

Journal of Organometallic Chemistry, 377 (1989) 59–67
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20273

Organo-*f*-element thermochemistry. Actinide–ligand bond disruption enthalpies in tris(indenyl)actinide hydrocarbyls

S. Bettonville *, J. Goffart **,

Laboratory of Analytical Chemistry and Radiochemistry, University of Liège, Sart Tilman, B-4000 Liège (Belgium)

and J. Fuger

Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe (Federal Republic of Germany)

(Received June 1st, 1989)

Abstract

Thorium- and uranium–ligand bond disruption enthalpies ($D(\text{An-R})$) have been obtained for the series of complexes $\text{Ind}_3\text{An-R}$, where $\text{Ind} = \text{C}_9\text{H}_7$ or $1\text{-C}_2\text{H}_5\text{C}_9\text{H}_6$, $\text{An} = \text{Th}$ or U , $\text{R} =$ an alkyl group. All the new compounds have been characterised by microanalysis and spectroscopy. The thermodynamic data were determined by oxygen-free batch-titration, solution calorimetry from the enthalpies of solution of the organo-*f*-element complexes in toluene and from the subsequent enthalpies of alcoholysis with 2,2,2-trifluoroethanol. $D(\text{An-R})_{\text{gas}}$ values obtained (95% of confidence) were as follows: $(\text{C}_9\text{H}_7)_3\text{Th-CH}_2\text{Si}(\text{CH}_3)_3$, (397 ± 7) kJ mol^{-1} ; $(\text{C}_9\text{H}_7)_3\text{Th-CH}_3$, (371 ± 6) kJ mol^{-1} ; $(1\text{-C}_2\text{H}_5\text{C}_9\text{H}_6)_3\text{Th-CH}_3$, (365 ± 5) kJ mol^{-1} ; $(\text{C}_9\text{H}_7)_3\text{Th-CH}(\text{CH}_3)_2$, (357 ± 8) kJ mol^{-1} ; $(\text{C}_9\text{H}_7)_3\text{U-CH}_3$, (351 ± 2) kJ mol^{-1} ; $(1\text{-C}_2\text{H}_5\text{C}_9\text{H}_6)_3\text{U-CH}_3$, (350 ± 4) kJ mol^{-1} and $(\text{C}_9\text{H}_7)_3\text{Th-CH}_2\text{C}_6\text{H}_5$, (342 ± 9) kJ mol^{-1} . These bond disruption enthalpies parallel, but are significantly larger than, those for the identical R functionalities in the $(\text{C}_5\text{H}_5)_3\text{Th-R}$ series. For corresponding Th/U pairs, the difference $\{D(\text{Th-R}) - D(\text{U-R})\}$ is ca. 20 kJ mol^{-1} .

Organometallic chemical transformations such as β -hydride elimination, olefin and CO insertion into metal–carbon bonds, metal–carbon bond hydrogenolysis, are among the most important reactions in chemistry [1–6 and ref. cited therein]. To increase the knowledge and understanding of this class of processes, it is essential to

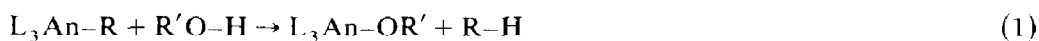
* Research Assistant, National Foundation for Scientific Research, Brussels (Belgium).

** Research Associate, Inter-University Institute for Nuclear Sciences, Brussels (Belgium).

establish a detailed account of the reaction thermodynamics and especially the metal–ligand bond energies.

Although the number of data accessible for middle and late first row transition metals is steadily expanding [7,8], only a few recent publications deal with the problem of *f*-element organometallic compounds [1–5]. This paper presents additional data for bond disruption enthalpies in indenyl complexes of thorium and uranium.

The determination of bond energies can be approached quantitatively by various techniques. We selected calorimetry involving the measurement of the reaction enthalpy between the organoactinides and an appropriate alcohol, according to eq. 1.



Experimental section

Synthetic methods

All the organoactinide compounds were handled in Schlenk-type glassware, and solid or solution transfers were performed in a glovebox under purified nitrogen or argon. Pentane and tetrahydrofuran were dried over sodium or potassium and distilled immediately prior to use. 2,2,2-Trifluoroethanol was dried and deoxygenated by vacuum transfer onto freshly activated 3 Å molecular sieves, and then degassed by freezing-thawing cycles. Ind_3ThCH_3 and Ind_3UCH_3 were prepared and purified as described elsewhere [9a].

Synthesis of $An(1-C_2H_5C_9H_6)_3CH_3$ ($An = Th$ and U). To a tetrahydrofuran solution of 0.010 mol of $An(1-C_2H_5C_9H_6)_3Cl$ [9b*] (ca. 100 ml) at $-78^\circ C$ was added 0.0105 mol of CH_3Li (1.6 mol dm^{-3} in diethyl ether). The mixture was allowed to warm to room temperature and stirred for two days. The solvent was then removed, in vacuo, and the yellow (for Th) or red-brown (for U) residue was extracted with pentane for two weeks. Crystals were produced [9b*]: (yield: 55% for Th and 60% for U). 1H NMR (Th compound [9c*], C_6D_6): δ 7.43 (m,3H), 7.34 (m,3H), 6.99 (m,3H), 6.95 (m,3H), 5.49 (d,3H), 5.02 (d,3H), 2.60 (m,6H), 1.10 (m,9H), 0.26 (s,3H). IR (CsI pellet, cm^{-1}), thorium compound: 3050(m), 2960(s), 2920(s), 2860(m), 1455(s), 1345(s), 1335(s), 1215(m), 1100(s), 1140(m), 1010(m), 755(s), 490(m), 445(s), 405(m), 210(m); uranium compound: 3050(m), 2960(s), 2930(s), 2880(m), 1460(s), 1350(m), 1040(m), 715(s), 760(s), 440(m). Anal. Found: C, 60.30; H, 5.36. $C_{34}H_{36}Th$ calcd.: C, 60.35; H, 5.36%. Anal. Found: C, 59.98; H, 5.30. $C_{34}H_{36}U$ calcd.: C, 59.82; H, 5.31%.

Synthesis of $Th(C_9H_7)_3CH_2C_6H_5$. To a THF solution (ca. 100 ml) of 0.0060 mol of $Th(C_9H_7)_3Cl$ at $-78^\circ C$ was added 0.0063 mol of $C_6H_5CH_2MgCl$ (2.0 mol dm^{-3} in THF). The solution was then allowed to warm to room temperature and stirred for two days. The solvent was removed, in vacuo, and the yellow residue extracted with pentane for one week: (yield 80%); 1H NMR (C_6D_6) δ 7.33 (d \times d,6H), 6.95 (d \times d,6H), 5.64 (t + d,9H), 7.39 (t,2H), 7.19 (d,2H), 1.54 (s,2H), one H of the $C_6H_5CH_2$ group (in *para* position in comparison with the CH_2) is not

* Reference number with asterisk indicates a note in the list of references.

observable. IR (CsI pellet, cm^{-1}): 3050(m), 2895(m), 2860(m), 1595(s), 1485(m), 1450(m), 1335(s), 1255(m), 1215(s), 975(s), 795(s), 750(s), 700(s), 440(s), 230(s). Anal. Found: C, 60.08; H, 4.37. $\text{C}_{34}\text{H}_{28}\text{Th}$ calcd.: C, 61.07; H, 4.22%.

Synthesis of $\text{Th}(\text{C}_9\text{H}_7)_3\text{CH}(\text{CH}_3)_2$. In a procedure similar to that employed for $\text{Th}(\text{C}_9\text{H}_7)_3\text{CH}_2\text{C}_6\text{H}_5$, 0.0084 mol of $(\text{CH}_3)_2\text{CHMgCl}$ (2.0 mol dm^{-3} in THF) was added to a cooled THF solution (-78°C) of $\text{Th}(\text{C}_9\text{H}_7)_3\text{Cl}$ (0.008 mol). The mixture was allowed to warm to room temperature and stirred for two days. The solvent was removed in vacuo and the yellow residue extracted with pentane for three weeks. Yellow crystals were obtained (yield 50%); ^1H NMR (C_6D_6): δ 7.43 (d \times d, 6H), 6.96 (d \times d, 6H), 5.63 (d, 6H), 5.34 (t, 3H), 1.97 (d, 6H), 0.44 (sept., 1H). IR (CsI pellet, cm^{-1}): 3050(m), 2960(m), 2920(m), 2870(m), 2820(w), 1460(m), 1340(s), 1220(m), 1145(m), 1080(m), 1040(m), 780(s), 750(s), 695(m), 440(s), 390(m), 220(s). Anal. Found: C, 57.56; H, 4.45. $\text{C}_{30}\text{H}_{28}\text{Th}$ calcd.: C, 58.06; H, 4.55%.

Synthesis of $\text{Th}(\text{C}_9\text{H}_7)_3\text{CH}_2\text{Si}(\text{CH}_3)_3$. To a THF solution (100 ml) of $\text{Th}(\text{C}_9\text{H}_7)_3\text{Cl}$ (0.006 mol) at -78°C was added 0.0063 mol of $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$ (1.0 mol dm^{-3} in pentane). The solution was allowed to warm to room temperature then stirred for two days, and the solvent was removed in vacuo. The extraction of the yellow residue with pentane for two weeks produced crystals (yield 70%); ^1H NMR (C_6D_6): δ 7.40 (d \times d, 6H), 6.98 (d \times d, 6H), 5.95 (t, 3H), 5.77 (d, 6H), 0.39 (s, 9H), -0.91 (s, 2H). IR (CsI pellet, cm^{-1}): 3050(m), 2940(m), 2880(w), 2830(w), 2790(w), 1335(s), 1250(m), 1240(s), 1215(s), 1040(m), 1000(m), 910(s), 850(s), 780(s), 740(s), 675(m), 450(m), 440(s), 385(m), 365(m), 220(s). Anal. Found: C, 55.93; H, 4.76 calcd.: C, 56.01; H, 4.85%.

Synthesis of $\text{Th}(\text{C}_9\text{H}_7)_3\text{OCH}_2\text{CF}_3$. To a solution of 0.010 mol of $\text{Th}(\text{C}_9\text{H}_7)_3\text{Cl}$ in 100 ml of THF at room temperature was added 0.010 mol of $\text{CF}_3\text{CH}_2\text{ONa}$. After being stirred for one day the solution was filtered and the solvent removed in vacuo. The yellow residue was extracted with pentane. A yellow compound was obtained, (yield 60%); ^1H NMR (C_6D_6): δ 7.44 (d \times d, 6H), 6.94 (d \times d, 6H), 6.21 (t, 3H), 5.86 (d, 6H), 3.63 (q, 2H, $J(\text{H}-\text{F})$ 9.7 Hz). IR (CsI pellet, cm^{-1}): 3050(m), 2920(m), 2870(w), 1340(s), 1285(s), 1220(m), 1160(s), 1045(m), 960(s), 780(s), 745(s), 680(s), 445(s), 390(m), 225(s). Anal. Found: C, 51.32; H, 3.41. $\text{C}_{29}\text{H}_{23}\text{OF}_3\text{Th}$ calcd.: C, 51.48; H, 3.43%.

Analytical methods

Proton NMR spectra were recorded on a Bruker AM400 (FT, 400.1 MHz) instrument. Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer with CsI pellets. Elemental analysis were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Titration calorimetry

The isoperibol calorimeter employed was the LKB 8700 model (Bromma, Sweden), especially modified to handle the air- and moisture-sensitive compounds. The titrant is injected into the reaction cell from a Gilmont precision 2.50 ml syringe, readable to ± 0.0001 ml. The titrant solution circulates through a long Teflon tubing immersed in the constant temperature bath and finally through a small diameter glass tube immersed in the reactant solution inside the calorimeter. In a typical experiment, a flat-bottom thin-walled glass ampoule is filled with 100 mg of compound and weighed in the inert atmosphere box to ± 0.01 mg on a Cahn Gram

electrobalance. A small plug inserted into the neck of the ampoule is sealed inside the glovebox with a high pyseal cement (suitable for sealing glass and rubber to produce air- and watertight joints insoluble in most organic solvents). This ampoule is placed on the stirring baffle and the entire calorimeter and syringe apparatus are loaded and sealed inside the glovebox. The stirring shaft is held in place by bearings contained inside a copper tube. These bearings allow nearly frictionless stirring while remaining nearly gas tight. As an additional precaution, the copper tube is flushed with argon during all calorimetric runs. The apparatus is removed from the glovebox and immersed in a water bath thermostatically controlled to $\pm 0.001^\circ\text{C}$. After temperature equilibration, an accurate electric calibration is carried out to determine the calorimeter energy equivalent.

This calibration is repeated after experiment because the energy equivalent varies slightly as a result of titrant addition. The sample ampoule is broken in the calorimeter cell and the heat effect upon dissolution is recorded on a strip-chart recorder. The titrant solution (0.08 mol dm^{-3} 2,2,2-trifluoroethanol in toluene) is added in 1 ml increments and heats of reaction measured.

The accuracy of the calorimeter was confirmed by measuring the enthalpy of solution of tris(hydroxymethyl)aminomethane "TRIS", (U.S. National Bureau of Standards, Standard Reference Material No. 724a) in 0.1 mol dm^{-3} hydrochloric acid to obtain a concentration of ca. 5 g l^{-1} and the reaction enthalpy of TRIS with 1 mol dm^{-3} hydrochloric acid, according to the procedure used by Öjelund and Wadsö [11]. For the former our value was $-(29.74 \pm 0.02)\text{ kJ mol}^{-1}$, which agrees well with the NBS accepted value of $-(29.77 \pm 0.03)\text{ kJ mol}^{-1}$ [10]. For the latter our value was $-(47.45 \pm 0.2)\text{ kJ mol}^{-1}$, which agrees well with the value reported by Öjelund and Wadsö of $-(47.45 \pm 0.04)\text{ kJ mol}^{-1}$ [11].

Results and discussion

An essential requirement in using titration calorimetry for determining metal–ligand bond disruption enthalpies via alcoholysis as in eq. 1 is that the reaction must be quantitative, selective, and rapid with respect to the An–R linkage. NMR studies have demonstrated that alcoholysis with 2,2,2-trifluoroethanol meets

Table 1

Experimental heat of solution data ^a ($\Delta H^\circ_{\text{soln}}$) for organoactinides and 2,2,2-trifluoroethanol ^b

Compound	$\Delta H^\circ_{\text{soln}}$ (kJ mol ⁻¹)
(C ₉ H ₇) ₃ ThCH ₃	19.1 (9)
(1-C ₂ H ₅ -C ₉ H ₆) ₃ ThCH ₃	18.2 (5)
(C ₉ H ₇) ₃ ThCH ₂ C ₆ H ₅	18.5 (4)
(C ₉ H ₇) ₃ ThCH ₂ Si(CH ₃) ₃	17.1 (3)
(C ₉ H ₇) ₃ ThCH(CH ₃) ₂	13.0 (3)
(C ₉ H ₇) ₃ UCh ₃	15.0 (4)
(1-C ₂ H ₅ -C ₉ H ₆) ₃ UCh ₃	22.1 (3)
(C ₉ H ₇) ₃ ThOCH ₂ CF ₃	12.3 (4)
CF ₃ CH ₂ OH	12.1 (3)

^a Quantities in parentheses are the number of measurements. ^b From ref. 2.

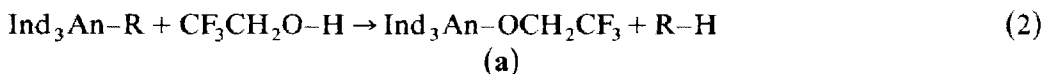
Table 2

Experimental alcoholysis thermochemical data and derived bond disruption enthalpies (D) for organoactinides (kJ mol^{-1})

Compound	$\Delta H_{2\text{alc}}^a$	$\Delta H_{2\text{gas}}^b$	$D(\text{An-R})_{\text{soln}}^b$	$D(\text{An-R})_{\text{gas}}^b$
$(\text{C}_9\text{H}_7)_3\text{ThCH}_3$	$-(131.0 \pm 5.4)$	$-(151.1 \pm 5.6)$	(391.5 ± 5.5)	(371.4 ± 5.7)
$(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{ThCH}_3$	$-(136.8 \pm 4.8)$	$-(157.8 \pm 5.0)$	(385.7 ± 4.9)	(364.7 ± 5.1)
$(\text{C}_9\text{H}_7)_3\text{ThCH}_2\text{C}_6\text{H}_5$	$-(121.3 \pm 7.7)$	$-(109.0 \pm 7.8)$	(329.7 ± 8.8)	(342.0 ± 8.9)
$(\text{C}_9\text{H}_7)_3\text{ThCH}_2\text{Si}(\text{CH}_3)_3$	$-(98.1 \pm 4.0)$	$-(100.7 \pm 4.2)$	(399.7 ± 6.4)	(397.1 ± 6.5)
$(\text{C}_9\text{H}_7)_3\text{ThCH}(\text{CH}_3)_2$	$-(109.0 \pm 5.8)$	$-(124.2 \pm 6.4)$	(371.8 ± 7.0)	(356.6 ± 7.5)
$(\text{C}_9\text{H}_7)_3\text{UCH}_3$	$-(109.6 \pm 1.5)$	$-(133.8 \pm 1.6)$	(375.3 ± 1.7)	(351.1 ± 1.8)
$(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{UCH}_3$	$-(117.8 \pm 2.5)$	$-(134.9 \pm 3.5)$	(367.1 ± 2.6)	(350.0 ± 3.6)

^a Error limits refer to the 95% confidence limits for 6–8 measurements. ^b Error limits do not include uncertainties that are constant throughout the series.

these three criteria, and can be represented by eq. 2.



The organoactinide product (a in eq. 2) at the end of the titration was identified as $\text{Ind}_3\text{AnOCH}_2\text{CF}_3$ for $\text{An} = \text{Th}$ by comparison with a sample of this compound prepared separately (see Experimental for details), and for $\text{An} = \text{U}$ by crystallographic study of single crystals which formed in the solution after the alcoholysis [12].

Enthalpies of solution (ΔH_{soln}) of the Ind_3AnR complexes in toluene and enthalpies of alcoholysis with $\text{CF}_3\text{CH}_2\text{OH}$ ($\Delta H_{2\text{alc}}$) are listed in Tables 1 and 2 respectively. The thermochemical cycle (Fig. 1), which can be described by eq. 3, represents the relationships of these measured quantities to other relevant thermodynamic parameters.

$$\begin{aligned} \Delta H_{2\text{gas}}^\circ &= \Delta H_{2\text{alc}} + \Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnOCH}_2\text{CF}_3) \\ &+ \Delta H_{\text{vap}}^\circ(\text{RH}) - \Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnR}) \\ &- \Delta H_{\text{vap}}^\circ(\text{CF}_3\text{CH}_2\text{OH}) - \Delta H_{\text{soln}}^\circ(\text{Ind}_3\text{AnOCH}_2\text{CF}_3) \\ &- \Delta H_{\text{soln}}^\circ(\text{RH}) + \Delta H_{\text{soln}}^\circ(\text{Ind}_3\text{AnR}) + \Delta H_{\text{soln}}^\circ(\text{CF}_3\text{CH}_2\text{OH}) \end{aligned} \quad (3)$$

In eq. 3, $\Delta H_{\text{sub}}^\circ$ refers to enthalpies of sublimation, $\Delta H_{\text{vap}}^\circ$ to enthalpies of vaporization, and $\Delta H_{\text{soln}}^\circ$ to enthalpies of solution. The $\Delta H_{\text{soln}}^\circ(\text{Ind}_3\text{AnR})$ values

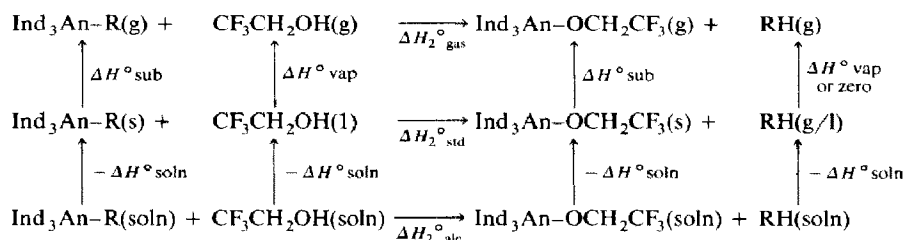


Fig. 1. Thermochemical cycle for determination of $D(\text{An-R})_{\text{gas}}$ ($\text{Ind} = \text{C}_9\text{H}_7$ or $1\text{-C}_2\text{H}_5\text{C}_9\text{H}_6$, $\text{An} = \text{Th}$ or U).

are measured by breaking ampoules containing the organoactinides in the calorimeter cell filled with the solvent (toluene) prior to the titration with $\text{CF}_3\text{CH}_2\text{OH}$ ($\Delta H_{2\text{ alc}}^\circ$). As assumed the enthalpies of solution are small and endothermic (12.9 to 22.1 kJ mol^{-1}); they were not measured at infinite dilution, but the corrections to zero concentration must be very small and negligible; in addition, they tend to cancel out on opposite sides of the thermochemical cycle. In any case, the enthalpies of solution represent only a small percentage of the final bond disruption enthalpies.

We did not measure $\Delta H_{\text{soln}}^\circ$ values for $(1\text{-C}_2\text{H}_5\text{C}_9\text{H}_6)_3\text{AnOCH}_2\text{CF}_3$ and $(\text{C}_9\text{H}_7)_3\text{UOCH}_2\text{CF}_3$, which can be reasonably assumed to be very similar to those for $\Delta H_{\text{soln}}^\circ$ of $(\text{C}_9\text{H}_7)_3\text{ThOCH}_2\text{CF}_3$ measured in separate experiments.

Also needed in the present treatment are the quantities $\Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnR})$ and $\Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnOCH}_2\text{CF}_3)$. We make a reasonable assumption [1-3,13], that all the $\Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnR})$ values are approximatively the same, and equal to $\Delta H_{\text{sub}}^\circ(\text{Ind}_3\text{AnOCH}_2\text{CF}_3)$. On the basis of this assumption the $\Delta H_{\text{sub}}^\circ$ terms cancel in eq. 3.

Data for $\text{CF}_3\text{CH}_2\text{OH}$ and the RH components of the reaction system are also necessary. For toluene, tetramethylsilane and 2,2,2-trifluoroethanol, the enthalpies of vaporization are 37.95, 24.48 and 43.97 kJ mol^{-1} , respectively [14].

$\Delta H_{\text{vap}}^\circ(\text{RH})$ is, of course, zero if the RH species produced in the alcoholysis process are gaseous at 25°C. The enthalpies of solution are not known for all the RH species, but enough data exist to estimate the values, which are relatively small [15].

The values of $\Delta H_{2\text{ gas}}^\circ$, derived from eq. 3 and the assumptions described above, are listed in Table 2.

The bond disruption enthalpy $D(\text{An-R})_{\text{gas}}$ is related to $\Delta H_{2\text{ gas}}^\circ$ by eq. 4.

$$\Delta H_{2\text{ gas}}^\circ = -D(\text{An-O})_{\text{gas}} - D(\text{R-H})_{\text{gas}} + D(\text{An-R})_{\text{gas}} + D(\text{O-H})_{\text{gas}} \quad (4)$$

The solution-phase bond disruption enthalpies $D(\text{An-R})_{\text{soln}}$ values can be determined from the solution data and eq. 5.

$$\Delta H_{2\text{ alc}}^\circ = -D(\text{An-O})_{\text{soln}} - D(\text{R-H})_{\text{soln}} + D(\text{An-R})_{\text{soln}} + D(\text{O-H})_{\text{soln}} \quad (5)$$

Such a procedure is useful if the plausible assumption is made that in dilute solutions of a non polar solvent such as toluene, $D(\text{R-H})_{\text{gas}} = D(\text{R-H})_{\text{soln}}$ and $D(\text{O-H})_{\text{gas}} = D(\text{O-H})_{\text{soln}}$.

Both gas-phase and solution-phase D parameters are reported in Table 2, it can be seen that these values are similar.

Within the particular series of $(\text{C}_9\text{H}_7)_3\text{ThR}$ the organoactinide titration product and reactant alcohol are the same, so that relative values of $D(\text{An-R})$ can be reached directly from the $D(\text{R-H})$ (known for all the R-H species) and the $\Delta H_{2\text{ gas}}^\circ$ values.

Equally desirable, however, are absolute $D(\text{An-R})$ values, so that these results can be correlated and compared with other data for d - and f -element organometallic complexes.

In order to achieve this the quantity $D(\text{An-O})$ must be estimated. A method similar to that used by Bruno and co-workers [1] was utilized for estimating the value of $D(\text{An-O})$ [2,3]. Use is therefore made of the mean bond disruption enthalpy (D) data for the complexes $\text{M}(\text{O-i-C}_3\text{H}_7)_4$ with $\text{M} = \text{Ti}$, Zr and Hf [16]

and of the pragmatic approximations described by eq. 6a and 6b below (X = a halogen):

$$\frac{\overline{D}(\text{An-OR})}{\overline{D}(\text{M-OR})} = \frac{\overline{D}(\text{An-X})}{\overline{D}(\text{M-X})} \quad (6a)$$

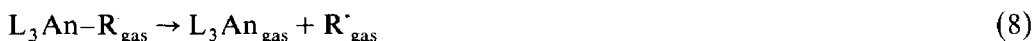
$$D(\text{An-OR}) = \overline{D}(\text{An-OR}) \quad (6b)$$

Within the M = Ti, Zr and Hf series, eq. 6a and 6b holds [17], and furthermore the $D(\text{M-OR})$ parameters are relatively insensitive to R. For all relevant tetrahalides extensive bond disruption enthalpy data are available [3,18]. Use of this proportionality for all M and X combinations yields a $D(\text{Th-OR})$ of 518.8 kJ mol⁻¹ and $D(\text{U-OR})$ of 481.2 kJ mol⁻¹. Justification for the approximation of eq. 6 derives from thermochemical data for AnF₄ [18] which show that $D(\text{Th-F})$ is 665.7 kJ mol⁻¹ and $D(\text{U-F})$ 612.1 kJ mol⁻¹, whereas $D_1(\text{Th-F})$ is 646.0 kJ mol⁻¹ and $D_1(\text{U-F})$ 618.8 kJ mol⁻¹. Moreover, this estimation procedure using ThCl₄ and UCl₄ data gives a $D(\text{Th-F})$ value of 682 kJ mol⁻¹ and a $D(\text{U-F})$ value of 609 kJ mol⁻¹. Nevertheless, the derived absolute $D(\text{An-O})$ values are probably not accurate to better than 40 kJ mol⁻¹ (in contrast to the high reliability of relative $D(\text{An-R})$ values).

The unknown $D(\text{O-H})$ value for 2,2,2-trifluoroethanol can be estimated to be 436.0 kJ mol⁻¹ (the value for ethanol) [19]. This appears to be a plausible approximation because, in all aliphatic alcohol investigated to date, the value $D(\text{O-H})$ has been found to fall in the range 435.1 ± 8.4 kJ mol⁻¹ [19].

The final $D(\text{An-R})_{\text{soln}}$ and $D(\text{An-R})_{\text{gas}}$ values for the complexes are given in Table 2, $D(\text{L}_3\text{An-R})$ being formally defined as in eq. 7 for the gas-phase reaction represented in eq. 8.

$$D(\text{L}_3\text{An-R})_{\text{gas}} = \Delta H^\circ_f(\text{L}_3\text{An})_{\text{gas}} + \Delta H^\circ_f(\text{R}^\cdot)_{\text{gas}} - \Delta H^\circ_f(\text{L}_3\text{An-R})_{\text{gas}} \quad (7)$$



It can be seen that the present $D(\text{Th-R})$ values are in good agreement with those derived for the Cp₃ThR series by Sonnenberger and co-workers [2]. The values for the Ind₃ThR series parallel but are slightly larger (by ca. 25 kJ mol⁻¹) than those for the analogous Cp₃ThR series.

For the present (C₉H₇)₃ThR compounds, the sequence of $D(\text{Th-R})$ values is CH₂Si(CH₃)₃ > CH₃ > CH(CH₃)₂ > CH₂C₆H₅, which closely parallels that in the Cp₃ThR series [2] and in *d*-element complexes [17a,20]. In the present case, it presumably reflects the Ind-R steric repulsions (which could be important) in the molecule, as well as the stability of the R[·] radical ($\Delta H^\circ_f(\text{R}^\cdot)_g$ in eq. 7). Bond disruption enthalpy values for ethylindenyl and corresponding indenyl complexes of Th and U are not indistinguishable from each other within their uncertainty range.

It is obvious that thorium and uranium hydrocarbyl bonds in the tetravalent tris(indenyl) series are rather strong. The observed $D(\text{An-R})$ values of 340–400 kJ mol⁻¹ are substantially in excess the values, in the 200 kJ mol⁻¹ range, reported for a number of types of middle and late transition metal complexes [13,20,21]. The present $D(\text{An-R})$ values are also somewhat larger than those of analogous $D(\text{M-R})$ values for Cp'₂MR₂ complexes of group 4 (Cp' = (CH₃)₅C₅), i.e., 271 kJ mol⁻¹ (M = Ti, R = CH₃), 280 kJ mol⁻¹ (M = Zr, R = CH₃), 269 kJ mol⁻¹ (M = Ti,

R = C₆H₅), 306 kJ mol⁻¹ (M = Zr, R = C₆H₅), 313 kJ mol⁻¹ (M = Hf, R = CH₃) [6,8].

Furthermore, uranium–hydrocarbyl bonds are weaker than those in corresponding thorium complexes by about 20 kJ mol⁻¹. Bruno and co-workers noticed the same behaviour in the bis(pentamethylcyclopentadienyl)actinide series; they observed a difference $D(\text{Th-R}) - D(\text{U-R})$ (with R = hydrocarbyl and hydride) of ca. 20 to 40 kJ mol⁻¹ [3]. At the most qualitative level, the general tendency towards rather high metal–ligand bond disruption enthalpies for actinides (and early transition elements) can be interpreted in terms of simple Pauling bond ionicity/bond energy concepts [22]. The highly electropositive character of the actinide metals, modified, of course, by bonding ligands, would be expected, a priori to give rise to relatively large bond energies; thus eq. 8 should correspond to highly endothermic process. The highly polar character of actinide to carbon sigma bonds is evident in their chemistry [23]. In respect of the difference between $D(\text{Th-R})$ and $D(\text{U-R})$, it should be noted that eq. 8 implies a formal An^{IV} → An^{III} reduction process. The tendency for actinides to show an increasing stable trivalent state with increasing Z is well known [24].

Why $D(\text{Th-R})$ values are consistently higher for the Ind₃ThR series than for the Cp₃ThR series is still an open question. For example, the three indenyl rings in Ind₃AnR may additionally stabilize the tetravalent or destabilize the trivalent thorium oxidation state, thus making more endothermic the process described by eq. 8.

In this study use was made of the value for $D(\text{An-O})$ employed for the study of cyclopentadienyl compounds [1–3], but $D(\text{An-O})$ may, in fact, be different and slightly dependent on the supporting ligands. Indications of a greater 5f covalency were found from photoelectron spectroscopy studies for bonding of the ring ligand in indenyl complexes [25]. Differential π-accepting tendencies of the Ind₃An and Cp₃An centres, may significantly influence the bonding of the hydrocarbyl and alkoxyde ligands, hence the observed exothermicity of eq. 2.

Acknowledgment

We are grateful to the Inter-University Institute for Nuclear Sciences (Brussels) for financial support of the Laboratory of Analytical Chemistry and Radiochemistry of the University of Liège.

References

- 1 J.W. Bruno, T.J. Marks and L.R. Morss, *J. Am. Chem. Soc.*, 105 (1983) 6824.
- 2 D.C. Sonnenberger, L.R. Morss and T.J. Marks, *Organometallics*, 4 (1985) 352.
- 3 J.W. Bruno, H.A. Stecher, L.R. Morss, D.C. Sonnenberger and T.J. Marks, *J. Am. Chem. Soc.*, 108 (1986) 7275.
- 4 G.M. Smith, H. Suzuki, D.C. Sonnenberger, V.W. Day and T.J. Marks, *Organometallics*, 5 (1986) 549.
- 5 L.E. Schock, A.M. Seyam, M. Sabat and T.J. Marks, *Polyhedron*, 7 (1988) 1517.
- 6 L.E. Schock and T.J. Marks, *J. Am. Chem. Soc.*, 110 (1988) 7701.
- 7 For leading references see: [1–6] and ref. cited therein.
- 8 (a) A.R. Dias, M.S. Salema, J.A.M. Simoes, J.W. Pattiasina and J.H. Teuben, *J. Organomet. Chem.*, 346 (1988) C4; (b) A.R. Dias, M.S. Salema, J.A.M. Simoes, J.W. Pattiasina and J.H. Teuben, *ibid.*, 364 (1989) 97.

- 9 (a) J. Goffart, B. Gilbert and G. Duyckaerts, *Inorg. Nucl. Chem. Lett.*, 13 (1977) 189. (b) M.R. Spirlet, J. Rebizant, S. Bettonville and J. Goffart, Crystallographic structures of the thorium compounds were determined and presented at "19^{èmes} Journées des Actinides" in Madonna di Campiglio, 29–31 march, Italy; to be published. (c) The NMR spectrum shows that slightly different ethylindenyl groups are present in the product. This is probably due in solution to constant exchange of the position of the ethyl groups. This seems to be corroborated by the crystal structure [9b], which indicates different conformations of the ethyl group in the solid.
- 10 E.J. Prosen and M.V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, A77, p. 581.
- 11 G. Öjelund and I. Wadsö, *Acta Chem. Scand.*, 22 (1968) 2691.
- 12 J. Rebizant, M.R. Spirlet, S. Bettonville and J. Goffart, to be published.
- 13 J.A. Connor, M.T. Zafarani-Moettar, J. Bickerton, N.A. Saied, S. Suradi, R. Carson, G.A. Takhin and H.A. Skinner, *Organometallics*, 1 (1982) 1166 and ref. cited therein.
- 14 (a) Thermodynamic Research Center Data Tables, Texas A&M University, College Station, TX; (b) C.H. Rochester and J.R. Symonds, *J. Chem. Soc., Faraday Trans. I*, 69 (1973) 1267.
- 15 (a) H.L. Clever and K.-Y. Hsu, *Sci. Data Mixtures, Ser. A14*, 1975; (b) B.S. Harsted and E.S. Thomsen, *J. Chem. Thermodyn.*, 7 (1975) 369; (c) J. Cone, L.E.S. Smith and W.A. Van Hook, *ibid.*, 11 (1979) 277; (d) R. Battino and K. Marsh, *Aust. J. Chem.*, 33 (1980) 1997.
- 16 M.F. Lappert, D.S. Patil and J.B. Pedley, *J. Chem. Soc., Chem. Commun.*, (1975) 830.
- 17 (a) J.A. Connor, *Top. Curr. Chem.*, 71 (1977) 71; (b) D.C. Bradley and M.J. Hillyer, *Trans. Faraday Soc.*, 62 (1966) 2367, 2374; (c) Y.K. Shaulov, V.G. Genchel, R.M. Aizatullova and N.N. Petrova, *Russ. J. Phys. Chem. (Engl. Transl.)*, 46 (1972) 1360; (d) V.G. Genchel, E.A. Volchkova, R.M. Aizatullova and Y.K. Shaulov, *ibid.*, 47 (1973) 643.
- 18 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm and R.L. Nuttall, *NBS Tech. Note (U.S.)*, 1981, No. 270-8.
- 19 D.F. McMillen and D.M. Golden, *Annu. Rev. Phys. Chem.*, 33 (1982) 493.
- 20 (a) G. Pilcher and H.A. Skinner, *In The Chemistry of the Metal-Carbon Bond in*; F.R. Hartley and S. Patai (Eds.), Wiley, New York, 1982, p. 43–90; (b) J. Halpern, *Acc. Chem. Res.*, 15 (1982) 238; (c) J.U. Mondal and D.M. Blake, *Coord. Chem. Rev.*, 47 (1982) 205; (d) M. Mansson, *Pure Appl. Chem.*, 55 (1983) 417; (e) H.A. Skinner and J.A. Connor, *Pure Appl. Chem.*, 57 (1985) 79; (f) R.G. Pearson, *Chem. Rev.*, 85 (1985) 41.
- 22 (a) G. Al-Takhin, J.A. Connor and H.A. Skinner, *J. Organomet. Chem.*, 259 (1983) 313; (b) J. Halpern, S.-H. Kim and T.W. Leung, *J. Am. Chem. Soc.*, 106 (1984) 8317; (c) F.T.T. Ng, G.L. Rempel and J. Halpern, *Inorg. Chim. Acta*, 77 (1983) L165; (d) F.T.T. Ng, G.L. Rempel and J. Halpern, *J. Am. Chem. Soc.*, 104 (1982) 621; (e) T.T. Tsou, M. Loots and J. Halpern, *ibid.*, 104 (1982) 623; (f) M.J. Calhorda, A.R. Dias, M.S. Salema and J.A.M. Simoes, *J. Organomet. Chem.*, 255 (1983) 81; (g) A.R. Dias, M.S. Salema and J.A.M. Simoes, *Organometallics*, 1 (1982) 971; (h) J.C.G. Calado, A.R. Dias, M.F.M. Piedade and J.A.M. Simoes, *Rev. Port. Quim.*, 22 (1980) 53; (i) R.G. Finke and B.P. Hay, *Inorg. Chem.*, 23 (1984) 3041; (j) R.G. Finke, B.L. Smith, B.J. Mayer and A.A. Molinero, *ibid.*, 22 (1983) 3677.
- 22 (a) L. Pauling, *The nature of the chemical bond*, 3rd edit., Cornell University Press, Ithaca, New York, 1960; Chapter 3; (b) J.E. Huheey, *Inorganic Chemistry*, 3rd edit., Harper and Row, New York, 1983, p. 144–160.
- 23 (a) T.J. Marks and I.L. Fragala, *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, D. Reidel, Dordrecht, Holland, 1979; (b) T.J. Marks and R.D. Ernst, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Chapter 21; (c) T.J. Marks, *Science (Washington, DC)*, 217 (1982) 989; (d) T.J. Marks and R.D. Fischer, *Organometallics of the f-Elements*, D. Reidel, Dordrecht, Holland, 1979; (e) P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam and T.J. Marks, *J. Am. Chem. Soc.*, 103 (1981) 6650.
- 24 (a) S.G. Bratsch and J.J. Lagowski, *J. Phys. Chem.*, 90 (1986) 307; (b) L.J. Nugent, in K.W. Bagnall (Ed.), *MTP Int. Rev. Sci., Inorg. Chem. Series two*; University Park Press, Baltimore, 1976, Vol. 7, Chapter 6.
- 25 I.L. Fragala, J. Goffart, G. Granozzi and E. Ciliberto, *Inorg. Chem.*, 22 (1983) 216.