of the ground and excited configurations.

IV. Conclusions

Calculated chemisorption properties of CO on Rh and Pd model clusters have been compared for two purposes. The first one was to verify whether DF calculations on small model clusters could reproduce experimental trends for the geometries and vibrational frequencies of CO adsorbed on Rh and Pd catalysts, with variation of both adsorption sites and metal substrates. Our second aim was more ambitious since it concerned a possible correlation between the site selection for CO chemisorption on Rh and Pd surfaces and some fundamental properties of these metals.

In a first step, the description of the metal–metal bond by the LCGTO-MCP-DF method has been checked by calculations on Rh_2 and Pd_2 dimers. Our results show that this description, at least for the ground states, is in good agreement with that given by very accurate CI calculations. It is worthwhile to note that these results show a stronger metal–metal bond for Rh_2 than for Pd_2, in agreement with experiment. We have then confirmed that LSD calculations on M_4CO models were able to reproduce the observed trends of the metal–CO and C–O bond lengths and stretching frequencies for an adsorbed CO molecule at three different sites of Rh and Pd (111) surfaces. All these results are consistent with a larger Rh–CO than Pd–CO bond strength.

The analysis of the wave functions of the different models has confirmed that the 4σ and 5σ CO MOs are strongly mixed, especially for multibonded sites, and that a σ donation from CO to the clusters occurs for all models. However, the σ charge transferred to the metal substrate is mainly distributed among metal orbitals in the surface for the adsorption at 3-fold site, whereas it provides the σ bonding between CO and the metal atom of the top site model. As reported previously, the metal–CO π bonding is achieved through bonding combinations of occupied metal MOs and $2\pi^*$ CO contributions, which increase with the coordination number of the site and are larger for Rh than for Pd models.

The gradient corrected binding energies of CO are clearly different for the three sites of Pd clusters, favoring the adsorption at the most highly coordinated site. In contrast, these energies are rather similar for the three sites of the Rh clusters. Examination of the Mulliken gross atomic populations has led to unexpected conclusion that the atomic configuration of the metal atom(s) bonded to CO is a characteristic of the adsorption site and is independent of the metal itself (except for the one d-electron difference between Rh and Pd). These results can be rationalized if we assume that the metal atom(s) of the surface, on which CO chemisorbs, has some "memory" of the energies of the isolated atom(s), which determines its ability to adopt a particular configuration and hence its bonding capability.

In other words, CO chemisorption can be viewed as local electronic rearrangements in the orbitals of the metal atom(s) of the site, in which the neighboring atoms can participate. These rearrangements, imposed by the bonding with CO, are different with different sites, and CO will bond preferentially to the site whose specific configuration is the closest to the GS configuration of the isolated metal atom. Small or large differences between adsorption energies at different sites could thus be related to the relative energies of ground and excited configurations of the isolated atom. Further calculations are in progress to verify if this concept of site configuration applies independently of the cluster size and if our interpretation can be extended to other metal systems.

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Homolytic Bond (H–A) Dissociation Free Energies in Solution. Applications of the Standard Potential of the ($H^+/H^\bullet$) Couple

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Abstract: Free energies of solvation [$\Delta G_{solv}(gas)_{aq}$'s] of the noble gases in water are linearly related to the atomic radii. These data allow $\Delta G_{solv}(H^\bullet)_{aq}$ to be calculated from the correlation line. The standard potential [$E°(H^+/H^\bullet)_{aq}$] for reduction of the proton in water (reaction i) was then determined using eq ii. The value of $E°_{NHE(aq)}(H^+/H^\bullet)_{aq}$ was observed to be −2.42

$$H^+ + e^- \rightleftarrows H^\bullet \tag{i}$$

$$E°_{NHE(aq)}(H^+/H^\bullet)_{aq} = -(\Delta G_{solv}(H^\bullet)_{aq} + \Delta G_f(H^\bullet)_{gas})/F \tag{ii}$$

V. Similarly, it was shown that the standard electrode potentials for the ($H^+/H^\bullet$) couple in other solvents (S) can be determined using eq iii. The standard potentials for the $(H^+/H^\bullet)_S$ couple are directly applicable in thermochemical cycles to the determination

$$E°_{NHE(S)}(H^+/H^\bullet)_S = -(\Delta G_{solv}(H^\bullet)_S + \Delta G_f(H^\bullet)_{gas})/F \tag{iii}$$

of the differences in free energies of heterolysis and homolysis of bonds in solution. The bond dissociation energies obtained in this manner are subject only to the experimental errors in the determination of anion redox potentials $E(A^\bullet/A^-)_S$ and pK_a's of the corresponding conjugate acids (H–A's). A less rigorous treatment in which electrode potentials in S are referred to NHE(aq) using extrathermodynamic quantities is also discussed.

Introduction

The normal hydrogen electrode [NHE(aq)] has long been the standard reference for electrode reactions. The hydronium ion in its standard state, activity of unity in water at 298.15 K, is in equilibrium with dihydrogen gas in its standard state, 1 atm pressure at 298.15 K. The NHE(aq) half-reaction is (1); the

$$H^+_{aq} + e^- \rightleftarrows \tfrac{1}{2}H_2(g) \tag{1}$$

standard free energy change of (1) is taken by convention to equal 0, and hence is assigned an electrode potential of 0. While the

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Table I. Thermodynamic Data for Solvation in Water and van der Waals Radii of Noble Gases

element	$\Delta H_{\text{solv}}(\text{gas})_{\text{aq}}$[a]	$-T\Delta S_{\text{solv}}(\text{gas})$[a]	$\Delta G_{\text{solv}}(\text{gas})$[b]	radius[c]	$\Delta G_{\text{solv}}(\text{calc})_{\text{aq}}$[d]
helium	−0.84	7.91	7.07	122	7.10 (−0.03)
neon	−1.88	8.55	6.67	160	6.61 (+0.06)
argon	−2.73	8.98	6.25	191	6.22 (+0.03)
krypton	−3.55	9.62	6.07	198	6.13 (−0.06)

[a] Thermodynamic parameters for solvation of the gas at 298.15 K at 1 atm gas pressure expressed in kcal/mol from ref 9. [b] Free energy of solvation of the gas in water calculated from data in columns 2 and 3. [c] van der Waals radii (*R*) in pm from: Emsley, J. *The Elements*; University Press: Oxford, U.K., 1989. [d] Calculated from the linear correlation equation ($\Delta G_{\text{solv}}(\text{calc}) = 8.66 = 0.0128\text{R}$); the correlation coefficient equals 0.99.

Scheme I

			Free Energy Change
$H^+(aq) + e^-$	$\rightleftarrows$	$1/2\ H_2(gas)$	0
$1/2\ H_2(gas)$	$\rightleftarrows$	$H^\cdot(gas)$	$\Delta G_f(H^\cdot)$
$H^\cdot(gas)$	$\rightleftarrows$	$H^\cdot(aq)$	$\Delta G_{solv}(H^\cdot)_{aq}$
$H^+(aq) + e^-$	$\rightleftarrows$	$H^\cdot(aq)$	$\Delta G_{solv}(H^\cdot)_{aq} + \Delta G_f(H^\cdot)_{gas}$

NHE(aq) serves to anchor the electrode potential scale for all other redox couples, it is not commonly used as a reference electrode.

In recent years, thermochemical cycles, in which electrode potentials are used to give reliable estimates of exprimentally inaccessible quantities, have been applied extensively.[1] Often, as exemplified by determination of C–H,[2] C–C,[3] O–H,[4,5] C–Si,[6] or metal–H[7] bond dissociation energies, the thermochemical cycles include the energy differences in heterolysis and homolysis of bonds. The electrode potentials that appear in these cycles are for electron-transfer reactions in the absence of accompanying chemical reactions. The proton reduction potential of interest in these applications is (2). In this paper, we derive the standard

$$H^+ + e^- \rightleftarrows H^\bullet \qquad (2)$$

electrode potentials for (2) in water and other common electrochemical solvents and apply these in thermochemical cycles to determine free energies of homolysis of H–A in solution [ΔG_{hom}(H–A)'s].

Results and Discussion

The following terminology is used throughout this discussion: (a) each standard electrode potential is referred to as $E^\circ_{\text{NHE(S)}}(\text{ox/red})_{\text{S}}$ where S is the solvent for either the reference (NHE) or the redox couple (ox/red). (b) Gas-phase energies such as the free energy of formation, ΔG_f, are written without a subscript indicating the phase. (c) Energies in solution as illustrated by the free energy of solvation of the hydrogen atom, $\Delta G_{\text{solv}}(H^\bullet)_S$, are written with a subscript S, which is the symbol for the solvent.

Scheme II

			Free Energy Change
$H^+(aq) + e^-$	$\rightleftarrows$	$H^\cdot(aq)$	$-FE^\circ_{NHE(aq)}(H^+/H^\cdot)_{aq}$
$H^\cdot(aq)$	$\rightleftarrows$	$H^\cdot(S)$	$\Delta\Delta G_{solv}(H^\cdot)$
$H^+(S)$	$\rightleftarrows$	$H^+(aq)$	$-\Delta G_{tr}^{aq\to S}(H^+)$
$H^+(S) + e^-$	$\rightleftarrows$	$H^\cdot(S)$	$-FE^\circ_{NHE(aq)}(H^+/H^\cdot)_S$

The standard electrode potential for reaction 2 in water can be related to the NHE(aq) (reaction 1) by the thermochemical cycle illustrated in Scheme I. The free energy of formation of the hydrogen atom (ΔG_f) is equal to 48.58 kcal/mol.[8] However, the free energy of solvation of the hydrogen atom [$\Delta G_{\text{solv}}(H^\bullet)_{\text{aq}}$] is experimentally inaccessible. In the following section, arguments are presented to justify taking the free energy of solvation of helium [$\Delta G_{\text{solv}}(\text{He})_{\text{aq}}$] to be very nearly equal to that expected for the hydrogen atom [$\Delta G_{\text{solv}}(H^\bullet)_{\text{aq}}$].

Standard Potential of the ($H^+/H^\bullet$) Couple in Water. The free energy of solvation of a given gas in liquid solution is given by eq 3, where X_{gas} is the mole fraction of that gas in solution under

$$\Delta G_{\text{solv}}(\text{gas})_S = -RT \ln (X_{\text{gas}})_S \qquad (3)$$

1 atm gas pressure. Enthalpies and entropies of solvation of the noble gases in water, derived from the temperature dependence of the Henry's law constant, have been tabulated.[9] The data for He, Ne, Ar, and Kr were used to calculate $\Delta G_{\text{solv}}(\text{gas})_{\text{aq}}$'s at 25 °C, which are listed in Table I along with the van der Waals radii (*R*'s). It is evident that $\Delta G_{\text{solv}}(\text{gas})_{\text{aq}}$'s are correlated to the van der Waals radii. Linear correlation results are presented in eq 4; the correlation coefficient is equal to 0.99. Including data for Xe and Rn lowers the correlation coefficient to 0.96. For the remaining noble gases, use of eq 4 to calculate $\Delta G_{\text{solv}}(\text{gas})_{\text{aq}}$'s results in an average deviation of ±0.05 kcal/mol from the experimental values. Equation 4 implies that ΔG_{solv}'s of spherical

$$\Delta G_{\text{solv}}(\text{calc})_{\text{aq}} = 8.66 - 0.0128R \qquad (4)$$

gaseous atoms, with *R* ranging from 198 to 122 pm, in aqueous solution are directly dependent upon *R*. Assuming that (4) is applicable to the hydrogen atom, the van der Waals radius of which is 120 pm, results in $\Delta G_{\text{solv}}(H^\bullet)_{\text{aq}}$ being equal to 7.12 ± 0.04 kcal/mol.[10]

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Table II. Standard Potentials of the $(H^+/H^\bullet)$ Couple in Various Solvents[a]

solvent	$\Delta G_{tr}{}^{aq\rightarrow S}$-$(H^+)$[b]	$\Delta\Delta G_{solv}{}^{S\rightarrow aq}$-$(H^\bullet)$[c]	$E^\circ{}_{NHE(aq)}$-$(H^+/H^\bullet)_S$	$E^\circ{}_{NHE(S)}$-$(H^+/H^\bullet)_S$
water			−2.42	−2.42
acetonitrile	+11.1	−1.4[d]	−1.88	−2.35
DMSO	−4.5	0.87[e]	−2.58	−2.38

[a] At 298.15 K, electrode potentials in V and free energies in kcal/mol. [b] Free energy of transfer of the proton from water to the solvent from: Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1972**, *76*, 2024. [c] The difference in free energy of solvation of the hydrogen atom between the solvent and water. [d] Taken to be equal to that for the hydrogen molecule. [e] Taken to be equal to that for helium.

Since a reliable estimate of $\Delta G_{solv}(H^\bullet)_{aq}$ has been obtained, the standard electrode potential $[E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_{aq}]$ for (2) can be proposed to be equal to −2.42 V. An uncertainty of 0.01 V in $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_{aq}$ corresponds to one of ±0.23 kcal/mol in $\Delta G_{solv}(H^\bullet)_{aq}$, which is well out of the range implied in the previous paragraph. Thus, assuming $\Delta G_{solv}(H^\bullet)_{aq}$ to be equal to $\Delta G_{solv}(He)_{aq}$ results in $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_{aq}$ being equal to −2.42 V. This suggests that $\Delta G_{solv}(He)_S$ determined in solvents other than water should provide reliable estimates of $\Delta G_{solv}(H^\bullet)_S$ in those solvents.

A previous estimate assumed that $\Delta G_f(H^\bullet)_{aq} = \Delta G_f(H^\bullet)_{gas}$.[13] That estimate is thus 0.31 V in error [i.e. −2.11 V vs NHE(aq)] due to the neglect of $\Delta G_{solv}(H^\bullet)_{aq}$. The same correction applies to $E^\circ(H^\bullet/H^-)_{aq}$, which was also estimated[13] and is equal to −0.12 V vs NHE(aq) after correction.

Standard Potential of the $(H^+/H^\bullet)$ Couple in Nonaqueous Solvents. In the previous section, it was shown that $\Delta G_{solv}(gas)_{aq}$'s are directly dependent upon the van der Waals radii of the atoms and that $\Delta G_{solv}(H^\bullet)_{aq}$ should be closely approximated by the corresponding term for helium. Scheme I can be modified to apply to any solvent S by substituting S for aq in the appropriate terms. This results in eq 5 for the standard potential for the $(H^+/H^\bullet)$

$$E^\circ{}_{NHE(S)}(H^+/H^\bullet)_S = -(\Delta G_{solv}(H^\bullet)_S + \Delta G_f(H^\bullet)_{gas})/F \quad (5)$$

redox couple. Evaluation of $E^\circ{}_{NHE(S)}(H^+/H^\bullet)_S$ then requires that $\Delta G_{solv}(H^\bullet)_S$ be estimated in S and the reference potential scale be the standard hydrogen electrode in S, NHE(S).

It is common practice[1] to convert electrode potentials measured in nonaqueous solvents to the NHE(aq) scale when applying thermochemical cycles. This practive involves, out of necessity, using the free energy of transfer of the proton from water to S $[\Delta G_{tr}{}^{aq\rightarrow S}(H^+)]$. The derivation of the latter involves extra-thermodynamic assumptions,[14] such as the tetraphenylborate assumption. The relationship between $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_S$ in S and $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_{aq}$ is illustrated in Scheme II. The free energies of transfer of the proton from water to a number of solvents $[\Delta G_{tr}{}^{aq\rightarrow S}(H^+)$'s] have been reported,[14] and Scheme II can be used to determine $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_S$, providing that $\Delta\Delta G_{solv}(H^\bullet)$, the difference in solvation energies of $H^\bullet$ in solvent S and in water, can be estimated.

The solubility of He in dimethyl sulfoxide at 298 K has been determined,[15a] and applying eq 3 results in a value of 6.20 kcal/mol for $\Delta G_{solv}(H^\bullet)_{DMSO}$. Solubility data for He in acetonitrile are not available. However, values of $\Delta G_{solv}(H_2)_S$ in all three solvents are available; 6.5 kcal/mol[9] (water), 5.1 kcal/mol[15b] (acetonitrile), and 5.7 kcal/mol[15b] (dimethyl sulfoxide) at 298 K have been reported. Thermodynamic solvation data for H_2 are not necessarily expected to fit in the correlation of the data for the spherical noble gas atoms. However, $\Delta G_{solv}(H_2)_{aq}$ falls between that for He (R = 122 pm) and that for Ne (R = 160 pm), which appears reasonable, since the van der Waals radius of $H^\bullet$ is 120 pm and H_2 is expected to be somewhat larger. This would appear to justify assuming that the change in solvation energy in going from water to S $[\Delta\Delta G_{solv}(H^\bullet)]$ is equal to that for the hydrogen molecule.

Scheme III

$$\begin{array}{lll}
 & & \underline{\text{Free Energy Change}} \\
H\text{-}A & \rightleftarrows \; H^+ + A^- & \Delta G_{het}(H\text{-}A)_S \\
H^\bullet + A^\bullet & \rightleftarrows \; H\text{-}A & -\Delta G_{hom}(H\text{-}A)_S \\
\hline\hline
H^\bullet + A^\bullet & \rightleftarrows \; H^+ + A^- & -FE^\circ{}_{NHE(S)}(A^\bullet - H^+)_S
\end{array}$$

This then results in $\Delta G_{solv}(H^\bullet)_S$ being equal to 5.7 kcal/mol in acetonitrile.

Application of Scheme I, using these estimates of $\Delta G_{solv}(H^\bullet)_S$ results in the $E^\circ{}_{NHE(S)}(H^+/H^\bullet)_S$ values found in the last column of Table II; −2.35 V (acetonitrile) and −2.38 V (dimethyl sulfoxide). Using the relationships in Scheme II and the data summarized in Table II then results in $E^\circ{}_{NHE(aq)}(H^+/H^\bullet)_S$ being equal to −1.88 V (acetonitrile) and −2.58 V (dimethyl sulfoxide). In the discussion that follows, values of $E^\circ{}_{NHE(S)}(H^+/H^\bullet)_S$ are used in thermochemical cycles to compute bond dissociation free energies. This choice of reference scale avoids the uncertainties associated with the use of $\Delta G_{tr}{}^{aq\rightarrow S}(H^+)$ estimated using extra-thermodynamic assumptions.

Application of $E^\circ{}_{NHE(S)}(H^+/H^\bullet)_S$ To Determine Bond Dissociation Free Energies. The difference in free energies of heterolytic and homolytic bond dissociation energies above the double line in Scheme III is directly related to the electrode potential difference below the double line.[1] Thus, $\Delta G_{het}(H\text{-}A)_S - \Delta G_{hom}(H\text{-}A)_S$ can be determined directly from the difference in reduction potentials of $A^\bullet$ and H^+. Since an abundance of $\Delta G_{het}(H\text{-}A)_S$ data (equal to $2.303RT(pK_a)$) exists, the most important application of Scheme III is for the determination of $\Delta G_{hom}(H\text{-}A)_S$. The gas-phase bond dissociation energy [BDE(H–A)] can be obtained from the relationship in eq 6. The last two terms in

$$\begin{aligned} \mathrm{BDE}(H\text{-}A) = {} & \Delta G_{hom}(H\text{-}A)_S - \Delta G_{solv}(H^\bullet)_S + TS^\circ{}_f(H^\bullet) - \\ & \Delta\Delta G_{solv}[A^\bullet - H\text{-}A]_S + TS^\circ{}_f[A^\bullet - H\text{-}A] \quad (6) \end{aligned}$$

(6), the differences in solvation energies ($\Delta\Delta G_{solv}[A^\bullet - H\text{-}A]_S$) and the entropy terms ($TS^\circ{}_f[A^\bullet - H\text{-}A]$) of $A^\bullet$ and H–A, are most often neglected in similar equations on the basis that the quantities for $A^\bullet$ and H–A cancel.

Bond Dissociation Free Energies in Solution. The major source of error in the use of Scheme III to determine BDE(H–A) is the uncertainty accompanying either the neglect of or the estimation of the last two terms in eq 6. On the other hand, $\Delta G_{hom}(H\text{-}A)_S$ is calculated directly without the need to evaluate any terms not included in Scheme III. Bond dissociation energies are often used to determine the feasibility of reactions in solution. When this is the case, $\Delta G_{hom}(H\text{-}A)_S$, rather than the gas-phase BDE(H–A), is the more pertinent quantity. In the following paragraphs, values of $\Delta G_{hom}(H\text{-}A)_S$ are evaluated for a number of different types of homolysis reactions.

One-electron redox potentials, determined by equilibrium measurements, of 4-substituted phenolates in water have recently been reported.[5] Upper limits of BDE(ArO–H) were evaluated using a thermochemical cycle. The estimations did not take into account the solvation energies of ArOH and $ArO^\bullet$, and for this reason the absolute values of BDE(ArO–H) are believed to be about 3 kcal/mol lower than the estimated upper limits. The electrode potential data,[5] along with pK_a values,[16] were used in the relationships of Scheme III to determine $\Delta G_{hom}(ArO\text{-}H)_{aq}$ values which are summarized in Table III. The gas-phase BDE(ArO–H)'s, derived using eq 6, are listed in the last column. Following Merenyi,[5] a value of −0.43 kcal/mol was assigned to $TS^\circ{}_f(PhO^\bullet - PhOH)$ and $\Delta\Delta G_{solv}(PhO^\bullet - PhOH)_{aq}$ was taken to equal 3.0 kcal/mol. it is of interest to note that the BDE(ArO–H)'s calculated using these assumptions are 2.8–2.9 kcal/mol lower than the upper limits estimated earlier with neglect of the $\Delta\Delta G_{solv}(PhO^\bullet - PhOH)_{aq}$ term. This remarkable correspondence suggests that any error in $\Delta G_{hom}(ArO\text{-}H)_{aq}$ is small

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Table III. Phenolic O–H Bond Dissociation Free Energies in Water^{a}

substituent	pK-(ArOH)$_{aq}$^{b}	E°(ArO$^\bullet$/ArO$^-$)$_{aq}$^{c}	ΔG_{hom}-(ArO–H)$_{aq}$^{d}	BDE-(ArO–H)^{e}
4-H	10.0	0.79	87.7	85.4
4-CH_3	10.3	0.68	85.5	83.2
4-OCH_3	10.1	0.54	82.0	79.7
4-F	9.9	0.76	86.8	84.5
4-Cl	9.4	0.80	87.1	84.8
4-Br	9.4	0.82	87.5	85.2
4-I	9.3	0.82	87.4	85.1
4-CO_2^-	9.4	0.90	89.4	87.1
4-$COCH_3$	8.0	1.00	89.8	87.5
4-CN	7.9	1.12	92.4	90.1
4-NO_2	7.1	1.22	93.6	91.3

^{a}Bond dissociation energies in kcal/mol. ^{b}pK_a from ref 16. ^{c}Standard electrode potentials from ref 5. ^{d}This study, calculated using relationships in Scheme III. ^{e}Calculated upper limits of gas phase bond dissociation energies from ref 5. BDE(ArO–H) = 1.363pK_a + 23.06$E°_{\mathrm{NHE(aq)}}$(ArO$^\bullet$/ArO$^-$) + 56.3.

Table IV. Bond Dissociation Free Energies of Selected H–A's

A^-	pK_a-(H–A)^{a}	$\Delta E°$ ^{b}	ΔG_{hom}-(H–A)$_{aq}$^{c}	BDE-(H–A)^{d}
$O_2^{\bullet -}$	4.7	2.23	57.8	
HSe^-	3.9	3.04	75.4	
$CH_3COCH_2^-$	19.1	3.06	96.6	93 ± 1
n-$C_3H_7S^-$	10.8	3.16	87.6	
PhS^-	6.5	3.18	82.2	
HO_2^-	11.7	3.25	90.9	87.2 ± 1
NO_2^-	3.4	3.31	81.0	78.3 ± 0.5
PhO^-	9.9	3.34	90.5	88 ± 5
ClO_2^-	2.0	3.35	78.6	
HS^-	6.9	3.50	90.1	90.5 ± 1
CH_3O^-	15.0	3.52	101.6	104.4 ± 1
$CF_3CH_2O^-$	12.5	3.70	102.4	
N_3^-	4.7	3.69	91.5	85
SCN^-	0.9	4.08	95.3	
HO^-	15.7	4.14	116.9	119 ± 1
$CH_3CO_2^-$	4.8	4.46	109.4	106
NO_3^-	−1.4	4.70	106.5	101.2 ± 0.5
Cl^-	1.4	4.73	111.0	103.13
CN^-	9.3	4.94	126.6	120 ± 1
F^-	3.5	5.80	138.5	136.2

^{a}Values compiled in ref 17. ^{b}Difference in redox potentials in V of (A$^\bullet$/A$^-$)$_{aq}$, obtained by converting the aqueous solution ionization potentials from ref 17, and (H$^+$/H$^-$)$_{aq}$. ^{c}Bond dissociation free energies in kcal/mol obtained using the relationships in Scheme III. ^{d}Gas-phase values in kcal/mol from ref 8.

Table V. Hydrocarbon (C–H) Bond Dissociation Free Energies in Dimethyl Sulfoxide

R–H	pK_a-(R–H)$_{\mathrm{DMSO}}$	E°-(R$^\bullet$/R$^-$)^{a}	BDE-(R–H)^{b}	ΔG_{hom}-(R–H)$_{\mathrm{DMSO}}$^{b}
An–CH_2–H^{c}	31.1	1.73	84.1	82.3
Ph_2C–H	32.3	1.68	84.5	82.8
Ph_3C–H	30.6	1.62	81.0	79.1
Cp–H^{d}	18.0	2.50	83.9	82.2
In–H^{e}	20.1	2.27	81.5	79.8
Fl–H^{f}	22.6	2.15	82.2	80.4

^{a}Anion redox potentials vs ferrocenium/ferrocene from ref 2b in V adjusted to $E°_{\mathrm{NHE(DMSO)}}$(H$^+$/H$^\bullet$)$_{\mathrm{DMSO}}$. $E°_{\mathrm{NHE(DMSO)}}$(ferrocenium/ferrocene)$_{\mathrm{DMSO}}$ = 0.732 V from: Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1972**, *76*, 2024. A kinetic shift of 0.11 V was applied to all potentials except that for Ph_3CH as explained in ref 1. ^{b}C–H bond dissociation energies in kcal/mol. ^{c}An = 9-anthracenyl. ^{d}Cp = cyclopentadienyl. ^{e}In = indenyl. ^{f}Fl = 9-fluorenyl.

Table VI. Dissociation Free Energies of Selected Bonds in Acetonitrile^{a}

substance	pK_a-(H–A)$_{\mathrm{AN}}$	E°-(A$^\bullet$/A$^-$)^{b}	BDE-(H–A)	ΔG_{hom}-(H–A)$_{\mathrm{AN}}$
2,6-di-*tert*-butyl-4-nitro-C_6H_2O-H	19.0^{c}	2.46	86.7^{e}	82.6
(η^5-C_5H_5)Cr$(CO)_3$H	13.3^{d}	1.71	61.5^{f}	57.6
(η^5-C_5H_5)Cr$(CO)_2$-(PPh_3)H	21.8^{e}	1.11	59.8^{f}	55.3

^{a}Energies in kcal/mol. ^{b}Anion redox potentials vs $E°_{\mathrm{NHE(AN)}}$(H$^+$/H$^\bullet$)$_{\mathrm{AN}}$ from ref 1. $E°_{\mathrm{NHE(AN)}}$(ferrocenium/ferrocene)$_{\mathrm{AN}}$ = 0.051 V from: Kolthoff, I. M.; Chantooni, M. M., Jr. *J. Phys. Chem.* **1972**, *76*, 2024. ^{c}From: Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23. ^{d}Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. ^{e}From ref 1. ^{f}Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

and that the uncertainty in BDE(ArO–H) arises almost entirely from the estimates of the values of the last two terms in eq 6.

The experimental errors in the determination of ΔG_{hom}(ArO–H)$_{aq}$ using Scheme III are those in the determination of pK_a-(ArO–H)$_{aq}$ and $E°_{\mathrm{NHE(aq)}}$(PhO$^\bullet$/PhO$^-$)$_{aq}$. These same experimental errors appear in the BDE(ArO–H) estimated using the thermochemical cycle.[5] In addition, the BDE(ArO–H)'s determined previously[5] or here (Table III) using eq 6 are associated with the additional uncertainty in the estimation of the last two terms in eq 6.

Aqueous solution ionization potentials of a number of inorganic anions have recently been compiled.[17] These were converted to $E°_{\mathrm{NHE(aq)}}$(A$^\bullet$/A$^-$)$_{aq}$ by subtracting 4.50 V, the number used[17] for the absolute potential of the NHE(aq).[18] The entries in Table IV are only those for which experimental values of pK_a(H–A)$_{aq}$ of the conjugate acids are available. The calculated values of ΔG_{hom}(H–A)$_{aq}$ may be compared to the available gas-phase BDE(H–A)'s found in the last column. Usually, but not always, values for BDE(H–A) are less than those for ΔG_{hom}(H–A)$_{aq}$ by a few kcal/mol. It seems likely that the greater variation in the differences between the two quantities in Table IV as compared to that in Table III is due to greater errors both in $E°_{\mathrm{NHE(aq)}}$(A$^\bullet$/A$^-$)$_{aq}$ and in the gas-phase BDE(H–A). The uncertainty in the former has been estimated to be ±3.5 kcal/mol (±0.15 V).[17] In this regard it is of interest to note that ΔG_{hom}-(PhO–H)$_{aq}$ appears in both tables and that in Table IV is 3 kcal/mol greater than the other value. This discrepancy is due to a 0.13-V difference in $E°_{\mathrm{NHE(aq)}}$(PhO$^\bullet$/PhO$^-$)$_{aq}$. The experimental redox potentials in Table III have a reported[5] uncertainty of only ±0.02 V (±0.5 kcal/mol).

The hydrocarbon C–H bond dissociation energies listed in Table V were derived with the relationships in Scheme III along with experimental pK_a[20] and anion redox (A$^\bullet$/A$^-$) potentials in dimethyl sulfoxide.[2b] The redox potentials have been corrected for a kinetic contribution before calculating the BDE(R–H).[1] The BDE(R–H) values exceed the corresponding values for ΔG_{hom}(R–H)$_{\mathrm{DMSO}}$ by about 1.8 kcal/mol.

The anion redox potentials in acetonitrile (Table VI) are reversible values used together with pK_a(H–A)$_{\mathrm{AN}}$ in Scheme III to obtain ΔG_{hom}(H–A)$_{\mathrm{AN}}$.[1] In this case, BDE(H–A) − ΔG_{hom}(H–A)$_{\mathrm{AN}}$ is more positive than in either of the other two solvents. The effect of changing the solvent on this difference is predicted using eq 6 to be a function only of the relative solvation energies as summarized in eq 7. The use of eq 7 to discuss quantitative

$$\Delta[\mathrm{BDE(H{-}A)} - \Delta G_{\mathrm{hom}}(\mathrm{H{-}A})]^{\mathrm{aq}\to\mathrm{S}} = -\Delta\Delta G_{\mathrm{solv}}(\mathrm{H}^\bullet)^{\mathrm{aq}\to\mathrm{S}} + \Delta\Delta G_{\mathrm{solv}}(\mathrm{H{-}A} - \mathrm{A}^\bullet)^{\mathrm{aq}\to\mathrm{s}} \quad (7)$$

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(17) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(18) The value recommended by IUPAC is 4.44 ± 0.02 V,[19] which suggests that the aqueous ionization potentials reported by Pearson[17] may be 60 mV too high. However, this does not create any error in $E°_{\mathrm{NHE(aq)}}$(A$^\bullet$/A$^-$), since the value used[17] was subtracted to derive the electrode potentials.

(19) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955.

(20) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(21) BDE(PhO–H) determined by photoacoustic calorimetry in benzene[22] is similar to the aqueous value.[5] This work has been extended to BDE(ArO–H) in both acetonitrile and benzene, and results strongly suggest that ArOH, but not ArO, is stabilized in acetonitrile by hydrogen bonding.[23]

(22) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090.

(23) Mulder, P.; Wayner, D. D. M. Unpublished results.

Scheme IV

	Free Energy Change
$\mathrm{H{-}A(aq)} \rightleftarrows \mathrm{H^+(aq)} + \mathrm{A^-(aq)}$	$2.303RT\mathrm{p}K_a$
$\mathrm{H^+(aq)} + \mathrm{A^-(aq)} \rightleftarrows 1/2\ \mathrm{H_2(gas)} + \mathrm{A^\bullet(aq)}$	$FE^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{aq}}$
$\mathrm{H{-}A(aq)} \rightleftarrows 1/2\ \mathrm{H_2(gas)} + \mathrm{A^\bullet(aq)}$	$2.303RT\mathrm{p}K_a + FE^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{aq}}$

solvent effects is hampered by the uncertainty in $\Delta G_{\mathrm{solv}}(\mathrm{H^\bullet})_\mathrm{S}$ in acetonitrile and must await the determination of $\Delta G_{\mathrm{solv}}(\mathrm{He})_\mathrm{S}$ in this solvent. Some qualitative observations are in order. The observed change in going from water to dimethyl sulfoxide is 4.5 kcal/mol, suggesting that the contribution due to $\Delta\Delta G_{\mathrm{solv}}(\mathrm{H{-}A} - \mathrm{A^\bullet})_{\mathrm{DMSO}}$ is of the order of 3.5 kcal/mol. This can readily be accounted for by the differences in H–A's in the comparison. For the reactions in water, H–A refers to phenols which are strongly hydrogen bonded to the solvent, while, for the reactions in dimethyl sulfoxide, H–A refers to hydrocarbons which do not hydrogen bond.[18] On the other hand, $\Delta\Delta G_{\mathrm{solv}}(\mathrm{H{-}A} - \mathrm{A^\bullet})_{\mathrm{AN}}$ is calculated to be an additional 2.4 kcal/mol for the reactions in acetonitrile. It appears unlikely that the solvation energy of $\mathrm{A^\bullet}$ is more negative than that of H–A in acetonitrile, since existing[23] evidence suggests that there is no specific interaction between $\mathrm{A^\bullet}$ and acetonitrile. The alternative explanation is that the estimate of $\Delta\Delta G_{\mathrm{solv}}(\mathrm{H^\bullet})_{\mathrm{AN}}$, and hence $E^\circ_{\mathrm{NHE(AN)}}(\mathrm{H^+/H^\bullet})_{\mathrm{AN}}$, in Table II is in error by about 2.4 kcal/mol. A more detailed comparison, using the same H–A in all three solvents, will be warranted when a more reliable estimate of $\Delta G_{\mathrm{solv}}(\mathrm{H^\bullet})_{\mathrm{AN}}$ is available.

Relationships between the Enthalpy in the Gas Phase and Enthalpy and Free Energy of Bond Dissociation in Solution. The relationship between gas-phase and solution bond dissociation energies is given by eq 8. The latter is related to $\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_\mathrm{S}$ by eq 9, in which $T\Delta S_\mathrm{S}$ is defined by eq 10. Substituting (10) into (9) results in eq 11.

$$\mathrm{BDE(H{-}A)_{gas}} = \mathrm{BDE(H{-}A)_S} - \Delta H_{\mathrm{solv}}(\mathrm{H^\bullet} + \mathrm{A^\bullet} - \mathrm{H{-}A})_\mathrm{S} \quad (8)$$

$$\mathrm{BDE(H{-}A)_S} = \Delta G_{\mathrm{hom}}(\mathrm{H{-}A}) + T\Delta S_\mathrm{S} \quad (9)$$

$$T\Delta S_\mathrm{S} = TS^\circ_\mathrm{f}(\mathrm{H^\bullet} + \mathrm{A^\bullet} - \mathrm{H{-}A}) + T\Delta S_{\mathrm{solv}}(\mathrm{H^\bullet} + \mathrm{A^\bullet} - \mathrm{H{-}A})_\mathrm{S} \quad (10)$$

$$\mathrm{BDE(H{-}A)_S} = \Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_\mathrm{S} + TS^\circ_\mathrm{f}(\mathrm{H^\bullet} + \mathrm{A^\bullet} - \mathrm{H{-}A}) + T\Delta S_{\mathrm{solv}}(\mathrm{H^\bullet} + \mathrm{A^\bullet} - \mathrm{H{-}A})_\mathrm{S} \quad (11)$$

The common assumption that the thermodynamic quantities for $\mathrm{A^\bullet}$ and H–A differ negligibly leads to eqs 12 and 13, which

$$\mathrm{BDE(H{-}A)_{gas}} = \mathrm{BDE(H{-}A)_S} - \Delta H_{\mathrm{solv}}(\mathrm{H^\bullet})_\mathrm{S} \quad (12)$$

$$\mathrm{BDE(H{-}A)_S} = \Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_\mathrm{S} + TS^\circ_\mathrm{f}(\mathrm{H^\bullet}) + T\Delta S_{\mathrm{solv}}(\mathrm{H^\bullet})_\mathrm{S} \quad (13)$$

contain only terms for $\mathrm{H^\bullet}$ in addition to the bond dissociation energies. In water, $\Delta H_{\mathrm{solv}}(\mathrm{He})_{\mathrm{aq}}$ is equal to −0.8 kcal/mol, and assuming the same value for $\Delta H_{\mathrm{solv}}(\mathrm{H^\bullet})_{\mathrm{aq}}$ in eq 12 leads to the conclusion that the gas-phase and solution $\mathrm{BDE(H{-}A)_{aq}}$'s differ by only 0.8 kcal/mol. Similarly, assuming $\Delta S_{\mathrm{solv}}(\mathrm{H^\bullet})_{\mathrm{aq}}$ in (13) is equal to the corresponding term for He in water leads to the conclusion that $\mathrm{BDE(H{-}A)_{aq}}$ exceeds $\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_{\mathrm{aq}}$ by only 0.3 kcal/mol.

Conclusions. The free energies of solvation of the noble gases (He to Kr) in water are directly correlated to the van der Waals radii of the atoms, and this correlation provides a means of estimating the experimentally inaccessible free energy of solvation of the hydrogen atom. Having a reliable value of the latter, we derived the standard potential of the $(\mathrm{H^+/H^\bullet})$ couple using the relationships in Scheme I. The integrity of $E^\circ_{\mathrm{NHE(aq)}}(\mathrm{H^+/H^\bullet})_{\mathrm{aq}}$ derived, −2.42 V, is strongly supported by the fact that $\Delta\Delta G_{\mathrm{solv}}(\mathrm{ArO^\bullet} - \mathrm{ArOH})_{\mathrm{aq}}$ values are observed to be equal to 2.8–2.9 kcal/mol, which have previously been estimated to be equal to about 3 kcal/mol. Values of $E^\circ_{\mathrm{NHE(S)}}(\mathrm{H^+/H^\bullet})_\mathrm{S}$ were also derived in acetonitrile (−2.35 V) and dimethyl sulfoxide (−2.38 V). These potentials can be used to calculate reliable $\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_\mathrm{S}$ values in solution. For nonaqueous solvents, a less rigorous alternative involves evaluation of $E^\circ_{\mathrm{NHE(aq)}}(\mathrm{H^+/H^\bullet})_\mathrm{S}$ using the free energy of transfer of the proton from water to S.

Scheme V

	Free Energy Change
$\mathrm{H{-}A(aq)} \rightleftarrows 1/2\ \mathrm{H_2(gas)} + \mathrm{A^\bullet(aq)}$	$2.303RT\mathrm{p}K_a + FE^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{aq}}$
$\mathrm{H{-}A(gas)} \rightleftarrows \mathrm{H{-}A(aq)}$	$\Delta G_{\mathrm{solv}}(\mathrm{H{-}A})$
$1/2\ \mathrm{H_2(gas)} \rightleftarrows \mathrm{H^\bullet(gas)}$	$\Delta G_\mathrm{f}(\mathrm{H^\bullet})$
$\mathrm{A^\bullet(aq)} \rightleftarrows \mathrm{A^\bullet(gas)}$	$-\Delta G_{\mathrm{solv}}(\mathrm{A^\bullet})$
$\mathrm{H{-}A(gas)} \rightleftarrows \mathrm{H^\bullet(gas)} + \mathrm{A^\bullet(gas)}$	$\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_{\mathrm{gas}}$

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Appendix

In order to avoid possible confusion regarding the differences in thermochemical relationships derived in this paper compared to those previously used, more detail concerning the thermochemical relationships is provided here.

A. Thermochemical Cycles Using NHE(aq) as the Energy Reference for Reactions in Aqueous Solution. The free energy change involved in the homolytic cleavage of an H–A bond can be referenced to NHE(aq) by considering the following reactions:

$$\mathrm{H^+(aq)} + \mathrm{A^-(aq)} \rightleftarrows {}^1\!/_2\mathrm{H_2(g)} + \mathrm{A^\bullet(aq)} \quad (a)$$

$$\Delta G^\circ(\text{reaction a})_{\mathrm{aq}} = FE^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{aq}} \quad (b)$$

The free energy of reaction a is directly related to the reduction potential of $\mathrm{A^\bullet(aq)}$ by eqn b. A thermochemical cycle (Scheme IV) can be written in which reaction a is summed with the heterolytic cleavage of H–A in solution, resulting in a hypothetical homolytic cleavage reaction in which H–A is in solution, $\mathrm{A^\bullet}$ remains in solution, and $\mathrm{H^\bullet}$ generated ends up in the gas phase as ${}^1\!/_2\mathrm{H_2(g)}$. The hypothetical homolytic cleavage reaction, for which the free energy change is available via Scheme IV, has no direct physical meaning in terms of bond dissociation energies. However, the gas-phase bond dissociation free energy, $\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_{\mathrm{gas}}$, can be derived from this free energy change using the relationship in Scheme V. The enthalpic gas-phase bond dissociation energy, BDE(H–A), can then be calculated using eq c.

$$\mathrm{BDE(H{-}A)} = \Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_{\mathrm{gas}} + TS_\mathrm{f}^\circ(\mathrm{H^\bullet}) + TS_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A}) \quad (c)$$

The differences between scheme III, from which we derive $\Delta G_{\mathrm{hom}}(\mathrm{H{-}A})_{\mathrm{aq}}$, and the relationships in schemes IV and V and eq c are obvious. The rigorous use of eq c requires that $\Delta\Delta G_{\mathrm{solv}}(\mathrm{H{-}A} - \mathrm{A^\bullet})$ and $T\Delta S_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A})$ can be evaluated experimentally. This is seldom possible, and these terms are most often neglected. On the other hand, the use of the relationships in Scheme III does not require the evaluation of any of these terms.

B. Equations for Calculating Gas-Phase BDE(H–A) from Electrode Potentials. The general equation derived from Schemes IV and V is

$$\mathrm{BDE(H{-}A)} = 2.303RT(\mathrm{p}K_a) + FE^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_\mathrm{S} + \Delta G_\mathrm{f}(\mathrm{H^\bullet}) + TS_\mathrm{f}^\circ(\mathrm{H^\bullet}) + \Delta G_{\mathrm{tr}}^{\mathrm{aq}\rightarrow\mathrm{sol}} + TS_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A}) - \Delta\Delta G_{\mathrm{solv}}(\mathrm{A^\bullet} - \mathrm{H{-}A}) \quad (d)$$

When the solvent is water and values of known quantities are substituted in (d), the equation, at 298.15 K, becomes

$$\mathrm{BDE(H{-}A)} = 1.364\mathrm{p}K_a + 23.06E^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{aq}} + 56.7 + TS_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A}) - \Delta\Delta G_{\mathrm{solv}}(\mathrm{A^\bullet} - \mathrm{H{-}A}) \quad (e)$$

The corresponding equation when the solvent is dimethyl sulfoxide is

$$\mathrm{BDE(H{-}A)} = 1.364\mathrm{p}K_a + 23.06E^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{DMSO}} + 61.2 + TS_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A}) - \Delta\Delta G_{\mathrm{solv}}(\mathrm{A^\bullet} - \mathrm{H{-}A}) \quad (f)$$

When the solvent is acetonitrile, eq d becomes

$$\mathrm{BDE(H{-}A)} = 1.364\mathrm{p}K_a + 23.06E^\circ_{\mathrm{NHE(aq)}}(\mathrm{A^\bullet/A^-})_{\mathrm{AN}} + 48.4 + TS_\mathrm{f}^\circ(\mathrm{A^\bullet} - \mathrm{H{-}A}) - \Delta\Delta G_{\mathrm{solv}}(\mathrm{A^\bullet} - \mathrm{H{-}A}) \quad (g)$$