Absolute Uranium–Ligand Bond-disruption Enthalpies of $[U(C_5H_4R)_3X]$ Complexes ($X = I$ or H, $R = Bu^t$ or $SiMe_3$)

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The absolute uranium–ligand bond-disruption enthalpies (kJ mol^{-1}) of the series $[U(C_5H_4R)_3X]$ ($X =$ H or I, $R = Bu^t$ or $SiMe_3$) have been measured by iodinolysis batch-titration solution calorimetry in toluene: $R = Bu^t$, 246.3 ± 5.3 ($X = I$), 249.7 ± 5.7 ($X = H$); $R = SiMe_3$, 265.6 ± 4.3 ($X = I$), 251.7 ± 5.1 ($X = H$).

The breaking or formation of metal–hydrogen and –methyl bonds is an integral part of most elementary reaction steps in catalytic reactions.[1,2] A knowledge of the corresponding bond-disruption enthalpies is of fundamental importance in understanding/predicting organometallic reaction pathways. By alcoholytic isoperibol titration, Marks and co-workers have determined the relative solution-phase homolytic disruption enthalpies in the complexes $[\{Th(C_5Me_5)_2H_2\}_2]$,[3] $[Th(C_5Me_5)_2(OR)H]$[4] and $[U(C_5Me_5)_2(OSiBu^tMe_2)H]$[4] ($R = CHBu^t{}_2$ or $2,6\text{-}Bu^t{}_2C_6H_3$). The values of $\bar{D}$(Th–H) and D(U–H) were found to be *ca.* 388 and 342 kJ mol^{-1}, respectively, by using $\bar{D}(Th–O) = 518.8$ kJ mol^{-1} and $D(U–O) = 481.2$ kJ mol^{-1}. These values are much greater than those of the transition-metal hydride bond-dissociation energies which are all close to 250 kJ mol^{-1}.[5] It seemed to us of interest to measure absolute D(U–H) values and here we report and discuss briefly the results of thermochemical experiments leading to these values in the uranium(IV) hydrides $[U(C_5H_4R)_3H]$ ($R = Bu^t$ or $SiMe_3$).[6,7]

Results and Discussion

The absolute bond-disruption enthalpies D(U–H) and D(U–I) were calculated by published methods[8–12] illustrated by equations (1)–(6) ($L = C_5H_4Bu^t$ or $C_5H_4SiMe_3$). The thermochemical data corresponding to the oxidative-addition reaction (1) and the ligand-exchange reaction (2) are presented in Tables 1 and 2, respectively.

$$[UL_3I] \xrightarrow{-\Delta H_{ox}} [UL_3] + \tfrac{1}{2}I_2 \quad (1)$$

$$[UL_3H] + \tfrac{1}{2}I_2 \xrightarrow{\Delta H_{rx}} [UL_3I] + \tfrac{1}{2}H_2 \quad (2)$$

$$\tfrac{1}{2}H_2 \xrightarrow{\frac{1}{2}D(H\text{–}H)} H^* \quad (3)$$

$$[UL_3H] \xrightarrow{D(L_3U\text{–}H)} [UL_3] + H^* \quad (4)$$

$$D(L_3U\text{–}H) = \Delta H_{rx} - \Delta H_{ox} + \tfrac{1}{2}D(H\text{–}H) \quad (5)$$

$$D(L_3U\text{–}I) = -\Delta H_{ox} + \tfrac{1}{2}D(I\text{–}I) \quad (6)$$

The values of D(I–I) and D(H–H) which are necessary for the derivation of D(U–I) and D(U–H) have been taken from the literature.[5,13] The enthalpies of solution in toluene are quite small and very similar to those of a vast variety of complexes.[3,4,8–10,14–16] The derivation of D(U–R) values from solution data assumes that solvation effects in toluene can be cancelled out.

Table 1 Enthalpies of reaction with I_2 in toluene (per mol of I_2) and the derived bond-disruption enthalpies (kJ mol^{-1}) for uranium complexes (95% confidence)

L	ΔH_{ox}	$D(L_3U\text{–}I)_{soln.}$
$C_5H_4Bu^t$	-341.2 ± 10.6	246.3 ± 5.3
$C_5H_4SiMe_3$	-379.9 ± 8.6	265.6 ± 4.3

Table 2 Enthalpies of solution (ΔH_{soln}) in toluene, enthalpies of reaction with I_2 (per mol of I_2) and the derived bond-disruption enthalpies of L_3U–H complexes (kJ mol^{-1}) (95% confidence)

L	ΔH_{soln}	ΔH_{rx}	$D(L_3U\text{–}H)_{soln.}$
$C_5H_4Bu^t$	15.0 ± 1.3	-273.9 ± 4.0	249.7 ± 5.7
$C_5H_4SiMe_3$	15.5 ± 1.9	-308.6 ± 5.6	251.7 ± 5.1

The value of $D[U(C_5H_4SiMe_3)_3I]$, 265.6 ± 4.3 kJ mol^{-1}, is similar to that recently reported,[8] 261.1 ± 1.7 kJ mol^{-1}. It is also quite similar to those found for $D[U(C_9H_7)_3I]$,[9] 266.8 ± 3.2 kJ mol^{-1}, or calculated for $D_1(UI_4)$, 274.8 ± 26.6 kJ mol^{-1} from published data,[17] but is significantly greater than that determined for $D[U(C_5H_4Bu^t)_3I]$, 246.3 kJ mol^{-1}. This difference should be accounted for by the greater electron-donating ability of the $C_5H_4Bu^t$ ligands which would weaken the metal–halide bond.

The absolute uranium–hydrogen bond-disruption enthalpies in $[U(C_5H_4Bu^t)_3H]$ and $[U(C_5H_4SiMe_3)_3H]$ are respectively 249.7 ± 5.7 and 251.7 ± 5.1 kJ mol^{-1}. It is noteworthy that these values are similar to the small number of available D(M–H) data for transition-metal complexes, all of which fall near 250 kJ mol^{-1}.[5] These D(U–H) values can also be compared with $\bar{D}$(U–H) for UH_3 [equations (7) and (8)], 260.33 ± 0.04 kJ mol^{-1} calculated from literature thermochemical data.[13,18]

$$UH_3 \longrightarrow U + 3H^* \quad (7)$$

$$\bar{D}(U\text{–}H) = \tfrac{1}{3}[3\Delta H_f(H^*) - \Delta H_f(UH_3)] \quad (8)$$

The uranium–hydride bond-disruption enthalpy is similar to the uranium–iodide disruption enthalpy; a similar observation has already been made for the corresponding Group 4 complexes.[14] The D(U–H) values derived from $[U(C_5H_4R)_3]$/$[U(C_5H_4R)_3H]$ iodinolysis are much smaller than that derived from the alcoholysis of $[U(C_5Me_5)_2(OSiBu^tMe_2)H]$.[4] The origin of this disparity should reside in the difficulty in quantifying structural differences, but essentially in limitations on the transferability of $\bar{D}$(U–OR′) data. These problems have been already discussed in detail.[5,9,14,19]

It is interesting that the U–H bond disruption enthalpies in the complexes $[U(C_5H_4R)_3H]$ are not influenced by the nature of the cyclopentadienyl ring substituents R, *i.e.* Bu^t or $SiMe_3$, which are respectively an electron donor and an electron acceptor. These observations, and the aforementioned $\bar{D}(UH_3)/D[U(C_5H_4R)_3H]$ results, suggest that a hydride is a more reliable 'anchor' than an alkoxide or even a halide. Marks and co-workers[8] have predicted, from thermochemical considerations, that the tris(cyclopentadienyl)uranium hydrides should not be stable because 'bimolecular H_2 elimination from such hydrides may be sufficiently close to thermoneutrality to be entropically driven (as well as driven by typical work-up procedures)'. The enthalpy of reaction was estimated to be *ca.* 21 kJ mol^{-1}; this energy may be calculated accurately and is equal to *ca.* 65 kJ mol^{-1}, still in the range where entropic factors may render reaction (9) possible.

$$2[U(C_5H_4R)_3H] \longrightarrow 2[U(C_5H_4R)_3] + H_2 \qquad (9)$$

The remarkable stability of the hydrides $[U(C_5H_4R)_3H]$ ($R = Bu^t$ or $SiMe_3$), in contrast to that of $[U(C_5H_5)_3H]$ which, despite many attempts, could never be isolated, is likely due to kinetic factors: the bulkiness of the substituted cyclopentadienyl ligands R should impede the collision between two molecules for bimolecular hydrogen elimination. In addition, the decomposition of $[U(C_5H_5)_3H]$ should be favoured in co-ordinating solvents by solvation of the trivalent metallocene $[U(C_5H_5)_3]$, in particular, $[U(C_5H_4R)_3]$ ($R = Bu^t$ or $SiMe_3$) form very labile tetrahydrofuran (thf) adducts in contrast to $[U(C_5H_5)_3]\cdot$thf which is thermochemically stable[20] and can be sublimed in a high vacuum.

On the other hand, it has been emphasized that the difference $D(M\text{–}H) - D(M\text{–}CH_3)$ is a sensitive and chemically important parameter which reflects variations in metal–ligand polarity and metal–ligand orbital repulsions.[8,21] Knowledge of $D(M\text{–}H) - D[M\text{–}C(alkyl)]$ is essential to predict the thermodynamic feasibility of chemical transformations such as β-H elimination. The magnitude of $D[U(C_5H_4SiMe_3)_3H] - [U(C_5H_4SiMe_3)_3Me]$[8] is 65 kJ mol^{-1} and that of $D[U(C_5H_4SiMe_3)_3H] - D[U(C_5H_4SiMe_3)_3R]$ (R′ = Bu, CH_2SiMe_3 or CH_2Ph) is 94 kJ mol^{-1}. These values are smaller than those of the middle and late transition-metal complexes where $D(M\text{–}H) - D[M\text{–}C(alkyl)]$ is typically equal to 125 kJ mol^{-1} and should explain why the tendency to β-hydride elimination appears to be least for actinide alkyl compounds.

Experimental

All operations were performed in an atmosphere of purified argon or nitrogen. Solvents were purified by standard methods and distilled just prior to use. The syntheses, characterizations and reactivity of $[U(C_5H_4R)_3H]$ ($R = Bu^t$ or $SiMe_3$) were previously described.[6]

Titration Calorimetry.—Prior to a calorimetric experiment the reactions to be studied were checked by ^1H NMR, IR and NIR–VIS spectroscopies to be clean, quantitative and rapid, three criteria required for accurate and meaningful calorimetry. The isoperibol calorimeter employed in this study and the general experimental procedure are described elsewhere.[11] For the organometallic compounds, about 150 mg of a complex were weighed accurately and placed in a glass cell (1.5 cm^3) which was then broken under argon in the calorimeter containing very pure toluene. The absorbed heat during the dissolution of the organometallic compound was recorded. A freshly prepared solution of I_2 in toluene was then added and the reaction heat measured. The enthalpy of reaction per mol of titrant was obtained by the procedure described previously.[12]

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