TABLE III. Integral free enthalpies and entropies of formation on hydriding.

H/Pa	373–550 K		550–740 K	
	ΔH°_f kJ mol^{-1}	ΔS°_f J K mol^{-1}	ΔH°_f KJ mol^{-1}	ΔS°_f J K mol^{-1}
1.3	−46.5 ± 0.7	−65.0 ± 1.3	−42.4 ± 2.0	−58.5 ± 2.8
1.7	−62.1 ± 0.7	−88.5 ± 1.5	−52.1 ± 2.3	−72.9 ± 3.4
2.0	−74.9 ± 0.8	−109.7 ± 1.5	−59.7 ± 3.6	−86.4 ± 5.0
2.2	−82.5 ± 0.7	−122.2 ± 1.5	−69.3 ± 2.7	−102.1 ± 4.0
2.4	−91.8 ± 0.9	−138.9 ± 1.9	−72.3 ± 3.9	−108.7 ± 5.5
3.0	−110.9 ± 1.1	−176.4 ± 2.2	−90.1 ± 5.3	−143.1 ± 7.9

TABLE IV. Integral free enthalpies and entropies of formation on dehydriding.

H/Pa	550–740 K	
	ΔH°_f KJ mol^{-1}	ΔS°_f J K^{-1} mol^{-1}
1.3	−62.2 ± 2.0	−80.3 ± 2.9
1.7	−83.6 ± 0.8	−109.5 ± 1.3
2.0	−99.6 ± 1.2	−131.9 ± 1.9
2.4	−117.0 ± 1.0	−157.3 ± 1.5
3.0	−128.6 ± 6.9	−180.8 ± 9.9

All precisions are on the 0.95 confidence level.

change in slope at this temperature. Here again not enough data were available to proof this difference in slope on dehydriding. Enthalpies and entropies of formation derived from those graphs for selected compositions are presented in Tables III and IV.

The magnitude of hysteresis, expressed as the ratio of hydriding and dehydriding pressure, reaches a maximum of 45 in the II + III diphasic region near H/Pa = 2 at a temperature of 573 K. It decreases regularly to 11 as the temperature increases to 741 K. Cycling experiments were conducted to identify the origin of hysteresis and the true equilibrium conditions. Samples partially dehydrided at constant temperature and rehydrided reached their original hydriding hydrogen pressure. On the other hand during heating and cooling at constant composition the pressure of samples prepared on hydriding reversibly followed the lnp-1/T-lines for hydriding for that composition. In the same way the pressures of samples prepared on dehydriding reversibly follow the lnp-1/T-lines for dehydriding. This means that hysteresis is a matter of changes in compositions and not in gas pressure. At constant composition both, hydriding and dehydriding samples are in perfect equilibrium with the gas phase. Since the gas pressures are different, something must be different in the hydrides. This is confirmed by X-ray diffraction data for phases II and III; products formed on hydriding have larger lattice parameters than those observed for the same composition on dehydriding. Also the higher partial free entropy values indicate, that products, obtained on dehydriding must be in a more ordered state. Probably hysteresis is due to difficulties in the rearrangement of protoactinium atoms after phase changes or the ordering of hydrogen atoms or both. Calorimetric measurements and neutron diffraction studies should give a better insight in this problem. Since free energies of formation are more negative on dehydring the hydriding products are considered as metastable. The enthalpy and entropy of formation of β-PaH_3 on dehydriding is in excellent agreement with the values for its β-UH_3 analog: ΔH°_f (UH_3, β, 29.8 K) = −127.0 KJ mol^{-1} and ΔS°_f (UH_3, β, 298 K) = −184.2 J K^{-1} mol^{-1} [1].

1 H. E. Flotow, J. M. Haschke and S. Yamauchi, 'Chem. Thermod. of Actinide Elements and Comp'., IAEA, Vienna, part 9 (in press) (1983).

2 J. M. Haschke, W. Bartscher, J. Rebizant and J. W. Ward, *separate contribution to this conference.*

A21

The Thermal Oxidation of Tetrachlorobis(N,N,N′,N′-tetramethylurea)uranium(IV)

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The thermal oxidation of $UCl_4 \cdot 2$tmu (tmu ≡ N,N,N′,N′-tetramethylurea) was studied in an oxygen atmosphere by using thermogravimetry and differential scanning calorimetry.

Thermogravimetric results indicated that the oxidation reaction can be described as:

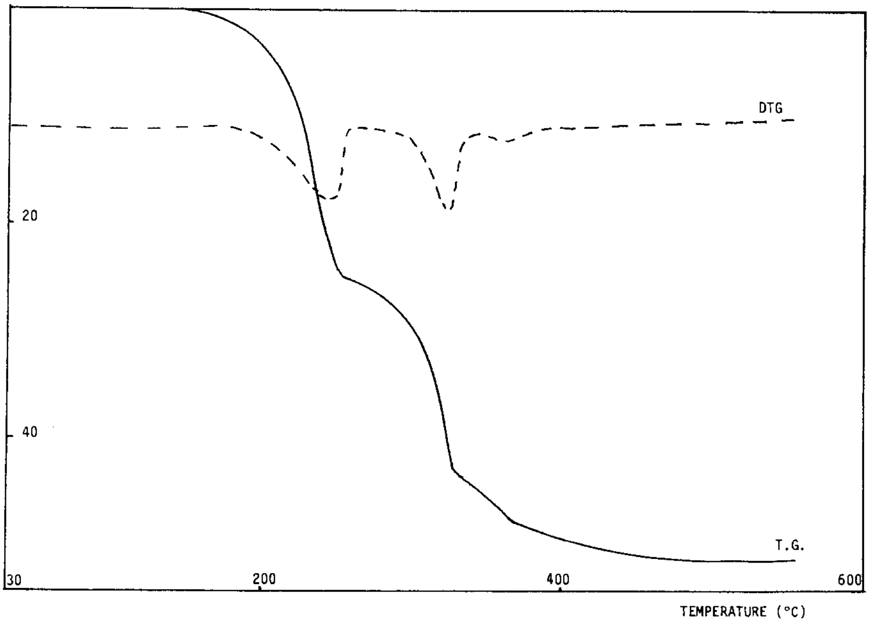

Fig. 1. TG and DTG curves for the oxidation of $UCl_4\cdot 2tmu$.

$$\text{(i) } UCl_4\cdot 2tmu + O_2 \longrightarrow UO_2Cl_2\cdot tmu + \text{ + volatile products}$$

This reaction started at ±150 °C and was completed at ±250 °C and

$$\text{(ii) } UO_2Cl_2tmu + O_2 \rightarrow U_3O_8 + \text{volatile products}$$

over the temperature range ±260 °C to ±480 °C.

Only the first reaction was studied fundamentally. The profiles of the TG and DTG curves, Fig. 1, suggested that the oxidation and dissociation reactions are occurring simultaneously. Isothermal measurements were performed over the temperature range 180–205 °C. The data suggested that the mechanism for the reaction can be described by the equation

$$1 - (1 - \alpha)^{1/2} = kt$$

where α = fraction decomposed. Using this equation an apparent activation energy was calculated and found to be 164 kJ mol^{-1}.

The DSC trace obtained for the oxidation reaction gave series of exothermic peaks over the temperature range 175–500 °C. The two overlapping peaks between 178 and 275 °C were assigned to the reaction,

$$UCl_42tmu + O_2 \longrightarrow UO_2Cl_2\cdot tmu + \text{volatile products}$$

The enthalpy of the reaction was estimated as –271 kJ mol^{-1}. The total enthalpy *i.e.* for the reaction

$$UCl_42tmu + O_2 \longrightarrow U_3O_8 + \text{volatile products}$$

was estimated as –765 kJ mol^{-1}. These results as well as isothermal measurements which were carried out in a argon atmosphere suggested that although the dissociation and oxidation reactions seem to occur simultaneously, the dissociation of the neutral ligand is a prerequisite for the reaction to occur.

A22

A Cone Packing Model Applied to Lanthanide(III) Organometallic Chemistry

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Statistics based on the structures of more than 30 organolanthanide(III) compounds give:

$$\overline{SAS} = 0.72 \text{ and } \delta = 0.05$$

where $\overline{SAS}$ is the average value of the solid angle sum (SAS), δ is the standard deviation [1]. A stable region can thus be defined for SAS around 0.72 ± 0.10 (Fig. 1) where 0.10 is the intrinsic error in our cone packing model [1, 2]. Steric parameters of common ligands are listed in Table I. In this way steric crowding around the metal ion in compounds of the