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Communications

Bond Dissociation Free Energies of the H−A Bonds in HA^{2-} Dianions

Yongyu Zhao* and Frederick G. Bordwell*

Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208-3113

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Introduction

Recently a potentially general method to estimate the equilibrium acidities of HA^{2+} dications in DMSO was devised by combining $pK_{HA^{\bullet+}}$ values for radical cations with their oxidation potentials and those of the corresponding $A^\bullet$ radicals by eq 1.[1]

$$pK_{HA^{2+}} = pK_{HA^{\bullet+}} + 16.8[E_{ox}(A^\bullet) - E_{ox}(HA^{\bullet+})] \quad (1)$$

The repulsive effect of the two positive charges was found to greatly weaken the $H-A^{2+}$ bond toward cleavage (eq 2). For example, the acidity of an N−H bond in the

$$HA^{2+} \rightleftharpoons H^+ + A^+ \quad (2)$$

$[p\text{-}PhNHC_6H_4NHPh]^{2+}$ dication was found to be about 43 kcal/mol stronger than that of its parent, p-$PhNHC_6H_4NHPh$, and about 13 kcal/mol stronger than that of the corresponding NH radical cation $[p\text{-}PhNHC_6H_4NHPh]^{\bullet+}$ (Henceforth kcal/mol will be abbreviated as kcal.)

It would be expected, then, that the bond dissociation free energy of the H−A bond in a HA^{2-} dianion, $BDE_{HA}{}^{2-}$, to form two negative ions (eq 3) would also be greatly weakened by the repulsive effects of the two negative charges.

$$H-A^{2-} \rightleftharpoons H^- + A^- \quad (3)$$

The chemistry of dianions has been explored extensively for synthetic purposes,[2] acid−base equilibria to form dianions have been examined in a number of instances,[3] and modes of cleavage of $A-B^{\bullet-}$ radical anions have been studied.[4] But, to the best of our knowledge, no bond dissociation energies of dianions of the type shown in eq 3 have been estimated.

Scheme 1

$$\begin{array}{lll}
HA^{2-} - e \rightleftharpoons HA^{-\bullet} & & E_{rd}(HA^{-\bullet}) \\
HA^{-\bullet} - e \rightleftharpoons HA & & E_{rd}(HA) \\
HA \rightleftharpoons H^+ + A^- & & pK_{HA} \\
H^+ + e \rightleftharpoons H^\bullet & & -E_{rd}(H^+) \\
H^\bullet + e \rightleftharpoons H^- & & -E_{rd}(H^\bullet) \\
\hline
HA^{2-} \rightleftharpoons A^- + H^- & & BDE_{HA}{}^{2-}
\end{array}$$

Results and Discussion

The bond dissociation free energy of cleavage of a dianion to form a hydride ion and an organic anion in DMSO can be obtained by eq 4, which is based on a thermodynamic cycle (Scheme 1).

$$BDE_{HA^{2-}} = 1.37pK_{HA} + 23.06[E_{rd}(HA) + E_{rd}(HA^{\bullet-})] + C \quad (4)$$

The experimental quantities needed to evaluate $BDE_{HA}{}^{2-}$ by eq 4 are (a) the pK_{HA} value in DMSO of the parent acid, HA, (b) the first and second reduction potentials of the parent acid in DMSO, and (c) the electrode potentials for the $(H^+/H^\bullet)$ and $(H^\bullet/H^-)$ redox couples. The latter redox potentials have been evaluated in DMSO and shown to be equal to −2.48 and −0.55 V, respectively, versus the normal hydrogen electrode, NHE_{aq}.[5] The sum of the free energies for these two half reactions is then equal to 3.03 V (69.9 kcal) in DMSO when the potentials are related to NHE_{aq} and is equal to 94.8 kcal when they are related to the Fc^+/Fc couple.[5] The latter value is used for the constant C in eq 4.

The data for estimating $BDE_{HA}{}^{2-}$ values for four weak acids are summarized in Table 1.

The acids in Table 1 were chosen because both their first and second reduction potentials are reversible, which allows good estimates of $BDE_{HA}{}^{2-}$ values, as well as $BDE_{HA^{\bullet-}}$ values, to be made. [Although the $E_{ox}(A^-)$ values used to estimate BDE_{HA} are not reversible, the BDE_{HA} values are believed to be accurate to ±3 kcal, or better, because of the good general agreement of the BDEs obtained by using eq 5 with literature values.[6]]

$$BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \text{ kcal} \quad (5)$$

The first reduction potentials for acids **1**, **2**, or **3** are associated with addition of a single electron to the nitro

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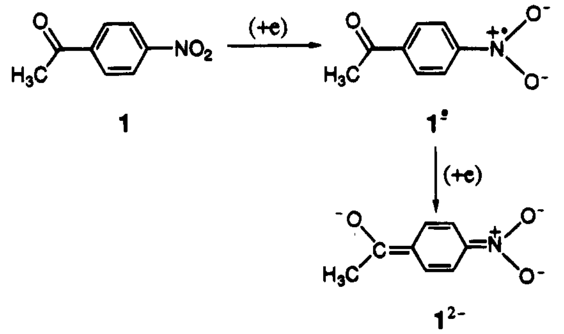
Table 1. Bond Dissociation Free Energies for Cleavage of the HA Bonds in Parent Acids, BDE_{HA}, and the Corresponding Radical Anions, $BDE_{HA^{\bullet-}}$, and Dianions, $BDE_{HA}2-$, in DMSO

acid	pK_{HA}[a]	$BDE_{(HA)}$[f]	$E_{rd}(HA)$[h]	$(BDE_{HA^{\bullet-}})$[i]	$E_{rd}(HA^{\bullet-})$[f]	$(BDE_{HA^{2-}})$[j]
p-$NO_2C_6H_4COCH_3$ (**1**)	21.8[b]	89	−1.263	70	−1.864	53
p-$NO_2C_6H_4SO_2CH_3$ (**2**)	26.3[c]	95	−1.238	77	−1.976	57
p-$NO_2C_6H_4SO_2C_6H_4NH_2$-p (**3**)	24.5[d]	92	−1.262	74	−1.983	53
$C_{60}H_2$ (dihydrobuckminsterfullerene) (**4**)	4.5[e]	59[g]	−0.88[e]	56[g]	−1.270[e]	52[g]

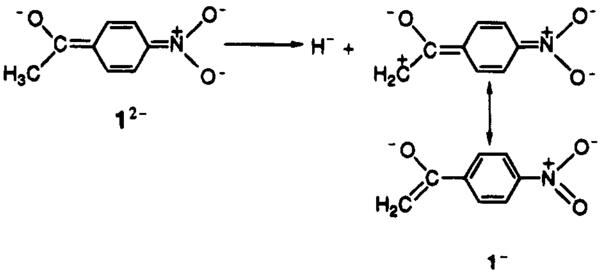
[a] In DMSO in pK_{HA} units. [b] Estimated from a Hammett plot.[7] [c] Estimated from a three-point Hammett plot for 3-$CF_3C_6H_4SO_2CH_3$, $3,5$-$(CF_3)_2C_6H_3SO_2CH_3$, $C_6H_5SO_2CH_3$ [$pK_{HA} = 28.87 - 3.30\ \sigma$; $r = 0.98$]. [d] Estimated from a Hammett plot.[8] [e] Reference 9. [f] Calculated by eq 5 and converted to free energies by subtracting 3.7 kcal. [g] Calculated from data given in reference 9. [h] Reversible potentials measured by cyclic voltammetry under the conditions described in earlier papers and referenced to the ferrocenium/ferrocene couple. [i] Calculated using the equation: $BDE_{HA^{\bullet-}} = 1.37pK_{HA} + 23.1E_{rd}(HA) + 69.6$ kcal/mol;[10] these values for homolytic cleavage of the H−A bonds are comparable to those estimated in earlier studies.[11] [j] Calculated using eq 4 with $C = 94.8$ kcal/mol.

group to form the radical anion, and the second reduction potentials are associated with the addition of a second electron to form a dianion, as shown for **1**.



The cleavage of the C−H bond in the methyl group of $\mathbf{1}^{2-}$ in the manner shown in eq 3 will give a hydride ion and anion $\mathbf{1}^-$ (Scheme 2). The data in Table 1 provides information that allows an estimate of the $BDE_{HA^{2-}}$ value for this bond cleavage to be made (53 kcal) and allow estimates for comparisons with the $HA^{\bullet-}$ bond cleavage of the corresponding radical anion, $\mathbf{1}^{\bullet-}$ ($HA^{\bullet-} \rightarrow H^\bullet + A^-$; 70 kcal) and with the homolytic cleavage of the C−H bond in **1** ($HA \rightarrow H^\bullet + A^\bullet$; 89 kcal). The bond dissociation energies for comparable C−H bond cleavages in **2** and **3** and their $HA^{\bullet-}$ and HA^{2-} derivatives are not greatly different from those for **1**, $\mathbf{1}^{\bullet-}$, and $\mathbf{1}^{2-}$, which is not surprising since the structures are not greatly different. It is surprising to find, however, that the $BDE_{HA^{2-}}$ value estimated for the cleavage of a C−H bond in a dianion derived from a very different structural type, namely, dihydrobuckminsterfullerene (**4**),[9] i.e., $C_{60}H_2^{2-} \rightarrow H^- + C_{60}H^-$, is remarkably similar (52 kcal) to those estimated for the dianions derived from **1**−**3**. The BDE_{HA} and $BDE_{HA^{\bullet-}}$ values for **4** and $\mathbf{4}^{\bullet-}$ are much smaller, however, than those for **1**−**3** and their radical anions (Table 1).

Scheme 2



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