

Letter to the Editor

O–H Bond Dissociation Free Energies of Hydroquinone and the Corresponding Radical Anion, Monoanion and Free Radical in Dimethyl Sulfoxide Solution

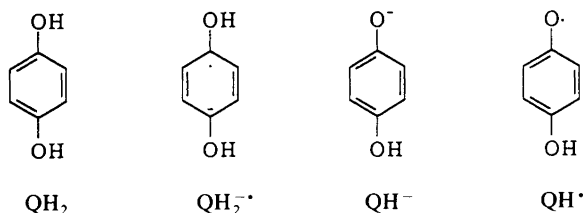
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The use of electrode potentials in thermochemical cycles to estimate experimentally inaccessible quantities has recently resulted in the availability of a number of different types of thermodynamic parameters including bond dissociation energies, acid dissociation constants, hydride affinities and halide affinities in solution.³ These data serve to establish the fact that either the addition to or the loss of an electron from an aromatic compound results in a profound change in various bond energies. For example, both radical cations and radical anions of alkylarenes have C–H bond dissociation energies of the order of 50 kcal mol⁻¹ lower than those of the neutral substrate.^{4–6}

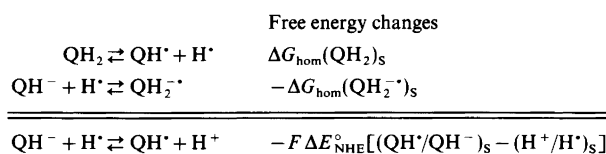
Consider the possible O–H bond dissociations of hydroquinone (QH₂) and the intermediates derived from QH₂; the radical anion (QH₂^{•-}), the monoanion (QH⁻) and the free radical (QH[•]). From previous work we expect a substantial lowering of the bond dissociation energy upon formation of the radical anion. But what is the effect of the charge in the monoanion and the unpaired electron in the radical on the O–H bond dissociation energies? There are no data available to draw upon in order to estimate the bond dissociation energies of either the monoanion or the free radical. We now report two new thermochemical cycles which allow these quantities to be derived from experimentally accessible quantities.



The O–H bond dissociation free energy in dimethyl sulfoxide (DMSO), $\Delta G_{\text{hom}}(\text{QH}_2)_{\text{DMSO}}$, of QH₂ can

be calculated using a thermochemical cycle reported previously^{7,8} which requires experimental values of $pK_a(\text{QH}_2)_{\text{DMSO}}$ and $E_{\text{NHE}}^\circ(\text{QH}^\bullet/\text{QH}^-)_{\text{DMSO}}$. The pertinent pK_a has been reported to be equal to 19.8.⁹ We estimate $E_{\text{NHE}}^\circ(\text{QH}^\bullet/\text{QH}^-)_{\text{DMSO}}$ to be equal to -0.247 V from electrode potential measurements. These data lead to a value of 78.5 kcal mol⁻¹ for $\Delta G_{\text{hom}}(\text{QH}_2)_{\text{DMSO}}$.

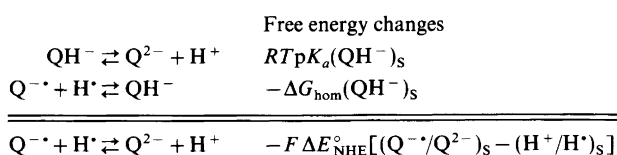
The difference in O–H bond dissociation free energies of QH₂ and QH₂^{•-} was obtained from the appropriate isodesmic reaction relationship¹⁰ shown in Scheme 1.



Scheme 1.

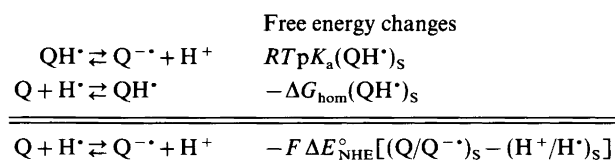
The subscript S designates the solvent. In addition to $\Delta G_{\text{hom}}(\text{QH}_2)_{\text{DMSO}}$ and $E_{\text{NHE}}^\circ(\text{H}^+/\text{H}^\bullet)_{\text{DMSO}}$ (equal to -2.48 vs. NHE⁸) the only experimental quantities necessary for this determination are $E_{\text{NHE}}^\circ(\text{QH}^\bullet/\text{QH}^-)_{\text{DMSO}}$ (-0.247 V) and $E_{\text{NHE}}^\circ(\text{Q}^{\bullet-}/\text{Q}^{2-})_{\text{DMSO}}$ (-1.208 V). We arrive at a value of 8.1 kcal mol⁻¹ for $\Delta G_{\text{hom}}(\text{QH}_2^{\bullet-})_{\text{DMSO}}$.

The thermochemical cycle shown in Scheme 2 was devised in order to estimate $\Delta G_{\text{hom}}(\text{QH}^-)_{\text{DMSO}}$. The experimental data required by this cycle are the second dissociation constant of QH₂ [$pK_a(\text{QH}^-)_{\text{DMSO}}$] which



Scheme 2.

we determined to be equal to 26.2 using a modification of the 'overlapping indicator method'⁸ and the electrode potential of the $(Q^{\cdot-}/Q^{2-})_{\text{DMSO}}$ couple which we find to be equal to -1.208 V vs. the NHE. We estimate a value of $65.0 \text{ kcal mol}^{-1}$ for $\Delta G_{\text{hom}}(QH^-)_{\text{DMSO}}$.



Scheme 3.

Finally, the O–H bond dissociation free energy of QH^{\cdot} can be estimated from the thermochemical cycle illustrated in Scheme 3. This requires $E_{\text{NHE}}^{\circ}(Q/Q^{\cdot-})_{\text{DMSO}}$ (-0.319 V) along with the acid dissociation constant of QH^{\cdot} . The latter was estimated to be equal to 8.1 using data cited above in Scheme 1 of Ref. 11. This leads to a value of $63.4 \text{ kcal mol}^{-1}$ for $\Delta G_{\text{hom}}(QH^{\cdot})_{\text{DMSO}}$. The thermochemical data are summarized in Table 1. The error associated with the estimation of the thermochemical parameters is believed to be of the order of $\pm 2 \text{ kcal mol}^{-1}$.

We can now answer the question posed earlier regarding the effect of the charge in the monoanion and the unpaired electron in the free radical on the O–H bond dissociation free energies. While the formation of the radical anion is accompanied by a 70 kcal mol^{-1} decrease in the O–H bond dissociation free energy, much more modest changes are observed in going to the monoanion and the free radical, 14 and 15 kcal mol^{-1} , respectively. This observation suggests that the enormous changes that take place in bond dissociation energies upon going from a neutral substrate to the corresponding radical ions cannot be attributed to either the charge or the open-shell character of these intermediates but rather to a combination of the two.

Table 1. Free energies of O–H bond dissociation reactions of hydroquinone and the corresponding radical anion, monoanion, and free radical in DMSO.

Process	$\Delta G^{\circ}/\text{kcal mol}^{-1}$ ^a
$QH_2 \rightleftharpoons QH^{\cdot} + H^{\cdot}$	78.5
$QH_2^{\cdot-} \rightleftharpoons QH^- + H^{\cdot}$	8.1
$QH^{\cdot} \rightleftharpoons Q^{\cdot-} + H^{\cdot}$	65.0
$QH^{\cdot} \rightleftharpoons Q + H^{\cdot}$	63.4

^aAt 298.15 K.

We estimate the reversible potential for the $(QH_2/QH_2^{\cdot-})_{\text{DMSO}}$ couple to be more negative than -3.0 V. This means that $QH_2^{\cdot-}$ is destabilized relative to $(QH_2 + e^-)$ in DMSO by about 70 kcal mol^{-1} or more. An important component of this is the large electronic ground state destabilization imparted by the odd electron occupying an antibonding π^* orbital. Since neither QH^{\cdot} nor QH^- are subject to a comparable destabilization, these species might be expected to have much higher O–H bond dissociation energies.¹²

The thermochemical relationship in Scheme 2 warrants further comment. The free energy change of the reaction above the double line, which represents the experimentally inaccessible quantity, can also be considered to be the free energy solution hydrogen atom affinity of the neutral aromatic compound. Such data have not previously been available and Scheme 2 offers the possibility of determining free energies of a variety of similar processes. These can be expected to be of both theoretical and practical value and will complement the recently determined free energy hydride affinities of carbenium ions,^{13,14} free radicals,^{13,15} and neutral molecules.¹⁶

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