

Organo-f-element thermochemistry

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Abstract

Actinide–oxygen bond disruption enthalpies $D(\text{An–O})$ in Cp^*_3AnR and $\text{Cp}^{**}_3\text{AnR}$ ($\text{Cp}^*_3 \equiv \text{C}_5\text{H}_4\text{Si}(\text{CH}_3)_3$; $\text{Cp}^{**}_3 \equiv \text{C}_5\text{H}_4\text{tBu}$; $\text{R} \equiv \text{H}$ or CH_3 ; $\text{An} \equiv \text{U}$ or Th) have been measured by iodinolysis and alcoholysis titration calorimetry. $D(\text{An–O})$ values are as follows (kJ mol^{-1}): 317 ± 15 for Cp^*_3UH , 319 ± 10 for $\text{Cp}^*_3\text{UCH}_3$ and 392 ± 11 and 371 ± 24 for the respective Cp^*_3ThR analogues. $D(\text{Cp}^{**}_3\text{U–O})$ is found at $307 \pm 9 \text{ kJ mol}^{-1}$. The influence of the nature of the titrants is observed in the series EtOH , $\text{CF}_3\text{CH}_2\text{OH}$, tBuOH .

1. Introduction

In the last decade the activity in actinide organometallic thermochemistry has been very intense. Initial efforts [1–4] focused upon determining relative solution phase bond disruption enthalpies D by alcoholic isoperibol titration calorimetry.

The measured enthalpy change can be expressed as the difference between the enthalpies of the bonds formed and ruptured during the reaction of alcoholysis:

$$\Delta H_{\text{react}} = D(\text{L}_n\text{An–R}) + D(\text{R'–O–H}) - D(\text{L}_n\text{An–OR}) - D(\text{R–H}) \quad (1)$$

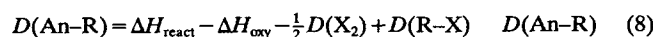
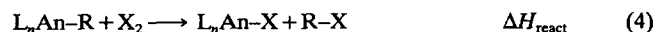
The main problem in these measurements is the knowledge of $D(\text{An–O})$. An estimate of this value was derived on the basis of the crude approximation [1–5]

$$\frac{D(\text{L}_n\text{An–OR}')}{D(\text{An–X}_4)} \approx \frac{\bar{D}(\text{M}(\text{OR})_4)}{\bar{D}(\text{MX}_4)} \quad (2)$$

where $\text{M} \equiv \text{Ti}$, Zr or Hf and X is a halogen.

The estimated values of 518.8 and 481.2 kJ mol^{-1} respectively for thorium and uranium compounds are probably affected by a substantial uncertainty and a serious problem of transferability. The enthalpies derived from alcoholysis are termed “relative” and are satisfactory for understanding most aspects of organoactinide chemistry; nevertheless, absolute $D(\text{An–R})$ values would allow comparison with thermochemical

data for other organometallic compounds. Schock *et al.* [6] have presented a new approach to measuring absolute actinide–hydrocarbyl bond disruption, namely halogenolytic calorimetry. The one-electron redox reaction is based on the following equations:



By combination of alcoholysis and iodinolysis experimental results, it is possible to deduce a so-called absolute bond disruption enthalpy $D(\text{U–O})$, keeping in mind that numerous assumptions have been made to obtain this value: the solvation effects in toluene, the possible U–U interactions in L_3U , the partial dimerization of Cp^*_3ThH [7], etc. have been neglected.

2. Experimental details

All procedures were performed using standard techniques for air-sensitive compounds.

Toluene, toluene- d^8 , tetrahydrofuran (THF) and pentane were dried over Na–K and distilled under an argon atmosphere.

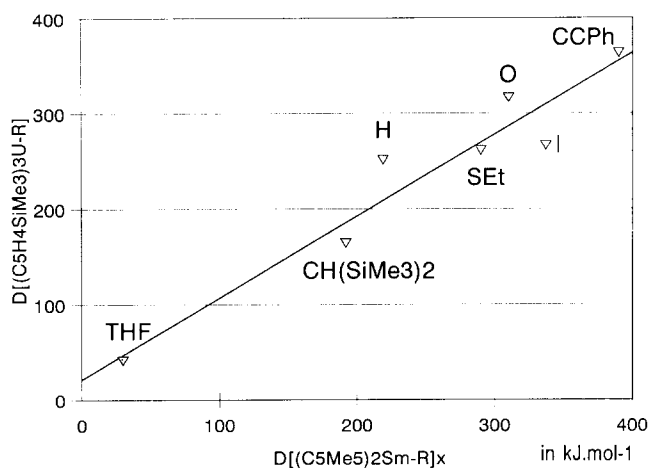
The complexes with trimethylsilyl cyclopentadienyl (Cp^*) and *tert*-butylcyclopentadienyl (Cp^{**}), *i.e.* Cp^*_3U

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TABLE 1. Enthalpies of reaction of I₂ and CF₃CH₂OH with organometallic compounds in toluene and bond disruption enthalpies (kJ mol⁻¹) [8, 14]

Compound	ΔH_{iod} per mole of complex	$D(\text{An-H/CH}_3)$	ΔH_{alc}	$D(\text{An-O})$
Cp* ₃ ThH	-171.4 ± 5.8	277 ± 6	-114 ± 5	392 ± 11
Cp* ₃ ThCH ₃	-196.7 ± 7.0	196 ± 7	-178 ± 22	371 ± 24
Cp* ₃ UH	-154.3 ± 2.8	253.7 ± 5.1	-63 ± 11	317 ± 15
Cp* ₃ UCH ₃	-	188 ± 5 [6]	-134 ± 4	319 ± 10

Fig. 1. Relationship between $D(\text{Cp}^*_3\text{U-R})$ and $D((\text{C}_5\text{Me}_5)_2\text{Sm-R})_x$.TABLE 2. Bond disruption enthalpies (kJ mol⁻¹)

Alcohol	$D(\text{Cp}^*_3\text{U-O})$	$D(\text{Cp}^{**}_3\text{U-O})$
EtOH	324 ± 24	
CF ₃ CH ₂ OH	317 ± 15	
'BuOH	280 ± 8	307 ± 9

[8], Cp*₃UCl [8], Cp*₃ThH [7], Cp**₃UCl [10], Cp**₃UH [11], Cp*₃UCH₃ [6], Cp*₃UOEt [11], Cp*₃UOCH₂CF₃, Cp*₃UO'Bu, Cp**₃UO'Bu, Cp**₃UOEt, Cp*₃ThCl, Cp*₃ThCH₃ and Cp*₃ThOCH₂CF₃ [12], were prepared in THF or toluene and purified by recrystallization in pentane as described in the literature (see ref. 12 and references cited therein).

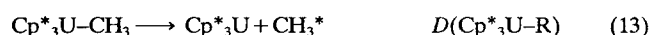
The titrants EtOH, 'BuOH and CF₃CH₂OH were dried over the corresponding magnesium alcoholate or CaH₂ [13], transferred over 4 Å molecular sieves and vacuum distilled prior to use. The calorimeter and the procedure employed in this study are described in ref. 4. In this work, sharp, well-defined end points were observed when a stoichiometrically appropriate amount of iodine or alcohol was added to the organometallic solutions. On monitoring by ¹H nuclear magnetic resonance (NMR, Bruker AM 400), it has been verified

that the titrant does not attack the η⁵ functionalities of the Cp ligand.

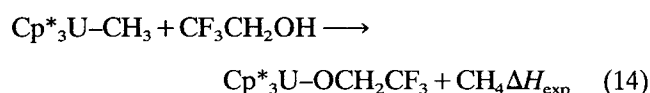
3. Results and discussion

The starting compounds chosen for this study, *i.e.* Cp*₃UH, Cp*₃UCH₃, Cp**₃UH, Cp*₃ThH and Cp*₃ThCH₃, are monomeric in common aromatic solvents [6, 8, 9, 12]. The enthalpies of solution of the complexes in toluene are rather small and well known [6, 8, 12, 14].

The reactions used in the iodinolysis of a uranium compound are as follows:



For the alcoholysis the main equations are as follows:



$$D(\text{Cp}^*_3\text{U-OCH}_2\text{CF}_3) = D(\text{O-H}) + D(\text{U-CH}_3) - D(\text{CH}_3\text{-H}) - \Delta H_{\text{exp}} \quad (15)$$

$D(\text{O-H})$ has been estimated to be 436 kJ mol⁻¹ [15], while $D(\text{R-H})$, $D(\text{I}_2)$ and $D(\text{CH}_3\text{-I})$ can be found in the literature [16–19].

Knowing the value of $D(\text{U-CH}_3)$ obtained by iodinolysis, eqn. (15) can be solved. The results of the thermochemical experiments for methyl and hydride derivatives are set out in Table 1.

The derived $D(\text{Cp}^*_3\text{U-O})$ values obtained from methyl and hydride derivatives are similar, 317 and 319 kJ mol⁻¹ respectively, but differ widely from Bruno *et al.*'s estimated value of 481.2 kJ mol⁻¹ [1]. On the other hand, Nolan *et al.* [20] have shown that a linear correlation exists between $D(\text{Cp}^*_3\text{U-R})$ and $D((\text{C}_5\text{Me}_5)_2\text{Sm-R})_x$ ($x=1$ for R ≡ alkyl, iodide, THF;

and $x=2$ for $R \equiv H$). The values that we have determined for Cp^*_3UH [14] and Cp^*_3USEt [21] confirm the validity of this correlation. By this graphical approach $D(U-O)$ should be estimated as about 310 kJ mol^{-1} [22], in very good agreement with our experimental value (Fig. 1).

For the thorium compounds the thermochemical datum corresponding to the oxidative reaction, ΔH_{oxy} , has not yet been measured. We employ the accepted parallelism between Th-alkyl and U-alkyl bond disruption enthalpies, $D(Th-R)$ being about 40 kJ mol^{-1} higher than $D(U-R)$ [3, 4] (Table 1) and the enthalpy of the oxidation reaction being about 230 kJ mol^{-1} [8]. The derived bond disruption enthalpies $D(Th-O)$ are 392 ± 11 and $370 \pm 24 \text{ kJ mol}^{-1}$ for Cp^*_3ThH and $Cp^*_3ThCH_3$ respectively.

'BuOH has been reported [1, 2] as titrant in calorimetric studies of Cp derivatives. One conclusion of these studies was that the bond disruption enthalpies obtained with 'BuOH and CF_3CH_2OH are mutually consistent for different thorium organometallics, $D((C_5Me_5)_2Th(C_2H_5)Cl)$ being 285.8 ± 8.4 [1] and $275.7 \pm 10.5 \text{ kJ mol}^{-1}$ [2] respectively.

In this work the reactions of EtOH, 'BuOH and CF_3CH_2OH with Cp^*_3UH and of 'BuOH with Cp^{**}_3UH are followed thermodynamically and the results are presented in Table 2.

It seems that a small decrease in the $D(U-O)$ values can be observed in the series $EtOH > CF_3CH_2OH > 'BuOH$, the nature of the alcohol being at least as important as the nature of the substituent on the Cp ring.

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