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Effect of Doping on the Thermal Decomposition of Zinc Oxalate

M.P. SURYANARAYANAN† and T.D. RADHAKRISHNAN NAIR*
Department of Chemistry
University of Calicut, Kerala-673 635, India

The influence of cation doping on the thermal decomposition of zinc oxalate was studied. Dopants such as Co^{2+} and Ni^{2+} have been found to decrease T_i, E, Z and ΔS^*. The phenomenon may be linked to the ability of Co and Ni to form carbonyls during pyrolysis. The effect of the dopants on mechanism of decomposition was also studied. The presence of dopants was detected by inductively coupled plasma atomic absorption spectrum.

INTRODUCTION

By doping with a cation having different valency, the extent of point defects can be increased and this may affect the kinetics as well as mechanism of solid state decomposition of inorganic salts. The size of the dopant also is important in this context.

EXPERIMENTAL

Doped sample of zinc oxalate dihydrate was prepared by adding the salts of the dopant at the time of preparation of the zinc oxalate dihydrate.[1]

Zinc oxalate dihydrate doped with ferric ion was prepared by adding ferric alum to zinc sulphate solution in required concentration and precipitating the salt by the addition of sodium oxalate solution with constant stirring. The precipitated doped zinc oxalate dihydrate was decanted, washed with water, filtered and dried. Similarly doped samples containing cobalt and nickel ions were prepared by adding cobalt nitrate and nickel sulphate respectively to $ZnSO_4$ solution at the time of preparation. Analytical studies using inductively coupled plasma atomic absorption spectrum (ICPAAS) revealed that Fe^{3+} ion was not introduced; but Co^{2+} and Ni^{2+} ions were introduced as dopants.

The thermograms of the samples doped with Co^{2+} amd Ni^{2+} as well as the pure sample were recorded on a Shimadzu TG analyser.

RESULTS AND DISCUSSION

The thermal decomposition of zinc oxalate dihydrate is shown by the following equations:

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†Deptartment of Chemistry, Government Victoria College, Palakkad-678 001, Kerala, India.

$$ZnC_2O_4 \cdot 2H_2O \rightarrow ZnC_2O_4 + 2H_2O \quad (1)$$

$$ZnC_2O_4 \rightarrow ZnO + CO + CO_2 \quad (2)$$

The second stage of the decomposition was studied (Eq. (2)). Kinetic parameters such as energy of activation E, frequency factor Z and entropy of activation ΔS^* calculated using Coats-Redfern (CR), Horowitz-Metzger (HM) and Freeman-Carroll (FC) methods[2–4] are given in Tables 1 and 2.

From Table-1 it can be noted that T_i values decreased when dopants are present. In the presence of Co^{2+} (0.5 mole per cent) T_i decreased from 633 K to 628 K and for Ni^{2+} to 610 K. The E values decreased by about 120 kJ for Co^{2+} and 210 kJ for Ni^{2+}. ΔS^* values also decreased considerably.

The thermal decomposition of ZnC_2O_4 doped with Co^{2+} was followed by varying the dopant concentration (Table-2). The T_i decreased in all cases. The E decreased and passed through a minimum (Fig. 1). The optimum dopant concentration is found to be near 1 mole % of Co^{2+}. The ΔS^* values also showed a similar pattern.

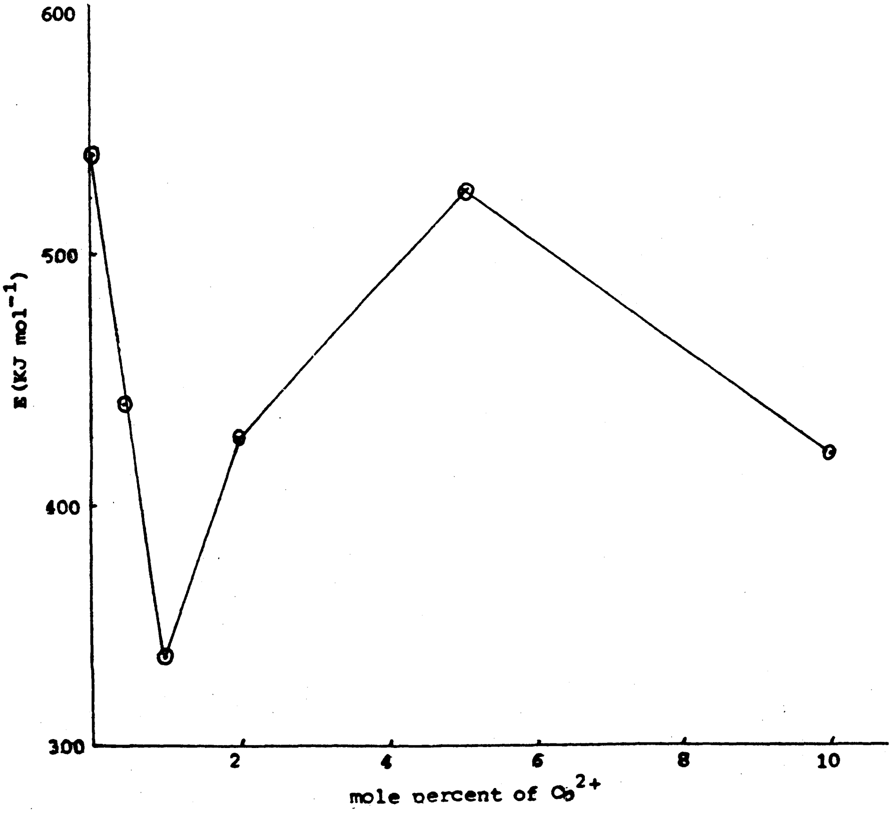

Fig. 1. Effect of doping with Co^{2+} on energy of activation.

TABLE-1

EFFECT OF DOPING WITH COBALT AND NICKEL IONS

Heating rate: 5 K per minute; nitrogen atomsphere; particle size: 106–90; mass of sample; 10 mg in each case; concentration of cobalt and nickel: 0.5 mole %

Sample	T_i K	T_f K	T_s K	E (kJ per mol)			Z (min^{-1})			ΔS* (JK^{-1} mol^{-1})		
				CR	HM	FC	CR	HM	FC	CR	HM	FC
Zinc oxalate	633	670.5	658.7	536.9	539.5	575.7	1.0×10^{42}	4.5×10^{42}	2.7×10^{45}	518.5	531.1	584.5
Zinc oxalate + cobalt	628	675.5	665.7	413.6	439.5	467.4	9.0×10^{31}	1.8×10^{34}	3.7×10^{36}	326.2	370.3	414.6
Zinc oxalate + nickel	610.4	671.3	663.7	322.9	358.2	353.3	4.8×10^{24}	7.6×10^{27}	2.3×10^{27}	186.4	248.2	238.4

TABLE-2

EFFECT OF DOPING WITH COBALT ON THE THERMAL DECOMPOSITION OF ZnC_2O_4

Heating rate: 5 K per minute; nitrogen atomsphere; particle size: 90–106; mass of sample in each case; 10 mg concentration of Co in mole %

Sample	T_i K	T_f K	T_s K	E (kJ per mol)			Z (min^{-1})			Δ S* (JK^{-1} mol^{-1})		
				CR	HM	FC	CR	HM	FC	CR	HM	FC
ZnC_2O_4	633	670.5	658.7	536.5	539.5	575.7	1.0×10^{42}	4.5×10^{42}	2.7×10^{45}	518.5	531.1	584.5
ZnC_2O_4 + Co (0.5)	628	675.5	665.7	413.6	439.5	467.4	9.0×10^{31}	1.8×10^{34}	3.7×10^{36}	326.2	370.3	414.6
ZnC_2O_4 + Co (1.0)	624	673.9	666.0	306.4	336.9	337.4	3.0×10^{23}	1.2×10^{26}	2.8×10^{26}	163.8	213.8	220.8
ZnC_2O_4 + Co (2.0)	623	675.5	667.5	392.9	426.5	458.4	1.9×10^{23}	1.4×10^{33}	7.1×10^{35}	294.3	348.8	400.8
ZnC_2O_4 + Co (5.0)	630.5	675.5	665.8	493.0	521.3	536.5	2.1×10^{38}	5.6×10^{40}	1.3×10^{42}	448.1	494.6	520.6
ZnC_2O_4 + Co (10.0)	618	665.5	659.5	385.7	417.3	352.3	1.4×10^{30}	6.5×10^{32}	5.0×10^{27}	291.4	342.6	244.7

The effect of doping on the thermal decomposition of strontiun nitrate doped with nitrite ions was studied[5] and it was reported that nitrate ion dopant decreased the activation energy while T_i remaining almost constant. The thermal decomposition of nickel oxalate doped with traces of Li^+ and Cr^{3+}, and sulphate and calcium ions on the decomposition of ammonium perchlorate[6] were studied. It was observed that the decomposition rate was generally increased by sulphate and decreased by calcium ions. These results were interpreted on the basis of electron transfer mechanism and vacancies produced by the presence of dopants. Boldyrev and co-workers[7] studied the effect of doping ammonium perchlorate with SO_4^{2-} and Ca^{2+} and obtained results in consistence with the above.

Here in the present case the valencies of the dopant cations are the same as Zn^{2+}. Further, the sizes of cations are also comparable. The Pauling ionic radii values are: Zn^{2+}, 0.74; Co^{2+}, 0.74; and Ni^{2+}, 0.69.[8] Therefore, the decrease in energy of activation cannot be explained on the basis of lattice vacancies or distortions. Cobalt and nickel easily interact with carbon monoxide to give carbonyls. One of the products of decomposition of ZnC_2O_4 is CO. The CO interact with cobalt and nickel to give carbonyls. Thus, the CO is removed from the reaction site which will enhance the reaction rate. Since the carbonyl of nickel is more stable than that of cobalt, the effect of nickel was found to be greater. But, at higher temperatures these carbonyls are not stable and, therefore, they decomposed. In effect, the function of Co^{2+} and Ni^{2+} seems to be the removal of CO from the reaction site. The ΔS^* values also showed a considerable decrease with decomposition of doped samples indicating a more ordered transition state.

Mechanism of thermal decomposition of pure zinc oxalate as well as the doped samples was deduced by using non-isothermal method suggested by Sestak and Berggren[9] and Satava.[10] The types of mechanism most frequently encountered are given in Table 3. Thus, log $g(\alpha)$ is plotted against $1/T$ using $g(\alpha)$ functions given in the above table by least square linear regression method.

TABLE-3

TYPES OF MECHANISM OF THERMAL DECOMPOSITION OF ZINC OXALATE

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	$(1-\frac{2}{3}\alpha) - (1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry (Ginstiling Brownshtein 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

Decomposition of pure zinc oxalate followed F_1 mechanism *i.e.* Mampel model equation with $-\ln(1-\alpha)$ for $g(\alpha)$. The rate controlling process is random nucleation with the formation of a nucleus on every particle. But, in the case of decomposition of ZnC_2O_4 doped with Co^{2+} and Ni^{2+} the mechanism was R_3, *i.e.*, the rate determining step is the phase boundary reaction, assuming spherical symmetry with $g(\alpha)$ value $[1-(1-\alpha)^{1/3}]$.

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