Thermochimica Acta, 48 (1981) 375—381
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL DECOMPOSITION OF MIXED LIGAND COMPLEXES OF MANGANESE(II), COPPER(II), ZINC(II) AND CADMIUM(II) CONTAINING *N*-(2-HYDROXYETHYL)-ETHYLENEDIAMINE AND OXALATE

G.N. RAO and C.S.R. MURTHY

Department of Chemistry, Indian Institute of Technology, New Delhi-110016 (India)

(Received 20 April 1981)

ABSTRACT

The kinetics of the thermal decomposition of mixed ligand complexes of Mn(II), Cu(II), Zn(II) and Cd(II) containing *N*-(2-hydroxyethyl)-ethylenediamine and oxalate have been studied employing thermogravimetry (TG) and differential scanning calorimetry (DSC). The activation energy of the first order reaction in which the complex loses one molecule of the amine was calculated using the equations of Dharwadkar and Karkhanavala (modified Horowitz and Metzger equation) and Coats and Redfern from the TG data, and Swarin and Wims from the DSC data. These values are 23.45, 16.83, 19.62 and 19.25 kcal mole^{-1} respectively, using the method of Dharwadkar and Karkhanavala. Infrared spectral studies of these complexes were carried out to determine the coordinating behaviour of the ligand in these complexes.

INTRODUCTION

The thermal decomposition of oxalate complexes has attracted the attention of several workers [1—3]. The decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$, $K_3[Co(C_2O_4)_3] \cdot 3\ H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3\ H_2O$ was studied by Wendlandt and Simmons [3]. In the decomposition process, manganese(III) and cobalt(III) are reduced to the divalent state but in the chromium(III) complex no reduction occurs. The decomposition of hydrated oxalate complexes of nickel(II), cobalt(II) and copper(II) have also been studied [4]. In the case of $K_2[Ni(C_2O_4)_2] \cdot 6\ H_2O$, it loses water first and is then converted to NiO and K_2CO_3, when heated in air. But in a nitrogen atmosphere, it is converted to Ni and K_2CO_3. Haschke and Wendlandt [5] studied the decomposition of mixed ligand complexes of zinc(II) and cadmium(II) containing ethylenediamine and oxalate. In the cadmium complexes it was found that the ethylenediamine was lost before rupturing of the oxalate group occurred.

According to Das Sarma and Bailar [6] the ligand *N*-(2-hydroxyethyl)-ethylenediamine(heen) may act as a bidentate as well as a tridentate ligand. In the first case, the two nitrogen atoms of the amino groups in the ligand coordinate with the metal, whereas in the latter case the additional —OH group may coordinate as such, or in a deprotonated form by using a suitable base. It was considered interesting to prepare and study the thermal decom-

0040-6031/81/0000—0000/$02.50

position of mixed complexes formed by using the potentially tridentate ligand *N*-hydroxyethylethylenediamine and oxalate with some metals as part of our programme on the thermal decomposition studies of mixed ligand complexes of metals.

EXPERIMENTAL

The ligand *N*(2-hydroxyethyl)ethylenediamine was obtained from Aldrich Chemicals and was used as such without further purification. The metal oxalates of manganese(II), copper(II), zinc(II) and cadmium(II) were prepared by adding equivalent amounts of oxalic acid to the solutions containing the above metal ions. The precipitated oxalates were air dried for 1 day at room temperature before use in the synthesis of the complexes. The oxalato bis[*N*-(2-hydroxyethyl)ethylenediamine] complexes were prepared according to the following method. Two-fold excess of the ligand was added to the metal oxalate, triturated and allowed to stand for 1 h. The resultant precipitate was filtered off, washed with ethanol and then with ether and dried in a vacuum desiccator. All the metal ions formed complexes of the type $M(II)(heen)_2C_2O_4$, except in the case of cadmium where $Cd(heen)C_2O_4$ only could be obtained. The yield was about 90% in all cases. The metal content of the complexes was estimated by complexometric titrations with EDTA using suitable metal ion indicators after decomposing the complex with aqua regia. These results were confirmed by atomic absorption spectrophotometry using a Pye Unicam SP 191 model single beam atomic absorption spectrophotometer. The oxalate content of the complexes was estimated by titrating the acidic solution of the complex with standard potassium permanganate solution. The carbon and hydrogen analyses were obtained employing a Coleman analyser. The IR spectra of the complexes were taken on a Unicam SP 1200 spectrophotometer as potassium bromide pellets.

The thermograms of the complexes were obtained on a Stanton HTD thermogravimetric analyzer with a heating rate of $6^\circ C\ min^{-1}$ in static air. The DSC curves were obtained using a Du Pont differential scanning calorimeter, with a heating rate of $10^\circ C\ min^{-1}$.

Methods used for calculating the activation energy (E)

The method proposed by Coats and Redfern [7] determines the order of the reaction on the basis of thermogravimetric data based on a plot of $\log[1-(1-\alpha)^{1-n}]/T^2(1-n) = A$ vs. $1/T \times 10^3$, where α is the thermal decomposition rate of the sample calculated from the TG curve from the formula $\alpha = (W_0 - W)/(W - W_K)$ in which W_0, W_k and W are initial weight, final weight and weight of the sample at temperature T, respectively; n is the order of the reaction.

For a number of assumed values of n a number of such relationships are plotted and the correct value of n for a given thermal decomposition reaction gives a straight line. These linear plots are shown in Fig. 1. The activa-

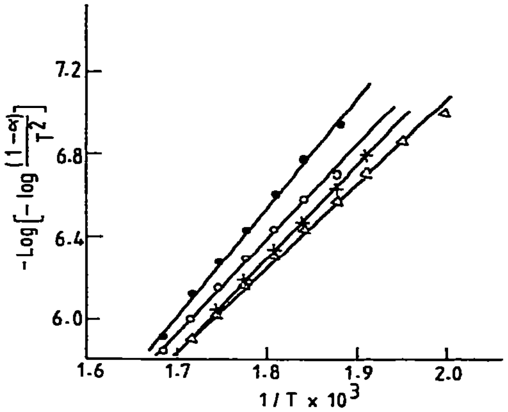


Fig. 1. Linear plots for the determination of activation energy ($n = 1$) using the Coats and Redfern equation. (———○———) $Cu(heen)_2C_2O_4$; (———●———) $Zn(heen)_2C_2O_4$; (———×———) $Mn(heen)_2C_2O_4$; (———△———) $Cd(heen)C_2O_4$.

tion energy E is then calculated from the equation

$$E = 2.303\, mR$$

where m is the slope of the straight line found, R is the gas constant, and if $n = 1$

$$A = -\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$$

Dharwadkar and Karkhanavala [8] have modified the equation of Horowitz and Metzger to yield values of activation energy which are independent of the variation in sample size and heating rate. According to them, the modified equation for the first order kinetics is

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E^*}{RT_i^2}\,\frac{100}{(T_f - T_i)}\,\theta + C$$

where α = fraction of the sample reacted; E^* = activation energy; R = gas constant; T_i = temperature of the inception of the reaction; T_f = temperature of the completion of the reaction; T_s = temperature at the point of inflection in the thermogravimetric curve; θ = difference between T_s and the temperature under consideration (T); C = constant.

The linear plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ are shown in Fig. 2.

In the method proposed by Swarin and Wims [9] for determining the activation energy from DSC curve, the following equation is used

$$K = \frac{(A)^{n-1}\, \mathrm{d}H/\mathrm{d}t}{(A-a)^n}$$

where K = rate constant; A = total area under the DSC curve; $\mathrm{d}H/\mathrm{d}t$ = height of the DSC curve; a = area up to temperature T; n = order of the reaction.

For different values of n, plots of $-\ln K$ vs. $1/T$ are made and the correct value of n gave a straight line from which the activation energy of the decomposition reaction was calculated.

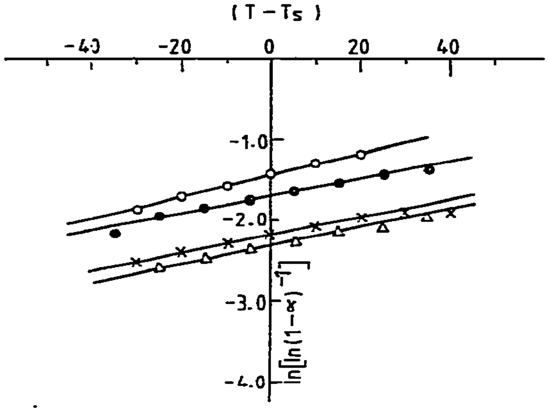
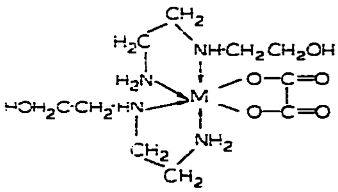


Fig. 2. Linear plots for the determination of activation energy using the Dharwadkar and Karkhanavala equation. (——○——) Zn(heen)$_2$C$_2$O$_4$; (——●——) Mn(heen)$_2$C$_2$O$_4$; (——×——) Cd(heen)C$_2$O$_4$; (——△——) Cu(heen)$_2$C$_2$O$_4$.

IR spectral studies

The IR band positions and their assignments are listed in Table 1. The free ligand shows a band at ~3300 cm^{-1} corresponding to the hydrogen bonded —OH group. In those complexes where the ligand is bidentate with a free —OH group, this band occurs at 3360 cm^{-1}. In the present case all the complexes have shown the ν(OH) band around 3340 cm^{-1}, indicating that here the ligand is bidentate. A strong band at 795 cm^{-1} is assigned to ν(M—O) and δ(O—C = O), and a strong band at 490 cm^{-1} is assigned to ν(M—N). These assignments of the bands indicate that the complexes have distorted octahedral structures, with the oxalate acting as a bidentate in the coordination sphere. Then the structure will be



Since the IR spectra of the intermediate monocomplexes did not show any change in the ν(OH) band position, they are apparently four-coordinate complexes. However, polymeric structure is not ruled out.

Thermal decomposition studies

The thermal decomposition curves of these complexes are shown in Fig. 3. Every complex shows a definite curve plateau after the loss corresponding to one amine molecule, indicating the formation of a stable complex with one amine ligand. In the case of the cadmium complex, stable anhydrous cadmium oxalate is formed. On further heating of the monoamine complexes,

TABLE 1

IR frequencies and band assignments of oxalato(heen) complexes

$Mn(heen)_2C_2O_4$	$Cu(heen)_2C_2O_4$	$Zn(heen)_2C_2O_4$	$Cd(heen)_2C_2O_4$	Band Assignment
3340	3330	3340	3340	ν(O—H)
3250	3240	3260	3260	$\nu(NH_2)$
2920 (s), 2880 (sh)	2930, 2890	2950, 2890	2920, 2830	$\nu(CH_2)$
2840				
1600 (vs)	1685 (vs), 1630	1630 (vs)	1610 (vs)	$\nu_{as}(C{=}O) + \delta(NH_2)$
1460	1440	1440	1460	$\delta(CH_2) + \nu_s(C{-}O) + \nu(C{-}C)$
1315 (s)	1310 (s)	1300 (s)	1310 (s)	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
1084	1095	1090	1090	$\nu(C{-}C)$
1045, 1020	1055, 1034	1050, 1030	1065, 1030	$\nu(C{-}N)$
960	970	980	970	$\gamma(NH_2)$
896	895	898	900	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
798 (vs)	795 (vs)	789 (vs)	793 (vs)	$\delta(O{-}C{=}O) + \nu(M{-}O)$
550	540	550	555	$\nu(N{-}M{-}N)$
500 (s)	500 (s)	499 (s)	490 (s)	$\nu(M{-}N'')$
410	420	420	420	$\nu(M{-}O)$ + ring diff.

TABLE 2

Analytical data of the oxalato(heen) complexes and intermediates

Complex	% Carbon		% Hydrogen		% Metal		% Oxalate	
	Obsd.	Theoret.	Obsd.	Theoret.	Obsd.	Theoret.	Obsd.	Theoret.
$Mn(heen)_2C_2O_4$	33.64	34.22	6.95	6.89	15.38	15.65	24.82	25.08
$Cu(heen)_2C_2O_4$	33.15	33.40	6.68	6.73	17.32	17.67	24.16	24.48
$Zn(heen)_2C_2O_4$	32.78	33.23	6.54	6.69	17.89	18.09	24.56	24.35
$Cd(heen)C_2O_4$	23.41	23.67	4.06	3.97	36.53	36.92	28.64	28.91
$Mn(heen)C_2O_4$	28.85	29.18	4.83	4.90	22.32	22.24	35.19	35.64
$Cu(heen)C_2O_4$	27.98	28.20	4.62	4.73	24.66	24.86	34.16	34.42
$Zn(heen)C_2O_4$	28.34	28.00	4.55	4.70	25.13	25.40	33.84	34.19
CdC_2O_4	11.77	11.98			55.85	56.08	43.57	43.90

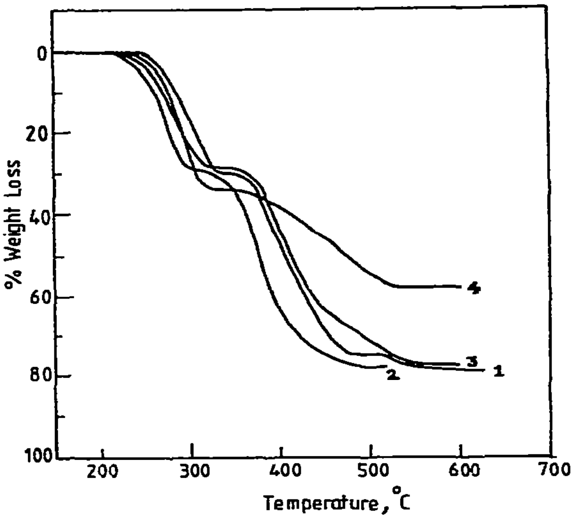


Fig. 3. Thermal decomposition curves of oxalato(heen) complexes. 1, $Mn(heen)_2C_2O_4$; 2, $Cu(heen)_2C_2O_4$; 3, $Zn(heen)_2C_2O_4$; 4, $Cd(heen)C_2O_4$.

simultaneous decomposition of the amine and oxalate occurred, with the metal oxide as the final product.

The stable intermediates were isolated in the case of Mn(II), Zn(II) and Cu(II) after careful heating of the complexes at the proper temperature range as ascertained from the thermograms. The carbon, hydrogen, metal and oxlate analyses have confirmed that these are [oxalato mono-(hydroxyethyl)ethylenediamine]metal(II) complexes. The analytical data are given in Table 2. The decomposition temperatures for the bis—mono transitions of these complexes are $[Mn(heen)_2C_2O_4]$ 250—330°C, $[Cu(heen)_2C_2O_4]$ 220—300°C, $[Zn(heen)_2C_2O_4]$ 230—320°C. The loss of one ligand molecule in the case of the $[Cd(heen)C_2O_4]$ complex occurred between 240 and 320°C.

The values of activation energy obtained from the three different methods are listed in Table 3. Considering the approximations involved in developing these equations and the precision of the experimental data, the agreement between the two sets of data (i.e. from TG and DSC methods) is quite satisfactory. From these values the order of decreasing activation energy is $Mn(II) > Cd(II) \simeq Zn(II) > Cu(II)$.

TABLE 3

Values of activation energy (kcal mole^{-1}) calculated by different methods

Complex	Method		
	Karkhanavala	Coats and Redfern	DSC
$Mn(heen)_2C_2O_4$	23.45	23.85	24.57
$Cu(heen)_2C_2O_4$	16.83	18.24	18.10
$Zn(heen)_2C_2O_4$	19.62	20.79	23.36
$Cd(heen)C_2O_4$	19.25	21.3	

Since Mn(II) ion contains the half-filled d^5 electron configuration, making it very stable, the corresponding complexes are thermally stable. In the 3*d* series, from Mn(II), electrons are added to the 3*d* energy level, until at Zn(II) a stable energy state with d^{10} electronic configuration is obtained. Due to this zinc(II) complexes could be expected to have a higher thermal stability than the complexes formed by copper(II). A similar trend in the thermal stability was obtained by Horowitz and Perros [10] for bis-(8-hydroxy-5-quinolyl)methane coordination polymers and metal oxinates. In the thermal decomposition of the mixed ligand complexes of zinc(II) and cadmium(II) containing oxalate and ethylenediamine, almost the same value of the activation energy was obtained for both the complexes, which is similar in the present case.

CONCLUSION

The ligand *N*-(2-hydroxyethyl)ethylenediamine acts as a bidentate ligand in the mixed ligand complexes of Mn(II), Cu(II), Zn(II) and Cd(II) containing oxalate. On heating, these complexes lose one mole of amine and kinetic analysis has indicated this step to be a first order reaction. The activation energies obtained are in the order: Mn(II) $>$ Cd(II) $\simeq$ Zn(II) $>$ Cu(II).

REFERENCES

1 W.W. Wendlandt and E.L. Simmons, Thermochim. Acta, 2 (1971) 217.
2 E.L. Simmons and W.W. Wendlandt, J. Inorg. Nucl. Chem., 27 (1965) 2325.
3 W.W. Wendlandt and E.L. Simmons, J. Inorg. Nucl. Chem., 27 (1965) 2317.
4 D. Broadbent, D. Dollimore and J. Dollimore, in R.F. Schwenker, Jr. and P.D. Garn (Eds.), Thermal Analysis, Vol. 2, Academic Press, New York, 1969, pp. 739—760.
5 J.M. Haschke and W.W. Wendlandt, Anal. Chim. Acta, 32 (1965) 386.
6 B. Das Sarma and J.C. Bailar, Jr., J. Amer. Chem. Soc., 91 (1969) 5958.
7 A.W. Coats and J.P. Redfern, Nature (London), 68 (1964) 201.
8 S.R. Dharwadkar and M.D. Karkhanavala, in R.F. Schwenker, Jr. and P.D. Garn (Eds.), Thermal Analysis, Vol. 2, Academic Press, New York, 1969, pp. 1049—1069.
9 S.J. Swarin and A.M. Wims, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 4, Plenum, New York, 1977, pp. 155—170.
10 E. Horowitz and T.P. Perros, J. Inorg. Nucl. Chem., 26 (1964) 139.