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THERMAL STUDIES ON THORIUM(IV) COMPLEXES OF 1-BUTYL-1-METHYLPIPERAZINIUM IODIDE

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Abstract

Thorium(IV) complexes of the type $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$, $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ and $Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$ (*L* = 1-butyl-1-methylpiperazinium iodide(I) have been synthesised. From thermogravimetric (TG) curves, the decomposition pattern of the compounds has been analysed. The order, activation energy and apparent activation entropy of the thermal decomposition reaction have been elucidated. The heat of reaction has been calculated from differential thermal analysis (DTA) studies.

Keywords: complexes, kinetics, TG-DTA

Introduction

In earlier communications [1–3], we have carried out synthesis and characterisation of complexes of uranium and thorium with some nitrogen ligands. In order to ascertain the decomposition pattern of such species, thermal studies on some thorium(IV) complexes involving 1-butyl-1-methylpiperazinium iodide ligand are reported in this paper. A number of kinetic and thermodynamic parameters have been elucidated from thermal studies.

Experimental

The ligand was prepared by a method described in our earlier publication [1]. The compounds of thorium(IV) sulphate and thiocyanate were prepared by adding dropwise with constant shaking an absolute ethanolic solution (ca. 10 ml) of the ligand in 1:2 and 1:1 mole ratio to an ethanolic solution (20 ml) of

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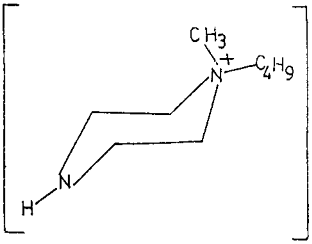
the metal salt (1 g) prepared in situ. The nitrate complex was prepared by adding the ethanolic solution of the ligand in the mole ratio of 1:3 to the solution of $Th(NO_3)_4 \cdot 6H_2O$ (1 g) in ethanol. In all the cases the products separated immediately which were filtered in a G_4 filtration unit under anhydrous conditions, washed 5–6 times with solvent ether and finally dried under vacuum.



I

(I)

Thermal studies were carried out by means of a derivatograph, containing platinum, platinum-rhodium thermocouples. The measurements were made in a platinum crucible in an air atmosphere, at a heating rate of 10 deg·min^{-1}; 0.098 to 0.107 g sample was used.

Results

The TG curves are shown in Fig. 1.

The steps involved in the thermal degradation of $Th(NO_3)_4 \cdot 3L \cdot C_2H_5OH$, $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ and $Th(SO_4)_2 \cdot 2L \cdot C_2H_5OH$ complexes are depicted in scheme I, II and III, respectively.

$$Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH \xrightarrow[\text{313–473 K}]{} Th(NO_3)_4 \cdot 3L \xrightarrow[\text{473–653 K}]{} ThO_2$$

Scheme I

$$Th(SCN)_4 \cdot L \cdot 2C_2H_5OH \xrightarrow[\text{313–423 K}]{} Th(SCN)_4 \cdot L \xrightarrow[\text{473–593 K}]{}$$

$$Th(SCN)_4 \xrightarrow[\text{593–673 K}]{} Th(SCN)_3^+ \xrightarrow[\text{>723 K}]{} ThO_2$$

Scheme II

$$Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH \xrightarrow[\text{313–473 K}]{} Th(SO_4)_2 \cdot 2L \xrightarrow[\text{473–663 K}]{} ThO_2$$

Scheme III

The compounds initially absorbed water of crystallisation and an increase in weight was recorded. Thereafter, the weight loss corresponded to the successive loss of water of crystallisation and ligand moieties. The weight loss in the final step corresponded to the formation of ThO_2.

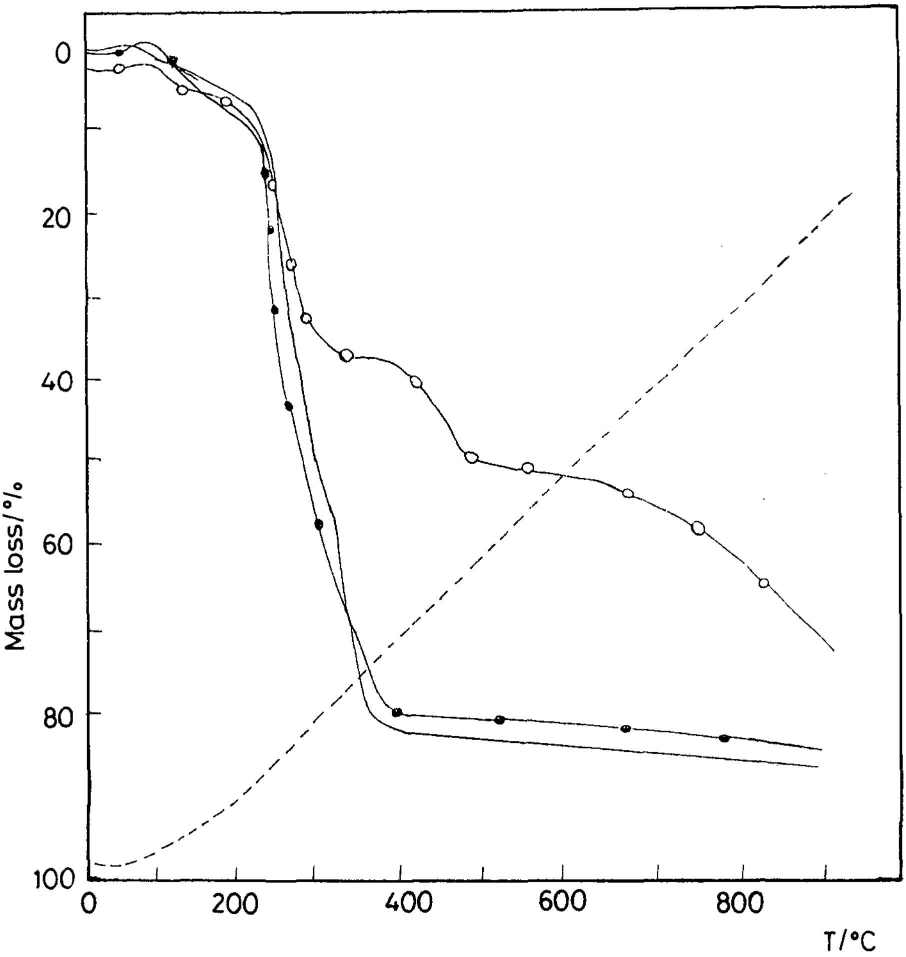


Fig. 1 TG curves of $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ (—), $Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$ (-•-•-) and $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ (-o-o-)

The DTA profile of the $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ complex showed a small endothermic peak with T_{max} 383 K. This was followed by a broad exothermic thermal effect with T_{max} 613 K. The decomposition pattern of $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ complex was indicated on the DTA curve by three exothermic thermal effect with T_{max} 373, 553 and 693 K. The DTA curve of $Th(SO_4)_2 \cdot 2L \cdot C_2H_5OH$ deriva-

Table 1 Thermal data

Compound	TG				DTA		
	Temperature range / K	n	E_a / kJ·mol^{-1}	S / J·mol^{-1}deg^{-1}	Thermal effect	T_{max} / K	ΔH kJ·mol^{-1}
$Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$	523–653	1	80.75	60.73	exothermic	613	14.04
$Th(SCN)_4 \cdot L \cdot C_2H_5OH$	523–583	1	54.63	35.90	exothermic	553	6.60
$Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$	523–638	1	16.59	0.86	exothermic	573	7.47

tives showed exothermic peak with T_{max} 373 K. It was followed by two sharp exothermic peaks with T_{max} 513 and 573 K.

Discussion

The results of TG and DTA evaluations are presented in Table 1. From the TG curves, the order (n) and activation energy (E_a) of the thermal decomposition reaction, involving the loss of ligand moiety, have been elucidated by the method of Coats and Redfern [4]. The linearization curves are shown in Fig. 2.

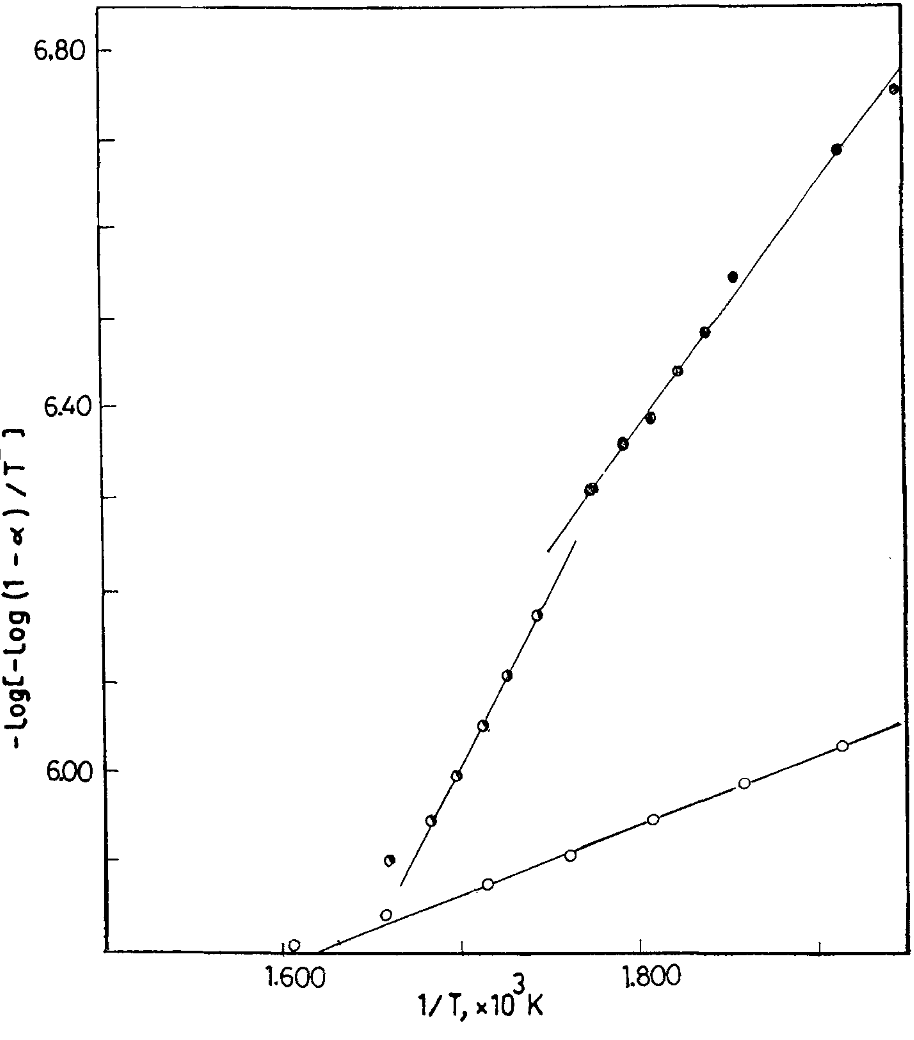


Fig. 2 Linearization curves of $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ (-o-o-), $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ (-•-•-) and $Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$ (-o-o-)

The order of reaction in each case is unity. A comparison of the activation energy data reveals that the $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ complex has the highest value of E_a. This may be explained on the basis of strong interactions between the thorium(IV) ion and the donor groups. The high charge on thorium(IV) ion makes it a hard acid [5]. Since the donor nitrogen atom in the piperazine moiety, as well as the nitrato anion are hard bases, the hard-hard interactions in $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ complex are quite strong; hence the exceptionally high value of E_a. For the remaining two complexes, the sulphur containing anions are quite soft in nature. The hard-soft interactions are comparatively weak. Therefore, thermal degradation of these complexes involves a lower value of activation energy.

The apparent activation entropy has been calculated by the method of Zsakó [6]. It has a positive value for $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$ and $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ complexes, and a negative value for the $Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$ analogue. Hence the latter decomposes with the least degree of randomness.

The TG data are supplemented by DTA studies. The heat of reaction (ΔH) has been calculated from the DTA curve [7]. The temperature dependent calibration coefficient was obtained from Currell equation [8].

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Zusammenfassung — Thorium(IV)-komplexe vom Typ $Th(NO_3)_4 \cdot 3L \cdot 2C_2H_5OH$, $Th(SCN)_4 \cdot L \cdot C_2H_5OH$ und $Th(SO_4)_2 \cdot 2L \cdot 2C_2H_5OH$ (mit L = 1 Butyl-1-Methyl-Piperaziniumjodid(I) wurden synthetisiert. Anhand der TG-Kurven wurde der Zersetzungsverlauf der Verbindungen analysiert. Reaktionsordnung, Akti- vierungsenergie und scheinbare Aktivierungsentropie der thermischen Zersetzungsreaktion wurden ermittelt. Die Reaktionswärme wurde anhand von DTA-Untersuchungen berechnet.