Organo-f-element thermochemistry. Absolute uranium–ligand bond disruption enthalpies of [UL_3–SX] complexes ($L = C_5H_4{}^tBu$, $C_5H_4SiMe_3$ or $C_9H_6SiMe_3$ and $X = Et$ or ${}^tBu$)

X. Jemine and J. Goffart

Laboratory of Analytical Chemistry and Radiochemistry, University of Liège, Sart Tilman, B4000 Liège (Belgium)

P.C. Leverd and M. Ephritikhine

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA / Saclay, 91191, Gif sur Yvette (France)

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Abstract

The absolute uranium–ligand bond disruption enthalpies for the series of compounds $U(Cp')_3SEt$, $U(Cp^*)_3SX$ ($X = Et$ or ${}^tBu$) and $U(Ind^*)_3SEt$ [$Cp' = C_5H_4{}^tBu$, $Cp^* = C_5H_4SiMe_3$ and $Ind^* = C_9H_6SiMe_3$] have been measured by an oxidative addition process involving batch-titration solution calorimetry in toluene. The derived values are as follows (kJ mol^{-1}): 252 ± 8 (Cp′, Et); 266 ± 9 (Cp*, Et); 158 ± 8 (Cp*, ^{t}Bu) and 158 ± 8 (Ind *, Et).

Key words: Uranium; Calorimetry

1. Introduction

The importance of sulphur in industry (vulcanisation of rubber [1]), in agriculture, in biology (protein transformations [2]) and in air pollution is well known. Although the breaking of formation of the metal–sulphur bond is of paramount importance to our understanding of a considerable number of chemical processes, no absolute thermodynamic data for the actinide–sulphur bond disruption enthalpies have been published. We report here the absolute bond disruption enthalpy [D(U–S)] for $U(Cp')_3SEt$, $U(Cp^*)_3SX$ ($X = Et$ or ${}^tBu$) and $U(Ind^*)_3SEt$.

2. Experimental details

All the organoactinide compounds were handled in Schlenk-type glassware, and solid or solution transfers were performed in a glove box under purified nitrogen or argon. Solvents were purified by standard methods and distilled immediately prior to use.

2.1. Synthesis of $U(Ind^*)_3$

To a tetrahydrofuran solution of 6×10^{-3} mol of UCl_3 was added a solution of 18×10^{-3} mol of Ind^*K [3] in a pentane (100 ml)/tetrahydrofuran (15 ml) mixture. The solution was stirred for 5 days, the solvents then removed *in vacuum*, and the brown residue extracted with pentane for 3 days (yield 76%). ${}^1H$ NMR (C_6D_6 in ppm from C_6D_5H 7.28 ppm): δ 7.02 (s, 3H); 4.20 (s, 3H); 4.11 (s, 3H); 0.48 (s, 27H); −11.78 (s, 3H); −17.73 (s, 3H); −18.95 (s, 3H). IR: (hexachlorobutadiene, Nujol, polyethylene) 2955m, 2900m, 1245m, 835s, 243s cm^{-1}. Anal. found: C, 53.74; H, 5.95; Si, 9.76; U, 30.71. Calc.: C, 54.06; H, 5.67; Si, 10.53; U, 29.76%.

2.2. Reactions of UL_3 ($L = Cp'$, Cp^* and Ind^*) with XSSX reagents ($X = Et$ and ${}^tBu$)

An NMR tube was charged with UL_3 (*ca.* 10 mg) and 0.5 molar equivalent of XSSX reagent in toluene

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Correspondence to: Professor J. Goffart.

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d_8 (0.4 ml). The solution immediately turned from green to red, and the spectrum showed the quantitative formation of UL_3SX.

As previously reported by Anderson and coworkers [4], triscyclopentadienyl uranium thiolate complexes can also be obtained by oxidation of L_3U with the corresponding thiol. The complete characterisation of these compounds, including the X ray crystal structure of $(C_5H_5)_3USMe$, their reaction and redox properties will be described elsewhere.

2.3. Analytical methods

Proton NMR spectra were recorded on Bruker AM400 (FT, 400.1 MHz) instrument, IR spectra on a Bruker IFS66 spectrophotometer and near-infrared visible (NIR-Vis) spectra on a Perkin-Elmer Lambda 9 spectrophotometer. Elemental analysis was carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany.

2.4. Titration calorimetry

The isoperibol calorimeter employed in this study, and the general experimental procedure, have been described elsewhere [5]. About 150 mg of the organometallic compound were dissolved under argon in very pure toluene and the solution was placed in the calorimeter. A freshly prepared solution of XSSX in toluene was then added, and the reaction heat measured. The enthalpy of reaction per mole of complex was obtained by the procedure described previously [5].

3. Results and discussion

The "absolute" bond disruption enthalpies [D(U–S)], neglecting solvent effects, possible U–U interaction in L_3U,..., were calculated from the oxidative-addition reaction illustrated in eqns. (1–3):

$$UL_3\ (L = Cp', Cp^{\star} \text{ or } Ind^{\star}) + \tfrac{1}{2}\ EtSSEt \longrightarrow UL_3SEt \quad \Delta H_{ox} \qquad (1)$$

$$U(Cp^{\star})_3 + \tfrac{1}{2}\ {}^tBuSS^tBu \longrightarrow U(Cp^{\star})_3S^tBu \quad \Delta H_{ox} \qquad (2)$$

$$D[UL_3\text{–}SX] = \tfrac{1}{2}\ D[XS\text{–}SX] - \Delta H_{ox} \qquad (3)$$

The thermochemical data are presented in Table 1. The values of D[EtS–SEt] and D[^{t}BuS–S^{t}Bu] needed for the derivation of D[UL_3–SX] were taken from the literature [2].

The uncertainty in the absolute D[UL_3–SX] values is mainly because of the large uncertainty in the value of D[XS–SX]. The disruption enthalpy of the sulphur–sulphur bond is given by the expression:

$$D[XS\text{–}SX] = 2\ \Delta H_f^0(XS)_g + \Delta H_f^0(XS\text{–}SX)_g \qquad (4)$$

However the heat of formation of the XS radical is not known with a high accuracy [2]. It is important to realise that the difference, ΔH_{ox} is not subject to this uncertainty; only the absolute D-values are affected.

TABLE 1. Enthalpies of reaction with XS–SX in toluene (per mole of complex) and the derived bond-disruption enthalpies (kJ mol^{-1}) for uranium complexes (95% confidence)

L	X	ΔH_{ox}	D[XS–SX]	D[UL_3–SX]
Cp′	Et	-109.8 ± 2.3	285 ± 16	252 ± 8
Cp*	Et	-123.1 ± 4.0	285 ± 16	266 ± 9
Ind*	Et	-15.8 ± 1.6	285 ± 16	158 ± 8
Cp*	^{t}Bu	-15.5 ± 2.3	285 ± 16	158 ± 8

It is immediately apparent from the data in Table 1 that U–S bond disruption enthalpies are influenced by the nature of the ligands. In contrast to the value of D[AnL_3–H] (An = Th, U)$^{\bullet}$, like that of the D[AnL_3–I] [6,7], the value of D[UL_3–SX] appears to be slightly influenced by the electron-donating ability of the ligands because D[UCp'_3–SEt] and D[$UCp^{\star}_3$–SEt] are respectively 252 ± 8 and 266 ± 9 kJ mol^{-1}. However, the value of D[UL_3–SX] is very much affected by the increase of the size of the L or X groups, and is lowered to 158 ± 8 kJ mol^{-1} for D[$UCp^{\star}_3$–S^{t}Bu] and D[$UInd^{\star}_3$–SEt].

Since the ΔH_{ox} value for reaction (2, L = Cp*) is about 100 kJ mol^{-1} less exothermic than the ΔH_{ox} value for reaction (1, L = Cp*), by subtracting this difference from the ΔH_{ox} values obtained for L = Cp′ and L = Ind* in reaction (1), the enthalpy values for the corresponding reactions (2) are given as *ca.* 0 and 100 kJ mol^{-1}, respectively. From this thermochemical finding and from the entropic driving, the synthesis of UL_3SX where L = Cp′ or Ind* from the oxidative-

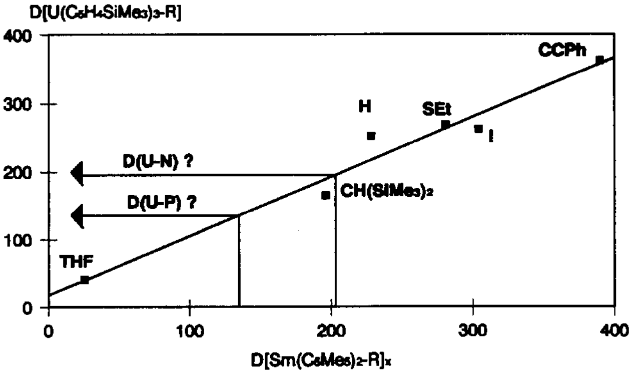

Fig. 1. Comparison of measured D[$Sm(C_5Me_5)_2$–R]$_x$ data to those of corresponding D[$U(C_5H_4SiMe_3)_3$–R] (kJ mol^{-1}).

addition reaction (5) seems to be impossible, and this is in agreement with the experiments.

$$\mathrm{UL_3\ (L = Cp'\ or\ Ind^*) + \tfrac{1}{2}\ {}^tBuSS{}^tBu \longrightarrow UL_3S{}^tBu} \quad \Delta H_{ox} \quad (5)$$

$\Delta H_{ox} \approx 0$ kJ mol^{-1} (L = Cp′)

$\Delta H_{ox} \approx 100$ kJ mol^{-1} (L = Ind*)

That ^{t}BuSS^{t}Bu reacts with UCp$^*_3$ but not with UCp$'_3$ can be explained by the more facile initial coordination of the sulphide reagent to the less electron-rich metallocene UCp$^*_3$; it was previously demonstrated that the latter gave a much less labile adduct with tetrahydrofuran than UCp$'_3$ [8].

Nolan *et al.* [9] have shown that a linear correlation exists between the D[U($C_5H_4SiMe_3)_3$–R] and D[Sm-$(C_5Me_5)_2$–R]$_x$ values ($X = 1$ for R = alkyl, I, THF and $X = 2$ for R = H) (estimated value for Sm$(C_5Me_5)_2$SEt from Sm$(C_5Me_5)_2$S^{n}Pr) for values about 30 kJ mol^{-1} lower than those for uranium compound (Fig. 1). The values that we have found for R = H [6] and R = SEt confirm the validity of this correlation. It can be predicted that the values of D[U–O] [10], D[U–N] and D[U–P] should be *ca.* 310, 190 and 130 kJ mol^{-1}, respectively.

Acknowledgments

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