



DYNAMIC THERMOGRAVIMETRIC ANALYSIS OF AMINE COMPLEXES OF COBALT (III) IN PRESENCE OF ZINC.

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ABSTRACT The dynamic thermogravimetric analysis (TGA) of chloropentaminecobalt(III)chloride (CPCC), nitropentaminecobalt (III)chloride (NPCC), and carbanatotetraminecobalt(III)chloride (CTCC) were carried out in absence and presence of metallic zinc under static air atmosphere. The various thermodynamic and kinetic parameters associated with the observed steps in the decomposition and reduction processes were calculated by fitting the observed weight losses to different expressions given by Horowitz and Metzger (H.M.), Coats and Redfern (C.R.), and Reich and Stivala (R.S.). The dynamic TGA data indicates the lowering of decomposition temperature, increase in the rate of decomposition, and the formation of cobalt metal as one of the decomposition products, in all three complexes. Moreover, the dynamic TGA data indicates an order of 1 for the decomposition and reduction processes suggesting that both processes follow approximately the first order kinetics in all three complexes.

KEYWORDS : CPCC, NPCC, CTCC, Dynamic TGA

INTRODUCTION

The cobalt amines and their analogues with certain donor molecules have been known for many years and played a key role in the evolution of the modern concepts of coordination chemistry. In spite of the voluminous work on cobalt amine complexes, there is still a continuing interest in their studies. The present work has been undertaken with a specific aspect, the thermal decomposition of CPCC, NPCC, and CTCC in absence and presence of zinc.

EXPERIMENTAL

The compounds, CPCC, NPCC, and CTCC were synthesized by the reported methods⁽¹⁻³⁾ and analyzed for cobalt, ammonia, and chloride by standard methods⁴. The dynamic thermogravimetric measurements of pure CPCC, NPCC and CTCC with 48 ± 2 mg size were carried out in static air atmosphere on the home-made calibrated thermobalance with heating rate of $3^\circ\text{C}/\text{minute}$ from room temperature to 700°C . The graphs of % weight loss against temperature were plotted and shown in Fig 1 to 3.

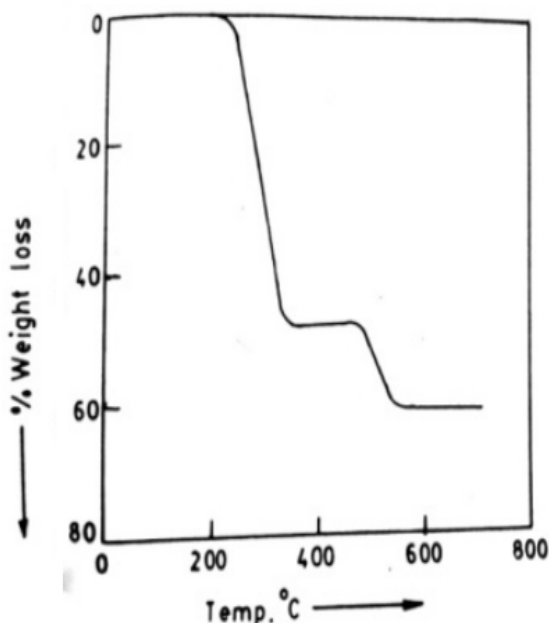


FIG.1. TGA of CPCC

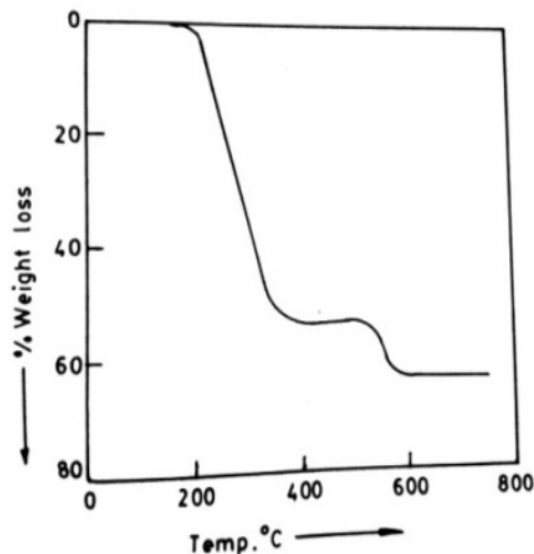


FIG.3. TGA of CPCC

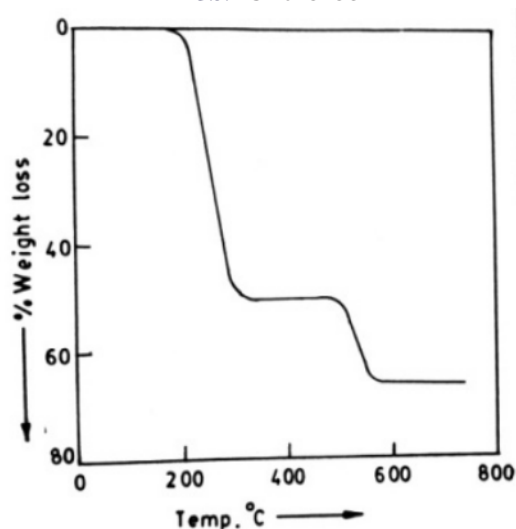


FIG.2. TGA of NPCC

Zinc powder was activated by treating with 0.5 N HCl and then washing it with oxygen free distilled water till free from acid followed by acetone.

The mixtures of CPCC, NPCC, and CTCC with zinc powder in 1:1, 1:2, 1:3, 1:4, and 1:5 mole ratios were prepared and their dynamic TGA curves were recorded. The gaseous and the residual decomposition products were chemically analyzed to ascertain the mechanism of thermal decomposition. During the reduction of Co (II) to Co metal

with Zn, the stoichiometric ratio of CPCC:Zn, NPCC:Zn and CTCC:Zn would be 1:1.5, 1:1, and 1:0.5 respectively. However, practically the ratio of 1:5 was preferred so that the reduction process became cleaner and the multistep decomposition changed to the two step process. From the dynamic TGA data, kinetic parameters such as the activation energy (Ea) and order of reaction (n) were calculated by using the well known kinetic expressions given by Horowitz and Metzger⁵ (H.M.), Coats and Redfern⁶ (C.R.), and Reich and Stivala⁷ (R.S.).

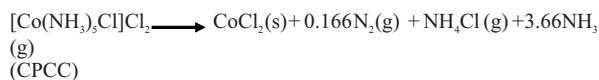
TABLE I. Data on Dynamic TGA of Cobalt (III) Amine Complexes

Complex	Step	Temp. ^a C		% weight loss		Probable expelled groups	Ea KJ mol ⁻¹		
		Obsd.	Calcd.	Obsd.	Calcd.		H.M.	C.R.	R.S.
[Co(NH ₃) ₅ Cl]Cl ₂ (CPCC)	I	235-355	48.5	48.11		3.66NH ₃ +0.166N ₂ +NH ₄ Cl xCl ₂ (x=0.46)	117(1.0) ^a	92(1.0)	122(1.4)
	II	475-550	13.0	13.03			202 (1.0)	218(1.0)	244(1.2)
[Co(NH ₃) ₅ Cl]Cl ₂ +Zn (1:5)	I	205-230	4.50	4.54		1.27 NH ₃ +0.166N ₂ 3.0NH ₃ +0.5ZnCl ₂ +0.5H ₂	265(1.0)	215(1.0)	191(0.9)
	II	485-565	20.5	20.81			273(1.2)	211 (1.0)	191(1.2)
[Co(NH ₃) ₅ NO ₂]Cl ₂ (NPCC)	I	195-315	50.0	50.22		3.66 NH ₃ +1.166N ₂ + 2H ₂ O xCl ₂ (X=0.6)	103(1.0)	86(1.0)	98(1.41)
	II	475-565	16.0	16.30			155(1.3)	104(1.0)	94 (0.92)
[Co(NH ₃) ₅ NO ₂]Cl ₂ +Zn (1:5)	I	195-220	8.0	8.45		NH ₃ +1.166N ₂ + 2H ₂ O 2.66NH ₃ +0.1 ZnCl ₂	206(1.0)	194(1.0)	187(0.97)
	II	520-555	12.0	16.13			191(1.0)	149(0.9)	191(1.0)
[Co(NH ₃) ₄ CO ₃]Cl (CTCC)	I	165-375	53.5	53.95		3.66NH ₃ +0.166N ₂ +CO ₂ +0.5H ₂ O xCl ₂ (x=0.35)	51(1.0)	34(1.0)	44(1.13)
	II	505-590	11.00	11.15			277(1.0)	291(1.1)	261(1.0)
[Co(NH ₃) ₄ CO ₃]Cl+Zn (1:5)	I	175-210	3.0	4.74		NH ₃ + 0.166N ₂ +0.1 CO ₂ 2.66NH ₃ +0.4 ZnCl ₂ + 0.9CO ₂ +0.5 H ₂ O	163(1.0)	123(1.0)	138(1.25)
	II	470-540	26.5	27.0			202(1.0)	200(1.0)	181(0.90)

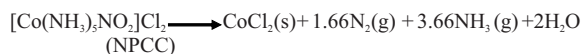
^aFigures in the parenthesis indicate the order of reaction (n)

RESULTS AND DISCUSSION

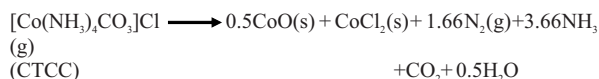
The thermal decomposition of CPCC was studied by Wendlandt and Smith⁸ by means of TGA and DTA. The decomposition reaction was given as



Recently, Miyokawa⁹ *et al* studied the thermal decomposition of NPCC. They postulated the following decomposition reaction,



Wendlandt and Woodlock¹⁰ studied the thermal decomposition of CTCC. They postulated the following decomposition reaction in helium atmosphere,



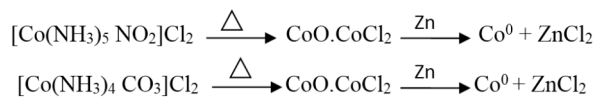
The metallic zinc plays an important role by three ways in the reduction of CPCC, NPCC and CTCC compounds. Firstly, Zn being higher in the electrochemical series (E⁰, -0.764 V) than Co (E⁰, -0.277 V), may reduce the cobalt (II) chloride formed to cobalt metal. Secondly, Zn may affect the decomposition temperature of CPCC, NPCC, and CTCC. A pure CPCC starts decomposing at about 235°C while in presence of zinc, it starts decomposing at 205°C. Similarly, NPCC and CTCC start decomposing from 195°C and 185°C, respectively whereas in the presence of zinc, these compounds start decomposing from 185°C and 175°C, respectively. The lowering of decomposition temperature is attributed to the higher specific heat¹¹ of Zn as compared to that of CPCC or NPCC or CTCC.

Thirdly, Zn reacts with NH₄Cl to give ZnCl₂, NH₃ and H₂, it appears that ZnCl₂ absorbs NH₃ and zinc-ammonia chloride complex¹² is formed which is stable in the temperature range 250°C to 490°C. The metallic Co formed is easily detected by taking the advantage of its ferromagnetic property. Hence, it can be collected from reaction mixture using the method of magnetic separation.

Zn reacts with NH₄Cl to give ZnCl₂, NH₃ and H₂ but the sublimation of NH₄Cl could not be observed in the TGA of CPCC and Zn mixture. A separate experiment was carried out to confirm the evolution of hydrogen in this reaction. It was observed that CoCl₂ reacts with Zn powder giving Co metal at room temperature by grinding. On the other hand, mere grinding of CPCC and Zn mixture did not result the Co metal suggesting that CoCl₂ did not form in the reduction process. It supported the formation of (NH₄)₂CoCl₄ during the decomposition of CPCC, which is reduced by Zn to Co metal. The overall reduction process could be written as



However, the mixtures of NPCC and Zn, CTCC and Zn on mere grinding result Co metal suggesting the formation of CoCl₂ in their reduction processes. This CoCl₂ gets reduced by Zn to Co metal. Hence the overall reactions for NPCC and CTCC would be written as



The data on dynamic TGA of CPCC, NPCC, and CTCC in absence and presence of zinc have been presented in Table 1. The good fit between the observed and calculated % weight losses corresponding to different decomposition steps of all complexes indicates that the assumed compositions of the expelled groups in the corresponding steps to be reasonably correct. The activation energies corresponding to various steps calculated by best fitting procedures from the three expressions viz. H.M. C.R. and R.S. are of comparable magnitude. The dynamic TGA data indicates i) the lowering of decomposition temperature ii) increase in the rate of decomposition iii) elimination of induction period iv) formation of cobalt metal as one of the decomposition products. From the dynamic data, the order of reaction (n) is found to lie within the range of 1 to 1.4 for decomposition and reduction reactions in all three complexes. This suggests that, the thermal decomposition and reduction processes are of first order kinetics in all three complexes. The activation energy for carbanato complex is lower than that of chloro and nitro complexes. The lower stability of carbanato complex as compared to chloro and nitro complexes is attributed to steric hindrance at the co-ordination sites in the former.

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