THERMAL DECOMPOSITION KINETICS
OF THORIUM(IV) CHELATES
OF TWO NAPHTHOLO DYES

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The thermal decomposition of thorium(IV) chelates of 1-(2-fluorenylazo)-2-naphthol and o-carboxyphenylazo-2-naphthol was studied by TG. Thermoanalytical data (TG and DTG) of these chelates are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, the energy and entropy of activation based on the differential method employing the Freeman–Carroll equation, the integral method using Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given. On the basis of experimental findings in the present course of studies the relative thermal stabilities of the thorium chelates can be given as [Th(FAN)2(N03)2] > [Th(CPAN)2(H2O)2]2H2O.

Very few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents [1]. Wendlandt [2–5] and Hill [6, 7] studied the thermal properties of metal chelates with different types of complexing ligands. Studies on thermal decomposition and kinetics of metal chelates with azo and azomethine ligands have been done by a few workers [8–12]. In continuation of our work [13] on thermal decomposition kinetics of metal chelates, we report in this paper, the thermal stability and kinetic parameters of thorium(IV) chelates of two novel azo dyes.

Experimental

Samples of thorium(IV) chelates of 1-(2-fluorenylazo)-2-naphthol and o-carboxyphenylazo-2-naphthol were prepared by adding aqueous solutions of Th(NO3)4·6H2O to DMSO solutions of the respective dye ligands in 1:2 ratio in presence of a few drops of dilute ammonium hydroxide and heating on a water bath for one hour. The precipitates were filtered, washed with an aqueous solution of
DMSO and dried in vacuum desiccator. The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis. The structures of these two chelates were found [14] to be $[\text{Th(FAN)}_2(\text{NO}_3)_2]$ and $[\text{Th(CPAN)}_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$.

**Apparatus**

A Stanton recording thermobalance Model TR-1 was used for recording TG traces. The heating rate was 5 or 6 deg min$^{-1}$ and chart speed was 6 in h$^{-1}$. The atmosphere was static air. Buoyancy correction was applied. The samples were taken in tall narrow crucibles to avoid loss by spattering.

**Treatment of data**

The instrumental TG traces were redrawn as mass vs. temperature (TG), curves and also as the rate of loss of mass vs. temperature (DTG) curves. TG and DTG traces of the two chelates are presented in Fig. 1.

**Mathematical analysis of the TG curves**

The curve for $[\text{Th(FAN)}_2(\text{NO}_3)_2]$ complex exhibited a two stage decomposition pattern and that for $[\text{Th(CPAN)}_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ complex exhibited a three stage

![Graph](image)

**Fig. 1** TG and DTG curves of $a = [\text{Th(FAN)}_2(\text{NO}_3)_2]$; $b = [\text{Th(CPAN)}_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}

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