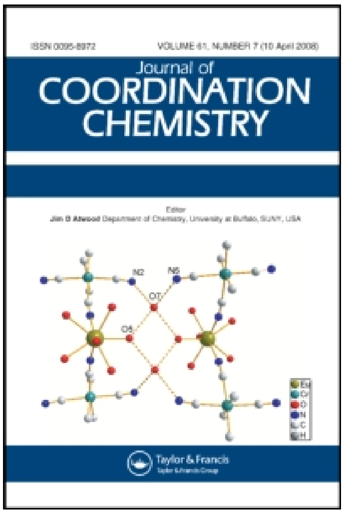

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THE CHEMISTRY OF URANIUM. XIV. THE THERMAL STABILITY OF SOME ACTINOID NITRATES

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The thermal decomposition of $Cs_2U(NO_3)_6$ has been investigated. The activation energy for the decomposition reaction was estimated to be ±120 kJ/mole, while the enthalpy of the reaction was calculated as 18 kJ/mole. These energy parameters were compared with similar parameters obtained for the decomposition of $Cs_2Th(NO_3)_6$ and $U(NO_3)_4$.2hmpa. It indicated that the nitrate ion is primarily responsible for the oxidation of the uranium with atmospheric oxygen having no effect at all. The dissociation reactions involved in the decomposition of $M(NO_3)_4$.4hmpa, (M = U and Th), are accompanied by intramolecular rearrangements of the nitrate groups.

INTRODUCTION

The behaviour of nitrate as an anionic ligand towards thorium and uranium(IV) has previously been studied by us in solid complexes as well as in non-aqueous solution by means of various physical methods. Enthalpimetric tritration of an acetone solution of $Th(NO_3)_4$ with strong neutral donor ligands, viz. hexamethylphosphoramide (hmpa) and trimethylphosphine oxide (tmpo) indicated to what extent stabilization occurs under such conditions.[1] $U(NO_3)_4$ is a very unstable compound and only exists in cold solution. Solid $Cs_2U(NO_3)_6$ can be isolated from an aqueous acidic solution and is much more stable with respect to decomposition. Upon standing at room temperature, however, slow decomposition takes place. The decomposition products were identified as $Cs_2UO_2(NO_3)$ and oxides of nitrogen, mainly NO and NO_2.[2, 3]

It was therefore of interest to determine the energy parameters involved in the decomposition of solid $Cs_2U(NO_3)_6$ and to compare it with other solid nitrato complexes of uranium(IV) of the type $U(NO_3)_4.xl$ as well as with their thorium analogues. (l = strong neutral donor). Isothermal kinetic studies were thus conducted on $Cs_2M(NO_3)_6$, $M(NO_3)_4$.4hmpa, $M(NO_3)_4$.2hmpa at a variety of temperatures and activation energies calculated. Differential scanning calorimetry (D.S.C.) studies of the compounds allowed calculation of the enthalpies for the decomposition reactions. The comparison between the behaviour of uranium(IV) and thorium analogues was of interest, not only because of the differences in cationic size and Lewis acidity of the two species, but especially since nitrate oxidation of the metal ion species will occur in the one instance, but not in the other.

EXPERIMENTAL

The preparation of the nitrato complexes $Cs_2U(NO_3)_6$, $U(NO_3)_4$.4hmpa, $Cs_2Th(NO_3)_6$ and $Th(NO_3)_4$.4hmpa were described previously.[1,6]

Thermal analysis (T.G.A. and D.S.C.) of the compounds were carried out under vacuum (0.3 mm Hg) using a DuPont 990 Thermal Analyzer. Samples of 10–20 mg were used.

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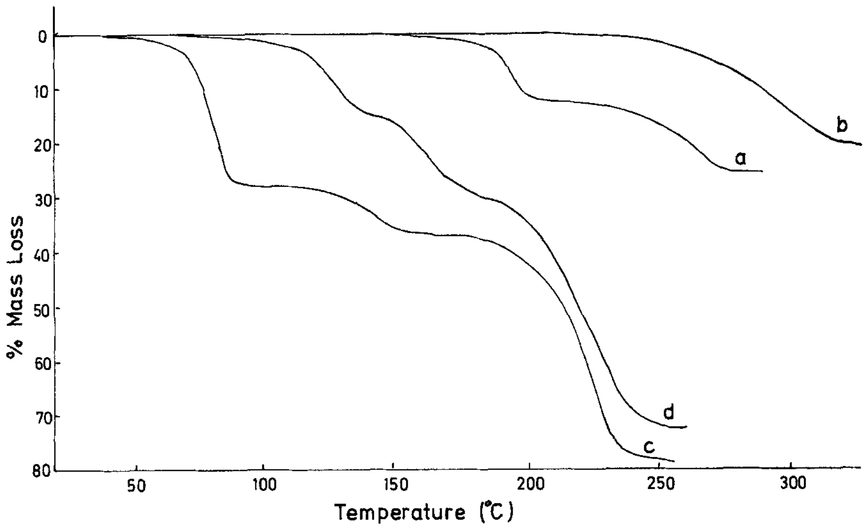

FIGURE 1 Thermogravimetric analysis of:
(a) $Cs_2U(NO_3)_6$; (b) $Cs_2Th(NO_3)_6$; (c) $U(NO_3)_4$.4hmpa;
(d) $Th(NO_3)_4$.4hmpa.

Isothermal kinetic studies on $U(NO_3)_4$.2hmpa were performed using $U(NO_3)_4$.4hmpa as starting material. A suitable amount of $U(NO_3)_4$.4hmpa was held at approximately 90°C until no mass change could be detected and the mass loss observed was checked against the theoretically calculated mass loss to ensure that the compound was actually present as $U(NO_3)_4$.2hmpa. The temperature was then raised to the required temperature and the mass loss recorded as a function of time. Dynamic thermogrammes were obtained at constant heating rates of 20°, 10°, 5°, 2° and 1°C/min. following Flynn and Wall.[4] D.S.C. studies were conducted at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

$Cs_2U(NO_3)_6$

Vacuum thermolysis (Figure 1, curve a) of the compound showed the existence of a stable intermediate, viz. $Cs_2UO_2(NO_3)_4$. The decomposition reaction started at 150°C and was completed at 200°C. The decomposition of $Cs_2UO_2(NO_3)_4$ started at 220°C and was completed at 280°C. Fractional isothermal mass losses as a function of time are shown in Figure 2. The decomposition kinetics fit the Avrami-Erofeyev equation ($[-\ln(1-\alpha)]^{1/n} = k(t-t_0)$ ($t_0 \equiv$ induction time)) with $n = 3$ over the α range

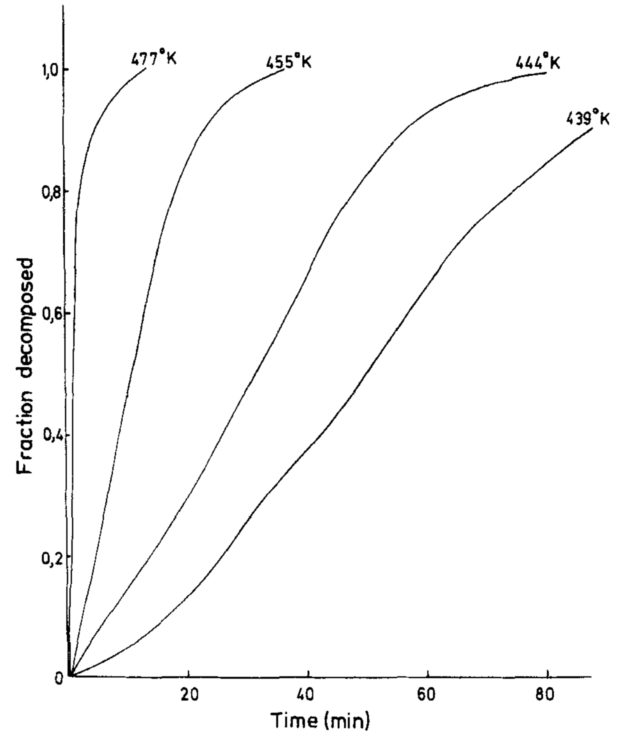

FIGURE 2 Isothermal decomposition of $Cs_2U(NO_3)_6$.

0.08 to 0.98. This rate law suggests a random nucleation with rapid growth of the nuclei in three dimensions. The activation energy calculated for this process from the Arrhenius plot was found to be 113 kJ/mole which was in fair agreement with the activation energy of 124 kJ/mole obtained from the dynamic method of Flynn and Wall[4] in the α range 0.43 to 0.86. A higher activation ±175 kJ/mole, was obtained for the initial stages of the reaction ($\alpha = 0.08$ and 0.17). This relatively high activation energy indicated that the compound is initially relatively stable. Once the reaction had nucleated further reaction was fast due to its auto-catalytic nature.

The enthalpy of the overall decomposition reaction was obtained from D.S.C. measurements. Figure 3, curve a, shows that the reaction started exothermically (peak at 178°C) but became endothermic (peak at 198°C). The overall enthalpy calculated from this curve was 18 kJ/mole. The exothermic reaction observed initially, is most likely due to rapid nitrate oxidation of uranium(IV) which produced some intermediate species which subsequently decomposed in an endothermic reaction. Once the intermediate accumulated to a sufficient concentration, its rate of decomposition exceeded its rate of formation, as can be seen from the D.S.C. curve where the overall heat flow changes from exothermic to endothermic.

The decomposition of the compound was also studied in an oxygen atmosphere to estimate the importance of gaseous oxygen in the oxidation reaction. No real difference in the decomposition kinetics could be detected. The kinetics fitted the Avrami-Erofeyev equation. The activation energy obtained was 135 kJ/mole and was slightly higher than that obtained in vacuum. The D.S.C. curve showed again two peaks – an exothermic peak at 178°C followed by an endothermic peak at 192°C. The enthalpy was found to be similar to that of the decomposition reaction in vacuum, i.e. $\Delta H = 21$ kJ/mole. It, therefore, appeared that it was mainly the nitrate ion which was responsible for the oxidation of the uranium in the complex.

$Cs_2Th(NO_3)_6$

The complex was found to decompose between 200°C and 330°C (Figure 1, curve b). The isothermal decomposition curves (α vs t) are given in Figure 4. A characteristic feature of the decomposition curves was the absence of an induction period. The decomposition kinetics was

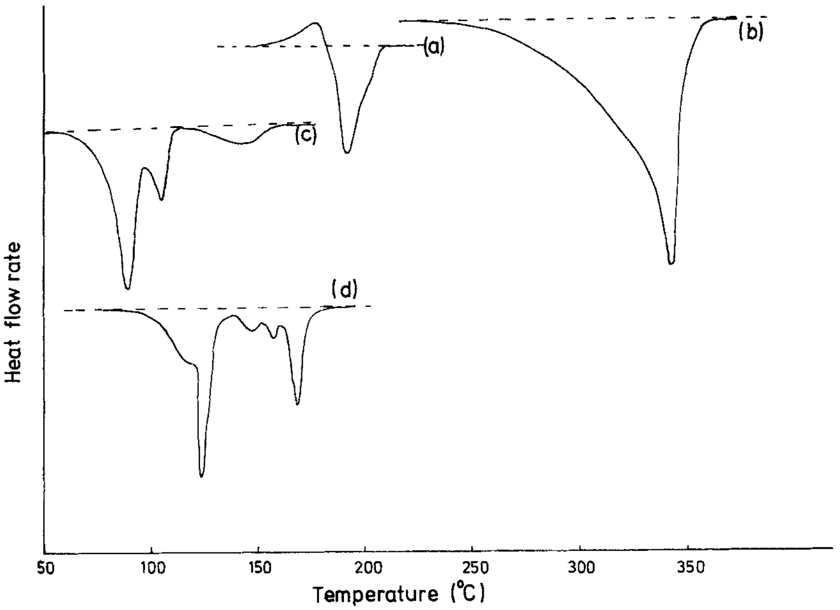

FIGURE 3 Differential scanning calorimetry curves of: (a) $Cs_2U(NO_3)_6$; (b) $Cs_2Th(NO_3)_6$; (c) $U(NO_3)_4$.4hmpa; (d) $Th(NO_3)_4$.4hmpa.

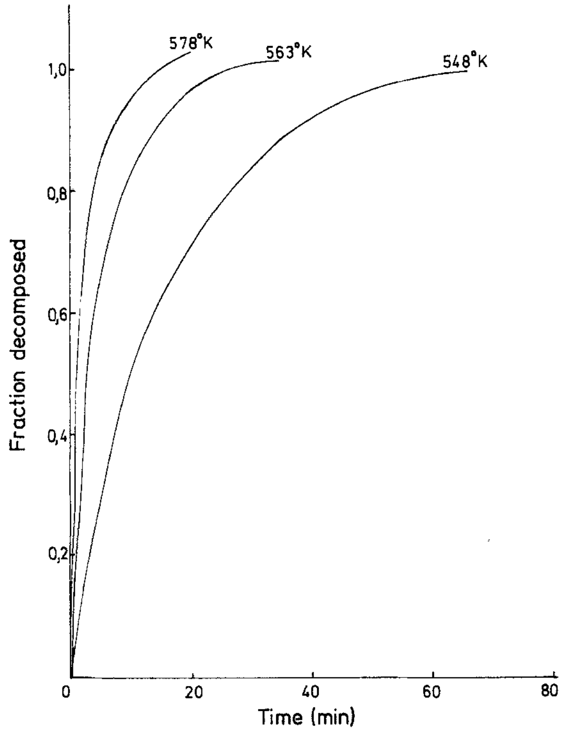

FIGURE 4 Isothermal decomposition of $Cs_2Th(NO_3)_6$.

described by a random nucleation law followed by rapid surface growth, $[-\ln(1-\alpha)] = kt$ and gave an activation energy of 196 kJ/mole. The activation energies calculated from the dynamic method was found to decrease fairly rapidly as the reaction progressed and levelled off to a value of approximately 190 kJ/mole in the α 0.5 to 0.9 (see Table I).

TABLE I

Activation energies calculated from the dynamic method according to Flynn and Wall for various nitrato complexes

Compound	α	E_{act} (kJ/mole)
$Cs_2U(NO_3)_6$	0.08	170
	0.17	180
	0.43	124
	0.87	124
$Cs_2Th(NO_3)_6$	0.21	242
	0.42	214
	0.64	191
	0.85	186

α = the fraction decomposed in the technique followed by Flynn and Wall.

The D.S.C. curve of this compound showed a strongly endothermic reaction with a peak at 345°C (Figure 3, curve b). The enthalpy for the overall decomposition reaction was found to be 225 kJ/mole.

The results indicated that the $Cs_2Th(NO_3)_6$ was much more stable than the $Cs_2U(NO_3)_6$. This was not unexpected since the nitrate oxidation of the metal occurring in $Cs_2U(NO_3)_6$ was absent during the decomposition of $Cs_2Th(NO_3)_6$.

$U(NO_3)_4$.4hmpa *and* $Th(NO_3)_4$.4hmpa

Thermolysis of $U(NO_3)_4$.4hmpa (Figure 1, curve c) indicated the existence of two stable intermediates, viz. $U(NO_3)_4$.2hmpa and $UO_2(NO_3)_2$.2hmpa. This suggested that the thermolysis of the compound could be described by two different reactions: (i) A dissociation reaction, $U(NO_3)_4$.4hmpa → $U(NO_3)_4$.2hmpa + 2hmpa followed by (ii) an oxidation reaction $U(NO_3)_4$.2hmpa → $UO_2(NO_3)_2$.2hmpa + oxides of nitrogen. The former dissociation reaction was found to obey the Avrami-Erofeyev equation with $n = 3$, i.e. $[-\ln(1-\alpha)]^{1/3} = k(t - t_0)$. This type of mechanism, rapid nucleation followed by three dimensional growth of the nuclei, was completely different from similar reactions studied by other workers.[5] The activation energy was found to be 110 kJ/mole. D.S.C. measurements on this compound gave some interesting results, (Figure 3, curve c). The curve showed three different endothermic peaks, at 90°, 105° and 145°C, respectively. The two peaks at 90° and 105° were ascribed to the dissociation reaction while the one at 145° was associated with the oxidation reaction, since thermogravimetric results suggested that the dissociation reaction occurred between 40° and 90°C with the oxidation reaction between 115° and 150°C. The two peaks at 90° and 105°C respectively, suggested two different reactions – the dissociation reaction followed by a rearrangement in the molecule. Such a rearrangement could be the change of coordination mode of the nitrate ion. It was shown earlier[6] that the hmpa molecules in $U(NO_3)_4$.4hmpa provided steric hindrance to such an extent that some of the nitrato groups are coordinated as monodentate groups. If some of these hmpa molecules are now removed from the coordination sphere of the uranium, the monodentate nitrato groups can rearrange and coordination to the uranium will become bidentate, as was observed in $U(NO_3)_4$.2hmpa, the final product. Since the rearrangement reaction is not accompanied by any mass change this rearrangement was not detected by T.G.A., but the D.S.C. curve showed a clear peak at 105°C. The total heat calculated for this process from the endothermic peaks at 90° and 105° was found to be 155 kJ/mole. The complex $Th(NO_3)_4.4hmpa$ started to lose hmpa at 40° ± 5°C. Thermogravimetric analysis (Figure 1, curve d) indicated the dissociation process to take place in two different processes:

(i) $Th(NO_3)_4.4hmpa \rightarrow Th(NO_3)_4.3hmpa + hmpa$;

and

(ii) $Th(NO_3)_4.3hmpa \rightarrow Th(NO_3)_4.2hmpa + hmpa$

The endothermic peaks at 115°C and 166°C (Figure 3, curve d) were assigned to the dissociation reactions and the peak at 125°C as well as the other smaller peaks due to the intramolecular rearrangement of the nitrato groups, as was the case with the uranium analogue. The total heat involved in the process was found to be 180 kJ/mole. It was, however, not possible to calculate accurate values for the various processes but rough estimations from the peak areas indicated that the energy amounts in the process

$$M(NO_3)_4.4hmpa \rightarrow M(NO_3)_4.2hmpa + 2hmpa,$$

for M = uranium and thorium, were approximately 120 kJ/mole. Although these are approximate values it does seem to indicate that the energy amounts are very similar for both uranium and thorium, suggesting that the $M(NO_3)_4.2hmpa$/hmpa interactions are very similar.

$U(NO_3)_4.2hmpa$

Decomposition of $U(NO_3)_4.2hmpa$ started at 115°C and was completed at 155°C. The α vs t plots fit the contracting cube law, i.e. decomposition starts on the surface of the particles and progresses inwards. The equation governing such a process is given as $1 - (1 - \alpha)^{1/3} = kt$. The activation energy was calculated from the Arrhenius plot as 147 kJ/mole. An enthalpy of 18 kJ/mole for the decomposition reaction was calculated from the D.S.C. scan. The very low enthalpy obtained for the decomposition reaction and relatively high activation energy was analogous to that observed for $Cs_2U(NO_3)_6$. It indicated again that the compound was relatively stable with respect to decomposition (oxidation–reduction) but once decomposition had started, the reaction proceeded very readily.

CONCLUSIONS

Isothermal and non-isothermal decomposition studies indicated that the nitrato complexes of uranium(IV) were relatively stable initially. Once decomposition (oxidation of the uranium(IV)) had started, the reaction took place very easily. The overall enthalpy change was very small, $\Delta H = 18$ kJ/mole. The nitrate ion was responsible for the oxidation with atmospheric oxygen having no effect at all. When oxidation of the metal ion was eliminated as in $Cs_2\ Th(NO_3)_6$, the compound tends to be much more stable. The complexes $U(NO_3)_6.4hmpa$ and $Th(NO_3)_4.4hmpa$ lost hmpa under vacuum upon heating. Both ligand dissociation reactions were associated with intramolecular rearrangement reactions. The energy amounts associated with these processes were very similar.

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REFERENCES

1. J. G. H. du Preez and C. P. J. van Vuuren, *J. Chem. Soc.*, Dalton 1548, (1975).
2. W. Kedev, J. Ryan and A. Wilson, *J. Inorg. Nucl. Chem.*, **20**, 131 (1961).
3. K. W. Bagnall, P. S. Robinson and M. A. A. Stewart, *J. Chem. Soc. (A)*, 4060 (1961).
4. J. H. Flynn and L. A. Wall, *J. Polym. Sci.*, **B4**, 323 (1966).
5. O. G. Stroder and J. E. House, *Thermochim. Acta.*, **3**, 461 (1972).
6. J. G. H. du Preez and C. P. J. van Vuuren, *J. Inorg. Nucl. Chem.*, **36**, 81 (1974).