

Thermodynamics of Benzylic C–H Activation in 18- and 19-Electron Iron Sandwich Complexes: Determination of pK_a values and Bond Dissociation Energies

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The pK_a values and bond dissociation energies of 19-electron complexes have been determined for the first time, supporting the concept of proton and hydrogen atom reservoirs for late transition-metal sandwich complexes.

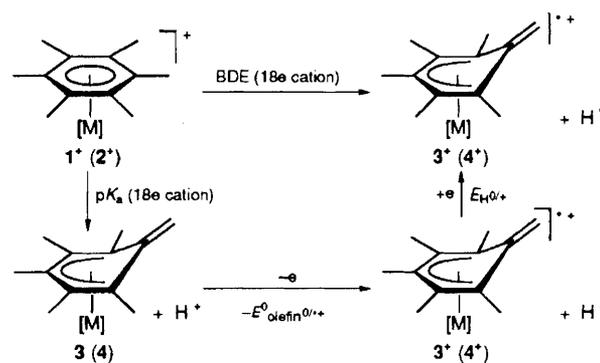
Organotransition-metal radicals are involved in redox catalysis,^{1a} electrocatalysis^{1b} and material science.^{1c} However, little thermodynamic information is available concerning, for instance, C–H bond dissociation energies (BDEs) and pK_a values. Recently, Tilset and Parker determined such parameters in 17-electron (17e) transition-metal hydrides from thermodynamic cycles, which constitute a first entry into the field.² Since the seminal studies by Breslow and coworkers³ in the late 1960s, thermodynamic cycles have proven very useful to determine thermodynamic parameters such as pK_a values and BDEs.⁴ A smaller class of organotransition-metal radicals is that involving 19 valence electrons, yet these radicals are involved in most radical mechanisms.^{5,6} We have sought to determine the pK_a values and C–H bond dissociation energies BDEs in the 19e complexes $[\text{Fe}^{\text{I}}(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{Me}_6)]$ **1** and $[\text{Fe}^{\text{I}}(\eta\text{-C}_5\text{Me}_5)(\text{C}_6\text{Me}_6)]$ **2**.^{6a} The first step of this research involves the determination of the thermodynamic parameters for the corresponding 18e complexes **1**⁺ and **2**⁺, which are unknown. The pK_a values of fluorene^{4f} and diphenylmethane⁷ complexes have been published, yet simple polymethylbenzene derivatives examined here are expected to be much less acidic. For these determinations, we have used the direct method, in which a known quantity of base, of a strength similar to that of the compound under investigation, is added to the solution containing this compound for spectroscopic observation of the resulting equilibrium.² This method has not yet been used to find the pK_a values of transition-metal arene complexes. We have sought to determine the pK_a values of the cationic 18e forms and their reduction potentials as well as the oxidation and reduction potentials of their deprotonated forms in Me_2SO at 20 °C. Using thermodynamic cycles, we have then calculated the pK_a values of the corresponding 19e neutral forms and the C–H BDEs in these 18e and 19e complexes. Given the extended use of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{arene})]^+$ complexes as proton reservoirs in starburst perfunctionalizations of polymethyl aromatics,⁸ the comparison of the pK_a values of the 18e and 19e complexes of aromatics and of the free aromatics is useful. The reactions of 19e complexes with radicals can proceed either by direct

H-atom abstraction or by electron transfer followed by proton transfer,⁸ hence the comparison of BDEs in isostructural 18e and 19e complexes is of mechanistic interest.

The equilibrium concentrations of $[\text{Fe}(\text{C}_5\text{R}_5)(\text{C}_6\text{Me}_6)]^+\text{PF}_6^-$ [$\text{R} = \text{H}$ (**1**⁺) or Me (**2**⁺)] were measured by ¹H NMR and UV–VIS spectroscopy using NaOMe ($pK_a = 29$) or Bu^tOK ($pK_a = 32.2$) in Me_2SO ,^{2c} which allowed calculation of the pK_a values (Table 1). In this solvent, the 18e cations **1**⁺ and **2**⁺ and their deprotonated forms **3** and **4**¹¹ are sufficiently stable.

The BDE's of **1**⁺ and **2**⁺ were determined from the thermodynamic cycle of Scheme 1 by coupling their acidities with the oxidation potentials of their deprotonated forms (see Table 1). A value of $73.5 \pm 1 \text{ kcal mol}^{-1}$, published by Parker and Tilset,^{2c} was used for the constant C_{Fc} containing the solvation of H^+ and H^\cdot and the energy of formation of the radical, and taking into account the expression of E^0 versus the ferrocene–ferrocenium reference (Fc) [eqn. (1)].

$$\begin{aligned} \text{BDE}(\text{18e cation}) &= 2.301 RT pK_a + FE^0_{\text{vs.Fc}} + C_{\text{Fc}} \\ &= (1.365 \text{ kcal mol}^{-1})pK_a(\text{18e cation}) \\ &+ 23.06 \text{ kcal mol}^{-1}(E^0_{\text{olefin}^{0/+}} \text{ vs. Fc}) + 73.5 \text{ kcal mol}^{-1} \quad (1) \end{aligned}$$



Scheme 1 [M] = $\text{Fe}(\eta\text{-C}_5\text{H}_5)$ or $\text{Fe}(\eta\text{-C}_5\text{Me}_5)$

Table 1

	$pK_a(\text{DMSO})^a$	$E^{1/2}_{\text{red}}/\text{V}^b$	$E^{1/2}_{\text{ox}}/\text{V}^b$	C–H BDE ^{a,c}
$[\text{Fe}^{\text{II}}(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{Me}_6)]^+\text{PF}_6^-$ 1 ⁺ ^{9a}	29.2 ± 0.2	-1.99 ± 0.01		86.5 ± 1.5 (361.9 ± 6.2)
$[\text{Fe}^{\text{II}}(\eta\text{-C}_5\text{Me}_5)(\text{C}_6\text{Me}_6)]^+\text{PF}_6^-$ 2 ⁺ ^{9a}	31.4 ± 0.4	-2.22 ± 0.01		85.5 ± 2 (357.7 ± 8.3)
$[\text{Fe}^{\text{II}}(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{Me}_6\text{CH}_2)]$ 3 ^{9b}		-2.80 ± 0.05^d	-1.165 ± 0.01	
$[\text{Fe}^{\text{II}}(\eta\text{-C}_5\text{Me}_5)(\text{C}_6\text{Me}_5\text{CH}_2)]$, 4 ^{9b}		-3.11 ± 0.05^d	-1.34 ± 0.01	
$[\text{Fe}^{\text{I}}(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{Me}_6)]$ 1 ^{9a,c}	43.5 ± 2.5		-1.99 ± 0.01	67.5 ± 1.5 (282.4 ± 6.2)
$[\text{Fe}^{\text{I}}(\eta\text{-C}_5\text{Me}_5)(\text{C}_6\text{Me}_6)]$ 2 ^{9a,c}	46.4 ± 2.5		-2.22 ± 0.01	65 ± 2 (271.9 ± 8.3)
PhCH_3	43^e			$87\text{--}90^f$ ($364\text{--}376$)

^a All the measurements were done at 20 °C. ^b $E^{1/2}$ values of reversible waves (closely approximating the thermodynamic potential E^0) were determined versus the ferrocene–ferrocenium redox potential as the average of the anodic and cathodic peaks of the cyclic voltammograms in $\text{Me}_2\text{SO} + \text{Bu}^n_4\text{NPF}_6$ (0.1 mol dm^{-3})/Pt. Unless otherwise noted, the waves are reversible, thus the uncertainty on E^0 is very low ($\pm 0.01 \text{ V}$). ^c BDE in kcal mol^{-1} (kJ mol^{-1}). ^d Peak potential of an irreversible wave ($E_{\text{peak}} \neq E^0$); in order to minimize the error in the determination of E^0 , and thus in the calculation of the BDE, a 0.05 V correction ($\Delta E = E_{\text{peak}} - E^0$) was applied to the recorded E_{peak} to give the estimated E^0 value. This correction corresponds to a kinetic peak potential shift for an EC mechanism with a pseudo first-order reaction between the solvent and the radical substrate with a rate constant equal to 10^2 s^{-1} . Since an ESR spectrum of the radical anion **3**[−] has been reported,¹¹ the k value is expected to be not greater than 10^4 s^{-1} , which gives an uncertainty of $\pm 0.05 \text{ V}$. For discussion of the uncertainties related to such follow-up reactions, see ref. 2(c). ^e From ref. 4(c); see also ref. 10(a). ^f From ref. 10(b).

The pK_a values of the 19e complexes were determined by analogy with the method used by Tilset and coworkers for 17e organotransition-metal hydrides.² This method relates the pK_a values of two oxidation states using the redox potentials [Scheme 2 and eqn. (2)]. The pK_a values of the 19e complexes are given by eqn. (2) and the data are gathered and their uncertainties are discussed in Table 1.

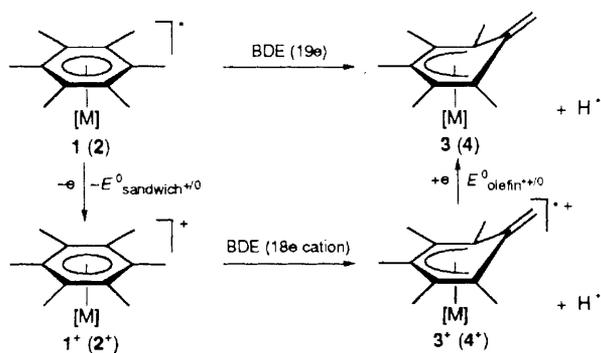
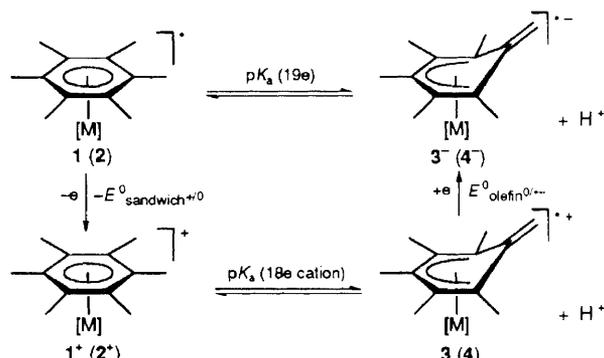
$$pK_a(19e) = pK_a(18e \text{ cation}) - \frac{F}{2.301RT} (E^0_{\text{olefin}^{0/+}} - E^0_{\text{sandwich}^{+/0}}) \quad (2)$$

Lastly, the cycle of Scheme 3 relates the BDEs of the 18e cations with those of their monoreduced 19e complexes [eqn. (3)]. The required redox potentials (E^0 values) and the calculated BDE values are also reported (and their uncertainties discussed) in Table 1.

$$\text{BDE}(19e) = \text{BDE}(18e \text{ cation}) - F(E^0_{\text{olefin}^{0/+}} - E^0_{\text{sandwich}^{+/0}}) \quad (3)$$

As can be seen from eqn. (3), the difference in BDEs between the analogous 18e and 19e complexes is just the difference between the thermodynamic oxidation potentials E^0 of the neutral deprotonated form, *i.e.* the olefin **3** (or **4**) and of the 19e complex **1** (or **2**).

The present data indicate that coordination of a polymethylbenzene to a $[\text{Fe}(\eta\text{-C}_5\text{H}_5)]^+$ fragment *enhances* the acidity of the benzylic hydrogens by *ca.* 14 pK_a units (*cf.* 12 pK_a units in the case of Ph_2CH_2),⁷ whereas this value is reduced to 12 pK_a units for $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)]^+$. On the other hand, in the 19e complexes, there is *no* acidity enhancement with respect to the uncoordinated arene.¹⁰ Tilset has reported a similar difference in a series of hydridotris(pyrazolyl) borate hydride complexes, for which the radical cations are about 19 units more acidic than the neutral complexes.^{2d} The electron density increase incurred on permethylation of the $\eta\text{-C}_5\text{H}_5$ ring raises the pK_a by 2.2 units. The effect discussed above for the pK_a values is just the opposite



for the BDEs. Here, the BDEs of the 18e iron complexes are close to those of the uncoordinated arenes, while those of the 19e complexes are 20–35 kcal mol⁻¹ (83–146 kJ mol⁻¹) smaller. This lower energy arises from the fact that, with a 19e complex, a radical starting material becomes a product which has an even-electron form, whereas the 18e cationic complexes are transformed into products having an unpaired electron. Comparison with the C–H BDEs of uncoordinated polymethyl aromatics^{10b} shows that coordination in a 19e complex produces a *considerable labilization* of the benzylic hydrogens, bringing their BDEs into the range typical for M–H bonds in transition-metal hydride complexes.² These low C–H BDEs in the 19e complexes show that direct H-atom abstraction reactions should be easy, *i.e.* these 19e complexes are excellent ‘H-atom reservoirs’.⁸

In conclusion, we have determined the first pK_a values and C–H BDEs of 19e complexes, which allows a meaningful comparison with those of 18e analogues, also determined in this work, and of the free arene ligand.

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