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NOTE

Thermal Decomposition Kinetics of Samarium(III) Isothiocyanate Complexes with Schiff Base Ligands

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Parameters related to thermal decomposition kinetics, *viz.*, E*, A and ΔS^* are computed on the basis of thermal decomposition data of the complexes of samarium(III) isothiocyanate with Schiff base ligands, *viz.*, 4-[N-(cinnamalidene) amino] antipyrine (CAAP) and 4-[N(furfural) amino] antipyrine (FFAAP), using three different methods and it was inferred that the values of E^* are sufficiently high and positive while values of ΔS^* are negative.

Thermogravimetric analytical studies of lanthanide(III) metal complexes were of great interest for many workers in the past[1–3]. Thermal decomposition kinetics parameters, *viz.*, E*, A and ΔS^* were also computed for transition metal complexes[4] and of thorium(IV) and dioxouranium(VI) complexes[5–9]. Continuing with the studies, the authors wish to report thermal decomposition kinetics parameters for two representative complexes $Sm(NCS)_3(CAAP)_3$ and $Sm(NCS)_3(FFAAP)_3$. (CAAP = 4[N-(cinnamalidene) amino] antipyrine and FFAAP = 4[N-furfural) amino] antipyrine.

The complexes $[Sm(NCS)_3(CAAP)_3]$ and $[Sm(NCS)_3(FFAAP)_3]$ were prepared by reported method[10] TGA of these complexes were recorded on Santon Red-Craft thermobalance model TG-750 at heating rate 10% min and these TGA curves were used to draw the rate of loss of mass *vs.* temperature (DTG) curves for these complexes. The decomposition data for the complexes is presented in Table-1.

Three different methods, Freeman-Carroll[11] (FC), Coats-Redfern[12] (CR) and Horowitz-Metzger[13] (HM), were used to evaluate kinetic parameters from these TGA traces mentioned in Table-1.

$$-\frac{(E^*/2.303R)\,\Delta T^{-1}}{\Delta \log W_r} = -n + \frac{\Delta \log dw/dt}{\Delta \log W_r} \qquad \text{(FC)}$$

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\left\{\frac{ZR}{AE^*}\frac{(1-2RT)}{E^*} - \frac{E^*}{2.3RT}\right\} \quad \text{for } n \neq 1 \qquad \text{(CR)}$$

$$\log\left\{\frac{-\log(1-\alpha)}{T^2}\right\} = \log\left\{\frac{ZR}{AE^*}\frac{(1-2RT)}{E^1} - \frac{E^*}{2.3RT}\right\} \quad \text{for } n = 1$$

$$\log \log \left\{\frac{W_\alpha}{W_r}\right\} = \frac{E^*}{2.303RT_S^2} - \log 2.303 \qquad \text{(HM)}$$

ΔS^* value for each of the reactions is obtained from the following equation:

$$\Delta S^* = R \ln \{Ah/KT_S\}$$

where all the symbols have usual meanings.

The kinetic parameters obtained employing Coats-Redfern, Horowitz-Metzger and Freeman-Carroll equations are summarized in Table-2. On application of these equations to our present thermal decomposition data, it was inferred that all the reactions mentioned in Table-1 are of order unity. The values of E^*, A and ΔS^* are appreciable and E^* values are sufficiently high and positive while ΔS^* have negative values; these are comparable with other observations[4–9]. These complexes show similar type of thermal behaviour as shown by the E^* and A values for each reaction. Horowitz-Metzger method gives reasonably good results but it is less accurate mathematically than integral methods. Coats-Redfern method seems to be more accurate but it is a considerably time-consuming method.

TABLE-1
THERMAL DECOMPOSITION DATA FOR SAMARIUM(III) THIOCYANATE COMPLEXES WITH 4-[N(CINNAMALIDENE) AMINO] ANTIPYRINE (CAAP) AND 4-[N(FURFURAL) AMINO] ANTIPYRINE (FFAAP)

Complexes	Stage of Decomposition	Reaction	Peak Temperature in DTG (°C)	Temperature Range in DTG (°C)
$Sm(NCS)_3(CAAP)_3$	I Stage	$Sm(NCS)_3(CAAP)_3 \rightarrow Sm(NCS)_3(CAAP)_2$	240	215–300
	II stage	$Sm(NCS)_3(CAAP)_2 \rightarrow Sm(NCS)_3(CAAP)$	390	350–460
	III stage	$Sm(NCS)_3(CAAP) \rightarrow Sm(NCS)_3$	500	480–540
	IV stage	$Sm(NCS)_3 \rightarrow Sm_2O_3$	730	*ca.* 810
$Sm(NCS)_3(FFAAP)_3$	Ist stage	$Sm(NCS)_3(FFAAP)_3 \rightarrow Sm(NCS)_3(FFAAP)$	240	215–305
	II stage	$Sm(NCS)_3(FFAAP) \rightarrow Sm(NCS)_3$	400	350–465
	III stage	$Sm(NCS)_3 \rightarrow Sm_2O_3$	620	560–680

TABLE-2
KINETIC PARAMETERS OF COMPLEXES OBTAINED USING EQUATIONS OF FREEMAN-CARROLL, COATS-REDFERN AND HOROWTZ-METZGER

Complex	Decomposition stage	quation	Parameters		
			E* kJ mol^{-1}	A S^{-1}	S* JK^{-1} mol^{-1}
$Sm(NCS)_3(CAAP)_3$	I stage	FC	20.66	—	—
	II stage	CR	19.66	4.06×10^4	-154.87
		HM	22.67	4.09×10^4	-157.78
	II stage	FC	26.23	—	—
		CR	24.22	1.90×10^4	-165.20
		HM	25.32	2.05×10^4	-167.28
	III stage	FC	18.42	—	—
		CR	14.36	6.88×10^5	-137.45
		HM	17.63	6.50×10^5	-139.05
	IV stage	FC	37.50	—	—
		CR	33.87	7.60×10^5	-139.77
		HM	35.78	7.87×10^5	-142.72
$Sm(NCS)_3(FFAAP)_3$	I stage	FC	24.73	—	—
		CR	22.77	4.70×10^4	-153.66
		HM	26.75	5.10×10^4	-155.10
	II stage	FC	9.81	—	—
		CR	7.18	5.41×10^5	-137.59
		HM	8.18	5.14×10^5	-139.50
	III stage	FC	16.05	—	—
		CR	14.55	4.54×10^5	-142.69
		HM	15.15	4.95×10^5	-145.59

REFERENCES

1. R.K. Agarwal and R.K. Sarin, *Polish J. Chem.*, **67**, 1209 (1993); *Polyhedron*, **12**, 2411 (1993).
2. R.K. Agarwal and S.K. Gupta, *Thermochim. Acta*, **99**, 357 (1986).
3. _____, *Polish J. Chem.*, **61**, 341 (1987).
4. S. Laly and Geetha Parameswaran, *Asian J. Chem.*, **3**, 142 (1991).
5. R.K. Agarwal and K. Arora, *Oxidation Commun.*, **16**, 317 (1993).
6. _____, *Oxidation Commun*, **17**, 10 (1994).
7. Kishor Arora, *Asian J. Chem.*, **7**, 506 (1995).
8. Kishor Arora and M.C. Pathak, Oxidation Commun. (in press).
9. Kishor Arora, *J. Indian Chem. Soc.*, **74**, 589 (1997).
10. Arun Kumar, Ph.D. Thesis, Meerut University (1993).
11. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
12. A.W. Coats and J.P. Redfern; *Nature*, **210**, 68 (1964).
13. H.H. Horowtiz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1958).

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