

## Thermal Decomposition Behaviour of Mg(II) and Zn(II) Complexes of *cis*-2,6-diphenyl-3-ethoxycarbonylpiperidin-4-one

A. MANIMEKALAI\* and R. MAHENDHIRAN

*Department of Chemistry*

*Annamalai University, Annamalainagar-608 002, India*

The TG-DTA and IR spectral analysis of complexes of Mg(II) and Zn(II) with *cis*-2,6-diphenyl-3-ethoxycarbonylpiperidin-4-one was investigated. The results from thermal analysis have shown that mainly two step decomposition occurred in both the complexes. Various kinetic and thermodynamic parameters for these steps were estimated employing Horowitz-Metzger and Coats-Redfern methods.

### INTRODUCTION

Although transition metal complexes of acetylacetonate and several  $\beta$ -diketones are well known<sup>1-5</sup>. Comparatively less work has been done on the complexation behaviour of 1,3-diketo functional groupings, which form part of the ring structure. *cis*-2,6-Diphenyl-3-ethoxycarbonylpiperidin-4-one (DECP) which resemble quite closely the  $\beta$ -diketones in its complexation behaviour has been characterised recently using IR, NMR and microanalysis in our laboratory.<sup>6</sup> Interesting complexation behaviour of DECP with some transition metals has already been investigated by us.<sup>7</sup> As an extension of these studies we now report an investigation on spectral and thermal decomposition behaviour of Mg(II) and Zn(II) complexes of DECP.

### EXPERIMENTAL

The ligand DECP is prepared from a mixture of ethylacetoacetate, benzaldehyde and ammonium acetate by adopting the procedure followed by known method. 10 mmol of ligand and 3 mmol of appropriate metal salt [magnesium nitrate or zinc nitrate] were mixed in 50 mL of methanol and refluxed for 8-12 h. Further the reaction solution was concentrated and kept overnight. The resulting yellow [Mg(II)-DECP] and white [Zn(II)-DECP] coloured complexes were filtered, washed thoroughly with benzene to remove any unreacted ligand and finally with hot water and dried in a desiccator. The analytical data are as follows: Mg(II)-DECP [found (%) C, 44.80; H, 5.12; N, 7.91; Calc. (%) C, 44.20; H, 5.34;

N, 7.73]; Zn(II)-DECP [found (%) C, 40.20; H, 5.44; N, 7.22; Calc. (%) C, 39.94; H, 5.16; N, 6.99].

Infrared spectra of the ligand and metal complexes in the region 4000–400  $\text{cm}^{-1}$  were recorded on JASCO-IR-700 model using potassium bromide pellets. Thermal analysis was done on a Mettler TA 3000 microprocessor with a TG 50 thermobalance and on STA 1500 PL thermal sciences [heating rate is  $10^\circ\text{C min}^{-1}$ ].

## RESULTS AND DISCUSSION

*cis*-2,6-Diphenyl-3-ethoxycarbonylpiperidin-4-one can form anion as a result of enolisation and ionisation similar to acetylacetone and acetoacetic ester. If enolic hydrogen of ligand is removed during complexation there is a possibility that nitrogen present in the piperidone may be protonated and the complex may be isolated as piperidinium nitrate since the ligand itself has been recovered from the corresponding hydrochloride by neutralisation with ammonia.

IR spectra of Mg(II)-DECP and Zn(II)-DECP complexes revealed absence of bands for  $\nu(\text{C}=\text{O})$  around  $1700\text{ cm}^{-1}$  thus indicating coordination occurring through enol form *i.e.*, Mg(II) and Zn(II) form type A complexes with DECP. A band at  $1620\text{ cm}^{-1}$  in Mg(II)-DECP and  $1582\text{ cm}^{-1}$  in Zn(II)-DECP is due to both  $\nu(\text{C}-\text{C})$  and  $\nu(\text{C}-\text{O})$  of enolic form of DECP ligand. The band at  $553\text{ cm}^{-1}$  in Mg(II) complex and  $616\text{ cm}^{-1}$  in Zn(II) complex is probably due to  $\text{M}-\text{O}$  stretching mode.

The IR spectrum of Mg(II)-DECP also displayed new bands at  $1382\text{ cm}^{-1}$ ,  $1019\text{ cm}^{-1}$  and a broad band at  $1269\text{ cm}^{-1}$  for the presence of monocoordinate nitrate ion. In addition new peak is observed at  $840\text{ cm}^{-1}$ . The peak at  $699\text{ cm}^{-1}$  is attributed to the  $\text{C}-\text{H}$  deformation of benzene ring and the ionic nature of nitrate group. Thus, the peaks at  $840\text{ cm}^{-1}$  and  $699\text{ cm}^{-1}$  show the presence of

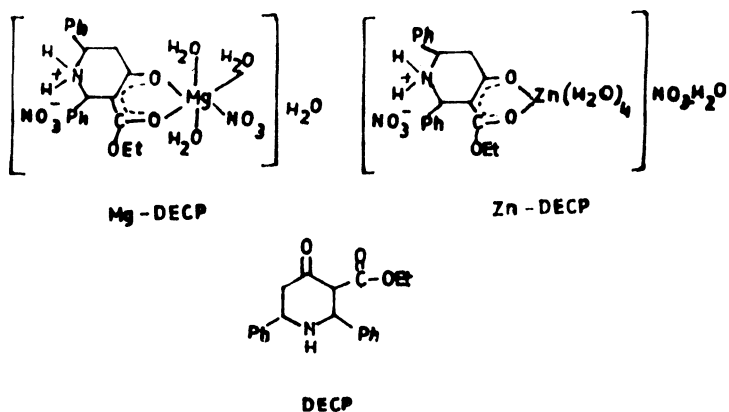


Fig. 1

ionic nature of nitrate also in the complex. The presence of ionic nature of nitrate group alone is present in Zn(II)-DECP complex is evidenced from the peaks at

1026, 823 and 764  $\text{cm}^{-1}$ . Based on microanalysis and infrared spectral studies the structures of the complexes are shown in Fig. 1 along with that of ligand.

### Thermal behaviour

Analysis of the thermograms shows that both the complexes lose water molecules below 100°C and major decomposition takes place in two stages.

Mg(II)-DECP complex is degraded in two steps. The complex is stable up to 350 K. In step 1 the complex splits off two molecules of nitrate ion, four molecules of  $\text{H}_2\text{O}$  and one molecule of  $\text{CO}_2$  and one molecule of ethylene (from  $\text{COOC}_2\text{H}_5$  group at C-3) in the temperature range 353–623 K. The decomposition suffers a weight loss of 50% as against the calculated value of 49.4%. In the next step one molecule of *cis*-2,6-diphenyl-3-ethoxycarbonyl-piperidin-4-one is eliminated in the temperature range 643–828 K. The observed weight loss is 42% as against the calculated value of 46.2%. There is no appreciable change after the temperature of 830 K and possibly MgO is formed. The residual weight was found to be 8% as against the calculated value of 7.2%.

Zn(II)-DECP complex is stable up to 340 K. The complex loses five  $\text{H}_2\text{O}$  molecules, one molecule of ethylene and one molecule of  $\text{CO}_2$  in a single step between 343–523 K. The observed weight loss is 32% as against the calculated value of 27%. In the second step the decomposition of one molecule of *cis*-2,6-diphenylpiperidin-4-one occurs between 543 and 838 K. The observed weight loss is found to be 36% as against the calculated value of 41.8%. After the complete decomposition of the complex mass loss data shows that the residue is a nitrate of zinc whose percentage corresponds to 32% [calcd. 31.3%].

### Kinetic studies

We have adopted (1) Horowitz-Metzger method [H-M method]<sup>8</sup> and (2) Coats and Redfern method [C-R method]<sup>9</sup> for the determination of order of reaction ( $n$ ) and kinetic parameters. The order was found to be one in I stage and zero in the second stage of both the complexes.

According to Horowitz and Metzger method the following expressions were used.

$$\ln(-\ln(1-\alpha)) = \ln\left[\frac{ART_s^2}{qE^*}\right] - \frac{E^*}{RT_s} + \frac{E^*Q}{RT_s^2} \quad \text{for } n = 1$$

and

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \ln\left[\frac{ART_s^2}{qE^*}\right] - \frac{E^*}{RT_s} + \frac{E^*Q}{RT_s^2} \quad \text{for } n \neq 1$$

where  $A$  is frequency factor,  $\alpha$  is fraction decomposed,  $n$  is order of the reaction,  $E^*$  is energy of activation,  $R$  is gas constant;  $T_s$  is DTG peak temperature [or any reference temperature],  $q$  is rate of heating and  $\theta = [T - T_s]$

From the plot of  $\ln(-\ln(1-\alpha))$  vs.  $\theta$  for  $n = 1$  and  $\log[1-(1-\alpha)^{1-n}/(1-n)]$  vs.  $\theta$  for  $n \neq 1$ , the activation energy is calculated from the slope and  $A$  is calculated using the equation

$$\frac{E^*}{RT_s^2} = \frac{A}{q(e^{E^*/RT_s})_s}$$

The entropy of activation  $S^*$  values are calculated using equation

$$S^* = R \ln [Ah/KT_s]$$

The expressions used by Coats and Redfern are

$$\log_{10} \left[ \frac{-\log_{10}(1-\alpha)}{T^2} \right] = \log_{10} \frac{AR}{qE^*} \left[ 1 - \frac{2RT_s}{E^*} \right] - \frac{E^*}{2.303RT} \quad \text{for } n = 1$$

and

$$\log_{10} \left[ \frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log_{10} \frac{AR}{qE^*} \left[ 1 - \frac{2RT_s}{E^*} \right] - \frac{E^*}{2.303RT} \quad \text{for } n \neq 1$$

where  $\alpha$  is the fraction decomposed,  $A$  is the frequency factor,  $E^*$  is the activation energy and  $q$  is the heating rate. From the slope of the plot of  $\log -\log(1-\alpha)/T^2$  vs.  $1/T$  for  $n = 1$  and  $\log_{10} [1 - (1-\alpha)^{1-n}]/T^2(1-n)$  vs.  $1/T$  for  $n \neq 1$ , energy of activation  $E^*$  was calculated and from the intercept, the frequency factor  $A$  was calculated.

The kinetic parameters obtained by this way for both the complexes according to Coats and Redfern method and Horowitz and Metzger method are displayed in Table 1. In the determination of activation energies and frequency factor for the individual steps it was found that Horowitz and Metzger method equation gave somewhat higher values relative to Coats and Redfern equation in all cases. Higher activation energies corresponding to the second step decomposition in Mg(II) and Zn(II) complexes compared to the first step reveals that the thermal decomposition of the second step is slow. The entropy of activation values are negatives in all steps indicating more ordered structure of the activated complex than the reactants. It is also evident from Table 1 that the values of  $E^*$  and  $A$  increase in the order.

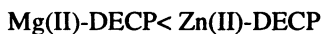


TABLE-1  
KINETIC PARAMETERS OF Mg(II)-DECP AND Zn(II)-DECP COMPLEXES

System	Decomposition range	Peak temperature (DTA)	Method	Parameters		
				$E^*$	$\log A$	$\Delta S$
Mg(II)-DECP	353–623 K (n = 1) I stage	477.9 K	CR	$1.69 \times 10^4$	0.78	$-2.34 \times 10^2$
			HM	$2.41 \times 10^4$	1.70	$-2.16 \times 10^2$
	643–828 K (n = 0) II stage	812.4 K	CR	$5.19 \times 10^4$	2.44	$-2.07 \times 10^2$
			HM	$7.44 \times 10^4$	3.94	$-1.78 \times 10^2$

Zn(II)-DECP	343–523 (n = 1) I stage	456.3 K	CR	2.44 × 10 <sup>4</sup>	1.82	– 2.14 × 10 <sup>2</sup>
			HM	3.60 × 10 <sup>4</sup>	3.37	– 1.84 × 10 <sup>2</sup>
	543–838 (n = 0) II stage	815.2 K	CR	6.56 × 10 <sup>4</sup>	3.32	– 1.90 × 10 <sup>2</sup>
			HM	8.86 × 10 <sup>4</sup>	4.86	– 1.60 × 10 <sup>2</sup>

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