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Organo-*f*-element thermochemistry. Uranium–ligand bond disruption enthalpies in the $(C_9H_7)_3U/(C_9H_7)_3U{-}I/(C_9H_7)_3U{-}CH_3$ system

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Abstract

Uranium–ligand bond disruption enthalpies have been obtained by application of iodinolysis batch-titration solution calorimetry to the $(C_9H_7)_3U/(C_9H_7)_3U{-}I/(C_9H_7)_3U{-}CH_3$ system. Derived values in toluene solution are as follows: $(C_9H_7)_3U{-}I$, 266.8 ± 3.2 kJ mol^{-1}; $(C_9H_7)_3U{-}CH_3$, 196.3 ± 6.6 kJ mol^{-1}. The correlation between the latter value and that obtained recently by alcoholysis confirms that the value of D(U–I) is certainly a better parameter for placing D data on an absolute scale than D(U–O).

Introduction

The rapid developments in organometallic chemistry and catalysis have given rise to increasing interest [1] in organometallic thermochemistry [2–4].

To increase our knowledge and understanding of catalysis by organometallic species it is necessary to have available quantitative information, especially thermochemical, on the metal–carbon and metal–hydrogen bonds often involved in the essential steps.

Alcoholytic isoperibol titration calorimetry was used to determine relative values of homolytic bond disruption enthalpies, D (defined in eq. 1 and 2) by providing a

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measurement of the enthalpy of the reaction of the alcoholysis shown in 3 [2,3b,3c,4].

$$L_nAn{-}R \rightarrow L_nAn + R^{\bullet} \qquad (1)$$

$$D(L_nAn{-}R) = \Delta H_f^0(L_nAn) + \Delta H_f^0(R^{\bullet}) - \Delta H_f^0(L_nAn{-}R) \qquad (2)$$

$$L_nAn{-}R + R'O{-}H \rightarrow L_nAn{-}OR' + R{-}H \qquad (3)$$

The measured enthalpy change associated with eq. 3 can be expressed as the difference between the enthalpies of the bonds formed and ruptured during the process (eq. 4).

$$\Delta H_r = D(L_nAn{-}R) + D(R'O{-}H) - D(L_nAn{-}OR') - D(R{-}H) \qquad (4)$$

If D(An–O) is known accurately (which has not been the case up to now) the $D(L_nAn{-}R)$ bond disruption enthalpies can be placed on an absolute scale. An estimate of this D(An–O) value was derived from the known absolute data for actinide and the Ti, Zr, and Hf group 4 compounds on the basis of the following crude approximation shown in eq. 5 (X = a halogen) [2,4]:

$$\frac{D(L_nAn{-}OR')}{\bar{D}(AnX_4)} \approx \frac{\bar{D}(M(OR)_4)}{\bar{D}(MX_4)} \qquad (5)$$

It became apparent that these estimated values (518.8 and 481.2 kJ mol^{-1}, respectively, for thorium and uranium) are not only probably subject to substantial uncertainty but also present a serious problem of transferability [$\bar{D}(M(OR)_4) \rightarrow \bar{D}(An(OR)_4) \rightarrow D(L_nAn{-}OR')$].

We have now determined the uranium–iodine and uranium–methyl bond disruption enthalpy values in indenyl compounds by use of an absolute approach (proposed by Schock and Marks [3a] and based on eq. 6–11) which refer to a one-electron redox reaction.

$$\begin{array}{rcllr}
L_nU{-}X & \rightarrow & L_nU + \frac{1}{2}X_2 & -\Delta H_{\text{oxid}} & (6) \\
L_nU{-}R + X_2 & \rightarrow & L_nU{-}X + R{-}X & \Delta H_{\text{reac}} & (7) \\
X^{\bullet} & \rightarrow & \frac{1}{2}X_2 & -\frac{1}{2}D(X_2) & (8) \\
R{-}X & \rightarrow & R^{\bullet} + X^{\bullet} & D(R{-}X) & (9) \\
\hline
L_nU{-}R & \rightarrow & L_nU + R^{\bullet} & D(U{-}R) & (10)
\end{array}$$

$$D(U{-}R) = \Delta H_{\text{reac}} - \Delta H_{\text{oxid}} - \tfrac{1}{2}D(X_2) + D(R{-}X) \qquad (11)$$

The comparison between the $D(U{-}CH_3)$ values obtained recently for the $(C_9H_7)_3U{-}CH_3$ by alcoholysis (eq. 3) [4] and that obtained by iodinolysis allows correlation of the two approaches and extrapolation to give a D(U–O) value.

Experimental

Synthetic methods

All operations were performed under purified argon by Schlenk techniques, and solid or solution transfers were performed in a special glovebox under pure argon or nitrogen. Solvents were purified by standard methods and distilled just prior to use. $(C_9H_7)_3U{-}I$ and $(C_9H_7)_3U{-}CH_3$ were prepared and purified as described elsewhere [5].

Synthesis of $(C_9H_7)_3U$

To 1.5 mmol of uranium trichloride was added a solution of 4.5 mmol of C_9H_7Na in benzene. The mixture was stirred under reflux for 4 days and then filtered in a glovebox under pure nitrogen. The filtrate was evaporated under reduced pressure at room temperature to give a black solid, which was extracted with benzene for one week to give pure solid $(C_9H_7)_3U$ (yield: 55%). ^1H NMR (C_6D_6): δ (in ppm from TMS) 3.59 (s, 6H), 1.26 (s, 6H), −8.41 (s, 3H), −14.10 (s, 6H). IR (CsI pellet, cm^{-1}): 3050(m), 1610(w), 1480(m), 1460(m), 1340(s), 1320(m), 1035(m), 900(m), 765(s), 440(m), 245(m). Anal. Found: C, 55.58; H, 3.73; U, 40.71. $C_{27}H_{21}U$ calcd.: C, 55.58; H, 3.63; U, 40.79%.

Analytical methods

Proton NMR spectra were recorded on a Bruker AM400 (FT, 400.1 MHz) spectrometer. Infrared and near-infrared visible (NIR-Vis) spectra were recorded on a Perkin Elmer 580 and a Perkin-Elmer Lambda 9 spectrophotometer, respectively. Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Titration calorimetry

The isoperibol calorimeter employed in this study and the experimental procedure are described elsewhere [4]. Briefly, a solution of the reactant (I_2 in toluene, for example) is introduced into the reaction cell containing the organoactinide in toluene solution and the heat of reaction is recorded. An alternative procedure involved breaking ampoules containing weighted quantities of reactant (I_2) within the calorimeter cell containing the organoactinide toluene solution. In this case, the heat of reaction corresponds to the combination of two effects; namely the enthalpy of dissolution of the reactant (measured separately) and the enthalpy of reaction with the organoactinide.

Results and discussion

Before the calorimetric study, the reactions to be studied were shown to be clean, quantitative and rapid, three essential requirements for accurate and meaningful calorimetry. NIR-Vis and ^1H NMR spectrometry showed clearly that all these requirements were met. Figure 1 shows the experimental ^1H NMR spectra from which it can be seen that $(C_9H_7)_3U$ and $(C_9H_7)_3U{-}CH_3$ react with I_2 to give $(C_9H_7)_3U{-}I$ (eq. 12 and 13).

$$(C_9H_7)_3U + \tfrac{1}{2}I_2 \rightarrow (C_9H_7)_3U{-}I \qquad (12)$$

$$(C_9H_7)_3U{-}CH_3 + I_2 \rightarrow (C_9H_7)_3U{-}I + CH_3{-}I \qquad (13)$$

The appearance of methyl iodide in the reaction mixture (eq. 13) was clearly revealed by the presence of a peak (singlet) at $\delta = 1.4$ ppm in C_6D_6 in the NMR spectrum (checked by recording the spectrum of pure methyl iodide in C_6D_6).

Enthalpies of reactions 12 and 13 (per mol of I_2) are shown in Table 1 along with the D(U–R) values derived from solution data on the assumption that solvation effects in toluene make a minor contribution or at least cancel out. The published values of ΔH_{soln} for organoactinide compounds [2–4] and the literature data or

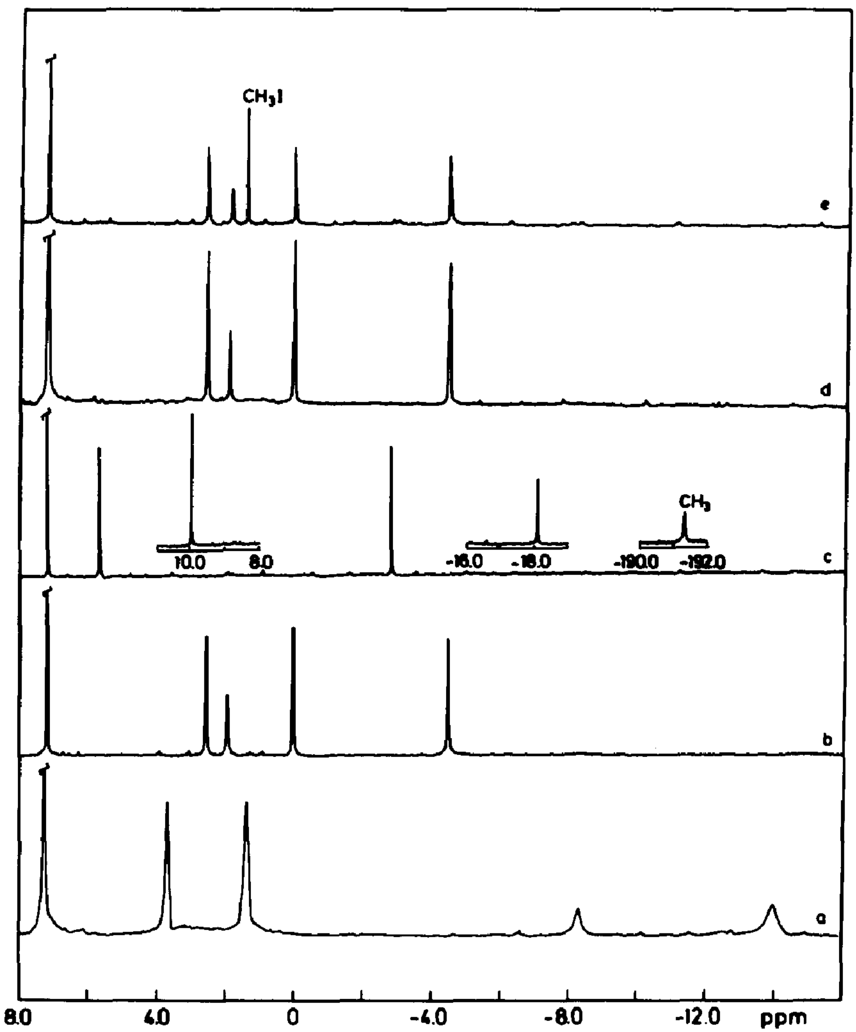

Fig. 1. ^1H NMR spectra (in C_6D_6): (a) $(C_9H_7)_3U$; (b) $(C_9H_7)_3U-I$; (c) $(C_9H_7)_3UCH_3$; (d) reaction $(C_9H_7)_3U+\frac{1}{2}I_2$; (e) reaction $(C_9H_7)_3U-CH_3+I_2$. Solvent peak is indicated by ~.

estimated values [6] for the other chemical components of the system confirm the cancellation of solvation effects in the $D(U-R)$ derivation.

$D(I-I)$ and $D(CH_3-I)$ data, needed for the determination of $D(U-I)$ and $D(U-CH_3)$, were calculated from literature data [7], as 151.2 and 239.5 kJ mol^{-1}, respectively, and the uncertainties in these values are taken into account in our final results.

The absolute value of $D[(C_9H_7)_3U-I]$ is 266.8 ± 3.2 kJ mol^{-1} (Table 1), which agrees well with the value of $D_1(UI_4) = 274.8 \pm 26.6$ kJ mol^{-1} defined in eq. 14 and 15 and calculated from published data [8].

$$UI_4(g) \rightarrow UI_3(g) + I^{\cdot}(g) \tag{14}$$

$$D_1(UI_4) = \Delta H_f^0(UI_3)(g) = \Delta H_f^0(I^{\cdot})(g) - \Delta H_f^0(UI_4)(g) \tag{15}$$

Table 1

Enthalpies of solution in toluene, enthalpies of reaction with I_2 in toluene (per mol of I_2)„ and derived bond disruption enthalpies for $(C_9H_7)_3U$–I and $(C_9H_7)_3U$–CH_3 complexes in kJ mol^{-1} (95% confidence limits)

Compound	ΔH_{soln}	$-\Delta H_{oxid/reac}$	$D(U-X/R)_{soln}$
$(C_9H_7)_3U$–I	19.2±2.4	–	–
$(C_9H_7)_3U$	14.4±1.3	382.3±3.2	266.8±3.2
$(C_9H_7)_3U$–CH_3	15.0±0.6	158.8±4.2	196.3±6.6

It can be concluded from this result that the three ancillary indenyl ligands in $(C_9H_7)_3U$–I do not significantly affect the nature of the uranium–iodide bond compared with that in I_3U–I. The U–I bond length in $(C_9H_7)_3U$–I of 3.041 Å [9a] is, in fact not much shorter than the sum of the ionic radii of U^{4+} and I^- (= 3.16 Å), and can be compared with the U–I (bridging) distances 3.08 and 3.11 Å and the U–I (terminal) distances 2.92 Å in UI_4 [9b].

The $D[(C_9H_7)_3U-CH_3]$ value derived in this work (Table 1) is lower by about 180 kJ mol^{-1} than the value derived from alcoholytic calorimetry and application of eq. 4 [4]. A major reason for the difference between the $D(U-CH_3)_{alc}$ and $D(U-CH_3)_{iod}$ values is probably uncertainty in the transferability of D(M–OR) values. The value of D(U–OR) (R = CH_2CF_3; $C(CH_3)_3$) was estimated as 481.2 kJ mol^{-1} by application of eq. 5 [2,4]. The transferability of observed D values between group 4 (Ti, Zr and Hf) tetrahalides and Th, U tetrahalides, and halide–alkoxide transferability within group 4 complexes, are generally very good [2,4]. In the case of the transferability $[\bar{D}(M(OR)_4) \rightarrow \bar{D}(U(OR)_4) \rightarrow D(Ind_3U-OR')]$, the transferability may be less reliable, especially for the step from $U(OR)_4$ to $(C_9H_7)_3U$–OR′. Indeed the latter conversion involves a substantial increase not only in the formal coordination number of the metal but also in interligand repulsion. Moreover, the indenyl-induced changes in metal electron density must

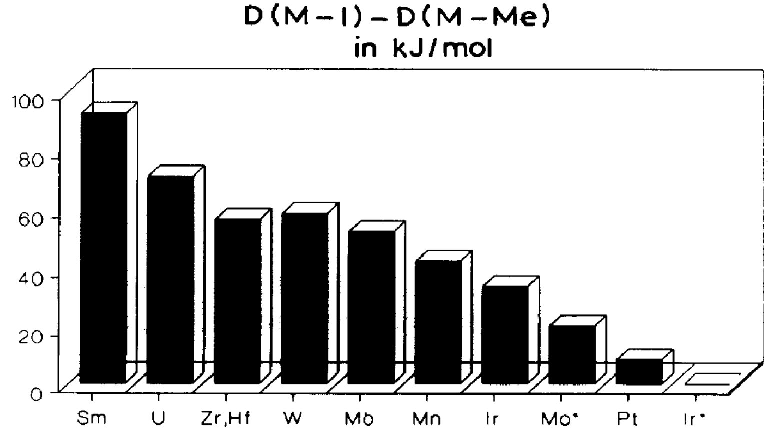

Fig. 2. Comparison of $D(M-I) - D(M-CH_3)$ for various metal complexes. Sm-Cp'_2SmR/X (R is $CH(SiMe_3)_2$) [3c]; U = this work; Zr,Hf = average $Cp'_2M(R/X)_2$ [3b]; W = $Cp_2W(R/X)_2$ [16]; Mo = $Cp_2Mo(R/X)_2$ [16]; Mn = $(CO)_5MnR/X$ [17]; Ir = $(PMe_3)(Cl)(I)(CO)IrR/X$ [18]; Mo* = $Cp(CO)_3MoR/X$ [19]; Pt = $(PPh_3)_2(I)PtR/X$ [18]; Ir* = $Cp'(PMe_3)Ir(R/X)_2$ [20].

influence to some extent the U–O bond. An important item of evidence in favor of this suggestion comes from a calorimetric study of Cp'_2ZrX_2 [3b], which revealed that the difference $D[Cp'_2Zr(OR)\text{–}OR] - D[CP'_2Zr(Cl)\text{–}Cl]$ is approximatively 110 kJ mol^{-1} lower than the reported value of $\bar{D}[Zr(OR')_4] - \bar{D}(ZrCl_4)$ [10] (whereas the value of $\bar{D}(ZrCl_4)$ is very close to that of $D_1(ZrCl_4)$; the values are 491.2 [7,10] and 486.0 kJ mol^{-1}, respectively [7]).

On the other hand Nolan et al. [3c] recently determined "in an absolute manner" (eq. 16) the bond disruption enthalpies for bis(pentamethylcyclopentadienyl)-samarium–L complexes (L = R, X, H, OR,...), and for $D(Cp'_2Sm\text{–}OC(CH_3)_3)$ found a value of 344.8 kJ mol^{-1}.

$$2\ Cp'_2Sm + (CH_3)_3CO\text{–}OC(CH_3)_3 \rightarrow (Cp'_2Sm\text{–}OC(CH_3)_3)_2 \qquad (16)$$

A very good linear correlation between $D(U\text{–}L)$ and $D(Sm\text{–}L)$ was observed (Fig. 3 of ref. 3c), the values being about 30 kJ mol^{-1} lower for uranium. If there is no serious discontinuity in this trend for L = OR, it is reasonable to assume that the value of $D(U\text{–}O)$ is fairly similar to that of $D(Sm\text{–}O)$. This seems to be confirmed by very recent works by Martinho Simoes et al., which indicate that the value of $D(U\text{–}O)$ is close to 380 kJ mol^{-1} [11].

Another important feature contributing the disparity between $D(U\text{–}CH_3)$ values derived from iodinolysis and alcoholysis may be steric effects, which are rather difficult to quantify. In terms of steric hindrance the transformations of $(C_9H_7)_3U$ or $(C_9H_7)_3U\text{–}CH_3$ into $(C_9H_7)_3U\text{–}I$, as (see eq. 12 and 13) by reaction with I_2, should show significant differences. The crystal structure of $(C_9H_7)_3U\text{–}I$ [9] reveals that each indenyl ring deviates significantly from planarity and there is an average bending of about 7° between the five and six-membered rings, in contrast with the situation for $(C_9H_7)_3U$, which has a zero dihedral angle [12].

Our $D(U\text{–}I)$ and $D(U\text{–}CH_3)$ values are in good agreement with those determined by Shock et al. for $Cp''_3U\text{–}R$ compounds [3a]. An interesting measure of the nature of the metal–ligand bonding may be provided by the parameter $D(M\text{–}I) - D(M\text{–}CH_3)$ (and its variants) [3a,b,c]. Figure 2 shows that the value of this parameter tends to decrease for the transition metals on going to the right in the Periodic Table. This effect can be accounted for in terms of arguments based on the Pauling electronegativity of the metal (Sm: X = 1.2 → Pt:X = 2.3 [13]), the polarisability of iodine [14] (its ability to adjust energetically to various bond polarity situations), and the attractive (or repulsive) interactions between filled ligand orbitals and empty (filled) metal orbitals [15].

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