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Effect of Gamma-irradiation on Thermal Decomposition of Tris(1,2-diaminoethane) Cobalt(II) Sulphate

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ABSTRACT

Tris(1,2-diaminoethane)cobalt(II)sulphate was prepared and characterised. Pure dry sample of uniform mesh size was then irradiated with ^{60}Co γ-rays for varying doses up to 900 kGy. Non-isothermal decomposition of the complex was studied before and after irradiation. Unirradiated and irradiated samples decompose in three stages. Kinetic parameters E, Z and ΔS were evaluated by Coats-Redfern (integral), Freeman-Carroll (differential) and Horowitz-Metzger (approximation) equations. Results showed that irradiation enhanced thermal decomposition, lowering thermal as well as kinetic parameters. Mechanism of decomposition for each stage has been established. Irradiation modifies the reaction mechanism of the first stage of decomposition.

Key words: Tris(1,2-diaminoethane) cobalt(II)sulphate, γ-irradiation, Thermal decomposition kinetics, Mechanism.

INTRODUCTION

Pre-exposure to energetic radiation considerably affect the thermal decomposition kinetics of crystalline solids, the contributing factors being structural as well as topochemical. Inorganic salts containing oxyanions like acetates, chlorates, thiosulphates etc. have been extensively studied in this regard[1-3] while those of complexes are scanty[4,5]. In our earlier work we have reported the effect of gamma irradiation on non-isothermal decomposition kinetics of bis(diethylenetriamine) cobalt(II)nitrate[6]. In the present investigation the ligand is replaced by ethylenediamine and the counter ion nitrate, by sulphate. Thus the present paper reports the effect of gamma irradiation on non-isothermal decomposition kinetics of tris(1,2- diaminoethane)cobalt(II)sulphate. The study proposes evaluation of kinetic parameters by non-mechanistic equations for unirradiated and irradiated samples. The non-mechanistic equations employed are Coats-Redfern (integral), Freeman-Carroll (differential) and Horowitz-Metzger (approximation)[7-9]. In order to establish the mechanism of thermal decomposition, evaluation of kinetic parameters by mechanistic equation is also intended.

EXPERIMENTAL

All chemicals used were of AR grade or of high purity. Hydrated cobalt sulphate and ethylenediamine were obtained commercially and used without further purification. Tris (1,2-diaminoethane)cobalt(II) sulphate was prepared by known procedure (10). The sample was purified by recrystallisation and dried over P_2O_5, characterized by elemental analysis, spectral and magnetic studies. The IR spectrum of the sample was recorded on a Perkin Elmer infrared spectrophotometer in the range 4000 to 500cm^{-1}. Electronic spectrum was recorded on a Shimadzu uv-2450 uv-visible spectrophotometer in the range 300-900 n.m. at room temperature. Magnetic susceptibility was measured by Gouy method. Octahedral geometry of the complex ion was confirmed by electronic spectral and magnetic studies. Pure dry sample was ground and sieved to uniform mesh size and sealed in Pyrex ampoules. The sample was irradiated using ^{60}Co gamma rays to varying doses as 300 kGy, 600 kGy and 900 kGy at constant intensity under room temperature at a dose rate of 6 kGy/hr. After irradiation each sample was mixed uniformly and stored over P_2O_5 in a vacuum desiccator. Thermograms providing simultaneously TG and DTG were recorded in a Perkin Elmer STA 6000 model instrument in nitrogen atmosphere at a heating rate of 10°C/min. The sample mass was kept constant around 3±0.5mg. Thermal studies were carried out within one week of irradiation.

RESULTS AND DISCUSSION

Thermal and kinetic analysis

The TG curves recorded in nitrogen atmosphere were redrawn as percentage mass versus temperature curves (Fig 1).

Thermograms of unirradiated and irradiated samples are of the same pattern indicating that irradiation does not modify the decomposition pathway. Both the unirradiated and irradiated samples (300 kGy, 600 kGy and 900 kGy) of the complex decompose in three stages. Percentage mass loss during the first stage corresponds to the removal of two mols of the ligand while that of the second stage to the remaining one mole. The third stage involves the oxidation of the deaminated complex to the metal oxide (Table 1).

The percentage of final residue in all cases corresponds to oxide of cobalt, which is confirmed by independent pyrolysis data. Phenomenological data with T_i- temperature of inception, T_f- temperature of completion and T_s- peak temperature for the unirradiated and irradiated samples are presented in Table 1. It can be seen that T_i, T_f, and T_s are lowered upon irradiation, indicating decomposition is relatively faster in the irradiated samples. Non-isothermal data were analyzed by Coats-Redfern, Freeman-Carroll and Horowitz-Metzger methods (non-mechanistic equations). Kinetic parameters viz.,

Table 1: Thermal Decomposition Data

Sample $[Co(en)_3]SO_4$	$T_i(K)$	$T_f(K)$	$T_s(K)$	% mass loss
Stage **I**				
unirradiated	481	590	539	35.5
300kGy	463	575	531	36.2
600kGy	448	556	512	36.8
900kGy	434	532	496	37.2
Stage **II**				
Unirradiated	618	708	660	28.2
300kGy	606	684	644	28.7
600kGy	594	673	635	29.0
900kGy	580	661	631	29.2
Stage **III**				
Unirradiated	751	873	826	51.5
300kGy	732	860	813	52.0
600kGY	720	849	800	52.2
900kGy	706	836	789	52.7

activation energy E, frequency factor Z and entropy of activation "S along with the correlation coefficient (r) evaluated by these methods, are presented in Tables 2, 3 and 4.

Calculations were done by the statistical linear regression method using excel pre-defined functions. The order parameter n was assumed as unity. From Tables 1 - 4 it is clear that thermal as well as kinetic parameters are lowered upon irradiation and the extent of lowering increases with increase in absorbed dose. Thus the reactivity parameters follow the order, unirradiated > 300 kGy > 600 kGy > 900 kGy. The decomposition of the complex [Co

Table 2: Kinetic parameters evaluated by evaluated by coats-Redfern equation

$[Co(en)_3]SO_4$	$T_i(K)$	$T_f(K)$	$T_s(K)$	% mass loss
Stage **I**				
unirradiated	481	590	539	35.5
300kGy	463	575	531	36.2
600kGy	448	556	512	36.8
900kGy	434	532	496	37.2
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300kGy	732	860	813	52.0
600kGY	720	849	800	52.2
900kGy	706	836	789	52.7

Table 3: Kinetic parameters evaluated by evaluated by Freeman-Carroll Equation

Sample $[Co(en)_3]SO_4$	$T_i(K)$	$T_f(K)$	$T_s(K)$	% mass loss
Stage **I**				
unirradiated	481	590	539	35.5
300kGy	463	575	531	36.2
600kGy	448	556	512	36.8
900kGy	434	532	496	37.2
Stage **II**				
Unirradiated	618	708	660	28.2
300kGy	606	684	644	28.7
600kGy	594	673	635	29.0
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Stage **III**				
Unirradiated	751	873	826	51.5
300kGy	732	860	813	52.0
600kGY	720	849	800	52.2
900kGy	706	836	789	52.7

(en)$_3$] SO$_4$ starts in the solid state. The decomposition reactivity of crystalline solids depends upon structural and energetic factors associated with the chemical nature of the reactants and products, lattice geometry and defect concentration. As irradiation leads to an increase in defect concentration and subsequent chemical damage, all these factors are modified. Thus the enhanced rate of decomposition may be attributed to lattice defects as well as products of chemical damage. These effects can influence both diffusion and nucleation which are the two fundamental steps in a solid state decomposition.

Table 4: Kinetic parameters evaluated by Horowtiz-Metzger equation

Sample [Co(en)$_3$]S O$_4$	E(KJmol^{-1})	Z(S^{-1})	$\square$S(JK^{-1}mol^{-1})	r
Stage I				
Unirradiated	166	6.7$\times 10^{15}$	53	0.9957
300kGy	162	2.9x10^{15}	47	0.9906
600kGy	147	7.8$\times 10^{14}$	35	0.9985
900kGy	135	1.3$\times 10^{14}$	21	0.9982
Stage II				
Unirradiated	234	2.3x10^{18}	100	0.9904
300kGy	220	4.6x10^{17}	87	0.9935
600kGy	201	2.0x10^{16}	61	0.9891
900kGy	198	1.5x10^{16}	58	0.9912
Stage III				
Unirradiated	310	2.0x10^{19}	117	0.9943
300kGy	286	1.0x10^{19}	94	0.9898
600kGy	269	2.0x10^{17}	78	0.9888
900kGy	252	2.0x10^{16}	60	0.9887

Table 5: Kinetic parameters evaluated by mechanistic equation

Sample [Co(en)$_3$]SO$_4$	E(KJmol^{-1})	Z(S^{-1})	r	Mechanism
Stage I				
Unirradiated	150	6.4$\times 10^{12}$	0.9943	R$_3$
300kGy	140	1.5$\times 10^{12}$	0.9967	R$_2$
600kGy	130	5.3$\times 10^{11}$	0.9959	R$_2$
900kGy	126	1.1$\times 10^{11}$	0.9940	R$_2$
Stage II				
Unirradiated	242	2.1x10^{18}	0.9933	F$_1$
300kGy	226	2.3x10^{17}	0.9949	F$_1$
600kGy	205	8.6x10^{15}	0.9915	F$_1$
900kGy	198	3.2x10^{15}	0.9924	F$_1$
Stage III				
Unirradiated	264	2.3x10^{15}	0.9935	R$_3$
300kGy	245	2.9x10^{14}	0.9915	R$_3$
600kGy	236	1.4x10^{14}	0.9925	R$_3$
900kGy	228	6.1x10^{13}	0.9927	R$_3$

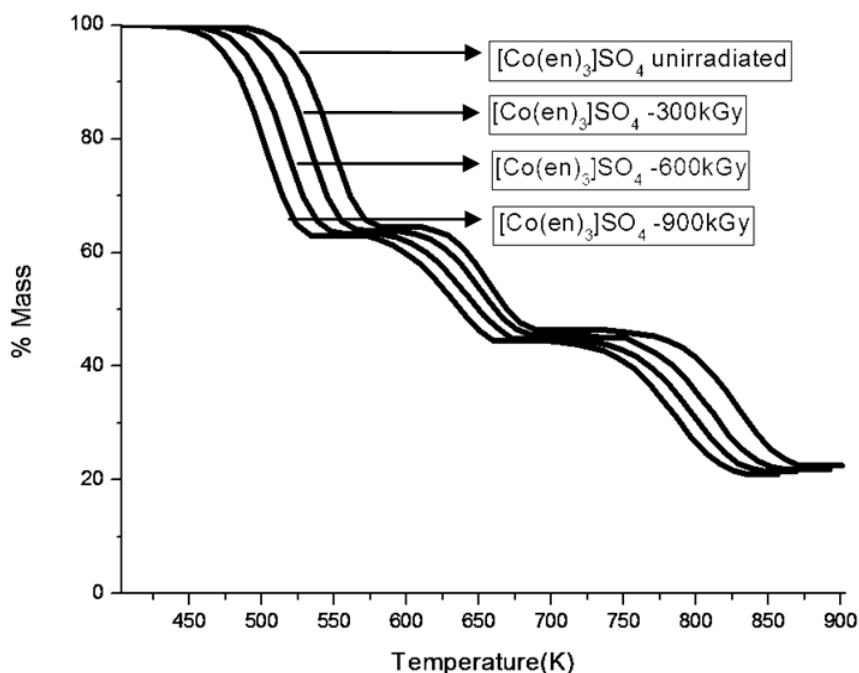**Fig. 1: Thermal decomposition curves redwarn as percentage of mass versus temperature curves for unirradiated and irradiated [Co(en)$_3$]SO$_4$**

Deduction of mechanism

In the present investigation the mechanism is established by following the method of Sestak and Berggren[11] and Satava[12]. In non-isothermal kinetic studies E is evaluated from the slope, tgα of the straight line approximation of the plot of ln gα versus 1/T by using the equations proposed by Sestak[13]. Computational details for arriving to the correct mechanism and the respective kinetic parameters have already been discussed[14]. The kinetic parameters evaluated by mechanistic equations are presented in table 5.

When the correlation coefficient is nearly the same the mechanism is chosen by comparing the E values with those obtained from the non-mechanistic equations. It is seen that in the first stage, the decomposition of unirradiated sample is governed by R$_3$ function i.e. phase boundary reaction with spherical symmetry. In phase boundary reactions the reactant is assumed to have a definite geometrical form. The surface nucleation of the reactant occurs instantaneously and an interface will be established. This interface moves with a constant velocity towards the centre of the particle and the reaction

is deceleratory throughout, because the reaction interface decreases continuously. Phase boundary reactions with spherical symmetry corresponds to three dimensional movement of the interface which is also known as contracting cube equation, i.e., $[1- (1-\alpha)^{1/3}] = kt$. The mechanism of decomposition changes to R$_2$ function in the irradiated samples, i.e., phase boundary reaction with cylindrical symmetry. Phase boundary reaction with cylindrical symmetry corresponds to the two dimensional movement of the interface and follow the equation, $[1- (1-\alpha)^{1/2}] = kt$. For the unirradiated and irradiated samples the second stage of decomposition is controlled by F$_1$ function ie., random nucleation, one nucleus on each particle., $-\ln(1-\alpha) = kt$ (Mampel equation). The third stage is governed by R$_3$ function for both the unirradiated and irradiated samples.

CONCLUSION

In this work, non-isothermal decomposition kinetics of the complex tris(1,2-diaminoethane) cobalt(II)sulphate was investigated before and after gamma irradiation. It was found that irradiation enhanced thermal decomposition, lowering thermal

as well as kinetic parameters, but did not change the decomposition path way. Irradiation modifies the reaction mechanism of the first stage of decomposition.

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