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The Solid State Chemistry of Uranium.
Part I: The Thermal Decomposition of $U(NO_3)_4 \cdot 2tdpo$ and $U(NO_3)_4 \cdot 2tppo$

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Abstract

The thermal decomposition of $U(NO_3)_4 \cdot 2tdpo$ (tdpo = tris-(dimethylamino)phosphine oxide) and $U(NO_3)_4 \cdot 2tppo$ (tppo = triphenyl phosphine oxide have been examined using thermogravimetry and differential scanning calorimetry. Decomposition of the crystals approximates to the general reaction

$$U(NO_3)_4 \cdot 2L(s) \longrightarrow UO_2(NO_3)_2 \cdot 2L(s) + \text{gases}$$

The general thermal behaviour of the two compounds were found to be different.

Introduction

Tetranitrato uranium(IV) can be stabilized and isolated from nonaqueous organic solvents as the neutral complex $U(NO_3)_4 \cdot 2L$ (L = neutral donor ligand) [1]. Once the compound is isolated as the solid, the thermal stability seems to be different for each complex isolated. Various factors, physical as well as chemical, are responsible for this observed tendency. The donor properties (Lewis basicity) of the ligand must be among the more important chemical factors in determining the stability of the compound. Physical factors such as imperfections in the crystal lattice and phase transitions are of importance, especially at higher temperatures.

The purpose of this study was therefore to investigate the thermal behaviour of some neutral complexes and to assess the relative importance of the chemical and physical factors which determine the stability of the complexes, especially the influence of the neutral donor ligand. For this reason, tppo and tdpo (where tppo = triphenyl phosphine oxide and tdpo = tris(dimethylamino)phosphine oxide) were chosen as neutral donor ligands. The experimental data were compared with that obtained for $U(NO_3)_4 \cdot 2tpyrp$ (where tpyrp = trispyrrolidino phosphine oxide) [2].

Experimental

Preparation of the Complexes

$U(NO_3)_4 \cdot 2tdpo$

A solution of 0.41 g of tris(dimethylamino)-phosphine oxide in 5 cm^3 acetone was added to 1.0 g $Cs_2U(NO_3)_6$ under 5 cm^3 acetone. The mixture was cooled in ice, stirred for 10 min and filtered. Petroleum ether, 5 cm^3, was added to the filtrate and left to crystallize at 0 °C. The crystals were dried in vacuum. These crystals were used within three days of preparation [*Anal.* Found: U(IV), 28.30. Calc. for $U(NO_3)_4 \cdot 2tppo$: U(IV) 28.20%].

$U(NO_3)_4 \cdot 2tppo$

A solution of 1.00 g of triphenyl phosphine oxide in 10 cm^3 CH_2Cl_2 was added to 1.70 g $Cs_2U(NO_3)_6$ in 5 cm^3 acetone. The mixture was cooled in ice, stirred for 10 min and filtered. Acetonitrile, 7 cm^3, and petroleum ether, ±10 cm^3, was added to the filtrate and left to crystallize at 0 °C. The crystals were filtered, washed with petroleum ether and dried in vacuum. [*Anal.* Found: U(IV), 22.60. Calc. U(IV), 22.80%].

$U(NO_3)_4 \cdot 2tpyrp$

This complex was prepared as described in a previous study [2].

Analysis

Uranium was determined as described previously [4]. The purity of the compound was confirmed by the mass losses observed on the thermobalance.

Thermal Studies

Thermogravimetric analysis

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. Helium was used as carrier gas at a flow rate of approximately 50 cm^3 min^{-1}. Platinum sample pans were used as sample holders. Temperature calibration of the equipment was achieved by using the

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ICTA recommended DTA temperature standards; GM 758, GM 759 and GM 760.

Isothermal measurements for $U(NO_3)_4 \cdot 2tdpo$ were performed in the temperature range 85 °C to 140 °C, and for $U(NO_3)_4 \cdot 2tppo$ in the temperature range 100 °C to 160 °C. The decomposition was strongly exothermic. Self-heating of the sample was reduced to a minimum by using low sample masses (approximately 10 mg) and by working in an atmosphere of helium. The crystals were ground to a powder before using.

Isothermal decomposition data collected were fitted to a variety of kinetic expressions [3]. The linearity of plots of calculated values of $F(\alpha_i)$ against time for each kinetic expression was taken as a criterion for identification of the rate equation.

Differential scanning calorimetry studies

A Du Pont 910 differential scanning calorimeter and high pressure cell which is controlled by a 1090 Thermal Analyser was used for the DSC studies. Peak integration and subsequent enthalpy calculations were performed by using the Du Pont Partial Area Integration data analysis program. The meltings of pure indium metal ($\Delta H_f = 28.4$ J g^{-1}) and pure zinc metal ($\Delta H_f = 102.0$ J g^{-1}) were used as reference materials.

Results and Discussion

Dynamic TG and DSC Measurements

The TG traces of the compounds are given in Fig. 1. The mass losses observed for both compounds agreed with the theoretical values calculated for the reaction

$$U(NO_3)_4 \cdot 2L(s) \longrightarrow UO_2(NO_3)_4 \cdot 2L(s) + \text{oxides of nitrogen}$$

For L = tdpo the reaction started at 98 °C and was completed at 156 °C. The observed mass loss was 11.2% (*cf.* 10.9% for the theoretical value). It was important to use slow heating rates and relatively small sample masses in order to avoid self-heating of the compound since the reaction was highly exothermic. Without these precautions, mass losses of up to 20% were observed, which can be explained in terms of oxidation of the ligand. This behaviour of the tdpo complex was very similar to that observed for the tpyrp complex [2]. The tppo complex started to decompose at 130 °C, which is much higher than either the tdpo (*ca.* 98 °C) or the tpyrp (*ca.* 84 °C) complexes. This characteristic as well as other thermal and kinetic characteristics are given in Table I. The decomposition was completed at 162 °C. Mass losses of between 8 and 9% (*cf.* 8.8% calculated) were observed for the various runs. Self-heating was not found to be a problem with the tppo complex.

The DSC traces of the compounds are given in Fig. 2. The shapes of the exotherms suggested different thermal behaviour for all three complexes. The enthalpies of the reactions are listed in Table I.

The reaction under consideration can be considered as an oxidation reaction in the solid state in which nitrate act as the oxidizing agent and the uranium(IV)-ion as reducing agent. Stabilisation of the uranium(IV) is accomplished by the donor properties of the netural donor ligand. By comparing

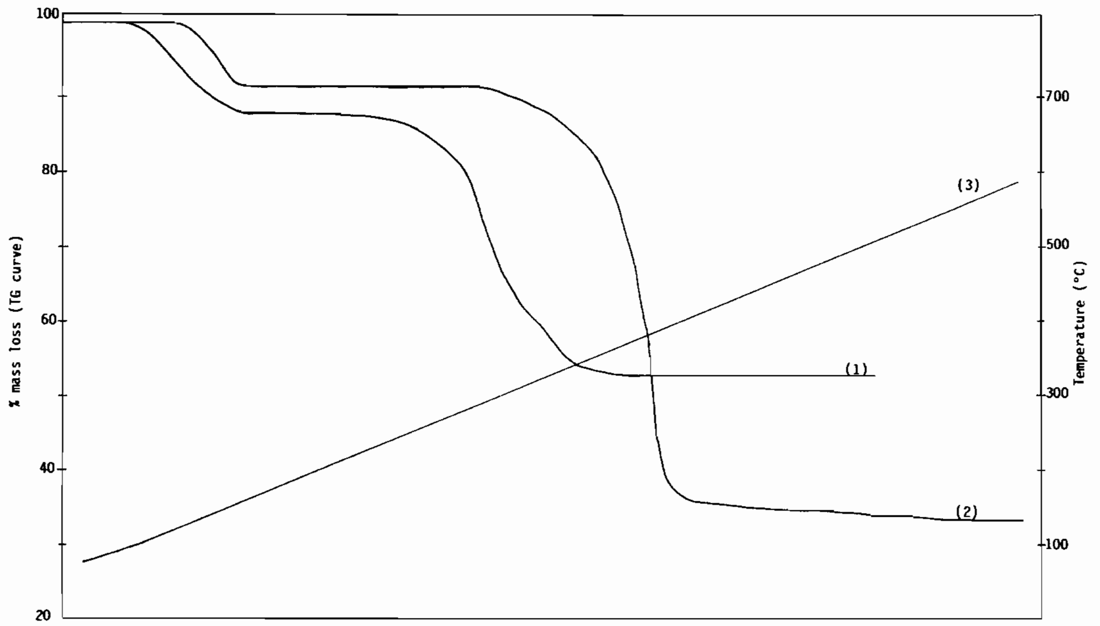

Fig. 1. TG traces for $U(NO_3)_4 \cdot 2L$ where L = tdpo and tppo. (1) tdpo; (2) tppo; (3) temperature.

TABLE I. Thermal Characteristics of the Nitrato Complexes of Uranium(IV)

Compound	T_i (°C)	ΔH_{rxn} (kJ mol^{-1})	Kinetic expression	References
$U(NO_3)_4 \cdot 2tpyrp$	84	−155	$(1-\alpha)^{-1/2} - 1 = kt$	2
		−165		This work
$U(NO_3)_4 \cdot 2tdpo$	98	−133.4	$-\ln(1-\alpha) = kt$	
$U(NO_3)_4 \cdot 2tppo$	130	−24.1	$1-(1-\alpha)^{1/2} = kt$	

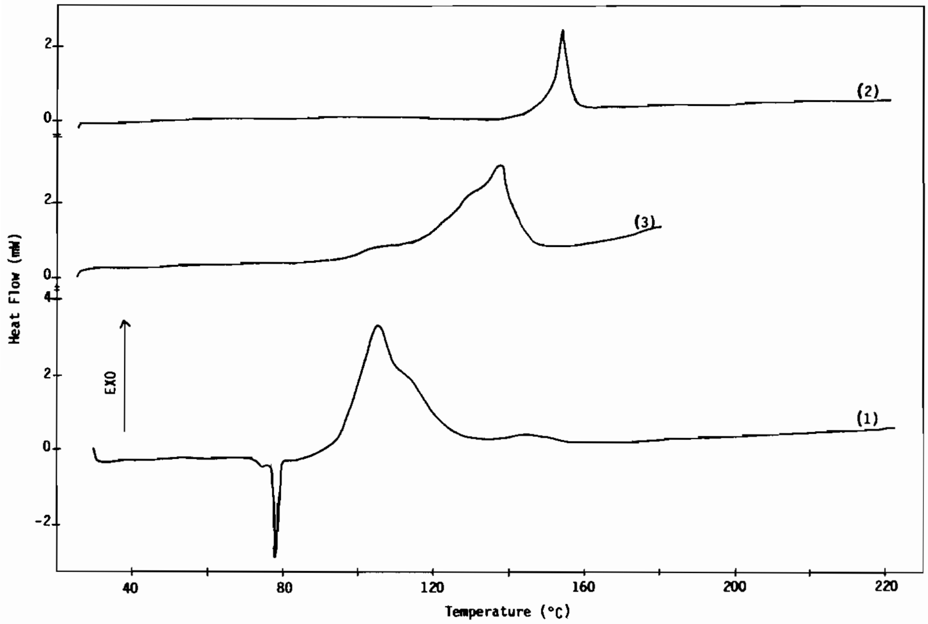

Fig. 2. DSC traces of $U(NO_3)_4 \cdot 2L$ (L = tdpo, tppo and tpyrp). (1) tdpo; (2) tppo; (3) tpyrp.

the temperature at which the reaction was initiated (T_i) and the enthalpy of the reaction (ΔH_{rxn}), as listed in Table I, it seems possible to establish an order of stability for the complexes;

$$U(NO_3)_4 \cdot 2tppo > U(NO_3)_4 \cdot 2tdpo > U(NO_3)_4 \cdot 2tpyrp$$

In addition to the exotherm which was observed for the tdpo complex, an endothermic peak was observed at 78 °C on heating. On cooling the sample from 85 °C, a small exothermic peak appeared at 76 °C. The enthalpy for the process occurring with the endothermic peak amounted to 10.1 kJ mol^{-1}. X-ray powder diffraction at room temperature and 83 °C showed a change in the symmetry of the crystal structure [5].

Isothermal TG Measurements

The isothermal decomposition curves for $U(NO_3)_4 \cdot 2tdpo$ at the indicated temperatures are given in Fig. 3. These rate data fit the equation for a first order solid state reaction; $-\ln(1-\alpha) = kt$. To calculate the Arrhenius parameters, the rate constants were estimated from the slopes of the isothermal decomposition curves. Values of 127 kJ mol^{-1} $U(NO_3)_4 \cdot 2tdpo$ for the apparent activation energy and $\ln(A\ (min^{-1})) = 40.0$ were obtained from the Arrhenius plot (linear regression factor > 0.970).

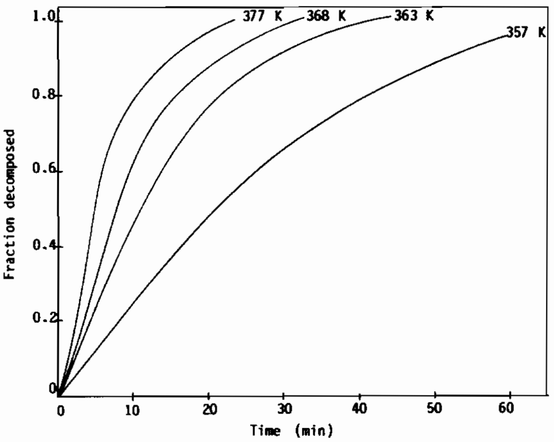

Fig. 3. Isothermal decomposition of $U(NO_3)_4 \cdot 2tdpo$ (α *vs.* time curves).

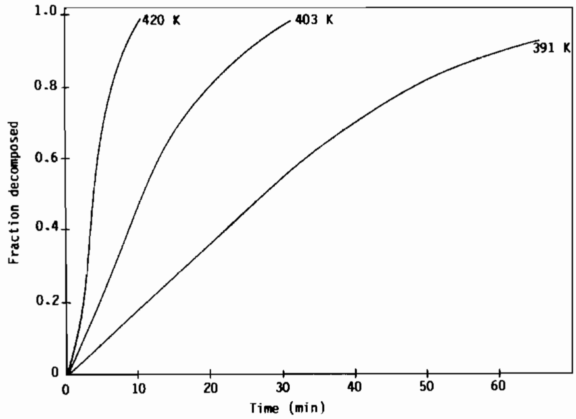

Fig. 4. Isothermal decomposition of $U(NO_3)_4 \cdot 2tppo$ (α *vs.* time curves).

Figure 4 represents some of the isothermal decomposition curves for $U(NO_3)_4 \cdot 2tppo$ at the indicated temperatures. The contracting area equation $1 - (1 - \alpha)^{1/2} = kt$ gave the best fit for the rate data. From the rate constants a value of 109.4 kJ mol^{-1} $U(NO_3)_4 \cdot 2tppo$ for the apparent activation energy and $\ln(A\ (min^{-1})) = 30.0$ was calculated. Activation energies need to be evaluated critically before conclusions regarding the stability of the complexes can be drawn from it [6]. However, it is significant that each of the decomposition reactions can be described by a different mathematical expression.

Preliminary X-ray powder diffraction data indicated that definite differences exist in the crystal structures of the three complexes. Studies to solve the structures of the various complexes and to correlate them with the decomposition kinetics and stability of the complexes are in progress.

Conclusions

The thermal decomposition of $U(NO_3)_4 \cdot 2L$ in the solid state is strongly influenced by the nature of the neutral donor ligand. TG and DSC methods of investigation indicate that the order of stability of the complexes is

$$U(NO_3)_4 \cdot 2tppo > U(NO_3)_4 \cdot 2tdpo > U(NO_3)_4 \cdot 2tpyrp$$

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