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Organo-*f*-element thermochemistry. Uranium(III)–Tetrahydrofuran bond disruption enthalpy in an indenyl compound

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Abstract

The U–THF (THF = tetrahydrofuran) bond disruption enthalpy in tris(indenyl)uranium tetrahydrofuranate has been obtained by iodinolysis batch-titration solution calorimetry. The $D[(C_9H_7)_3U–THF]$ value in toluene solution is (71.3 ± 5.2) kJ mol^{-1}.

Introduction

To understand thermochemically stoichiometric and catalytic reactions involving organometallic species it is necessary to have quantitative information, especially metal–ligand bond disruption enthalpies [1]. This is the reason for our present interest in organoactinides. In this paper we focus on the determination of the absolute bond disruption enthalpy of $(C_9H_7)_3U–THF$ by the measurement of the heat of reaction associated with the iodinolysis process described by eq. 1:

$$(C_9H_7)_3U–THF + \tfrac{1}{2}I_2 \rightarrow (C_9H_7)_3UI + THF \qquad (1)$$

Experimental

All the organoactinide compounds were handled in a glovebox under purified nitrogen or argon. Pentane and toluene were dried over sodium or potassium and distilled immediately prior to use.

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Synthesis of $(C_9H_7)_3U{-}THF$

Potassium (69.5 mmol) was added to a dry and degassed tetrahydrofuran solution of indene. When reaction was complete a stoichiometric amount of UCl_3 was added. The mixture was stirred at room temperature for 4 days. The solvent was removed *in vacuo* and the brown residue extracted with pentane for 8 days (yield 35%): ^1H (C_6D_6 in ppm from C_6D_5H 7.15): δ 7.29 (s, 6H), 5.84 (s, 6H), −13.17 (s, 3H), −28.41 (s, 6H). IR (CsI pellet, cm^{-1}): 3061.0(m), 2971.1(m), 2887.4(m), 1605.1(w), 1477.4(m), 1459.0(m), 1334.6(s), 1318.5(w), 1217.0(m), 1067.0(m), 1036.0(m), 1012.6(m), 863.9(m), 765.2(s), 715.8(m), 438.0(s), 205.5(m). Analysis: Found: C, 56.64; H, 4.35; U, 36.58. Calc.: C, 56.79; H, 4.46; U, 36.31.

Analytical methods

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

Results and discussion

Three important differences can be seen between the IR-spectrum of $(C_9H_7)_3U$ previously described [2] and that of $(C_9H_7)_3U{-}THF$: (1) The aliphatic C–H stretching vibrations are observed at 2971.1 and 2887.4 cm^{-1} respectively. (2) For the THF adduct there is a bond at 863.9 cm^{-1}, assigned to the C–O–C stretching vibration of THF (909 cm^{-1} in free THF) [3]. (3) The IR band observed at 250 cm^{-1} in the $(C_9H_7)_3U$ spectrum which can be assigned to the metal–η^5 ring vibration [4], is shifted to 210 cm^{-1} in THF adduct. In this kind of molecule the signals from the THF in the ^1H NMR spectrum are broad, and moreover one of them is probably superimposed upon another.

The isoperibol calorimeter and the experimental procedure employed to measure the heats of reaction have been described elsewhere [2,5]. For meaningful calorimetric measurements it is necessary to have a reaction which is quantitative, selective and rapid, and that these criteria were met was confirmed by NMR and IR spectroscopy for the iodinolysis process described by eq. 1.

The bond disruption enthalpy $D[(C_9H_7)_3U{-}THF]$ is derived from the following thermochemical cycle:

$$\begin{array}{ll}
(C_9H_7)_3U{-}THF + \frac{1}{2}I_2 \rightarrow (C_9H_7)UI + THF & \Delta H_1 \\
(C_9H_7)_3UI \rightarrow (C_9H_7)_3U + \frac{1}{2}I_2 & -\Delta H_{react} \\
\hline
(C_9H_7)_3U{-}THF \rightarrow (C_9H_7)_3U + THF & D(U{-}THF)
\end{array}$$

The results are summarized in Table 1.

Table 1

Enthalpy of reaction with I_2 in toluene solution (kJ mol^{-1})

	Per mole of I_2 [a]	Per mole of complex
ΔH_1	-239.8 ± 10.0	-119.9 ± 5.0
ΔH_{react}	-382.3 ± 3.2 [2]	-191.2 ± 1.6
$D(U{-}THF)$		71.3 ± 5.2

[a] Error limits refer to the 95% confidence limits.

Schock and al. [6] previously obtained a value of D(U–THF) of 41.0 ± 0.8 kJ mol^{-1} for (η^5-$(CH_3)_3SiC_5H_4)_3U$–THF. The difference between the D(L_3U–THF) values for $L = \eta^5$-$(CH_3)_3SiC_5H_4$ and $L = \eta^5$-C_9H_7 may result from ligand steric hindrance, which is more important in the cyclopentadienyl than the indenyl organouranium compound [7]. It thus appears that the bond disruption enthalpy D(U–THF) is rather sensitive to the steric hindrance by the ancillary ligands.

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