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Thermal decomposition kinetics of mixed ligand complexes of cobaloxime with 1-benzyl-2-phenylbenzimidazole

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Abstract

Cobaloxime complexes of the type $[Co(DH)_2(BPBI)X]$, where BPBI is 1-benzyl-2-phenylbenzimidazole and X = Cl, Br, I or SCN, were subjected to a systematic thermogravimetric, differential thermogravimetry and differential thermal analysis. All the complexes decompose just after melting, and the decomposition process consists essentially of three stages. The final residue in all cases was found to be CoO. The mass loss data indicate the formation of intermediate complexes with an approximate composition of $[Co(DH)_2(BPBI)]$ at the end of the first stage of decomposition. The kinetic parameters were calculated using the Coats–Redfern equation. The E_a values for the first stage of the decomposition are seen to decrease in the following order: thiocyanato complex > chloro complex > bromo complex > iodo complex. The E_a and ΔS values for the second and third stages of decomposition indicate catalytic activity of the intermediate complexes formed during these stages.

INTRODUCTION

Cobaloximes are a class of complexes which contain the $Co(DH)_2^+$ moiety (DH is the monoanion of dimethylglyoxime, DH_2). They are known to simulate the reactions of vitamin B_{12} [1,2] and are useful reagents in synthetic organic chemistry [3]. They also find use as catalysts for oxidation reactions involving molecular oxygen. In view of these, several mixed-ligand cobaloxime complexes have been synthesized and characterized [4–7]. TG studies have also been done in a few cases [8]. However, thermal decomposition kinetic studies have not yet been reported on any of these complexes. In this paper the results of our studies on the thermal decomposition kinetics of some interesting cobaloxime complexes of the type *trans*-$[Co(DH)_2(BPBI)X]$, where BPBI is 1-benzyl-2-phenylbenzimidazole and X = Cl, Br, I or SCN (Fig. 1), are presented.

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EXPERIMENTAL

Materials

The ligand BPBI was prepared according to the procedure given in the literature [9]. All the other reagents used were Analar grade and were used without further purification.

Synthesis of the complexes

The complexes were prepared by interacting cobalt(II) salts with dimethylglyoxime and BPBI in *n*-butanol medium according to the procedure given in the literature [10].

Analytical methods

Magnetic susceptibilities were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. IR spectra of the complexes were taken as KBr discs in the region 400–4000 cm^{-1} on a Perkin–Elmer PE-983 IR spectrophotometer.

The thermogravimetric analysis and the differential thermal analysis were carried out on a Dupont 990 thermal analyser. The analysis was done under a nitrogen atmosphere at a heating rate of 10°C min^{-1} using a platinum crucible. In all the experiments 10 mg of the sample was taken. The evaluation of kinetic parameters (i.e. order n, energy of activation E_a, entropy of activation ΔS, and pre-exponential factor A) using the Coats–Redfern equation was based on a computer program which was developed

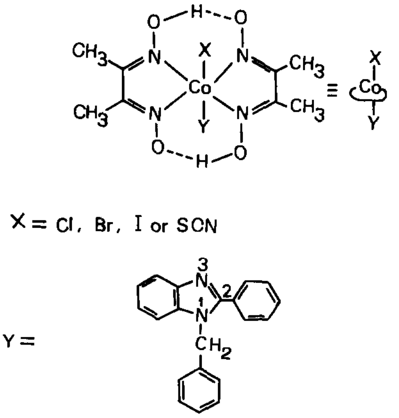

Fig. 1. Schematic structure of *trans*-$[Co(DH)_2(BPBI)X]$.

for use on a Busybee PC/XT computer (HCL Ltd.), and had been used earlier for the determination of kinetic parameters [11].

RESULTS AND DISCUSSION

Thermal behaviour

The TG, DTG and DTA curves for all the complexes are shown in Fig. 2. Thermoanalytical data for the complexes are presented in Table 1. The percentage mass loss and the probable composition of the expelled groups are also given in this table.

All the complexes have a fairly wide stability range and have almost the same pattern of thermal decomposition. The DTG curves show three peaks for all the complexes. All the DTG peaks have their parallel DTA peaks. The DTA peak corresponding to the first stage is a weak endothermic peak followed by an exothermic peak. Similar behaviour in nitrogen has been reported for the first stage thermal decomposition of organo(aquo)cobaloxime and organo(pyridine)cobaloxime complexes [8]. The endothermic peak may be due to the melting of the complexes. Independent studies revealed that the complexes decompose just after melting.

The mass loss at the first stage of decomposition corresponds to the expulsion of halogen atom in the case of the halogeno complexes and the SCN group in the case of the thiocyanato complex. The unexpected exothermic nature of the decomposition step may be due to subsequent reactions involving the halogen or thiocyanate radical formed during this stage. The residue left after the first stage was isolated and analysed. The intermediate complexes were found to have an approximate composition of $[Co(DH)_2(BPBI)]$. The IR spectra of these complexes show the presence of DH and BPBI. Furthermore, magnetic susceptibility measurements were also carried out on these complexes. Their μ_{eff} values around 4.6 BM indicate that these intermediate complexes are five-coordinate cobalt(II) complexes. In all the complexes the first DTG peak is followed by a medium DTG peak. The mass loss at this stage corresponds to the removal of a BPBI molecule, except in the case of the iodo complex. For the iodo complex, the mass loss corresponds to the expulsion of 0.7 BPBI only. The temperature range for the last stage of decomposition is almost the same for all the complexes. This might be due to the thermal breakdown of the common core complex, $[Co(DH)_2]$. For the iodo complex, 0.3 BPBI is also removed at this stage. In all the cases the residue after the final stage of decomposition was found to be CoO.

Decomposition kinetics

The kinetic parameters, n, E_a, ΔS and A, calculated using the Coats–Redfern equation are presented in Table 2. In the present study, the

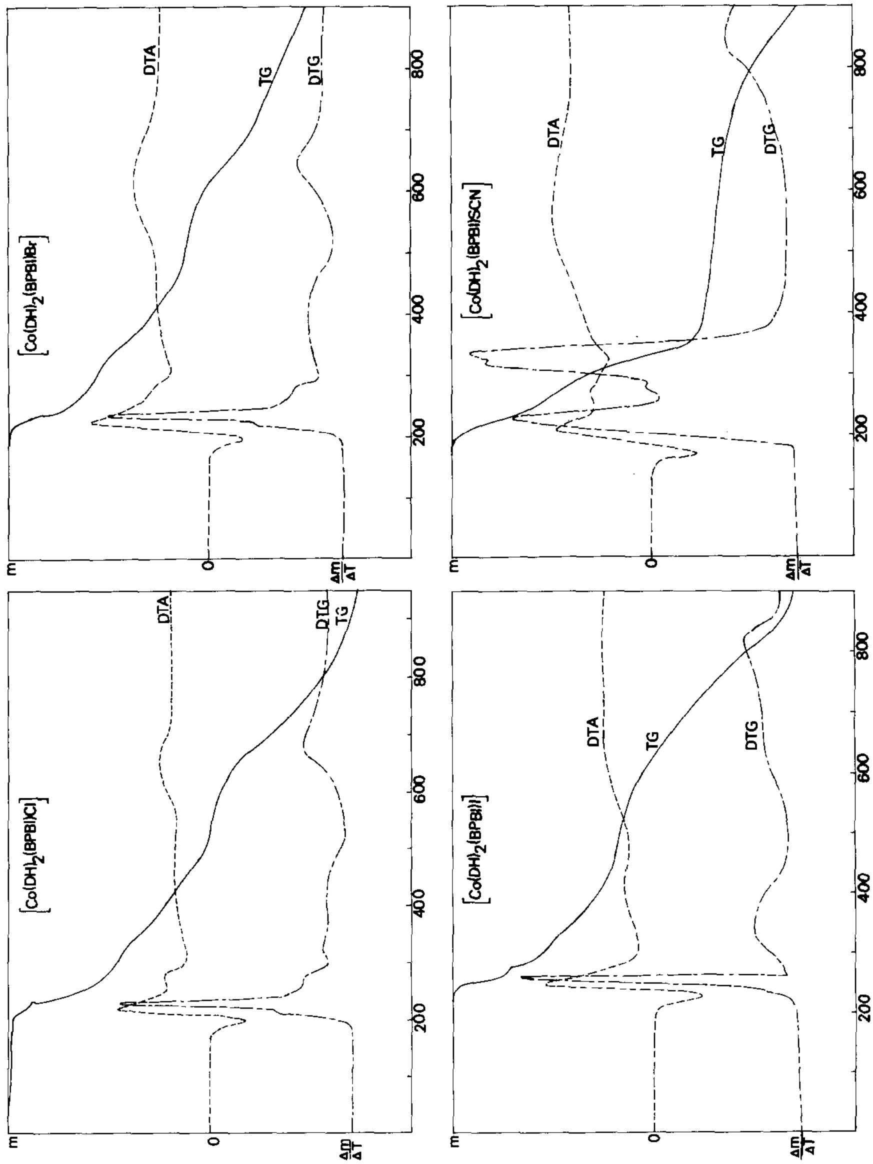

Fig. 2. TG, DTG and DTA curves of complexes.

TABLE 1

Thermal decomposition data

Substance	DTA		DTG		Stage of decomposition	Loss (%) from TG (calc.)	Probable composition of expelled group
	Peak temperature (°C)	Temperature range (°C)	Peak temperature (°C)	Temperature range (°C)			
$[Co(DH)_2(BPBI)Cl]$	215 exo (s)	190–220	220 (s)	190–230	I	5.94 (5.82)	Cl
	260 exo (m)	230–520	255 (m)	230–520	II	43.56 (46.66)	BPBI
	640 exo (m)	520–890	675 (m)	550–890	III	36.44 (37.76)	DMG core
$[Co(DH)_2(BPBI)Br]$	225 exo (s)	190–240	230 (s)	190–240	I	11.22 (12.24)	Br
	265 exo (m)	240–480	265 (m)	240–480	II	32.74 (43.48)	BPBI
	630 exo (m)	480–900	650 (m)	480–900	III	30.84 (35.25)	DMG core
$[Co(DH)_2(BPBI)I]$	240 exo (s)	210–260	250 (s)	210–260	I	13.96 (18.10)	I
	380 exo (m)	260–450	340 (m)	260–460	II	27.36 (40.56)	0.7 BPBI
	660 exo(m)	530–900	820 (m)	530–900	III	43.30 (32.88)	0.3 BPBI and DMG core
$[Co(DH)_2(BPBI)SCN]$	215 exo (s)	170–230	225 (s)	170–230	I	15.66 (9.34)	SCN
	270 exo (m)	230–380	333 (m)	230–380	II	46.32 (45.00)	BPBI
	540 exo (m)	520–900	850 (m)	520–900	III	22.64 (36.79)	DMG core

TABLE 2

Kinetic data

Substance	Stage	Order (n)	E_a (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	A (s^{-1})
[Co(DH)$_2$(BPBI)Cl]	I	0.15	141	−189	1.216×10^{3}
	II	1.99	26	−123	3.948×10^{6}
	III	1.61	112	−192	1.755×10^{3}
[Co(DH)$_2$(BPBI)Br]	I	1.12	124	−81	6.139×10^{8}
	II	1.34	31	−255	6.300×10^{-1}
	III	1.26	47	−264	3.016×10^{-1}
[Co(DH)$_2$(BPBI)I]	I	1.81	63	−223	2.395×10^{1}
	II	1.66	63	−193	9.417×10^{2}
	III	1.03	71	−241	5.828×10^{0}
[Co(DH)$_2$(BPBI)SCN]	I	0.56	159	+35	7.321×10^{14}
	II	0.82	76	−167	2.223×10^{4}
	III	0.28	35	−287	2.226×10^{-2}

parameters E_a and ΔS have been evaluated for similar compounds using the same equation for nearly the same experimental conditions (same heating rate, furnace atmosphere, sample mass etc.) and hence can be used for the comparison of the decomposition processes [12]. However, the order n does not provide any meaningful information about the mechanism of complex decomposition [12].

The activation energies for the first stage of the decomposition are seen to decrease in the following order: thiocyanato complex > chloro complex > bromo complex > iodo complex. This order is almost the same as that of the Co–X bond strength, which indicates that in all cases the dissociation of the Co–X bond takes place during this stage. The stoichiometry of the intermediate complex formed after the first stage of decomposition (see Table 2) also indicates this aspect.

Even though the intermediate complexes obtained after the first stage of decomposition have nearly the same composition, [Co(DH)$_2$(BPBI)], the different kinetic parameters for the second stage of decomposition of the chloro, bromo, iodo and thiocyanato complexes indicate that the decomposition mechanisms are different for these complexes. This might be due to the subsequent reactions of the gaseous products and also to slight differences in stoichiometries of the intermediate complexes involved in these decomposition steps. Such slight differences in composition and structure are known to alter the rate in many catalytic reactions [13].

The E_a values for the second stage of decomposition are found to be smaller than those for the first stage in the case of all the complexes, indicating an increased rate of decomposition during the second stage. This might be due to the catalytic activity of the intermediate five-coordinate complex, which, due to its vacant coordination site, can adsorb gaseous products and thus facilitate easy decomposition. The E_a values for the third stage also suggest an increased rate of reaction, especially for the thiocyanato complex. Here also the increased rate may be due to the catalytically active four-coordinate $[Co(DH)_2]$ complex formed after the second stage.

Negative ΔS values for the first stage of decomposition suggest that the activated complexes have a more ordered structure than the reactants which are in the liquid state just before the decomposition. The more ordered nature may be due to polarization of bonds in the activated state, which might happen through charge transfer electronic transitions. The ΔS values for the second and third stages are found to be more negative, except for the chloro complex, than those for the first stage, which might be due to the chemisorption of the gaseous decomposition products by the intermediate complexes with vacant coordination sites involved in these respective steps. The five-coordinate complex, $[Co(DH)_2(BPBI)]$, formed after the first stage of decomposition and the four-coordinate complex, $[Co(DH)_2]$, formed after the second stage have vacant coordination sites. In fact, these type of complexes are known to act as catalysts in many oxidation reactions [14].

REFERENCES

1 G.N. Schrauzer and G. Kiatel, Angew. Chem., 77 (1965) 180.
2 G.N. Schrauzer and R.J. Windgassen, J. Am. Chem. Soc., 88 (1966) 3738.
3 H. Eckert, G.N. Schrauzer and I. Ugi, Tetrahedron, 31 (1975) 1399.
4 J.K. Das and K.C. Dash, Polyhedron, 4 (1985) 1109.
5 J.K. Das and K.C. Dash, Synth. React. Inorg. Met.-Org. Chem., 15 (1985) 839.
6 J.K. Das and K.C. Dash, Indian J. Chem., Part A, 24 (1985) 387.
7 J.K. Das and K.C. Dash, Proc. Natl. Acad. Sci., India, Sect. A, 56 (1986) 14.
8 K.L. Brown, G. Jang, R. Segal and K. Rajeswar, Inorg. Chim. Acta, 128 (1987) 197.
9 N.V. Subba Rao and C.V. Ratnam, Proc. Indian Acad. Sci., 43 (1956) 174.
10 K.K.M. Yusuff and A.R. Karthikeyan. Synth React. Inorg. Met-Org. Chem., 21(6/7) (1991) 903.
11 K.K.M. Yusuff and R. Sreekala, Thermochim. Acta, 159 (1990) 357.
12 G.N. Natu, S.B. Kulkarni and P.S. Dhar, J. Therm. Anal., 23 (1982) 101.
13 R. Pearce and W.R. Patterson, Catalysis and Chemical Processes, Blackie, London, 1981.
14 S. Nemeth, Z. Szeverenyl and L.I. Simandi, Inorg. Chim. Acta, 44 (1980) L107.