalt oxalate + M | 478 | 559 | 553 | 238.0 | $1.2 \times 10^{22}$ | 172.4 |

M = doped with malonate

Doping with cation having different valency may alter the concentration of point defects and affect the decomposition kinetics as well as mechanism. The size of the dopant ion is also an important factor since it may distort the lattice. Many studies have been conducted in this field. These factors may also have influence in the case of anionic doping. Some studies have been done in this field also, which showed that anionic doping decreasesd activation energy[2] (E).

Here in the case of lead oxalate doping with malonate ion slightly increases the temperature at which the decomposition began ($T_i$), no appreciable change in temperature of completion ($T_f$) and temperature of maximum decomposition ($T_s$). The energy of activation (E) and entropy of activation ($\Delta S^*$) also increases slightly. For zinc oxalate $T_i$, $T_f$ and $T_s$ remain constant, whereas E and $\Delta S^*$ increase slightly. Manganese oxalate follows the same pattern, except that $T_s$ shows an increase.

The decomposition of cobalt oxalate and nickel oxalate proceeded with a considerable decrease in the energy of activation (E) and entropy of activation ($\Delta S^*$). For cobalt oxalate E decreases from 233.8 to 188.3 kJ mol$^{-1}$ and $\Delta S^*$ from 419.2 to 238.1 J K$^{-1}$ mol$^{-1}$. In the case of nickel oxalate E changes from 307.0 to 209.8 kJ mol$^{-1}$ and $\Delta S^*$ from 553.5 to 232.5 J K$^{-1}$ mol$^{-1}$. $T_i$ and $T_f$ decrease whereas $T_s$ increases for cobalt oxalate and remains constant for nickel oxalate. The values quoted are from Coats-Redfern method. The values obtained by Freeman-Caroll method also follow the same trend.

Thus, malonate doping has influence on the thermal decomposition of metal oxalates in certain cases. Since the size of malonate ion is bigger than oxalate ion it may bring about strain in the crystal lattice which may be the probable reason for the decrease in the E and $\Delta S^*$ values of cobalt oxalate and nickel oxalate. The size of the cation may be another influencing factor. The Pauling ionic radii of different cations in Å units are: $Pb^{2+}$, 1.21; $Mn^{2+}$, 0.80; $Zn^{2+}$, 0.74; $Co^{2+}$, 0.74; $Ni^{2+}$, 0.69. This effect may be used in altering the decomposition pattern of these compounds used in the preparation of oxides, pure or mixed, which are having

magnetic, piezoelectric and ceramic properties. It may be noted that doping with malonate will not affect the composition of the final product whereas it may sometimes bring about desirable changes in the properties of the product oxides.

## Mechanism

The method suggested by Sestak and Berggren[8] and Satava[9] has been used for determining the mechanism of thermal decompoaition. For correct mechanism the plot of log $g(\alpha)$ vs. $1/T$ should be a straight line. The different possible mechanisms and the corresponding $g(\alpha)$ functions are given in Table-3.

TABLE-3

| Function | Equation $g(\alpha) = kt$ | Rate controlling process |
|---|---|---|
| $D_1$ | $\alpha^2 = kt$ | One-dimensional diffusion (parabolic law) |
| $D_2$ | $(1-\alpha)\ln(1-\alpha)+\alpha = kt$ | Two-dimensional diffusion, cylindrical symmetry |
| $D_3$ | $[1-(1-\alpha)^{1/3}]^2 = kt$ | Three-dimensional diffusion, spherical symmetry (Jander equation) |
| $D_4$ | $(1-2/3\alpha)-(1-\alpha)^{2/3} = kt$ | Three-dimensional diffusion, spherical symmetry (Ginstiling Brownstein equation) |
| $F_1$ | $-\ln(1-\alpha) = kt$ | Random nucleation; one nucleus on each particle (Mampel equation) |
| $A_2$ | $[-\ln(1-\alpha)]^{1/2} = kt$ | Random nucleation (Avrami equation I) |
| $A_3$ | $[-\ln(1-\alpha)]^{1/3} = kt$ | Random nucleation (Avrami equation II) |
| $R_2$ | $1-(1-\alpha)^{1/2} = kt$ | Phase boundary reaction; cylindrical symmetry |
| $R_3$ | $1-(1-\alpha)^{1/3} = kt$ | Phase boundary reaction; spherical symmetry |

TABLE–4

| Sample | Mechanism | E (kJ mol$^{-1}$) [Mechanistic equation] | E (kJ mol$^{-1}$) [Coats-Redfern method] |
|---|---|---|---|
| Lead oxalate | $R_3$ | 308.3 | 309.8 |
| Lead oxalate + M | $R_3$ | 320.5 | 335.2 |
| Zinc oxalate | $F_1$ | 269.4 | 256.8 |
| Zinc oxalate + M | $F_1$ | 295.2 | 282.4 |
| Manganese oxalate | $R_3$ | 157.5 | 161.0 |
| Manganese oxalate + M | $R_3$ | 176.0 | 177.3 |
| Nickel oxalate | $R_3$ | 295.3 | 307.0 |
| Nickel oxalate + M | $R_3$ | 209.6 | 209.8 |
| Cobalt oxalate | $R_3$ | 228.8 | 233.8 |
| Cobalt oxalate + M | $R_3$ | 188.7 | 188.3 |

The least square linear regression method was used to arrive at the best linear fit. The mechanistic equation corresponding to maximum correlation coefficient gives correct mechanism. For nearly the same value of correlation coefficient the operating mechanism is chosen by comparing the E values, calculated by the

mechanistic equation, with those obtained by the non-mechanistic method, *viz.*, Coats-Redfern and Freeman-Carroll methods. For calculating E by mechanistic method MacCallum-Tanner equation was used[10]. The results are given in Table-4.

The mechanism of decomposition was found to be $R_3$, *i.e.*, phase boundary reaction with spherical symmetry except in the case of zinc oxalate for which the mechanism was $F_1$, *i.e.*, random nucleation with one nucleus on each particle. Further doping did not change the mechanism.

## Conclusion

The anionic doping of metal oxalate decreased the kinetic parameters like energy of activation (E), frequency factor (Z) and entropy of activation ($\Delta S^*$) of cobalt oxalate and nickel oxalate whereas it increased the values for oxalates of lead, zinc and manganese. The temperature at which the decomposition begins ($T_i$) and temperature of completion ($T_f$) decreased for cobalt oxalate and nickel oxalate whereas temperature of maximum decomposition ($T_s$) increased for cobalt oxalate and remained constant for nickel oxalate. In the case of lead oxalate doping with malonate ion increased $T_i$, no appreciable change was observed in $T_f$ and $T_s$. For zinc oxalate and manganese oxalate $T_i$, $T_f$ and $T_s$ remained practically constant. Thus, anionic doping has influence on the thermal decomposition of metal oxalates in certain cases. This effect may be used in altering the decomposition pattern of these compounds used in the preparation of oxides, pure or mixed, which are having special properties. The composition of the final product oxide is not changed by anion doping.

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