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PART IV. THE THERMAL DECOMPOSITION AND KINETICS OF TETRACHLOROBIS(*N*, *N*, *N*^{1}, *N*^{1}-TETRAMETHYLUREA) URANIUM(IV)

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ABSTRACT

The thermal decomposition of $UCl_4 2tmu$ in an oxygen atmosphere was studied. Decomposition of single crystals begins around 180°C and approximates to

$$UCl_4 2tmu_{(s)} + O_{2(g)} \rightarrow UO_2Cl_2tmu_{(s)} + tmu_{(g)} + \text{gases}$$

and is exothermic ($\Delta H = -270 \pm 5$ kJ mol^{-1}). The apparent activation energy for the initial stages (nucleation process) of the reaction was estimated as 362 kJ mol^{-1}. The growth period is described by a one-dimensional diffusion process and the decay period by the contracting-area model.

INTRODUCTION

The oxidation of uranium tetrachloride in an oxygen atmosphere has been described by von Wazer and John [1]. The reaction comprises two independent steps which are described as:

$$UCl_{4(s)} + O_{2(g)} \rightarrow UO_2Cl_{2(s)} + Cl_{2(g)} \qquad E_{act} = 50 \text{ kJ mol}^{-1}$$

$$UO_2Cl_{2(s)} + O_{2(g)} \rightarrow U_3O_{8(s)} + 3Cl_{2(g)} \qquad E_{act} = 189 \text{ kJ mol}^{-1}$$

Isothermal and dynamic thermogravimetric studies [2] on $(Et_4N)_2UCl_6$ in an oxygen atmosphere ruled out the formation of $(Et_4N)_2UO_2Cl_4$ as a stable intermediate in the decomposition reaction; this was a surprising result. In contrast to this, $(Et_4N)_2UO_2Br_4$ was found to exist as a stable intermediate when $(Et_4N)_2UBr_6$ was decomposed in an oxygen atmosphere. In order to obtain more information regarding the solid-state oxidation of uranium(IV), it was decided to extend the study to include neutral complexes such as $UCl_4 2L$, where L is a neutral donor ligand. The ligand *N*, *N*,

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N^1, N^1-tetramethylurea (tmu) was chosen as a neutral donor ligand since it is known to form a stable complex ($UCl_4$2tmu) in acetone which can readily be isolated as a crystalline solid. The results obtained were compared with those described for the thermal decomposition of $UO_2Cl_2$2tmu [3].

EXPERIMENTAL

Preparation of ($UCl_4$2tmu)

To prepare the complex ($UCl_4$2tmu), UCl_4 (1 mmol) was reacted with tmu (2 mmol) in acetone. The green crystals were vacuum dried and analysed. The analysis showed the composition: uranium = 38.83%, chloride = 23.29%. The calculation for $UCl_4$2tmu resulted in: uranium = 38.89%, chloride = 23.20%.

Thermogravimetry (TG)

A Du Pont 951 Thermogravimetric analyser was used to collect the thermogravimetric data. Oxygen and argon atmospheres were used at flow rates of approximately 50 cm^3 min^{-1}. Platinum sample pans were used. Isothermal measurements were made in the temperature range 177–227 °C. The data collected were applied to a variety of kinetic expressions [4]. The linearity of the plots of calculated values of fractional decomposition [$F(\alpha_i)$] vs. time (t) for each kinetic expression was taken as a criterion for identification of the rate equation. Activation energies were calculated from the temperature dependence of the rate constant.

Differential scanning calorimetry (DSC)

A Du Pont 910 differential scanning calorimeter controlled by a 1090 Thermal Analyser was used for the DSC studies. Peak integration and subsequent enthalpy calculations were performed using the Du Pont partial-area integration program. The melting endotherm 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 for calibration.

X-ray powder diffraction patterns were collected using a Seifert MZ IV diffractometer and Cu K_α radiation over the range $100° > 2\theta < 5°$. Only the five strongest peaks are listed for comparison (Table 2).

Raman spectra were recorded by the Spectroscopy group on a Z-24 Dilor spectrometer using a Coherent Radiation Innova Model 90-5 Ar laser as the excitation source.

Infrared spectra were recorded on a Beckman Spectrophotometer IR 4250.

RESULTS AND DISCUSSION

Thermal analysis and stoichiometry

The TG curve recorded at a rate of 3°C min^{-1} in an oxygen atmosphere (Fig. 1, curve A), indicated that the compound decomposed over the temperature range 175–530°C to yield U_3O_8 as the final product. The reaction consists of various overlapping processes as indicated by the DTG curve (Fig. 1, curve B). The DSC curve (Fig. 2) also suggested overlapping processes in the temperature range 180–530°C. An enthalpy for the total oxidation of $UCl_4 2tmu$ to U_3O_8 ($\Delta H_r = -765$ kJ mol^{-1}) was calculated from the curve. Both the DSC curve and the DTG curve suggested that the reactions occurring between 180 and 260°C could be isolated from the rest by means of carefully controlled isothermal decomposition experiments.

The isothermal decomposition curves (α vs. t where α = fractional decomposition) are given in Fig. 3. The percentage mass loss obtained for the various experiments varied between 25.2% and 25.8%, which suggested that the stoichiometry of the reaction occurring during the initial stages of the reaction could be written as:

$$UCl_4 2tmu_{(s)} + O_{2(g)} \rightarrow UO_2Cl_2tmu_{(s)} + tmu_{(g)} + \text{volatile products} \qquad (1)$$

(cf. calculated mass loss for the above reaction; 25.3%).

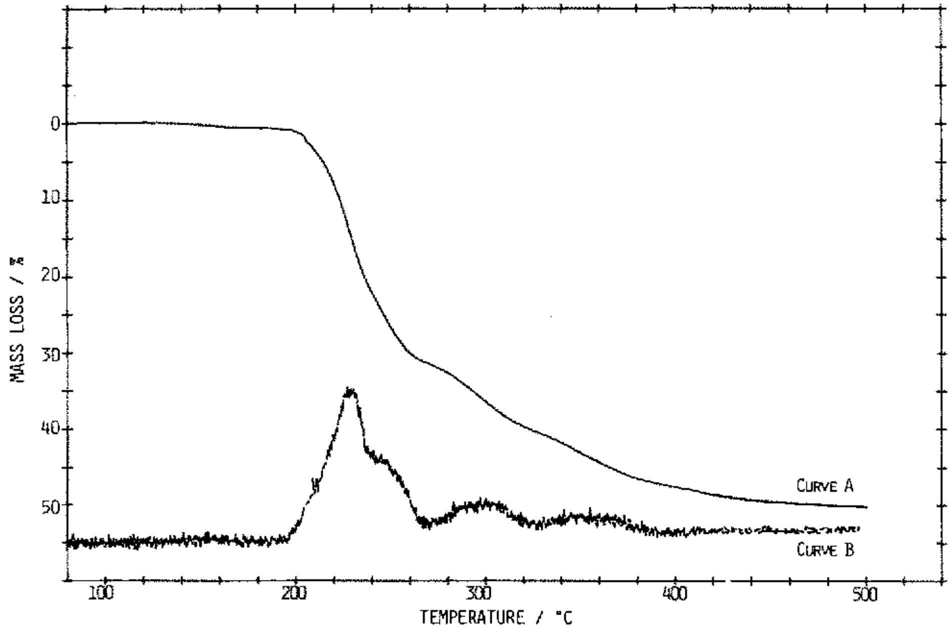

Fig. 1. TG and DTG curves for the thermal oxidation of $UCl_4 2tmu$ in oxygen (heating rate: 3°C min^{-1}).

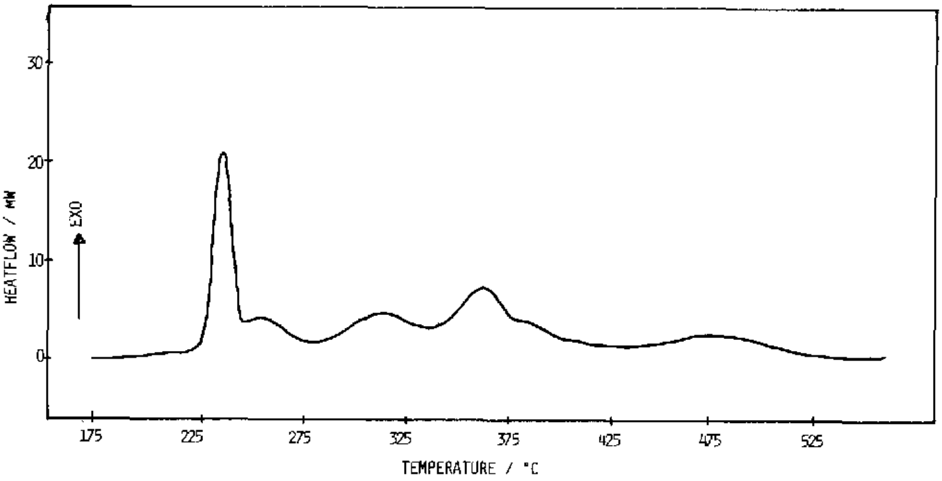

Fig. 2. DSC curve for the thermal oxidation of $UCl_4$2tmu in oxygen (heating rate: 3°C min^{-1}).

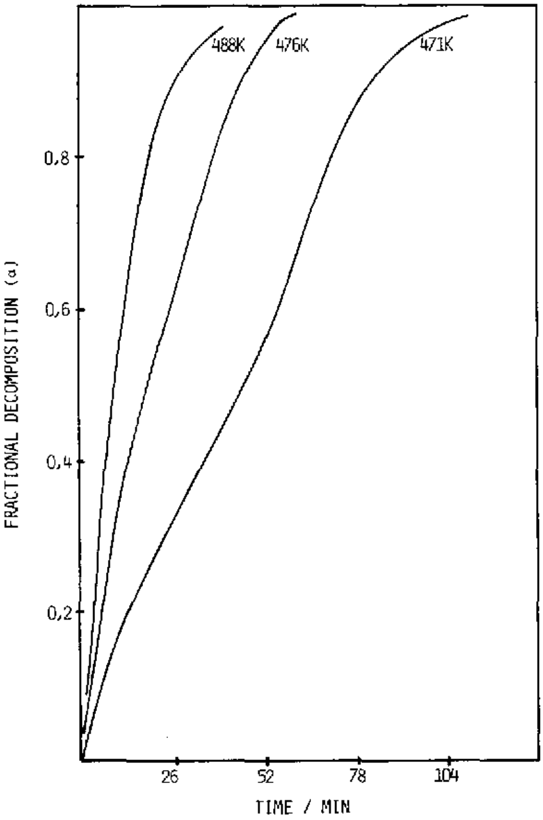

Fig. 3. Isothermal decomposition of $UCl_4$2tmu in oxygen (no pre-treatment).

TABLE 1

Raman vibrational bands (cm^{-1}) [a]

$UCl_4 2tmu$	$UO_2Cl_2 2tmu$	Decomposition products of	
		$UO_2Cl_2 2tmu$	$UCl_4 2tmu$
1060	834	865	865
1047	762	763	765
766	584 (br)	561 (br)	558 (br)
588	394	243	246
390	248	203	205
309	206	173	174
279	73		
117			
98			
86			
66			

[a] (br) = broad.

TABLE 2

X-ray powder diffraction data (Cu K_α radiation)

	2θ	d (Å)	Rel. I (%)
$UCl_4 2tmu$	12.20	7.25	100
	14.85	5.97	51
	19.51	4.55	52
	21.70	4.09	55
	24.42	3.64	48
$UO_2Cl_2 2tmu$	12.42	7.13	100
	13.21	6.70	59
	18.20	4.87	58
	22.31	3.98	51
	28.25	3.16	63
Decomposition product of $UCl_4 2tmu$	10.32	8.57	44
	11.42	7.75	44
	14.25	6.22	100
	16.44	5.39	33
	22.10	4.02	78
	27.20	3.28	50
Decomposition product of $UO_2Cl_2 2tmu$	10.29	8.59	56
	11.37	7.78	56
	14.22	6.23	100
	16.42	5.39	48
	22.08	4.03	69
	27.18	3.28	55

The Raman vibrational bands and X-ray powder diffraction data for the decomposition product of $UCl_4 2tmu$ are summarized in Tables 1 and 2, respectively. The data agreed very well with those obtained for the decomposition product of $UO_2Cl_2 2tmu$ which was proven to be $UO_2Cl_2 tmu$ [3]. The strong band occurring at 865 cm^{-1} in the Raman spectrum and at 945 cm^{-1} in the infrared spectrum can be assigned to the assymmetric O=U=O stretching frequency [5]. The assymmetric stretch in $UO_2Cl_2 2tmu$ was observed at 834 cm^{-1} in the Raman spectrum and at 925 cm^{-1} in the infrared spectrum. Infrared spectra of the decomposition product of $UCl_4 2tmu$, taken at α values of 0.16, 0.50 and 0.91, showed only a band at 945 cm^{-1}. This, together with the TG data, ruled out the existence of $UO_2Cl_2 2tmu$ as a stable intermediate in the reaction. Reaction (1), therefore, consists of at least three overlapping processes; i.e., the oxidation of $UCl_4 2tmu$; dissociation of the tmu from the coordination sphere of the uranium; and a molecular rearrangement [3], to give the bridged dimeric $(UO_2Cl_2 tmu)_2$ species. If it is assumed that the peaks which appeared between 180 and 260°C in the DSC trace (Fig. 2) could be assigned to these three processes, an approximate enthalpy value of $\Delta H_r = -270 \pm 5$ kJ mol^{-1} is obtained for the reaction.

Isothermal kinetics

It was noticed that the time which the sample spent in the oxygen atmosphere prior to the start of the reaction had a pronounced effect on the shape of the α–time curve. The shape of the curve changed continuously from one which could be described as fairly deceleratory (Fig. 4, curve A) to one which is fairly sigmoidal (Fig. 4, curve B).

Curve A was recorded immediately after the sample was loaded onto the thermobalance. It was not possible to fit the experimental data ($0 < \alpha < 1$) to a single kinetic expression. In addition it was found that two equations, $\alpha = kt$ and $\alpha^2 = kt$, could be used to describe the reaction over the range $0.05 < \alpha < 0.72$. Arrhenius activation energies were calculated assuming that either the linear law ($E_a = 329 \pm 10$ kJ mol^{-1}) or the one-dimensional diffusion equation ($E_a = 352 \pm 15$ kJ mol^{-1}) described the reaction. For $0.70 < \alpha < 0.95$ the reaction is described by the contracting-area model, $1 - (1 - \alpha)^{1/2} = kt$. An Arrhenius activation energy, $E_a = 203$ kJ mol^{-1} was calculated for the process.

Curve B was obtained when the sample was kept in a dynamic oxygen atmosphere for 24 h prior to the start of the reaction. This time limit was the minimum time required to give reproducible results in terms of the α vs. t curve at a specific temperature. The equation $\alpha = kt$ was found to describe the reaction over the range $0.02 < \alpha < 0.20$. The activation energy calculated for this process was $E_a = 362 \pm 15$ kJ mol^{-1}. The range $0.25 < \alpha < 0.70$ was found to be described by the one-dimensional diffusion equation, $\alpha^2 = kt$.

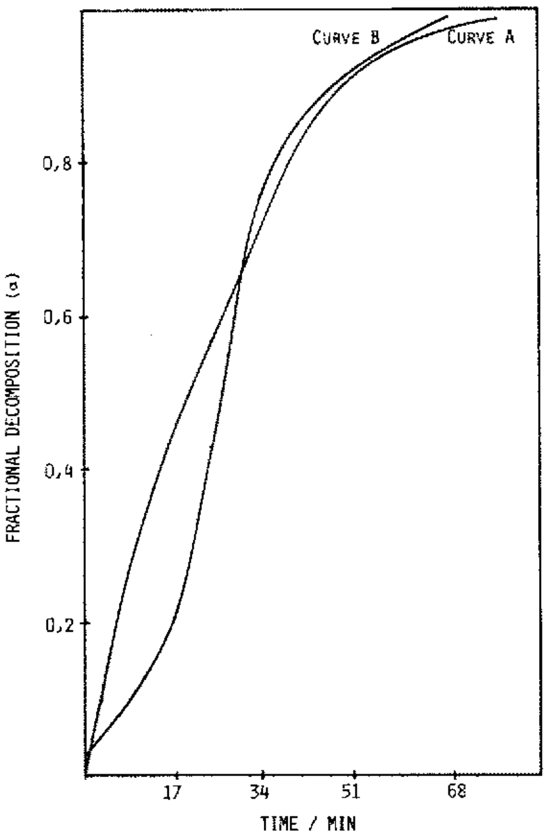

Fig. 4. Effect of oxygen treatment prior to the reaction on the decomposition of $UCl_4$2tmu: (A) no conditioning of the sample; (B) 24 h conditioning of the sample in oxygen. $T = 203°C$.

An activation energy $E_a = 349 \pm 10$ kJ mol^{-1} was calculated for the process. For $\alpha > 0.75$ the contracting-area model $1-(1-\alpha)^{1/2} = kt$ with an apparent activation energy of $E_a = 219 \pm 10$ kJ mol^{-1} was found to hold.

The differences in the kinetic behaviour of the two samples are further illustrated by the different types of nuclei formed during the initial stages ($\alpha = 0.1$) of the reaction. Micrograph A in Fig. 5 shows the nuclei formed on the surface of a sample which was decomposed immediately after loading onto the balance, while micrograph B shows the surface of a partly decomposed sample after 24 h of conditioning in oxygen. The observed differences in the kinetic behaviour of the compound could be attributed to weakly physically-adsorbed foreign molecules such as H_2O or organic solvent molecules on the crystal surface. During the conditioning time these impurities are removed from the surface, leaving a more homogeneous surface to react with the oxygen. Similar results (i.e., α vs. t curve and kinetics) were obtained when the oxygen used for the conditioning of the surface was

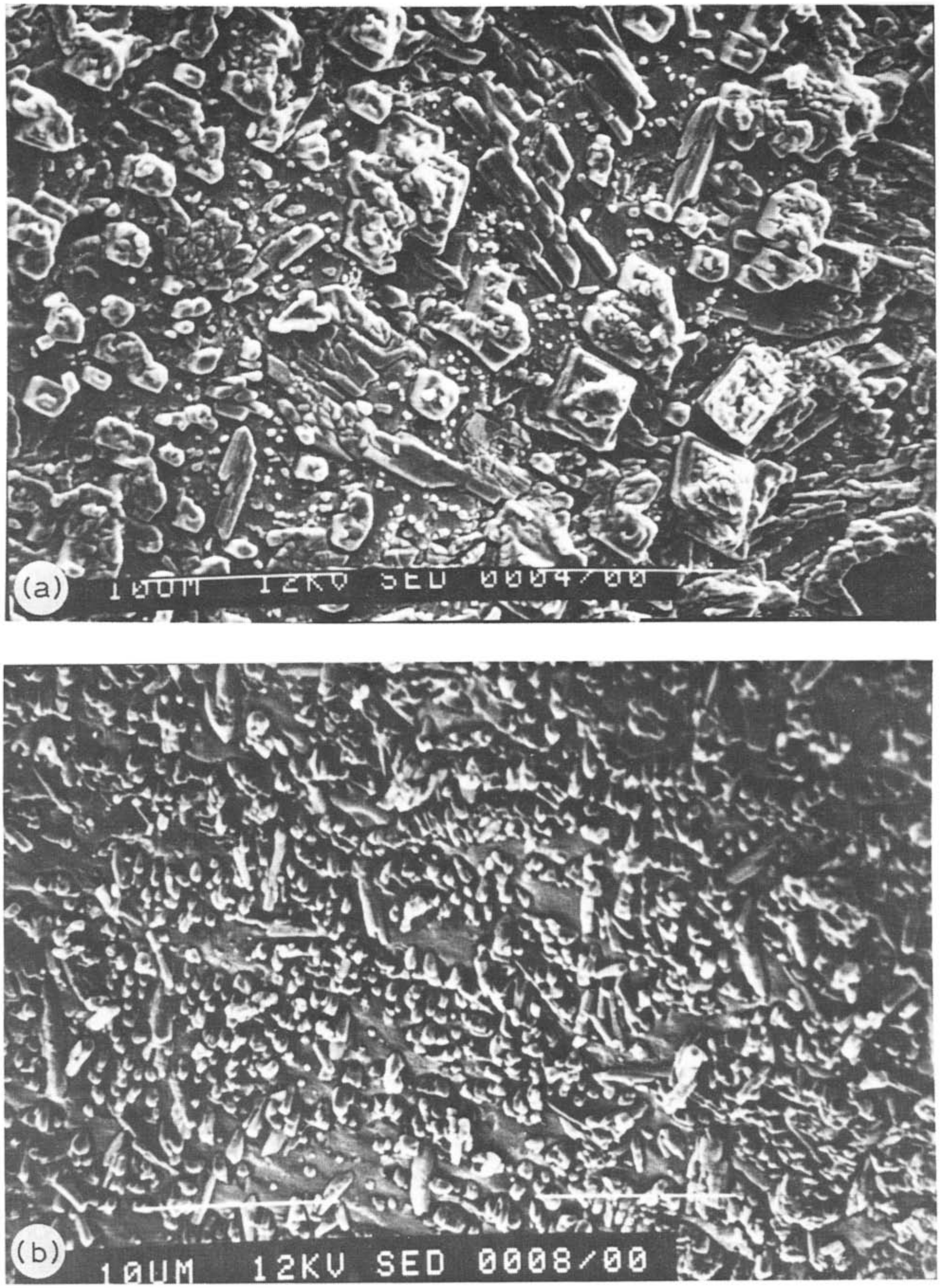

Fig. 5. Micrographs of the partly decomposed sample obtained by using a scanning electron microscope (magnification 2500×). (a) Decomposed sample without any pre-treatment in oxygen; (b) decomposed sample after 24 h pre-treatment in oxygen.

replaced with argon. This strengthens the idea that the function of the gas during the conditioning period is only necessary to produce a clean surface and not to create UO_2Cl_2Xtmu germ nuclei where $X = 1$ or 2.

The geometrical mechanism of decomposition can, therefore, be summarized as follows. The linear law of nucleus formation ($\alpha = kt$) describes the initial stages of the reaction on a clean surface which is followed by a one-dimensional growth process ($\alpha^2 = kt$). Eventually a contracting-area mechanism $[1 - (1 - \alpha)^{1/2} = kt]$ is used to describe the final stages of the reaction. It is not possible to draw definite conclusions regarding the geometric mechanism of decomposition if the surface of the crystals are contaminated with impurities. The decay period is however described in terms of the contracting-area model.

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