

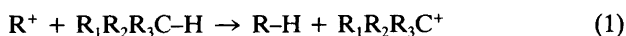
## Hydride Affinities of Organic Cations in Solution

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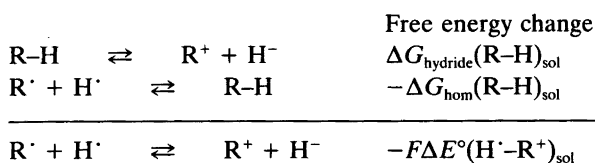
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The reactions of organic cations with active C-H containing compounds often result in a formal hydride transfer (1).



The mechanisms of these reactions are usually not obvious since a two-step process consisting of an initial electron transfer followed by a hydrogen-atom transfer gives rise to the same stoichiometry. Pertinent examples of formal hydride transfer reactions which have been interpreted as both single-step<sup>1a,2a</sup> and two-step electron/H atom transfer<sup>1b,2b</sup> processes include those from NADH models<sup>1</sup> and from some metal alkyls.<sup>2</sup> It has been proposed that in hydride transfer reactions between methylarenes and 9-arylfluoren-9-yl cations electron transfer progresses further in the transition state than nuclear motion of the migrating hydrogen.<sup>3</sup> While it is generally possible to evaluate the feasibility of an initial electron transfer reaction from the pertinent electrode potentials, thermochemical data for the hydride transfer step in solution are not available.

The free energy of (R-H) heterolytic bond dissociation can be derived from the isodesmic reaction relationship<sup>4</sup> illustrated in Scheme 1. The electrode potential difference



Scheme 1.

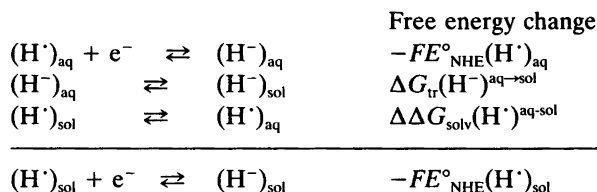
below the line is related to the difference in the free energy changes above the line by eqn. (2). The data required to

$$\Delta G_{\text{hydride}}(R-H)_{\text{sol}} = \Delta G_{\text{hom}}(R-H)_{\text{sol}} - F\Delta E^\circ_{\text{NHE}}(H^+ - R^+)_{\text{sol}} \quad (2)$$

evaluate  $\Delta G_{\text{hydride}}(R-H)$  include the bond dissociation free energy [ $\Delta G_{\text{hom}}(R-H)$ ] in solution and the difference in reduction potentials of  $H^+$  and  $R^+$ .

The standard reduction potential of  $H^+$  in aqueous solution [ $E^\circ_{\text{NHE}}(H^+)$ ] has been estimated to be equal to

+0.18 V.<sup>5</sup> Since the hydride transfer reactions of interest generally take place in non-aqueous solvents, it is necessary to derive the standard potentials for the reduction of  $H^+$  in these solvents. The thermochemical cycle for this conversion is illustrated in Scheme 2. The free energy of transfer



Scheme 2.

of hydride from water to solvent [ $\Delta G_{\text{tr}}(H^-)_{\text{aq} \rightarrow \text{sol}}$ ] and the difference in solvation energies of  $H^+$  [ $\Delta \Delta G_{\text{sol}}(H^+)_{\text{aq} \rightarrow \text{sol}}$ ] in water and the non-aqueous solvent are the quantities necessary to make the conversion. The former is experimentally inaccessible while the latter has recently been evaluated for acetonitrile (AN) and dimethyl sulfoxide (DMSO) solutions.<sup>6</sup>

Linear regression of  $\Delta G_{\text{tr}}(X^-)_{\text{aq} \rightarrow \text{sol}}$  data for  $I^-$ ,  $Br^-$  and  $Cl^-$  available<sup>7</sup> for AN ( $r = 0.98$ ), DMSO ( $r = 0.996$ ) and *N,N*-dimethylformamide (DMF) [ $r = 0.999$ ] with the corresponding free energies of hydration ( $\Delta G_{\text{hyd}}$ )<sup>5</sup> provided relationships to calculate  $\Delta G_{\text{tr}}(H^-)_{\text{aq} \rightarrow \text{sol}}$ . The predominant

Table 1. Hydrogen atom reduction potentials and hydride-ion free energies of transfer from water to non-aqueous solvents.

Solvent	$E^\circ_{\text{NHE}}(H^+)/V$	$\Delta G_{\text{tr}}(H^-)_{\text{aq} \rightarrow \text{sol}}/\text{kcal mol}^{-1}$
Water	+0.18 <sup>a</sup>	-
AN	-0.62 <sup>b</sup>	17.2 <sup>c</sup>
DMSO	-0.58 <sup>b</sup>	16.6 <sup>d</sup>
DMF	-0.60 <sup>b</sup>	17.9 <sup>e</sup>

<sup>a</sup>Value from Ref. 5 converted to the NHE. <sup>b</sup>Calculated with relationships in Scheme 2. <sup>c</sup>From the linear regression eqn. (see the text):  $\Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{AN}} = -0.465\Delta G_{\text{hyd}} - 23.3$  ( $r = 0.98$ ). <sup>d</sup>From the linear regression eqn. (see the text):  $\Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{DMSO}} = -0.50\Delta G_{\text{hyd}} - 26.8$  ( $r = 0.996$ ). <sup>e</sup>From the linear regression eqn. (see the text):  $\Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{DMF}} = -0.475\Delta G_{\text{hyd}} - 23.4$  ( $r = 0.999$ ).

Table 2. Free energies of heterolysis of C–H bonds to hydride ion and carbenium ions.<sup>a</sup>

R–H	Solvent	$\Delta G_{\text{hom}}(\text{R–H})^b$	$E^{\circ}_{\text{NHE}}(\text{R}^{\cdot})$	$\Delta G_{\text{hydride}}(\text{R–H})^c$
Ph <sub>3</sub> C–H	DMSO	79.3	0.43 <sup>d</sup>	102.6
PhCH <sub>2</sub> –H	AN	85.1	0.49 <sup>e</sup>	96.4
PhN(CH <sub>3</sub> )CH <sub>2</sub> –H	AN	80	–0.61 <sup>e</sup>	80.2

<sup>a</sup>All free energies in kcal mol<sup>–1</sup>. <sup>b</sup>Calculated using the relationship described in Ref. 6. <sup>c</sup>Relationships in Scheme 1. <sup>d</sup>Electrode potential from Ref. 8 adjusted to NHE. <sup>e</sup>Electrode potential from Ref. 9 adjusted to NHE.

factor in determining  $\Delta G_{\text{ir}}(\text{X}^-)^{\text{aq} \rightarrow \text{sol}}$  of the spherical halide ions appears to be the free energy of hydration. Since H<sup>–</sup> is spherical as well, it is reasonable to estimate  $\Delta G_{\text{ir}}(\text{H}^-)^{\text{aq} \rightarrow \text{sol}}$  from the regression equations. These values are summarized in Table 1 along with the corresponding  $E^{\circ}_{\text{NHE}}(\text{H}^{\cdot})$  evaluated using the relationships from Scheme 2.

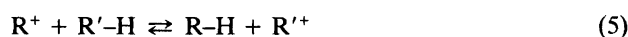
The recent evaluation of the reversible reduction potentials of the proton in water and non-aqueous solvents [ $E^{\circ}_{\text{NHE}}(\text{H}^+)_{\text{sol}}$ ] has provided eqn. (3) for the evaluation of

$$\Delta G_{\text{hom}}(\text{H–A})_{\text{sol}} = 1.364\text{p}K_{\text{a}}(\text{H–A})_{\text{sol}} + F\Delta E^{\circ}_{\text{NHE}}(\text{A}^{\cdot-}\text{–H}^+)_{\text{sol}} \quad (3)$$

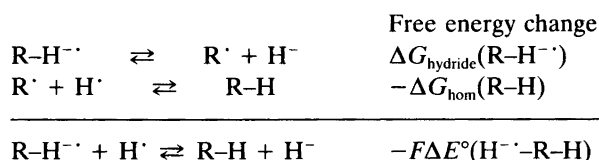
bond dissociation free energies in solution [ $\Delta G_{\text{hom}}(\text{H–A})_{\text{sol}}$ ].<sup>6</sup> The availability of electrode potentials for both the oxidation and reduction of methylarene radicals, eqn. (4),<sup>8,9</sup>



along with the pertinent  $\text{p}K_{\text{a}}$  values,<sup>10</sup> make it possible to evaluate  $\Delta G_{\text{hydride}}(\text{R–H})_{\text{sol}}$  using eqns. (2) and (3). The three examples illustrated by the data in Table 2 show that cleavage of hydride ion from these compounds in non-aqueous solvents is indeed a highly endergonic process and is not expected to take place in the absence of a hydride acceptor. The utility of the data, however, lies in the evaluation of equilibrium constants for reactions (5).<sup>11</sup>



Heterolytic (C–H) bond dissociation from methylarene radical anions is a much more favorable process. The thermochemical cycle which provides the relationship (6) to calculate  $\Delta G_{\text{hydride}}(\text{R–H}^{\cdot-})_{\text{sol}}$  is illustrated in Scheme 3.



Scheme 3.

$$\Delta G_{\text{hydride}}(\text{R–H}^{\cdot-})_{\text{sol}} = \Delta G_{\text{hom}}(\text{R–H})_{\text{sol}} - F\Delta E^{\circ}_{\text{NHE}}(\text{H}^{\cdot-}\text{–R–H})_{\text{sol}} \quad (6)$$

Application of eqn. (6) to the pertinent data for toluene radical anion in AN results in  $\Delta G_{\text{hydride}}(\text{PhCH}_2\text{–H}^{\cdot-})_{\text{AN}}$  equal

to 12 kcal mol<sup>–1</sup>. The equilibrium constant for reaction (7) in



AN at 298 K is thus equal to about 10<sup>62</sup>. In this case the mechanism of reaction (7) is not obvious from the thermochemical data since the equilibrium constant calculated for electron transfer is nearly as great as that for hydride transfer.

A previous attempt<sup>12</sup> to evaluate  $\Delta G_{\text{hydride}}(\text{R–H})_{\text{sol}}$  was hampered by the assumption that  $\Delta G_{\text{ir}}(\text{H}^-)^{\text{aq} \rightarrow \text{AN}}$  is negligibly small. This assumption was based on the fact that the free energy of hydration of H<sup>–</sup> is only a fraction of that of H<sup>+</sup> and thus the corresponding  $\Delta G_{\text{ir}}(\text{H}^-)^{\text{aq} \rightarrow \text{AN}}$  should also only be a fraction of that of H<sup>+</sup>. This assumption does not take into account the fact that anions are notoriously destabilized in non-aqueous solvents relative to water because of the lack of hydrogen bonding in the former.

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