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Review

Gas-phase hydride affinities of neutral molecules

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Abstract

In this review we report the hydride affinities for neutral molecules. The hydride affinity is defined as the enthalpy of reaction for the dissociation of RH^- to yield $R + H^-$. These important thermodynamic quantities, however, are not often measured experimentally. Instead, hydride affinities are typically calculated from thermochemical cycles. We show several methods for calculating hydride affinities and have compiled a list of hydride affinities for a large number of molecules. In addition to reporting hydride affinities for many common compounds, this review also details the hydride affinities of reactive intermediates, including radicals, carbenes, biradicals, and triradicals. The hydride affinities reported in this review are interpreted on the basis of thermochemical data and simple molecular orbital pictures.

Keywords: Hydride affinity; Thermochemistry; Radicals; Carbenes; Biradicals

Contents

1. Introduction

The hydride ion plays an important role in many chemical reactions. For instance, hydride shifts are common rearrangements of carbocations, such as the 1,2- or 1,3-hydride shifts of primary carbocations to form either secondary or tertiary carbocations [1,2]. Hydride shifts can also occur between molecules, such as the reaction of R^+ and $R'H$ to give $RH + R'^+$ [1,3]. In biochemistry, the interconversion of NADH and NAD^+ or other biologically relevant molecules has been the subject of intense debate [4–10] and is thought to occur either via a one-step hydride transfer or by a stepwise electron–proton–electron transfer. Similar reactions, hydride elimination or abstraction, are typically found in organometallic chemistry, and have important implications in catalysis [11,12]. Metal hydrides, especially LiH, $LiBH_4$, $LiAlH_4$, $NaBH_4$, and $NaAlH_4$, are important in a number of organic chemical reactions because of their capacity as hydride donors [13–15]. Recently, metal hydride systems are being studied for use as hydrogen storage devices [16–21]. Because hydride ions have an important and diverse

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role in chemical reactivity, it is important that they are characterized thermochemically. Perhaps the most useful thermochemical property for assessment of hydride transfer reactions is the hydride affinity (HA), defined as the enthalpy of reaction in Eq. (1a). Although hydride affinities of cations, the enthalpy of reaction for Eq. (1b), can also be determined, this review focuses on hydride affinities of neutral molecules. In principle, hydride affinities, like all thermochemical properties, can refer to any temperature. However, in this work we always refer to the hydride affinity as the 298 K enthalpy.

$$RH^- \rightarrow R + H^- \quad (1a)$$

$$RH \rightarrow R^+ + H^- \quad (1b)$$

The definition of hydride affinities, as shown in Eq. (1a), reveals that hydride affinities are readily obtained from enthalpies of formation of RH^- and R as shown in Eq. (2).

$$HA(R) = \Delta H_f(R) + \Delta H_f(H^-) - \Delta H_f(RH^-) \quad (2)$$

A large number of neutrals and anions have known heats of formation, and the corresponding HAs can be calculated directly by using Eq. (2). The two most common approaches for determining the heat of formation of anion RH^- involve either the gas-phase acidity of RH_2, $\Delta H_{acid}(RH_2)$, or the electron affinity, EA, of RH. Although the electron affinity technically corresponds to the 0 K energy for electron loss from the anion, the temperature correction involved to convert it to 298 K enthalpy is generally assumed to be small and is not included. It is possible to calculate hydride affinities directly by using the gas-phase acidity of RH_2 and the heat of formation of R, as shown in Eq. (3). However, HAs can also be calculated by using cycles involving other

$$RH_2 \rightarrow RH^- + H^+ \qquad \Delta H_{rxn} = \Delta H_{acid}(RH_2) = \Delta H_f(RH^-) + \Delta H_f(H^+) - \Delta H_f(RH_2)$$

$$RH^- \rightarrow R + H^- \qquad \Delta H_{rxn} = HA(R) = \Delta H_f(R) + \Delta H_f(H^-) - \Delta H_f(RH^-)$$

$$H^+ + H^- \rightarrow H_2 \qquad \Delta H_{rxn} = -\Delta H_{acid}(H_2) = \Delta H_f(H_2) - \Delta H_f(H^+) - \Delta H_f(H^-)$$

$$HA(R) = \Delta H_f(R) + \Delta H_{acid}(H_2) - \Delta H_{acid}(RH_2) - \Delta H_f(RH_2)$$

$$= BDE(RH{-}H) + BDE(R{-}H) - BDE(H_2) - \Delta H_{acid}(RH_2) + \Delta H_{acid}(H_2) \quad (3)$$

thermochemical properties, including the C–H bond dissociation energy (BDE), and the ionization energy, IE. As with the electron affinity, the small temperature corrections required to convert the IE, the 0 K energy, to 298 K enthalpy, are generally ignored. The chemical reactions to which these thermochemical properties refer and the relationships among the negative ion thermochemical properties of ions RH^- and R^+ are shown in Fig. 1. This figure illustrates familiar relationships, including that involving BDE, EA, and ΔH_{acid} (Eq. (4)) [22], but also reveals the interplay of other thermochemical properties. For example, there are two convenient routes for calculating HAs (Eqs. (5) and (6)), that require no knowledge of heats of formation and instead rely on the combination of electron affinities, bond dissociation energies, gas-phase acidities, and/or ionization energies. Because the IE(H) and EA(H) are well-defined thermochemical values (Table 1), only the thermodynamic properties on the left side of Fig. 1 are needed to calculate HA(R). Therefore, although few experimental studies have been aimed at determining HAs directly, these quantities can be readily calculated by using primary thermochemical measurements [22]. It should be noted that Eq. (6) is redundant as it is merely a combination of Eqs. (4) and (5).

$$BDE(RH) = \Delta H_{acid}(RH) + EA(R) - IE(H) \quad (4)$$

$$HA(R) = EA(RH) + BDE(RH) - EA(H) \quad (5)$$

$$HA(R) = EA(RH) + \Delta H_{acid}(RH) + EA(R) - IE(H) - EA(H) \quad (6)$$

Experimental methods have been developed for measuring HAs when none of the above methods can be applied. For example, forward and reverse hydride transfer reactions can be used to bracket the HA in select cases [23,24]. Similarly, the HA has been obtained from the measured energy barrier in translationally driven endothermic hydride transfer reactions (Eqs. (7) and (8)). These methods are relative approaches that require HAs for appropriate references.

$$AH^- + B \rightarrow A + BH^- \quad (7)$$

$$HA(A) = HA(B) + \Delta H_{rxn}\,(\text{Eq. (7)}) \quad (8)$$

Reaction-based approaches including bracketing, ion-equilibrium, and kinetic methods are generally challenging because hydride transfer often competes with other reaction processes. For example, because the hydride ion is a strong base, reactions of hydride containing ion often result in deprotonation of the neutral molecule (Eq. (9)). The

$$RH^- + AH \rightarrow R + H_2 + A^- \quad (9)$$

occurrence of this reaction has been used by Hajdasz and Squires to bracket the hydride affinities of silanes [25].

Gas-phase hydride affinities have been reviewed previously by Squires in 1987 [26]. In the nearly two decades since, additional hydride affinities have become available and many of the original values have been revised. Moreover, significant progress has been made in the last 20 years in the measurement of thermochemical properties of reactive species, including radicals, carbenes, and even triradicals, by using negative ion methods. As a result, there are currently a large number of hydride affini-

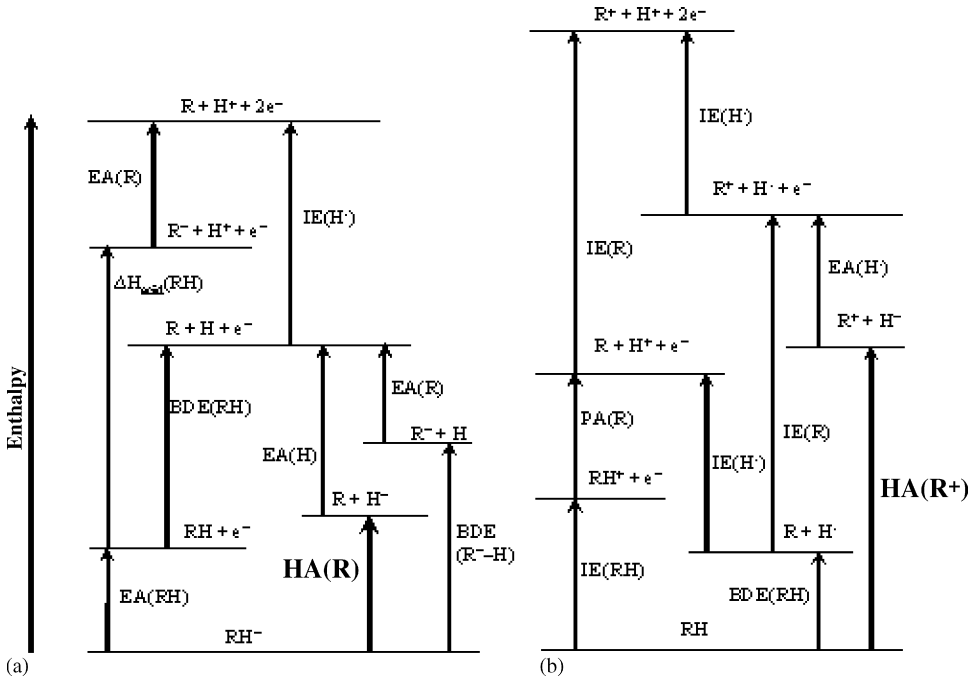

Fig. 1. Relationships among the thermochemical properties that can be used to determine hydride affinities of: (a) neutral molecules, R, and (b) cations, R^+.

ties available for these reactive species that were not known at the time of the last review.

In this review, we update the list of measured hydride affinities. We have chosen to arrange this review into four sections according to the electronic structure of the neutral. There are many similarities in the hydride affinities of these types of systems, both in regard to the magnitudes of the values and in terms of how they are obtained. Most of the hydride affinities listed in the tables have been calculated by using the relations in Eqs. (2), (3), (5), and (6), unless otherwise noted, using up-to-date thermochemical properties [27,28], including the data for hydrogen atom and the hydrogen molecule shown in Table 1. In all the hydride affinity tables, the hydride affinities have been organized in alphabetical order with respect to the molecular formula, and where there are several species of the same molecular formula the data have been placed in descending order of hydride affinity.

2. Hydride affinities of closed-shell molecules

The HAs of closed-shell organic and inorganic species are listed in Table 2. Unless otherwise noted, the HAs reported in this section were calculated by using the known enthalpies of formation of the neutral and the anion [27,28], which are included for reference. The HAs of closed-shell species range from very small (23 kJ mol^{-1}), for carbon monoxide, to very high (443 kJ mol^{-1}) for the boron trifluoride-acetaldehyde complex.

Most of the closed-shell species with positive HAs are unsaturated species, including carbonyls, thiocarbonyls, aromatic molecules, alkenes, and alkynes. In these systems the hydride binding can be described from the interaction between the hydride ($1s^2$) electrons and a π^* orbital, as shown in Fig. 2.

In saturated systems, the interaction occurs between hydride and a σ^* orbital. Because σ^* orbitals are generally much higher in energy than the π^* orbitals, the interactions with hydride tend to be weaker (Fig. 3). Thus, few saturated, closed-shell molecules have positive hydride affinity values, and the values for those that do, such as water and ammonia, tend to be very small. In fact, the hydride adducts of these species are often best described as either solvated hydride ions [29] or double-Rydberg states [30,31], as electrostatic repulsion is significant at the geometries of the covalently bound structures. Silanes have lower energy σ^* orbitals, and therefore have stronger covalent interactions with hydride.

On the other hand, molecules such as alane, AlH_3, and borane, BH_3, have a non-bonding p-orbital as the LUMO, which is very low energy and can readily accept the H^- ($1s^2$) electrons as shown in Fig. 4. The result of this advantageous orbital interaction is reflected in rather large HAs of 314 ± 17 kJ mol^{-1} [32] and 310 ± 12 kJ mol^{-1} [33] for alane and borane, respectively. Alane and borane are classic examples of good Lewis acids, and because H^- is a strong base, the large HAs of alane and borane are not surprising.

Table 1
Thermochemical properties of hydrogen (all values in kJ mol^{-1})

Property	Value	Ref.
BDE(H_2)	435.996 ± 0.012	[53]
EA($H^\bullet$)	72.770 ± 0.002	[54]
IE($H^\bullet$)	1312.073	[55]
$\Delta H_f(H^\bullet)$	217.998 ± 0.006	[53]
$\Delta H_f(H^-)$	145.228 ± 0.006	
$\Delta H_f(H^+)$	1530.071 ± 0.006	
$\Delta H_{acid}(H_2)$[a]	1675.299 ± 0.012	

[a] Evaluated using BDE(H_2) + IE(H) − EA(H).

Table 2
Hydride affinities of closed shell molecules (in kJ mol^{-1} unless noted)

Formula	Molecule (R)	EA(RH) (eV)	BDE(RH)[a]	ΔH_f(R)[b]	ΔH_f(RH$_2$)[b]	ΔH_{acid}(RH$_2$)	HA(R)[c]	Ref.[d]
AlC_3H_9	Trimethyl aluminum			−87 ± 5			>349 ± 5[e]	[56]
AlC_6H_{15}	Triethyl aluminum						356[e,f]	[57]
AlH_3	Alane						314 ± 17[g]	[32]
Al_2H_6	Dialane						322 ± 17[g]	[32]
BCH_2N	Cyanoborane						403 ± 15[g]	[33]
$BC_2F_3H_4O$	Boron trifluoride-acetaldehyde						443 ± 17[e]	[58]
BC_6H_{15}	Triethylborane						290 ± 10[g]	[33]
BH_3	Borane			107			310 ± 12[g]	[33]
B_2H_6	Diborane			41			309 ± 30[g]	[33]
CH_2O	Formaldehyde	1.572 ± 0.004	92 ± 4	−116	−201 ± 1	1597 ± 4	170 ± 4	
CH_2S	Thioformaldehyde	1.867 ± 0.004	213 ± 12	118 ± 8	−23 ± 1	1496 ± 8	319 ± 15	
CH_3N	Methanimine	0.504 ± 0.03		69 ± 8			99 ± 17	
CO	Carbon monoxide	0.313 ± 0.005	63 ± 1	−111 ± 1	−109 ± 1	1651 ± 1	23 ± 2	
COS	Carbonylsulfide			−139 ± 1		1467 ± 13	282[b,h]	[26]
CO_2	Carbon dioxide	2.180 ± 0.020	74 ± 5	−394 ± 1	−379	1449 ± 5	211 ± 5	
CS_2	Carbon disulfide			117 ± 1			281[b,h]	[26]
C_2H_2	Acetylene	0.667 ± 0.024	145 ± 4	227 ± 1	52	1713 ± 3	136 ± 3	
C_2H_2O	Ketene	1.817 ± 0.023	51 ± 5	−48 ± 3	−171 ± 2	1645 ± 4	153 ± 5	
C_2H_4	Ethylene	−0.260 ± 0.089	151 ± 12	52	−84 ± 1	1758 ± 8	53 ± 8	
C_2H_4O	Acetaldehyde	1.712 ± 0.004	64 ± 5	−171 ± 2	−235 ± 1	1583 ± 4	157 ± 5	
C_2H_4S	Thioacetaldehyde	1.953 ± 0.004	168 ± 12	50 ± 8	−46	1488 ± 9	283 ± 15	
C_3H_3N	Acrylonitrile	1.766 ± 0.012		180	51	1569 ± 9	235 ± 9	
C_3H_4	Allene	0.481 ± 0.008		191	20	1636 ± 1	210 ± 1	
C_3H_4	Propyne	0.56 ± 0.19	161 ± 20	185 ± 1	20	1636 ± 1	142 ± 2	
C_3H_4O	2-Propenal[i]	1.590 ± 0.020		−75	−189 ± 1	1528 ± 9	261 ± 9	
	2-Propenal[j]				−123.6 ± 1.5	1563 ± 12	161 ± 12	
C_3H_6O	*n*-Propanal	1.789 ± 0.033	70 ± 6	−189 ± 1	−256 ± 1	1572 ± 5	170 ± 6	
C_3H_6O	Acetone	1.874 ± 0.004	52 ± 4	−219 ± 1	−272 ± 1	1569 ± 4	160 ± 5	
C_4H_6	1,3-Butadiene	0.09 ± 0.12	125 ± 14	109 ± 1	−1 ± 1	1724 ± 8	60 ± 9	
C_4H_6O	2-Butenal	1.90 ± 0.15	141 ± 17	−110 ± 2	−212 ± 1	1526 ± 9	251 ± 12	
C_4H_8	Isobutene	0.05 ± 0.12	132 ± 15	−18 ± 1	134 ± 1	1728 ± 8	63 ± 10	
C_4H_8O	Butyraldehyde	1.78 ± 0.10	73 ± 13	−212 ± 1	−275 ± 1	1570 ± 8	172 ± 9	
C_4H_8O	2-Butanone	1.95 ± 0.10	49 ± 13	−239 ± 1	−293 ± 2	1565 ± 8	164 ± 9	
$C_4H_{12}Si$	Diethylsilane						84 ± 17[e]	[47]
$C_5H_{10}O$	3-Pentanone	1.95 ± 0.15		−254 ± 1	−315 ± 1	1560 ± 8	176 ± 9	
$C_5H_{10}O$	Pentanal	1.89 ± 0.13	61 ± 17	−230		1565 ± 9	171 ± 21	
$C_5H_{10}O$	Isopropyl methyl ketone	1.93 ± 0.15	57 ± 17	−263 ± 1	−316 ± 2	1559 ± 8	170 ± 9	
$C_5H_{14}Si$	*n*-Pentylsilane						84 ± 17[e]	[47]
$C_6H_4O_2$	*o*-Benzoquinone			−88 ± 13	−275 ± 1	1421 ± 9	442 ± 18	[59]
$C_6H_4O_2$	*p*-Benzoquinone			−116 ± 13	−277 ± 1	1466 ± 9	370 ± 18	[59]
$C_6F_3H_5Si$	Phenyl-trifluorosilane						268 ± 13[k]	[60]
C_6H_6	Benzene	1.67 ± 0.04	3 ± 18	83 ± 1	105 ± 1	1562 ± 17	91 ± 19	
$C_6H_{16}Si$	Triethylsilane						84 ± 17[e]	[47]
C_7H_5NO	Phenylisocyanate			−15 ± 2			276[b,h]	[26]
C_7H_6O	Benzaldehyde	2.142 ± 0.013	49 ± 10	−37 ± 3	−95 ± 3	1548 ± 9	183 ± 10	
$C_7H_{14}O$	*n*-Heptanal	1.86 ± 0.13	77 ± 16	−264 ± 4	−340 ± 2	1567 ± 9	184 ± 10	
C_8H_8	Styrene	0.91 ± 0.13	188 ± 15	147 ± 1	30 ± 1	1589 ± 9	203 ± 9	
C_9H_{10}	α-Methylstyrene	0.90 ± 0.13	191 ± 15	118 ± 1	4 ± 1	1585 ± 9	204 ± 9	
H_2O	Water	1.530 ± 0.02		−242 ± 1			72 ± 8[h]	[29]
N_2O	Nitrous oxide						152 ± 17[h]	[26]
OS	Sulfur monoxide	1.655 ± 0.04		5		1481 ± 15	312 ± 4	
SiH_4	Silane			34			93 ± 17[e]	[47]
SiO	Silicon monoxide						205 ± 21[e]	[61]

[a] BDE(RH) evaluated using the relationship $\Delta H_{acid}(RH) + EA(R) - IP(H)$.
[b] Values listed without uncertainty are provided without uncertainty in ref. [27].
[c] Calculated by using Eq. (3) or (6), using data from columns 3–7, unless otherwise noted.
[d] All data taken from refs. [27,28] unless otherwise noted.
[e] HA evaluated using gas-phase hydride transfer bracketing methods.
[f] No uncertainty listed in ref. [57].
[g] HA measured from endothermic hydride transfer reactions.
[h] HA obtained by using Eq. (2), $\Delta H_f(RH^-)$ obtained from the reference in right hand column and using the enthalpy of formation of hydride from Table 1.
[i] For addition of hydride to the 3-position (enolate formation).
[j] For addition of hydride to the 1-position (alkoxide formation).
[k] Evaluated using the relationship $HA(C_6H_5SiF_3) = \Delta H_{acid}(H_2) + \Delta H_f(C_6H_5SiF_3) - \Delta H_{acid}(C_6H_6) - \Delta H_f(C_6H_6) - \Delta H_f(SiHF_3) + DH_{298}(C_6H_5SiHF_3{}^-)$, where $DH_{298}(C_6H_5SiHF_3{}^-)$ is the dissociation energy of $C_6H_5SiHF_3{}^-$ to yield $C_6H_5{}^- + SiHF_3$.

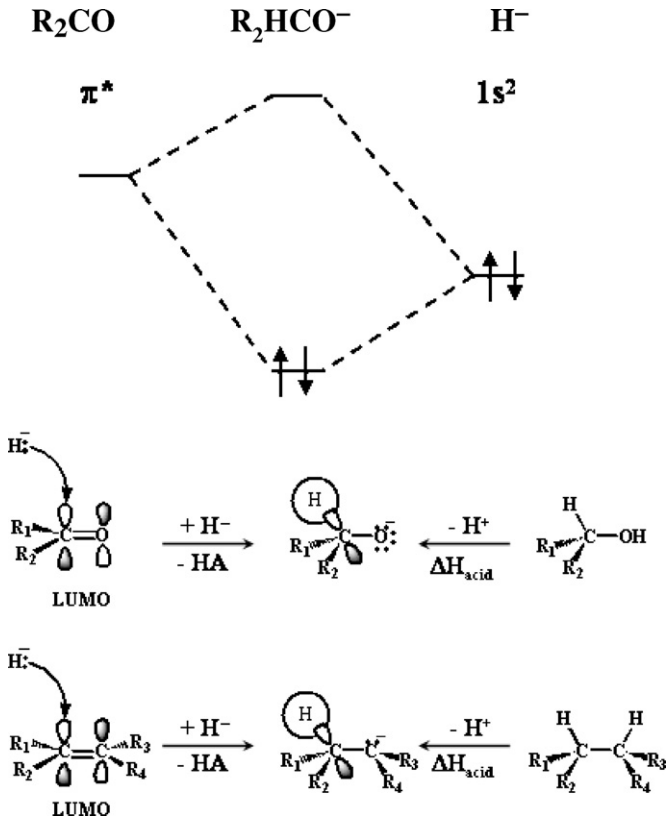

Fig. 2. Schematic orbital energy diagram for the interaction of an occupied 1s orbital in hydride ion with the π* orbital of a carbonyl or alkene. The resulting adduct is covalently bound, producing either a deprotonated alcohol or alkane.

Throughout this work, we deliberately avoid discussing the hydride affinities in the context of anion and neutral "stability." Because stability is a relative concept, invoking it as an explanation for thermochemical properties is tautological. The description of an anion as "more stable" essentially reflects the fact that it has a higher hydride or electron binding energy, or perhaps a lower proton affinity. As shown in Fig. 1, these thermochemical properties are not unrelated, and therefore such assessments merely reflect the relative contributions of the components in Eqs. (3) and (6).

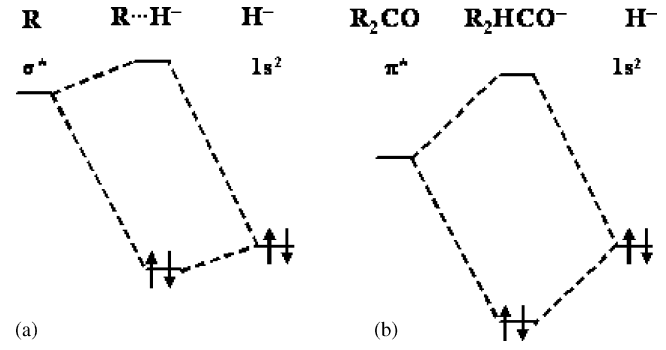

Fig. 3. Schematic orbital energy diagrams for interaction of the occupied 1s orbital in hydride with a: (a) σ* orbital in a saturated molecule or (b) π* orbital in an unsaturated molecule. Because the π* orbital is lower in energy than the σ*, the bonding interaction in (b) is stronger.

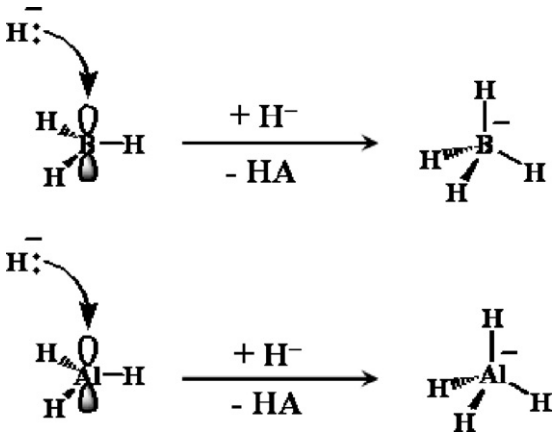

Fig. 4. Addition of hydride to the empty p-orbital on borane and alane.

3. Hydride affinities of radicals

The HAs of radicals are listed in Table 3. Very few radicals have positive hydride affinities because addition of hydride leads to an open-shell radical anion, with a singly occupied, generally anti-bonding orbital (Fig. 5). As such, the most important consideration for the hydride affinities of radicals is whether the anion is bound with respect to electron detachment. Surprisingly, Eq. (5) shows that systems for which the anion, RH^-, exists generally have very high hydride affinities, a consequence of the large homolytic bond dissociation energies in RH molecules. Thus, the HAs of radicals range from ca. 150 to 615 kJ mol^{-1}.

4. Hydride affinities of carbenes, biradicals, carbynes, and triradicals

Although there are few radical species that can form adducts with H^-, hydride addition is much more facile with more unsaturated species. As noted in Section 2, this can apply to molecules with π bonding, but it also applies to reactive molecules including carbenes, biradicals, and beyond. The molecular orbital picture shown in Fig. 6 applies to singlet carbenes, and similar arguments can be employed for other reactive intermediate systems. Hydride binding results in a stabilizing interaction of two orbitals to create a bonding pair of electrons and formation of a non-bonding orbital containing the

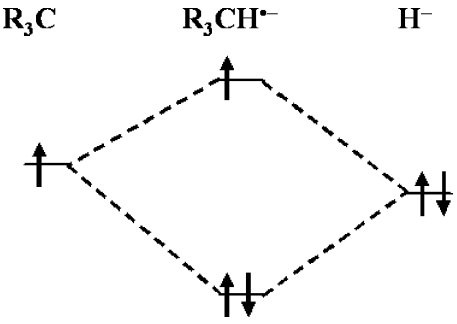

Fig. 5. Schematic orbital energy diagram for the interaction of hydride ion with the singly occupied orbital of a free radical. The resulting adduct contains a single electron in a high energy, generally anti-bonding, orbital.

Table 3
Hydride affinities of radicals (all units kJ mol^{-1})[a]

Formula	Molecule (R)	EA(RH) (eV)	BDE(RH)[b]	HA(R)
CCl_3	Trichloromethyl radical	0.62 ± 0.16	394 ± 13	389 ± 15
C_2H	Ethynyl radical	0.446 ± 0.002	374 ± 14	344 ± 15
CN	Cyano radical	>1.0017	529 ± 1	>615 ± 2
NO	Nitric oxide	0.338 ± 0.015	203 ± 1	163 ± 2
NO_3	Nitrogen trioxide	0.56 ± 0.17	426 ± 2	405 ± 15
OH	Hydroxyl radical		497 ± 1	218 ± 17[c]

[a] Calculated by using Eq. (5), unless otherwise noted.
[b] BDE(RH) = ΔH_{acid}(RH) + EA(R) − IP(H).
[c] HA evaluated using Eq. (2), $\Delta H_f(RH^-)$ obtained from the reference in right hand column and the enthalpy of formation of H^- from Table 1.

remaining pair of electrons. In polyradical species, a low energy LUMO is not required for favorable hydride binding as it was in closed-shell and radical species, because any polyradical with two or more singly occupied orbitals can participate in hydride binding, meaning that in these systems the HOMO must also be considered in the hydride bonding pictures. Addition of hydride to high spin species, such as triplet carbenes or biradicals, could lead to the formation of either a triplet or the spin-forbidden singlet electronic state. Thus, although formation of the singlet product may be thermodynamically favorable, it may be slow. The derived HAs of polyradical reactive intermediates are listed in Table 4. This section also includes isoelectronic species, such as nitrenes and silylenes, isoelectronic with carbenes, and silyne, SiH, isoelectronic with carbynes.

Table 4 also lists HAs of reactive species of small inorganic species also isoelectronic with carbenes and carbynes. For example, imidogen, NH, has a large HA, 410 ± 2 kJ mol^{-1}, and hydride addition yields NH_2^-, which is a strong base. Imidogen is isoelectronic with methylene and both have triplet ground states. Because imidogen and methylene have similar electronic properties it is not surprising that they have similar HAs.

The use of Eq. (5) is very helpful for interpreting the HAs of a number of reactive intermediates. For example, the α,*n*-dehydrotoluenes, α,*n*-dehydrophenols (*n* = 2–4), and *o*-, *m*-, and *p*-benzynes make up several series of biradicals that have different topology, but give the same respective anions upon addition of H^-. As shown in Fig. 7a, removal of H^- from phenyl anion at various positions around the benzene ring results in formation of *o*-, *m*-, or *p*-benzyne. The value EA(RH) (RH = phenyl radical) is the same for all three benzynes, such that the differences in HA of *o*-, *m*-, and *p*-benzyne are solely due to the differences in BDEs at the *ortho*-, *meta*-, and *para*-positions of phenyl radical.

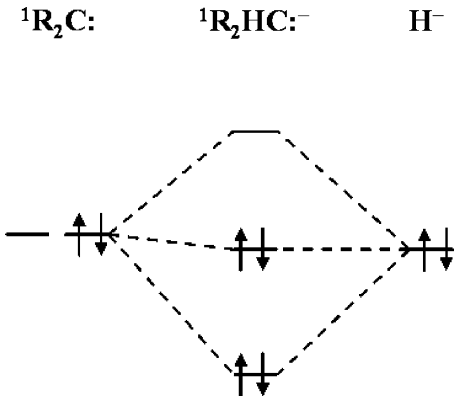

Fig. 6. Schematic orbital energy diagram for the interaction between hydride and the non-bonding molecular orbitals of a singlet carbene.

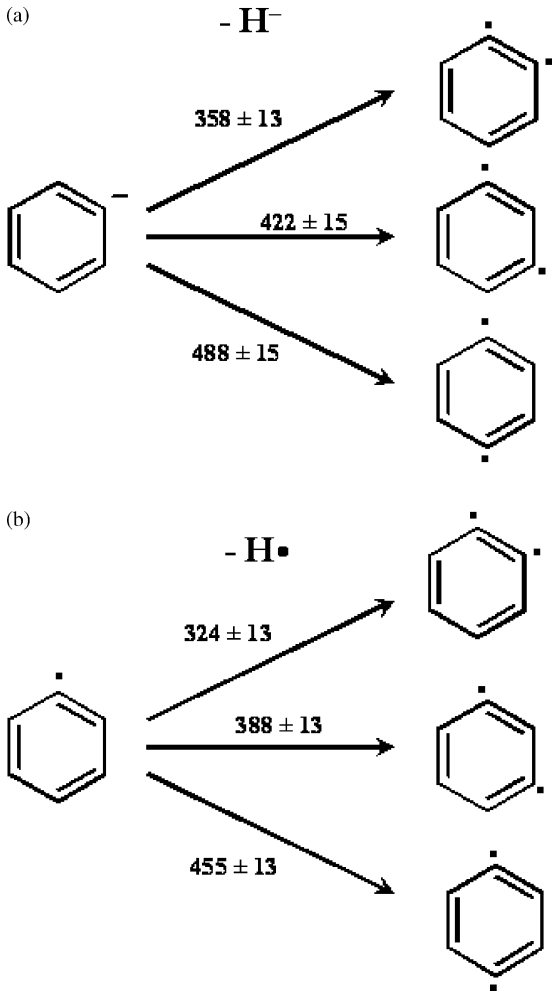

Fig. 7. Enthalpies for loss of: (a) H^- from phenyl anion or (b) H from phenyl radical to form either *o*-, *m*-, and *p*-benzyne. Because the three isomeric products are all formed from the same anionic precursor, RH^-, the pattern in hydride affinities mirrors that for the homolytic BDEs, as indicated by Eq. (5).

Table 4
Hydride affinities of carbenes, biradicals, carbynes, and triradicals and isoelectronic species (in kJ mol^{-1})

Formula	Molecule (R)	EA(RH) (eV)	BDE(RH)[a]	ΔH_f(R)[b]	ΔH_f(RH$_2$)[b]	ΔH_{acid}(RH$_2$)[b]	HA(R)[c]	Ref.
Carbenes								
CBrH	Bromo-	0.79 ± 0.14	427	373 ± 18	−38 ± 1	1660 ± 10	426 ± 22	[62]
CClF	Chlorofluoro-			31 ± 13	−264 ± 8	1615 ± 4	355 ± 18	[63]
CClH	Chloro-	0.74 ± 0.16	426 ± 13	326 ± 8	−82 ± 1	1674 ± 8	409 ± 15	[63]
CCl_2	Dichloro-	1.472 ± 0.043	355 ± 13	229 ± 11	−96 ± 1	1572 ± 9	427 ± 17	[63]
CFH	Fluoro-	0.25 ± 0.18	394 ± 13	143 ± 13	−238 ± 8	1711 ± 17	345 ± 24	[63]
CF_2	Difluoro-	1.21 ± 0.16	272 ± 13	−182 ± 13	−452 ± 1	1628 ± 15	317 ± 22	[63]
CHI	Iodo-		433	428 ± 21	14 ± 1	1616 ± 21	472 ± 31	[62]
CH_2	Methylene	0.08 ± 0.03	462 ± 1	391 ± 1	−75 ± 1	1743 ± 3	397 ± 3	[64]
C_2O	Dicarbon-monoxide	2.338 ± 0.008	332 ± 9	287 ± 1	−48 ± 3	1526 ± 9	484 ± 10	[65]
C_3H_4	Vinyl-	0.481 ± 0.008	435 ± 14	390 ± 14	17 ± 3	1636 ± 1	412 ± 17	[66]
C_6H_5N	Phenylnitrene	1.704 ± 0.030	393 ± 8[d]	430 ± 13[d]	87 ± 1	1533 ± 9	485 ± 16	[67,68]
C_7H_6	Phenyl-	0.912 ± 0.006	440 ± 15	434 ± 10	50 ± 1	1587 ± 9	468 ± 19	[66]
NH	Imidogen	0.771 ± 0.005	389 ± 2	377 ± 1	−46 ± 1	1688 ± 1	410 ± 1	[69]
PH	Phosphinidene	0.96 ± 0.11	334 ± 34	254 ± 1	6	1551 ± 9	373 ± 9	[67]
SiH_2	Silylene	1.405 ± 0.026	291 ± 6	273 ± 6	34	1564 ± 9	354 ± 7[e]	[70]
Biradicals								
C_4H_6	Trimethylenemethane (TMM)	0.505 ± 0.006	369 ± 10	293 ± 13	−18 ± 1	1644 ± 8	342 ± 17	[71]
C_6H_4	*p*-Benzyne	1.096 ± 0.006	455 ± 13	577 ± 13	83 ± 1	1681 ± 2	488 ± 15	[36]
C_6H_4	*m*-Benzyne	1.096 ± 0.006	388 ± 13	510 ± 13	83 ± 1	1681 ± 2	421 ± 16	[36]
C_6H_4	*o*-Benzyne	1.096 ± 0.006	392 ± 13	448 ± 14	83 ± 1	1681 ± 2	359 ± 17	[36]
C_6H_4O	α,2-Dehydrophenol	2.253 ± 0.006	451 ± 16	290 ± 16	−96 ± 1	1466 ± 3	595 ± 18	[34]
C_6H_4O	α,4-Dehydrophenol	2.253 ± 0.006	451 ± 16	290 ± 16	−96 ± 1	1466 ± 3	595 ± 18	[34]
C_6H_4O	α,3-Dehydrophenol	2.253 ± 0.006	449 ± 16	288 ± 16	−96 ± 1	1466 ± 3	593 ± 18	[34]
$C_6H_4O_2$	*m*-Benzoquinone	2.42 ± 0.13	377 ± 15	−28 ± 17	−285 ± 1	1451 ± 9	480 ± 21	[59]
C_7H_6	α,2-Dehydrotoluene	0.912 ± 0.006	448 ± 13	431 ± 13	50 ± 1	1587 ± 9	469 ± 18	[35]
C_7H_6	α,3-Dehydrotoluene	0.912 ± 0.006	448 ± 13	431 ± 13	50 ± 1	1587 ± 9	469 ± 18	[35]
C_7H_6	α,4-Dehydrotoluene	0.912 ± 0.006	448 ± 13	431 ± 13	50 ± 1	1587 ± 9	469 ± 18	[35]
C_8H_8	*m*-Xylylene	0.88 ± 0.17	377 ± 7	335 ± 16	17 ± 1	1601 ± 7	392 ± 19	[39]
$C_{10}H_6$	2,6-Dehydronaphthalene	1.3 ± 0.1	448 ± 17	632 ± 21	151 ± 1	1655 ± 5	501 ± 23	[72]
$C_{10}H_6$	2,3-Dehydronaphthalene	1.3 ± 0.1	322 ± 17	506 ± 21	151 ± 1	1655 ± 5	376 ± 23	[72]
Carbynes								
CH	Methyne	0.652 ± 0.006	424 ± 1	594 ± 1	147 ± 1	1710 ± 1	412 ± 2	[73]
SiH_1	Siylidyne	1.123 ± 0.022	313 ± 10	377 ± 1			349 ± 10[e]	[74]
Triradicals								
C_6H_3	1,3,5-Tridehydro-benzene	0.846 ± 0.013	457 ± 23	749 ± 19	339 ± 8		466 ± 23[e]	[38]
C_6H_3	1,2,3-Tridehydro-benzene	0.564 ± 0.007	456 ± 24	649 ± 16			438 ± 24[e]	[37]
C_6H_3	1,2,4-Tridehydro-benzene	0.565 ± 0.007	421 ± 22	684 ± 21			403 ± 22[e]	[37]
C_8H_7	5-Dehydro-*m*-xylylene	0.919 ± 0.008	469 ± 17	590 ± 21			485 ± 17[e]	[75]

[a] BDE(RH) evaluated using the relationship ΔH_{acid}(RH) + EA(R) − IP(H).
[b] All values taken from refs. [27,28].
[c] HA determined using Eq. (3) or (6) unless otherwise noted.
[d] Values for phenylnitrene revised using ref. [68].
[e] HA calculated using Eq. (5).

The large variation in these BDEs (324, 388, and 455 kJ mol^{-1}, respectively, Fig. 7b) leads to large variations in the hydride affinities of the benzynes. On the other hand, the BDEs at the *ortho*-, *meta*-, and *para*-positions of benzyl and phenoxyl radicals are essentially invariant [34,35], and the resulting hydride affinities are the nearly the same for each set of isomers (Table 4).

Table 4 also includes the HAs of several triradicals, including the series of 1,3,5-, 1,2,4-, and 1,2,3-tridehydrobenzenes. The hydride adducts of these ions result in formation of *m*-benzyne anion from the 1,3,5-tridehydrobenzene, and *o*-benzyne anion from the 1,2,4- and 1,2,3-tridehydrobenzenes, because formation of *o*-benzyne anion is energetically favored over formation of *m*-benzyne anion [36]. The difference in HA of 1,2,4- and 1,2,3-tridehydrobenzene reflects the differences in BDEs at various positions around *o*-benzyne (421 kJ mol^{-1} in the 3-position versus 456 kJ mol^{-1} in the 4-position [37]). Differences in BDEs at various positions have been attributed to differences in electronic structure of the isomeric products [36–39].

The recommended heats of formation of reactive species listed in Table 4 were obtained by using primary measurements reported in the original studies along with the currently accepted values for auxiliary data [27,28].

5. Hydride affinities of atoms and elemental clusters

Oxygen has the largest hydride affinity of any atomic species (Table 5), 533 ± 1 kJ mol^{-1}. This is not surprising because, of the atomic species listed, oxygen is the most electronegative

Table 5
Hydride affinities of atoms and elemental clusters (in kJ mol^{-1})

Formula	Molecule (R)	EA(RH) (eV)	BDE(RH)	ΔH_f(R)[a]	ΔH_f(RH$_2$)[a]	ΔH_{acid}(RH$_2$)[a]	HA(R)[b]	Ref.[a]
Atoms								
B	Boron	0.30 ± 0.25	337 ± 9	565 ± 5	201		293 ± 26[c]	[76]
Be	Beryllium	0.70 ± 0.10	220.8				215 ± 10[c]	[77]
C	Carbon	1.2380 ± 0.0078	338 ± 1	717 ± 1	386	1618 ± 1	388 ± 1	
Ca	Calcium	0.930 ± 0.050	166 ± 4	178 ± 1			183 ± 6[c]	[77]
Co	Cobalt	0.671 ± 0.010	194 ± 13	427			186 ± 13[c]	[78]
Fe	Iron	0.934 ± 0.010	157 ± 26	415			174 ± 26[c]	[79]
Li	Lithium	0.342 ± 0.012	237 ± 1	159 ± 1			197 ± 2[c]	[80]
N	Nitrogen	0.370 ± 0.004	314.1	473 ± 1	190	1665 ± 2.1	293 ± 2	
O	Oxygen	1.8277	430 ± 1	249 ± 1	−242 ± 1	1633	533 ± 1	
P	Phosphorus	1.028 ± 0.010	298 ± 33	317 ± 1	126	1547 ± 34	319 ± 34	
S	Sulfur	2.317 ± 0.002	354 ± 2	277 ± 1	−21 ± 1	1468 ± 12	505 ± 12	
Se	Selenium	2.212525	305 ± 4	227 ± 6		1429 ± 3	446 ± 4[c]	[81]
Si	Silicon	1.2771 ± 0.0087	299 ± 11	450 ± 8		1502 ± 10	349 ± 11[c]	[74]
Te	Tellurium	1.947 ± 0.096	272 ± 5				387 ± 11[c]	[82]
Miscellaneous								
C_2	Dicarbon	2.969 ± 0.006		838 ± 1	227 ± 1	1584 ± 1	702 ± 2	
C_4	Tetracarbon			971 ± 1	464	1507 ± 13	675 ± 13	
O_2	Dioxygen			0	−136	1575 ± 2	236 ± 2	

[a] All values taken from refs. [27,28] unless otherwise noted.
[b] Calculated using Eq. (3) or (6) unless otherwise noted.
[c] HA evaluated using Eq. (5), where BDE(RH) = ΔH_{acid}(RH) + EA(R) − IP(H).

element and the product formed is hydroxide, which has a very high electron binding energy. Among the atomic species, the metal atoms generally have lower HAs than non-metals, presumably because interactions with d-orbitals are weaker than those with s- or p-orbitals. This aspect is also manifested as weaker M–H bonds in the neutral hydrides (Table 5). The relative hydride affinities within the transition metals also reflect differences in electronegativities. Among the elemental clusters we find that C_2 has the largest HA, reflecting the large electron affinity of HC_2 (Eq. (5)) and the large BDE of acetylene as shown in Eq. (3).

6. Hydride affinities of organometallic species

The hydride affinities of a small number of metal-carbonyl compounds have been measured, and are listed in Table 6. The hydride affinity of $Fe(CO)_4$ was determined by measuring the acidity of $H_2Fe(CO)_4$ [40]. Because the hypovalent complex has an empty d-orbital to which the hydride can add, the HA of $Fe(CO)_4$ is much higher than that of $Fe(CO)_5$, wherein the hydride adds to the carbonyl [23,24,41]. Ab initio studies of hydride addition to iron pentacarbonyl, $Fe(CO)_5$, indicate that complexation of the CO with the d_{z^2}-orbital on iron center activates the carbonyl toward hydride addition as compared to bare CO [41,42]. The hexacoordinated carbonyls, $Mo(CO)_6$, $W(CO)_6$, and $Co(CO)_6$, have HAs similar to each other, but lower than those for the iron carbonyls. Lane and Squires explain the trends in light of competing effects between the d-orbital energies and the extent of orbital-interaction arguments [24].

Table 6
Hydride affinities of organometallic species (all units kJ mol^{-1})[a]

Formula	Molecule (R)	HA(R)	Ref.
$Cr(CO)_6$	Chromium hexacarbonyl	184 ± 17	[24]
$Fe(CO)_4$	Iron tetracarbonyl	446 ± 31[b]	[40]
$Fe(CO)_5$	Iron pentacarbonyl	241 ± 21	[23]
$Mo(CO)_6$	Molybdenum hexacarbonyl	191 ± 17	[24]
$W(CO)_6$	Tungsten hexacarbonyl	191 ± 17	[24]

[a] Measured by using bracketing methods unless otherwise noted.
[b] Evaluated using Eq. (2) with values from refs. [27,28], $\Delta H_f(RH^-)$ obtained from the reference in right hand column and using the enthalpy of formation of hydride from Table 1.

7. Computational studies of hydride affinities

Although hydride affinity values can readily be calculated, few direct computational studies of hydride affinities have been reported. Rosenberg described a G2(MP2) study of the hydride affinities of carbonyl compounds [43]. In an examination of a large number of substituted carbonyl compounds XYCO (X, Y = H, CH_3, NH_2, OH, F, etc.) it was found that the hydride affinities are largely dependent on the inductive effects of the substituent groups X and Y. It was also found that there is a strong correlation between the calculated atomic charge (from Mulliken analysis) on the carbonyl carbon and oxygen, and the calculated hydride affinity [43]. In the study, hydride affinities were not calculated directly but were determined by calculating the hydride transfer between the substrate and formaldehyde. Rosenberg's results imply hydride affinities of 164 and 162 kJ mol^{-1} for acetaldehyde and acetone, respectively, in fair agreement with the experimental values of 157 ± 5 and 160 ± 5 kJ mol^{-1} (Table 2). However, the calculated hydride affinity of the carbonyl position of 2-propenal, corresponding to formation of the alkoxide ion, is 177 kJ mol^{-1}, 16 kJ mol^{-1} higher than the experimental value of 161 ± 12 kJ mol^{-1}.

Vianello and Maksic have also used G2(MP2) calculations in an investigation of the Lewis acidities of borane derivatives [44]. They analyzed hydride affinities in light of the relationship shown in Eq. (10), which utilizes the homolytic bond dissociation enthalpy in the ion, BDE(R^-–H), as shown in Fig. 1a.

$$HA(R) = BDE(R^-–H) + EA(R) - EA(H) \quad (10)$$

They found little correlation between the hydride affinity of the borane and the "hardness" of the substrate, in contrast to earlier proposals. However, a high correlation between HA(R) and EA(R) indicates that the homolytic BDEs are less important in determining the hydride affinities of borane compounds.

Wenthold has reported a computational study of the hydride affinities of the Group I and Group II metals and metal hydrides, including Li, LiH, Na, NaH, BeH, BeH_2, MgH, and MgH_2, by using the MP2, MP4, BLYP, and B3LYP methods. When experimental values were available, the agreement with the calculated hydride affinities was very good. These calculations showed that BeH has a relatively large HA, ca. 280 kJ mol^{-1}, and the large HA was shown to reflect the large bond dissociation energy of BeH_2 [45].

In that work, as well as in others [43,45,46], many of the difficulties in obtaining good agreement with experimental and calculated hydride affinities is a direct result of the poor description of the hydride ion at low levels of theory. Wenthold noted that HAs obtained from G2 calculations are too high because the G2 energy for the hydride ion is too low [45]. The low energy of hydride in G2 results because the calculation lacks diffuse functions on hydrogen. In a study of hydride transfer in cationic systems, Gronert and Keeffe used MP2/6-311G** theory, but mention that the enthalpy of H^- at this level of theory is still not well described [46]. On the other hand, these difficulties are avoided by calculating hydride affinities using isodesmic reactions [43].

Hydride affinities have been reported in select cases as components of other computational studies. The hydride affinity of silane, for example, has been calculated in the course of studies of the hydridosiliconate anion, SiH_5^- [25,47,48], and Damrauer and co-workers have examined the effect of alkyl substitution on the hydride affinity values of silanes. Similarly, in early computational studies, Kari and Csizmadia used the LCAO-MO-SCF approach and obtained a hydride affinity of 540 kJ mol^{-1} for S atom [49], in fair agreement with the value of 505 kJ mol^{-1} recommended in this work (Table 5), whereas Liu et al. [50] predicted a bond dissociation energy of 203 kJ mol^{-1} for LiH^-, in good agreement with the recommended value of 197 kJ mol^{-1}.

8. Hydride affinities in solution

Although the focus of this review has been on hydride affinities in the gas-phase, some condensed phase hydride affinities have been determined and can be compared to the gas-phase results. The relationship between gas-phase hydride affinities and the corresponding solution-phase values is shown in Fig. 8. Gas-phase values are related to those in the condensed-phase by the solvation energies (ΔH_{solv}) of the ions and neutral species.

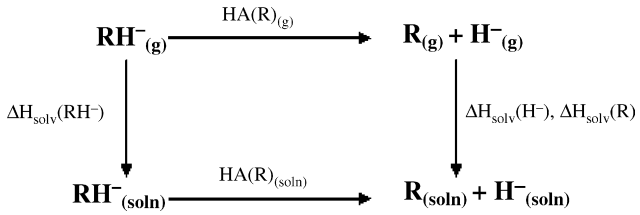

Fig. 8. Thermochemical cycle indicating the relationship between gas-phase ($HA(R)_{(g)}$) and solution-phase ($HA(R)_{(soln)}$) hydride affinities. The quantities are related by the solvation energies, ΔH_{solv}, of RH^-, R, and H^-.

Because neutral solvation energies are generally smaller than those for ions, the main differences between gaseous and solution hydride affinities of neutral molecules are due to differences in the solvation energies of RH^- and the hydride ion. Cation hydride affinities are much more strongly dependent on the medium because the heterolytic cleavage requires creation of charged species, as opposed to simple separation of the charge from the neutral substrate.

Parker and co-workers have determined the free energy of hydride attachment ($\Delta G_{hydride}$, Eq. (11)) for *o*- and *p*-benzoquinone by using electrochemical measurements of dimethyl sulfoxide solutions [51].

$$R + H^- \rightarrow RH^- \quad (11)$$

The measured free energies for hydride loss, which are $-\Delta G_{hydride}$, are 268 kJ mol^{-1} for the *ortho*-isomer and 293 kJ mol^{-1} for the *para*-isomer [51]. By comparison, the gas-phase hydride binding enthalpies are HA(*o*-benzoquinone) = 442 ± 18 kJ mol^{-1} and HA(*p*-benzoquinone) = 370 ± 18 kJ mol^{-1} (Table 2). Thus, the combination of entropy and solvation effects switches the relative ordering of the binding strength.

Free energies of hydride attachment have also been measured for benzyl and other arylmethyl radicals [52]. The values of $-\Delta G_{hydride}$ for benzyl radicals range from ca. 80 to 300 kJ mol^{-1}, whereas those for anthracene-based radicals are 190–290 kJ mol^{-1}. The hydride binding energies for these substrates generally reflect the reduction potential for the closed-shell species, RH.

9. Conclusions

Consideration of the relationships among thermochemical parameters allows for assessment of the major contributors to molecular hydride affinities. High hydride affinities for stable molecules result from high hydrogen binding energies, forming RH, and high electron binding energies in the hydride adduct, RH^-, as shown by Eq. (5). As a result, it is not surprising to find high hydride affinities of polar, unsaturated molecules such as ketones and aldehydes, and the differences between the hydride affinities of carbonyls and olefins are due to the differences in electron binding energies of enolates and hydrocarbon anions. Radicals, meanwhile, have very high hydrogen binding energies but hydride addition results in the formation of open-shell anions, most of which are unbound. Hence, only few radicals have meaningful hydride affinities.

Reactive intermediates, such as carbenes and biradicals, generally have very high hydride affinities, a consequence of two important effects, which can be seen in Eq. (3). The first component is the difference between two BDEs in the precursor, RH_2, and that in H_2, which is generally a large, positive value, especially in organic systems. The second component is the acidity difference between H_2 and RH_2. Because most molecules are more acidic than H_2, this component is generally favorable. Moreover, although alkanes are the exception, in that they are more acidic than H_2, the difference in acidity is not enough to overcome the benefits of the BDEs. Thus, carbenes and biradicals have HAs in the range 300–600 kJ mol^{-1}, whereas HAs for triradicals are all over 400 kJ mol^{-1}. The combination of high BDEs and a high electron binding energy in the anion accounts for the highest hydride affinity known, 702 kJ mol^{-1} for C_2.

The overall range of the HAs of the molecules evaluated in this review is 23–702 kJ mol^{-1}. These HAs have been interpreted based on simple molecular orbital energy diagrams, which account for the fact that hydride binding is favorable in molecules that have low energy unoccupied orbitals which can accommodate the electron pair from H^-. Borane and alane, with empty, non-bonding p-orbitals, are good examples of Lewis acids with high hydride affinities. Unsaturated compounds such as carbonyls, alkenes and alkynes have low-energy π^* LUMO's that are amenable to hydride bonding, giving these classes of compounds reasonably large HAs.

The hydride affinities of reactive intermediates have also been interpreted using molecular orbital diagrams. For radical species, few HAs are known, and as shown, the hydride adduct results in an electron which occupies an anti-bonding orbital or can result in a weakly bound ion–radical complex. The situation changes dramatically for other reactive intermediates such as carbenes and polyradical species, which have low energy empty or partially filled degenerate or nearly degenerate orbitals that can participate in adduct formation with H^-, resulting in large HAs.

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