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Thermal Decomposition Studies on Amine Complexes of Copper(II) Nitrate in Solid State

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Synopsis. Thermal decomposition of tetraamminecopper(II) nitrate and bis(ethylenediamine)copper(II) nitrate has been studied using TG, DTG, and DTA. The kinetic parameters for the thermal deamination of the former were evaluated. The thermal decomposition of bis(ethylenediamine)copper(II) nitrate involves the concurrent deamination and the oxidation of the liberated amine by the decomposition products of $Cu(NO_3)_2$.

Solid state thermal decomposition of different complexes and salts has been extensively studied employing both isothermal and nonisothermal methods to evaluate the kinetics of their thermal decompositions. Although transition metal amine complexes were known for a long time, investigations on their thermal decomposition behavior have been carried out only recently.[1—4] Thermal studies on the amine complexes containing nitrate anion are relatively few, because of their self oxidative decomposition.

The thermal decomposition studies on tetraamminecopper(II) nitrate and bis(ethylenediamine)copper(II) nitrate in the solid state using TG, DTA, and other accessory techniques are described in this paper. The objectives of this investigation are to explore the kinetic and thermodynamic aspects of the thermal deamination of $[Cu(NH_3)_4](NO_3)_2$ and $[Cu(en)_2](NO_3)_2$.

Experimental

Preparation of Complexes: The preparative methods of $[Cu(NH_3)_4](NO_3)_2$ and $[Cu(en)_2](NO_3)_2$ are given elsewhere.[5] Both complexes were characterized by spectral and chemical methods.

Measurements: The experimental methods and the equipments used to measure TG-DTG, DTA curves, and X-ray powder diffractograms were the same as those described in our earlier work.[3,4] The heating rates employed here are 10, 2, 0.5 °C min^{-1} and sample mass 5±0.3 mg. Area under the DTA curves was evaluated by the sigmoidal curve integration and calibrated using pure indium metal.

Mathematical Treatment of Data: Kinetic parameters were evaluated from the TG and DTA curves using four nonmechanistic methods., viz. Coats-Redfern,[6] MacCallum-Tanner,[7] Horowitz-Metzger,[8] and MKN equations.[9] The iterative determination of the order parameter '*n*' is described in our earlier papers.[3,4] The entropy of activation was calculated from the equation.

$$A=[(kT_s/h)\exp(\Delta S^{\neq}/R)]$$

where k=Boltzmann constant, h=Planck's constant, and $\Delta S^{\neq}$=entropy of activation. The heat of reaction ΔH was evaluated from the DTA curve by area integration of the peak.

Results and Discussion

Thermal Decomposition of $[Cu(NH_3)_4](NO_3)_2$: The TG-DTG and DTA curves of tetraamminecopper(II) nitrate are given in Fig. 1. The TG trace revealed a clear cut decomposition state (125—225 °C) but on further heating, the complex gets exploded (ca. 257 °C) at a heating rate of 10 °C min^{-1}. This can be attributed to the presence of the reducing (NH_3) group and the oxidant nitrate group in the same compound. At a lower heating rate of 2 °C min^{-1} neat thermograms could be recorded. The phenomenological data from TG and DTA curves for each stage of decomposition are given in Table 1. From the mass loss data, the two stages of decomposition of tetraamminecopper(II) nitrate can be represented as follows:

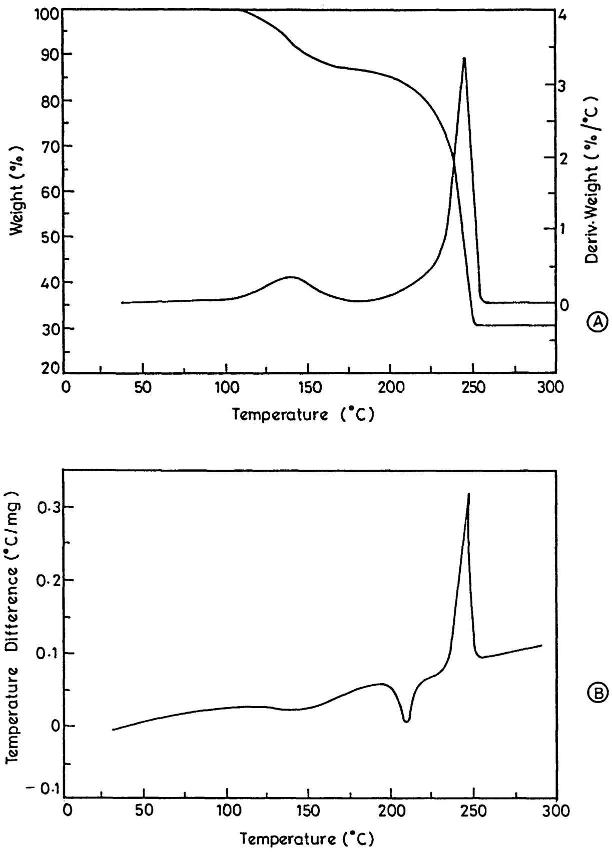

Fig. 1. A: TG and DTG curves of $[Cu(NH_3)_4](NO_3)_2$ at 2 °C min^{-1}. B: DTA curve of $[Cu(NH_3)_4](NO_3)_2$ at 2 °C min^{-1}.

$$[Cu(NH_3)_4](NO_3)_2\,(s) \longrightarrow Cu(NH_3)_2(NO_3)_2\,(s) + 2NH_3\,(g)$$
$$Cu(NH_3)_2(NO_3)\,(s) \longrightarrow CuO\,(s)$$

The DTA profile of the complex shows three peaks. The first endothermic peak in the DTA curve at 146 °C is due to the first stage of deamination resulting in the formation of the diammine complex. The second

Table 1. Phenomenological Data for the Thermal Decomposition of Tetraamminecopper(II) Nitrate and Bis(ethylenediamine)copper(II) Nitrate

		$[Cu(NH_3)_4](NO_3)_2$						$[Cu(en)_2](NO_3)_2$				
	Stage	T_i	T_f	T_s	%wt loss		ΔH	T_i	T_f	T_s	%wt loss	ΔH
		°C	°C	°C	Theoretical	Observed	J gm^{-1}	°C	°C	°C	Observed	J gm^{-1}
TGA	I	90	176	140	13.31	13	—	230	252		37	—
	II	185	250	248	42.26	42	—	252	261		23	—
	III							261	272	266	3	—
	IV							276	338	296	10	—
DTA	I	98	181	146	—	—	297	230	248	245	—	−934
	II	190	218	211	—	—	180	248	258	255	—	−280
	III	227	254	249	—	—	−873	258	271	264	—	−435
	IV	—	—	—	—	—	—	271	335	293	—	−664

endothermic peak is immediately followed by a sharp exotherm, contrary to the expected enthalpy changes accompanying the decomposition of a stable complex. The exothermic peak can, however, be explained on the basis of the decomposition of $Cu(NO_3)_2$, overlapping the diammine complex. $Cu(NO_3)_2$ on decomposition gives rise to oxides of nitrogen and oxygen which in turn would oxidize the liberated ammonia. Thus the decomposition of the diammine complex initiates with a small endothermic peak (corresponding to the initial deamination), immediately followed by a sharp exotherm.

The thermal decomposition of tetraamminecopper(II) nitrate is consistent with the crystal structure of the complex.[10] The first deamination stage corresponds to the removal of two molecules of ammonia. From the single crystal study it is revealed that Cu–N bond distance for one pair is 2.03 Å and for the other pair is 2.008 Å. Hence normally the two NH_3 molecules coordinated to the copper at a distance of 2.03 Å can be expected to get liberated first. On subsequent heating, the remaining two NH_3 molecules are lost.

The intermediate diammine complex and the final residue of decomposition were identified by XRD. The final residue is found to be copper(II) oxide. The temperature values agree reasonably with the corresponding values of TG, except that the last two stages of DTA appear as a single stage in TG. However, the DTG peak temperature T_s corresponds to the T_{max} of the third stage in DTA. The ΔH for the first stage of deamination is 297 J gm^{-1} (endo), whereas for the second stage of deamination it is only 180 J gm^{-1} (Table 1). The reduction in enthalpy supports our contention that this stage corresponds only to a partial loss of ammonia. This is followed by the simultaneous loss of the rest of ammonia and the decomposition of $Cu(NO_3)_2$, leading to the exothermic oxidation of the liberated NH_3 by the decomposition products ($\Delta H = -873$ J gm^{-1}).

Thermal Decomposition of $[Cu(en)_2](NO_3)_2$: In order to avoid the explosive decomposition due to the presence of a powerful reductant (en) and the oxidizing nitrate group the TG and DTA curves were recorded at a lower heating rate of 0.5 °C min^{-1} (Fig. 2). The decomposition temperature regime reveals that bis(ethylenediamine) complex is thermally more stable than tetraammine complex, which could be attributed to the bidentate nature of the ligand and hence a stable chelate. The weight loss corresponding to each stage of decomposition is given in Table 1. The powder diffraction pattern of the residue obtained revealed that it is pure copper(II) oxide.

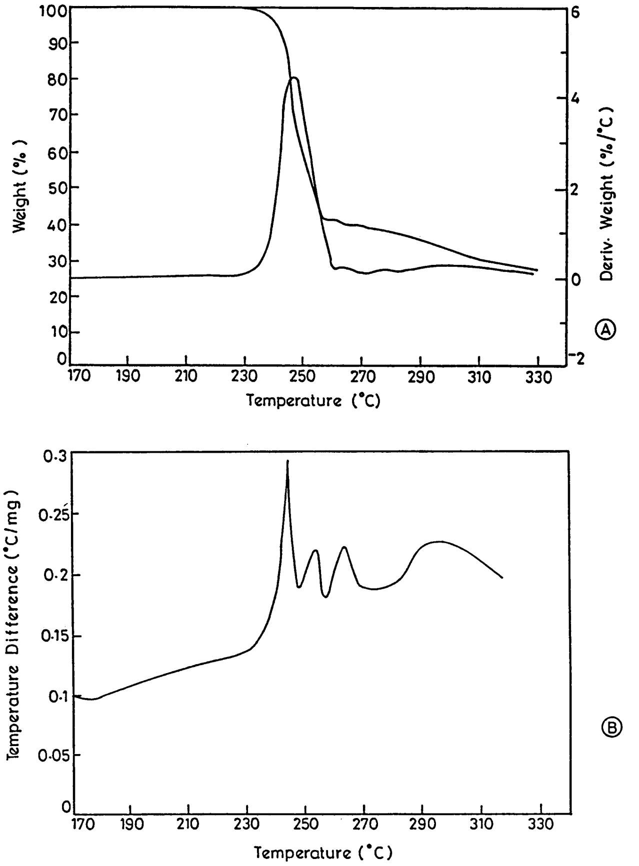

Fig. 2. A: TG and DTG curves of $[Cu(en)_2](NO_3)_2$ at 0.5 °C min^{-1}. B: DTA curve of $[Cu(en)_2](NO_3)_2$ at 0.5 °C min^{-1}.

The bis(ethylenediamine) complex starts decomposing at 230 °C. At this temperature, $Cu(NO_3)_2$ also starts to decompose. Due to this overlap, the whole process appears as pseudo exothermic in several steps. It is reasonable to assume that the exothermic peaks in

Table 2. Kinetic Parameters for the Deamination of $[Cu(NH_3)_4](NO_3)_2$ to $Cu(NH_3)_2(NO_3)_2$ Using Nonmechanistic Equations[a]

		TG	DTA
n		1.56	1.56
E ($kJ\,mol^{-1}$)	CR	125.4	150.6
	MT	124.6	150.2
	HM	133.9	156.3
	MKN	125.6	150.7
A (s^{-1})	CR	2.35×10^{13}	1.26×10^{16}
	MT	1.62×10^{13}	9.65×10^{15}
	HM	2.67×10^{14}	6.09×10^{16}
	MKN	2.44×10^{13}	1.30×10^{16}
$\Delta S^{\neq}$ ($J\,K^{-1}\,mol^{-1}$)	CR	8.36	60.5
	MT	5.26	58.3
	HM	28.6	73.6
	MKN	8.67	60.8
r	CR	0.9999	0.9985
	MT	0.9999	0.9987
	HM	0.9993	0.9975
	MKN	0.9999	0.9985

a) CR: Coats-Redfern, MT: MacCallum-Tanner, HM: Horowitz-Metzger, MKN: Madhusudanan-Krishnan-Ninan.

DTA are due to the simultaneous deamination and the insitu oxidation of the liberated amine. This process takes place in four stages, and all the stages are exothermic. The first sharp exotherm corresponds probably to the loss of one en, overlapping with its partial oxidation by the decomposition products of $Cu(NO_3)_2$.

The value of ΔH computed from the area under the DTA curve along with the T_i, T_f, and T_s values for the four stages of decomposition are given in Table 1. The four exothermic peaks in DTA add upto a heat of reaction $-2313\ J\,gm^{-1}=-711\ kJ\,mol^{-1}$. The heat of combustion of ethylenediamine is $1894\ kJ\,mol^{-1}$[11] and therefore a complete oxidation of the two moles of en would have given rise to a heat of reaction of $-3787\ kJ\,mol^{-1}$. However the minimum requirement for the complete oxidation of two ethylenediamine molecules is 16 oxygen atoms, whereas only 6 oxygen atoms are available in $Cu(NO_3)_2$. Further, some of the ethylenediamine is likely to escape oxidation in the open system. These result in only partial oxidation of the liberated ethylenediamine. This, coupled with the endothermicities of the deamination process and the decomposition of $Cu(NO_3)_2$ to CuO, leads to an overall heat of reaction much below the heat of combustion of two ethylenediamine molecules.

The kinetic parameters were evaluated for the deamination of tetraamminecopper(II) nitrate to the diammine complex. The data using the four kinetic equations from TG and DTA are tabulated in Table 2. The correlation coefficients indicate nearly perfect fits. This table shows that the order parameter for the deamination process is a fraction, as is possible.[12,13]

Table 2 shows that the kinetic parameters computed with Horowitz-Metzger equation are higher than the values from the other three equations. This is due to the inherent error involved in the approximation method employed in the derivation of the Horowitz-Metzger equation. The deamination reaction of tetraammine complex has a positive value of entropy, indicating a less ordered structure of the activated complex than the reactant and hence the reaction may be described as "faster than normal".[14] The higher values of activation energy from DTA technique may be due to the lag in the measurement of temperature as compared to mass measurement.

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