diverse experimental methods are in such good agreement, not only with each other but with theory as well.

Additional thermodynamic properties for diatomic metal hydrides may be derived by combining our D[M–H] values with other data from the literature (Table I). For example, ΔH_f[MH,g] is obtained from metal sublimation enthalpies[74] and eq 10, and recent measurements of D[M$^+$–H][2] together with IP(M)[69] yield IP(MH) according to eq 11. Furthermore, homolytic bond energies for MH$^-$ ions may be derived from eq 12 and measured values for EA(MH) and EA(M). Properties derived in this way for each of the five metals are listed in Table V.

$$\Delta H_f^\circ [\text{MH,g}] = \Delta H^\circ_{\text{sub}}(\text{M}) + \frac{1}{2}D[\text{H–H}] - D[\text{M–H}] \quad (10)$$

$$\text{IP(MH)} = D[\text{M–H}] + \text{IP(M)} - D[\text{M}^+\text{–H}] \quad (11)$$

$$D[\text{M}^-\text{–H}] = D[\text{M–H}] + \text{EA(MH)} - \text{EA(M)} \quad (12)$$

Conclusions

The gas-phase chemistry of atomic metal anions is a rich new area for research. In this paper, we report the first in-depth study of the reactivity of these species. Pulsed techniques using FTMS are shown to be well suited for both the generation of atomic transition-metal anions by CID and the subsequent investigation of their reactions with neutral substrates. Atomic metal anions are observed to react with their parent neutral metal carbonyls. In all cases, dissociative electron-transfer reactions occur, while V$^-$, Cr$^-$, Co$^-$, and Mo$^-$ also produce dinuclear adduct ions from which one or more CO ligands are expelled. Bracketing methods have provided estimates of the proton affinities for several of the atomic metal anions from which new values for homolytic metal–hydrogen bond-dissociation energies have been derived. A striking feature of the metal hydride acidities measured in this study is that they are all very nearly the same. The generality and origins of this remarkable trend are explored in the following paper in this issue.

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Correlation of Electron and Hydrogen Atom Binding Energies for Transition-Metal Atoms

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Abstract: A collection and analysis of thermochemical data for neutral metal atoms, atomic negative ions, and diatomic metal hydrides is described which exposes a new periodic property correlation for transition-series elements. Diatomic metal hydrides are shown to exhibit a constant gas-phase acidity (ΔH_{acid}) equal to 341 ± 5 kcal/mol. This behavior is unique to neutral monohydrides since cationic metal hydrides (MH$^+$), main-group monohydrides, and polyatomic metal hydride complexes each exhibit a wide range in ΔH_{acid} as the metal atom is varied. The origin of this trend is shown to be a general linear correlation between transition-metal atom electron affinity and homolytic bond-dissociation energy for the corresponding diatomic hydride, i.e., D[M–H] = EA(M) + 27.5 kcal/mol. Detailed consideration of the electron configurations of atomic transition-metal negative ions and diatomic metal hydrides exposes a simple analogy between electron and hydrogen atom binding by most all metal atoms. Formation of most atomic negative ions and neutral monohydrides from transition-metal atoms generally results in an electron configuration characterized by an additional (nonbonding) d electron and a stabilized, doubly-occupied s or σ orbital. Atomic electron affinities and diatomic hydride bond energies for the first-row transition metals except Sc and Ti are found to inversely parallel the atomic promotion energies ΔE[3d^{n}4s$^2 \rightarrow$ 3d^{n+1}4s^1] required to achieve the nominal H atom and electron binding configurations of the atoms. Deviation by Sc and Ti is ascribed to enhanced ionic character of the monohydrides which makes the electron configurations of the atomic anions and diatomic hydrides dissimilar. The weak metal–hydrogen bonds known for FeH and MnH are shown to be due to the relatively high promotion energies required for bonding and a minimal ionic character of the hydrides due to high atomic ionization potentials. On the basis of the correlation equation given above and measured electron affinities, bond-dissociation energies for several second- and third-row transition-metal diatomic hydrides are predicted. The columnar trends in MH bond energies so exposed are discussed.

Diatomic transition-metal hydrides represent one of the simplest classes of molecules with which to study periodic bonding patterns of the transition series elements and the role of d electrons in prototype metal σ bonds.[1–3] Small molecular metal hydrides are of long-standing astrophysical and cosmochemical interest since many examples have been detected from electronic and infrared spectra of cool stellar atmospheres.[4,5] Furthermore, diatomic metal hydrides and polyhydrides continue to play a key role in the development of models for catalytic activation of molecular hydrogen on metal surfaces.[6–9] Accordingly, a large number of

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Table I. Metal–Hydrogen Bond-Dissociation Energies

M–H	SLSF[a]	Birge–Sponer extrapolation[b]	KM[c]	other	theory[i]
			D[M–H], kcal/mol		
ScH		43.0	47.5 ± 2		28.5,[d] 41.5[e]
TiH					36.9,[f] 37.3,[d] 46.9[g]
VH	37.9 ± 3				38.5,[d] 50.8[g]
CrH	41.2 ± 3	66.9 ± 11.9	<45		43.9,[d] 46.3[g]
MnH		55.9 ± 6.9	<32		41.8,[d] 37.1[g]
FeH	29.6 ± 3	39.9 ± 6.9[l]	<43		31.1,[d] 42.7[g]
CoH	42.2 ± 3		45.1 ± 3	38.9 ± 4.5[m]	47.9[d]
NiH		69.1 ± 3.1	58.4 ± 3, 59.4 ± 2		54.9,[d] 61.5,[g] 60.9,[h] 60.9[i]
CuH		66.9 ± 1.9	59.7 ± 1, 58.3 ± 2	64 ± 3[n]	59.7,[d] 60.3[j]
ZnH		20.5 ± 0.5			
MoH	46.1 ± 3				
PdH				<76[o]	
AgH		54.0 ± 1.9	54.3 ± 1, 50.5 ± 2	58.3 ± 6[p]	45.1,[j] 35.1[k]
CdH		16.5 ± 0.09			
PtH		84.1 ± 9.1			
AuH		75.0 ± 2.4	71.9 ± 6, 68.9 ± 2, 74.3 ± 2		
LiH		55.6 ± 1.4[s]			55.3[q]
NaH		44.7 ± 1.1[s]			42.7[q]
KH		41.9 ± 1.1[s]		46.2 ± 3.8[r]	
RbH		40.8 ± 1.7[s]			
CsH		41.7 ± 1.1[s]			

[a] Reference 17. [b] Reference 14. [c] Reference 20. [d] Reference 24. [e] Reference 11; cf.: Scott, P. R.; Richards, W. G. *J. Phys. B* **1974**, *7*, 1679–1682. [f] Reference 11; cf.: Scott, P. R.; Richards, W. G. *J. Phys. B* **1974**, *7*, 500–504. [g] Reference 25. [h] Blomberg, M. R. A.; Siegbahn, P. E. M.; Roos, B. J. *Mol. Phys.*, in press. [i] Goddard, W. A. III; Walch, S. P.; Rappe, A. K.; Upton, T. H. *J. Vac. Sci. Technol.* **1977**, *14*, 416. [j] Stöll, H.; Fuentealba, P.; Dolg, M.; Flad, J.; Szentpaly, L. V.; Preuss, H. *J. Chem. Phys.* **1983**, *79*, 5532–5542. [k] Boeyens, J. C. A.; Lemmer, R. H. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 321–326. [l] Dendramis, R. J.; Van Zee, R. J.; Weltner, W., Jr. *Astrophys. J.* **1979**, *231*, 632–636. [m] Reference 21. [n] Reference 22. [o] Malmberg, C.; Scullman, R.; Nylen, P. *Ark. Fys.* **1969**, *39*, 495–499. [p] Reference 23. [q] Meyer, W.; Rosmus, P. *J. Chem. Phys.* **1975**, *63*, 2356–2375. [r] Farber, M.; Srivastava, R. D.; Moyer, J. W. *J. Chem. Thermodyn.* **1982**, *14*, 1103–1113. [s] Experimental Rydberg–Klein–Rees potential curve extrapolation, ref 42. [t] Calculated values corrected to D_0 when vibrational constants available in original report.

experimental and theoretical accounts of transition-metal hydrides have been published and several critical reviews of their properties, spectroscopy, and electronic structures are available.[10–16]

In the preceding paper in this issue a new experimental method was described for obtaining thermochemical information for diatomic metal hydrides from gas-phase ion–molecule reactions of the corresponding atomic metal anions.[17] Reactions between atomic negative ions and a series of neutral reference acids with established gas-phase acidities provided quantitative estimates of metal-hydride acidities, ΔH_{acid}(MH), for VH, CrH, FeH, CoH, and MoH. From these data, homolytic bond-dissociation energies for the diatomic hydrides, D[M–H], could be evaluated from eq 1 since the corresponding atomic electron affinities,[18] EA(M), and

$$\Delta H_{acid}(MH) = D[M\text{–}H] - EA(M) + IP(H) \qquad (1)$$

the hydrogen ionization potential, IP(H),[19] are accurately known. An especially striking feature of these new data is that the measured acidities for the five metal hydrides are all very nearly the same: ΔH_{acid}(MH) ≈ 340 ± 3 kcal/mol. In this paper, the scope and generality of constant diatomic metal-hydride acidity

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Table II. Heterolytic and Homolytic Transition-Metal Hydride Bond Energies and Metal Atom Electron Affinities

M–H	D[M–H][a]	EA(M),[b] kcal/mol	ΔH_{acid}(MH)[c]
first row			
ScH	47.5 ± 2	4.35 ± 0.46	356.7 ± 2
TiH	38 ± 3	1.84 ± 0.32	349.7 ± 3
VH	37.9 ± 3	12.1 ± 0.3	339.4 ± 3[d]
CrH	41.2 ± 3	15.4 ± 0.3	339.4 ± 3[d]
MnH	<32	<0	>355
FeH	29.6 ± 3	3.78 ± 0.81	339.4 ± 3[d]
CoH	42.2 ± 3	15.3 ± 0.2	340.5 ± 3[d]
NiH	60 ± 3	26.7 ± 0.2	346.9 ± 3
CuH	60 ± 3	28.3 ± 0.2	345.3 ± 3
ZnH	20.5 ± 0.5	<0	>334
second row			
MoH	46.1 ± 3	17.2 ± 0.2	342.4 ± 3[d]
PdH	<76	12.9 ± 0.2	<378
AgH	54 ± 3	30.0 ± 0.2	337.6 ± 3
CdH	16.5 ± 0.1	<0	>330
third row			
PtH	84.1 ± 9.1	49.1 ± 0.05	348.6 ± 9
AuH	72 ± 3	53.2 ± 0.0	332.4 ± 3
alkali metals			
LiH	55.6 ± 1.4	14.2 ± 0.0	354.0 ± 1.4
NaH	44.7 ± 1.1	12.6 ± 0.0	345.7 ± 1.1
KH	41.9 ± 1.1	11.6 ± 0.0	343.9 ± 1.1
RbH	40.8 ± 1.7	11.2 ± 0.0	343.2 ± 1.7
CsH	41.7 ± 1.1	10.9 ± 0.0	344.4 ± 1.1

[a] Preferred value from Table I, see text. [b] Reference 18. [c] Calculated from eq 1 unless otherwise noted. [d] Direct measurement, ref 17.

is explored and its thermodynamic and electronic origins are considered.

Gas-Phase Acidities of Diatomic Transition-Metal Hydrides

The results described in the preceding paper[17] represent the first and only direct experimental measurements of diatomic transition-metal-hydride acidities. Gas-phase acidities for several other metal hydrides may be derived by use of eq 1 along with homolytic M–H bond energies and metal atom electron affinities from the literature. Table I summarizes the currently available metal-hydride bond-dissociation energies: including values from both

Table III. Ground-State Electron Configurations for First-Row Metal Atoms, Metal Anions, and Diatomic Hydrides

	M^a		M^{-b}		MH^c		$\Delta E(3d^n4s^2 \rightarrow 3d^{n+1}4s^1)^a$
Sc	$3d^14s^2$	$(^2D_{3/2})$	$3d^14s^24p^1$	$(^1D$ or $^3D)$	$4s^2\sigma^2$	$(^1\Sigma^+)$	32.9
					$3d^14s^1\sigma^2$	$(^3\Delta)$	
Ti	$3d^24s^2$	$(^2F_2)$	$3d^34s^2$	(^4F)	$3d^24s^1\sigma^2$	$(^4\Phi)$	18.7
V	$3d^34s^2$	$(^4F_{3/2})$	$3d^44s^2$	(^5D)	$3d^34s^1\sigma^2$	$(^5\Delta)$	6.0
Cr	$3d^54s^1$	$(^7S_3)$	$3d^54s^2$	$(^6S_{5/2})$	$3d^5\sigma^2$	$(^6\Sigma^+)$	−22.2
Mn	$3d^54s^2$	$(^6S_{5/2})$			$3d^5\sigma^2\sigma^{*1}$	$(^7\Sigma^+)$	48.4
Fe	$3d^64s^2$	$(^5D_4)$	$3d^74s^2$	(^4F)	$3d^7\sigma^2$	$(^4\Delta)$	19.8
Co	$3d^74s^2$	$(^4F_{9/2})$	$3d^84s^2$	(^3F)	$3d^8\sigma^2$	$(^3\Phi_4)$	9.9
Ni	$3d^84s^2$	$(^3F_4)$	$3d^94s^2$	$(^2D_{5/2})$	$3d^9\sigma^2$	$(^2\Delta_{5/2})$	0.6
Cu	$3d^{10}4s^1$	$(^2S_{1/2})$	$3d^{10}4s^2$	$(^1S_0)$	$3d^{10}\sigma^2$	$(^1\Sigma^+)$	−32.0
Zn	$3d^{10}4s^2$	$(^1S_0)$					

^{a} Reference 29. ^{b} Reference 30. ^{c} Reference 11 and 25.

experiment and theory as well as the five new values derived in the preceding paper by Sallans, Lane, Squires, and Freiser (SLSF). The alkali metals are also included for comparison. A preferred value for each bond energy is given in Table II along with the corresponding atomic electron affinity and the resulting metal-hydride acidity calculated via eq 1. In selecting an MH bond energy from among the values listed in Table I, preference was given to experimentally derived bond energies, when available. Of these, the high-temperature equilibrium studies of Kant and Moon (KM),[20] the one-ion beam result for CoH,[21] and the 5 new values given by SLSF are considered to be the most reliable. Linear Birge–Sponer extrapolations of vibrational levels for diatomic hydrides[13,14] lead to consistently higher bond energies when compared with other experimental data. Thus, the selected values for ZnH, CdH, and PtH should be considered upper limits. The experimental values for CuH (64 ± 3 kcal/mol)[22] and AgH (58.3 ± 6 kcal/mol)[23] are derived from H⁻ abstraction reactions of Cu⁺ and a high-temperature kinetic study, respectively. The theoretical values are mainly those due to Das,[24] Scott and Richards (SR),[11] and Walch and Bauschlicher (WB),[25] who used various MCSCF techniques to derive molecular constants for first-row metal hydrides. The variation among calculated bond energies is generally larger than the spread among experimental values. In most cases WB report higher values than those of Das—presumably due to the higher level of electron correlation employed by WB. The particular bond energy selected in Table II is either that given by SLSF or an average value when separate experimental determinations are in good agreement. A conservative uncertainty interval of ±3 kcal/mol is assigned to accommodate the typical spread among most values.

The metal-hydride acidities listed in Table II all fall within a narrow range of ca. 343 ± 5 kcal/mol, except for ScH, AuH, LiH, and the three hydrides corresponding to elements with unstable atomic negative ions.[18] Constant metal-hydride acidity has also been noted recently by Simoes and Beauchamp.[12] It appears to be a unique phenomenon of diatomic transition-metal hydrides. The known acidities for main group diatomic hydrides span almost the entire range of the gas-phase acidity scale from BH (ΔH_{acid} = 386 ± 6 kcal/mol) and OH (ΔH_{acid} = 382 ± 0.4 kcal/mol) to SH (ΔH_{acid} = 350 ± 4 kcal/mol) and HI (ΔH_{acid} = 314 ± 1 kcal/mol).[26] Furthermore, constant acidity appears to be unique to neutral metal hydrides. The acidities of MH⁺ ions (proton affinities of neutral metal atoms) deduced from ion beam studies[12,21] exhibit a ~60 kcal/mol range of magnitudes and a sys-
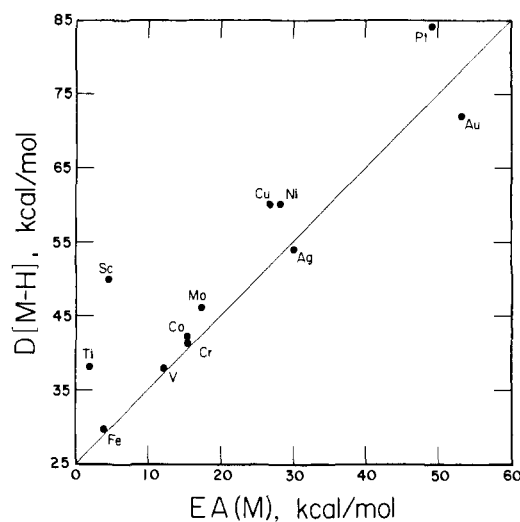

Figure 1. Plot of metal atom electron affinity vs. homolytic bond-dissociation energy for the corresponding diatomic metal hydride. A line of unit slope is drawn corresponding to constant metal-hydride acidity.

tematic decrease across the first transition series with increasing atomic number. Metal-hydride complexes, such as metal carbonyl hydrides, exhibit 20–30 kcal/mol greater acidities than the corresponding diatomics,[27] thereby placing them near the currently known lower limit of the gas-phase acidity scale.[26] For example, HMn(CO)₅ (ΔH_{acid} = 318 ± 3 kcal/mol) and H₂Fe(CO)₄ (ΔH_{acid} = 319 ± 5 kcal/mol) possess nearly equal acidities, while the upper limit for HCo(CO)₄ is somewhat lower ($\Delta H_{acid} \leq 314$ kcal/mol).[27] Insufficient gas-phase data are available to establish a clear trend. Thermodynamic acidities for metal-hydride complexes in solution show a range of pK_a values spanning over ten orders of magnitude.[28] Solvation and ion-pairing effects are likely to obscure trends in the intrinsic MH acidities.

The constancy of $\Delta H_{acid}(MH)$ can be qualitatively understood in terms of its thermodynamic components as given by eq 1. As the metal atom is varied, changes in $D[M-H]$ and EA(M) evidently offset one another. That is, an increase or decrease in the *hydrogen atom affinity* of a metal atom is almost exactly matched by a corresponding increase or decrease in the metal atom *electron affinity*. The general correlation between these two properties is illustrated in Figure 1 which is a plot of M–H bond energy vs. the corresponding metal atom electron affinity given in Table II. A line of unit slope is drawn, corresponding to $\Delta D[M-H] = \Delta EA$-(M), i.e., constant metal-hydride acidity. A general linear correlation is evident over the ~60 kcal/mol range of either property, with significant aberrance exhibited by Sc, Ti, and Pt.

The origins of this remarkable and previously unnoted relationship may be understood by considering the electronic details of hydrogen atom and electron binding by transition-metal atoms.

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Table III summarizes the ground-state electron configurations for first-row transition-series elements[29] and the corresponding atomic negative ions, the latter being assigned from laser photoelectron measurements.[18,30] Also shown are the dominant ground-state electron configurations for each hydride as assigned from MCSCF calculations[10,11] and limited spectroscopic observations.[13,31] Let us first consider some qualitative features of metal–hydrogen bonding. Extensive accounts of the electronic structures of diatomic metal hydrides are available.[10,11,25,32,33] These molecules are generally characterized by several closely spaced, low-lying, electronic states. This fact has rendered unambiguous ground-state assignments difficult in many cases since the energy ordering of states is complicated by strong configuration mixing. Thus, transition-metal monohydrides are not well described theoretically at the Hartree–Fock (HF) level and extensive configuration interaction calculations are often required to achieve agreement with measured electronic spectra.

A useful qualitative picture of bonding in first-row transition-metal monohydrides has been described[10,11,25,32] wherein a σ bond to an H atom involves mainly the 4s and 4p metal orbitals and the 3d electrons are largely nonbonding. The metal atom $3d^n4s^2$ and $3d^{n+1}4s^1$ electronic configurations feature most strongly in covalent interactions, with the $3d^n4p^14s^1$ state also of importance in some cases. The $3d^n4s^2$ atomic configuration gives rise to the ground state for all first-row metals but Cr and Cu where a half-filled and filled 3d subshell, respectively, is achieved with a $3d^{n+1}4s^1$ configuration. The energy difference between the lowest fine-structure levels for these two states, $\Delta E(3d^n4s^2 \rightarrow 3d^{n+1}4s^1)$, for each metal is tabulated in the last column of Table III.[29] The promotion energies (PE) defined in this way decrease monotonically for the early transition metals, becoming strongly negative at Cr. An anomaly occurs at Mn where the $3d^54s^2$ configuration is strongly favored, followed by a second decreasing trend to Cu. Direct H-atom bonding to the $3d^n4s^2$ atomic state involves formation of a pair of 4s/4p hybrid-metal orbitals, one of which forms a doubly occupied σ-bonding orbital with H(1s) while the other is singly occupied and somewhat antibonding. This molecular configuration may be loosely described[32] as high-spin, $3d^n\sigma^2\sigma^{*1}$. Alternatively, promotion of a 4s electron yields a $3d^{n+1}4s^1$ configuration which may directly bind to H(1s) to give a low-spin, $3d^{n+1}\sigma^2$ molecular configuration. This latter bonding mode characterizes the ground states for $^6\Sigma^+$ CrH and the later transition-metal hydrides $^4\Delta$ FeH through $^1\Sigma^+$ CuH. The covalent picture for the early transition-metal hydrides ScH, TiH, and VH is somewhat different in that high-spin ground states exhibiting a single, "nonbonding" 4s electron are favored.[10,11] This difference may be attributed to both a decrease in the extent of d–s mixing due to higher lying 3d orbitals, as well as an increase in the ionic character (M^+ H^-) of the early metal hydrides since the metal atom ionization potentials are relatively low[19] (vide infra).

With this bonding scheme in mind, the qualitative similarly between hydrogen atom and electron binding by a metal atom now becomes clear. Electron binding by all first-row metals except Sc and Mn produces $3d^{n+1}4s^2$ atomic negative ion configurations (Table III) which may be equated with the $3d^{n+1}\sigma^2$ ground-state molecular configurations found for the low-spin hydrides. Formation of a negative ion results in an additional 3d electron and a stabilized, doubly occupied 4s atomic orbital, while the hydride is also characterized by an added 3d electron (through initial promotion of a 4s electron) and a low-lying, doubly occupied σ orbital which is largely H(1s) in character. It is interesting to note in this context that the assigned ground-state term for each
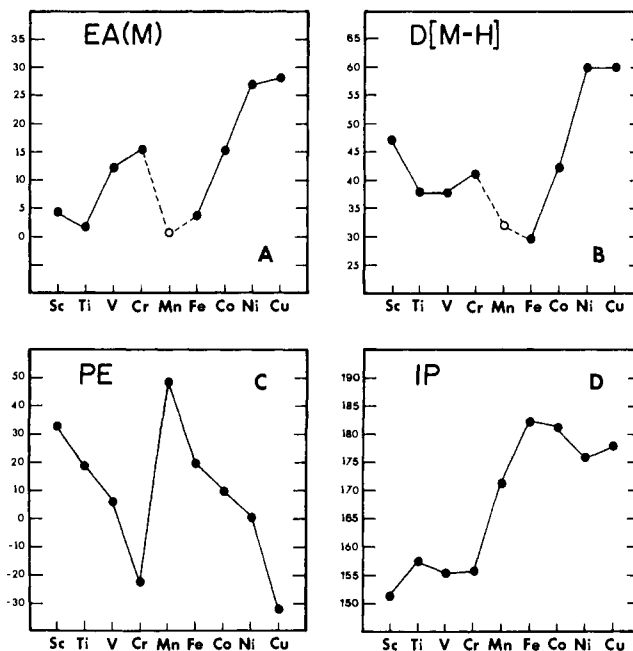

Figure 2. Periodic property plots for first-row transition-metal atoms: (A) metal atom electron affinity, (B) diatomic metal-hydride bond-dissociation energy, (C) atomic promotion energy PE = $\Delta E(3d^n4s^2 \rightarrow 3d^{n+1}4s^1)$, (D) metal atom ionization potential. All data in kcal/mol.

of the monohydrides listed in Table III except FeH is directly derived from the ground-state term for the corresponding atomic anion.[34] This simple empirical observation underscores the electron and H atom binding analogy presented above and it should be a useful qualitative guide in future studies of diatomic metal hydrides. Here the "extra" proton of the monohydride makes no net contribution to the spin multiplicity of the atomic metal anion and the highest orbital angular momentum component of the metal anion is selected for the molecular term.

Note that the bond energies for the five low-spin hydrides CrH, FeH, CoH, NiH, and CuH obey the electron affinity correlation illustrated in Figure 1 quite closely. Vanadium hydride also correlates well, although the assigned[10,11,35] high-spin $^5\Delta$ ground state $(4s^13d^3\sigma^2)$ is not strictly analogous to the atomic anion ^5D $(3d^44s^2)$ configuration in the same sense as the other metals. However, it may be noted that strong mixing between the $3d^44s^1$ and $3d^34s^2$ atomic states generally has been found in calculations on VH,[11] with a net 3d orbital population of ca. 3.4 found from CI wave functions.[25] This is consistent with the relatively low promotion energy for vanadium (6.0 kcal/mol).[29] Therefore, it is not surprising that VH exhibits behavior which is characteristic of the low-spin hydrides, i.e., correlation between D[M–H] and EA(M). The correlation clearly breaks down for Sc and Ti, which possess stronger bonds than might be expected on the basis of their low electron affinities. Unfortunately, these two bond energies are the least well established. A large spread among separate values is evident for both, and there are no experimental data for TiH. In the case of Sc and Ti, the negative ion and monohydride electron configurations are dissimilar. Because the 3d orbitals are higher lying in the beginning of the first transition series, Sc⁻ prefers a $3d^14s^24p^1$ (^1D or ^3D) configuration in which the extra electron occupies a 4p orbital.[36] In contrast, ScH has two nearly degenerate configurations which contend for the ground state: a low-spin $4s^2\sigma^2$ ($^1\Sigma^+$) state involving $3d\sigma$ bonding and a high-spin $3d^14s^1\sigma^2$ ($^3\Delta$) state with an unpaired 4s electron.[11,25] Similarly, TiH has a high-spin ground state and an unpaired 4s electron.[11,25]

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Correlation of Electron and H Atom Binding Energies

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These latter two configurations bear little resemblance to those of the corresponding negative ions; indeed, these states most strongly resemble the atomic states of the corresponding *cations* in that unpaired 4s electrons are present.[37] ScH and TiH are expected to be the most ionic ($M^+ H^-$) of the first-row transition element monohydrides in which almost complete metal-to-hydrogen electron-transfer occurs. Therefore, electron and H atom binding by Sc and Ti have quite different electronic consequences.

A semiquantitative rationale for the observed relationship between bond energy and electron affinity can be formulated in terms of other key atomic properties. Figure 2 represents a schematic illustration of metal–hydrogen bond strengths, atomic electron affinities, ionization potentials, and ($3d^n4s^2 \rightarrow 3d^{n+1}4s^1$) promotion energies for the first-row transition elements. The qualitatively similar appearance of the EA(M) and D[M–H] plot restates the correlation illustrated in Figure 1. A general inverse relationship between either EA(M) or D[M–H] and the atomic promotion energies is also evident from Figure 2. Here, an increase/decrease in promotion energy is generally reflected by a corresponding decrease/increase in the electron and H atom binding energies, with the early transition metals showing the greatest deviation from the trend. Beauchamp and co-workers have noted a similar relationship between homolytic bond energies for diatomic metal hydride cations, D[M$^+$–H], and the corresponding promotion energies required to achieve the nominal bonding configuration in the atomic metal ion, $\Delta E(3d^n \rightarrow 3d^{n-1}4s^1)$.[21,38] The fact that this type of correlation reappears for the neutral metal hydrides offers additional support for the view that the first metal–hydrogen σ-bond mainly involves the 4s orbital. The key energy term is simply the electronic rearrangement which is necessary to liberate a 4s electron for bonding in either M or M$^+$. Similar considerations apply to electron binding by neutral metal atoms. Lineberger and co-workers have noted smooth trends in plots of "s-electron binding energies" vs. the number of d electrons for each of the three transition series.[39] The s-electron binding energy is defined as the difference between the lowest energy d^ns^1 configuration of the neutral metal atom and the d^ns^2 configuration of the atomic anion. For elements with s^2 ground states this is simply given by EA(M) + PE. A linear increase with increasing d-electron count (n) is observed, with significant dispersion-like behavior for $1 \leq n \leq 5$ for each transition series.[39] It is interesting to note that the same two first-row elements, Sc and Ti, are aberrant in both the s-electron binding plots and the EA(M) vs. D[M–H] plot. In the previous discussion it was shown that deviation from the correlation in Figure 1 by Sc and Ti is expected on the basis of the differences in electron and H atom binding configurations. Moreover, Sc strongly deviates from the s-electron binding energy trend since the corresponding atomic anion actually involves an unusual $3d^14s^24p^1$ configuration.[36] Ti still represents somewhat of a puzzle; however, the deviation is not large.

Though the inverse relationship between atomic promotion energies (Figure 2C) and metal–hydrogen bond energies (Figure 2B) is qualitatively visible in the figures, a direct plot of these two properties yields only a crude correlation. However, by considering the promotion energies and atomic ionization potentials[19] (Figure 2D) together, we can account for certain critical features in the bond-energy plot. For example, the bond energies for ScH and TiH are somewhat higher than what might be expected on the basis of their relatively high atomic promotion energies and low atomic electron affinities. That is, while Ti and Fe have nearly equal promotion energies (Table III), TiH has a roughly 8 kcal/mol stronger bond than FeH. Similarly, ScH has both a high atomic promotion energy *and* a high bond energy, in contrast to the more general inverse relationship. The relatively low ionization potentials for Sc and Ti may account for this

(37) Cheetham and Barrow have noted that the multiplicity of the ground state of MH is partly determined in many cases by the multiplicity of the ground state of M$^+$. For a discussion of this point, see ref 10.

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Table IV Predicted Transition-Metal Hydride Bond-Dissociation Energies

M	EA(M),[a] kcal/mol	$\Delta E(d^ns^2 \rightarrow d^{n+1}s^1)$,[b] kcal/mol	IP(M),[c] kcal/mol	D[M–H],[d] kcal/mol
second row				
Zr	9.84	13.9	149.9	37.3
Nb	20.6	3.3	156.1	48.1
Ru	(24.2)	−21.4	169.7	51.7
Rh	26.2	−36.3	172.0	53.7
third row				
W	18.8	8.4	184.0	46.3
Os	(25.8)	14.7	200.6	53.3
Ir	36.1	8.1	208	63.6

[a] Taken from ref 18. Values in parentheses are based on semi-empirical estimates, ref 41. [b] Reference 29. [c] Reference 19. [d] Estimated bond energy with eq 2.

behavior. Stabilization of the $M^+ H^-$ ionic component of the total bonding in the hydride is achieved by a reduction of the metal ionization potential; this may, in turn, act to increase the bond strength. In support of this, it may be noted that the alkali-metal hydrides, which are known to be substantially ionic,[40] exhibit moderately strong M–H bonds relative to the transition metals.

Using this simple picture, we can identify the origins of the weak FeH bond as the high atomic promotion energy and high ionization potential for Fe, viz., electronic rearrangement for bonding is costly, and the ionic character of the monohydride is minimal. It is interesting to note in this regard the near perfect colinearity of the group 8 elements in most all the periodic plots of Figure 2, as well as in the correlation plot in Figure 1. This gives strong support for the new values for D[FeH] and D[CoH] determined by SLSF.[17]

A similar analysis may be applied to MnH. Since Mn has the highest promotion energy of the series and a moderately high IP, MnH should be only weakly bound. Stated in different terms, the high promotion energy for Mn forces occupancy of the σ^* orbital in the hydride (bond weakening) with only relatively weak Mn$^+$ H$^-$ ionic character (bond strengthening) available to offset it. These considerations weigh against the higher estimates for D[Mn–H] listed in Table I and lend credence to the upper limit of 32 kcal/mol reported by Kant and Moon.[20b] Finally, NiH and CuH are observed to have similar bond strengths since little or no promotion energy is required as a prelude to low-spin bonding by either metal atom, and the ionic bonding contributions are likely to be comparable. Despite the qualitative appeal of this apparent interplay between bond energy, promotion energy, and ionization potential, no simple linear combination of PE and IP could be found which satisfactorily predicts D[M–H] to better than 8 kcal/mol (rms error). This is probably due to a varying balance between the contributions of these two properties to the bond energy as one proceeds across the transition series.

Prediction of Diatomic Metal Hydride Bond-Dissociation Energies

The preceding discussion and the general relationship in Figure 1 make it possible to predict metal hydride bond energies. The ten data points in Figure 1, excluding Sc and Ti, define a least-squares line of unit slope (1.00 ± 0.09) and intercept 27.5 ± 2.8 kcal/mol. This corresponds to a constant ΔH_{acid}(MH) = 341 kcal/mol and the empirical equation given below (eq 2). This simple relationship is expected to be valid for metals with $d^{n+1}s^1$

$$D\text{[M–H]} = \text{EA(M)} + 27.5 \ (\text{kcal/mol}) \qquad (2)$$

ground-state atoms and those possessing d^ns^2 atomic configurations with modest [$d^ns^2 \rightarrow d^{n+1}s^1$] promotion energies ($\leq 20$ kcal/mol). In other words, it should hold best when a low-spin $d^{n+1}\sigma^2$ ground-state configuration can be expected for the diatomic metal hydride. Predicted metal–hydrogen bond energies for several second- and third-row transition metals fitting these criteria are

(40) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press, 1960; Chapter 3.

given in Table IV. Other metals are probably ineligible. For example, Y resembles Sc in its atomic[29] ($4d^1 5s^2$) and negative ion[36] ($4d^1 5s^2 5p^1$) configurations as well as in its high promotion energy (31.2 kcal/mol). Therefore, a YH bond energy in excess of that calculated by eq 2 (EA(Y) = 7.1 kcal/mol;[36] D[Y–H] = 34.6 kcal/mol) is anticipated. Likewise, Pd($4d^{10}$) and Pd$^-$($4d^{10}5s^1$)[39] possess unusual ground-state configurations, and the hydride is calculated to have significant $4d\sigma$ bonding character.[11] Technitium is interesting since, unlike Mn, it has a low [$d^5s^2 \rightarrow d^6s^1$] promotion energy (7.4 kcal/mol) and is calculated to yield a bound negative ion (EA(Tc) = 12.7 kcal/mol).[41] A low-spin quintet ground state for TcH is therefore possible for which a bond energy of 40.2 kcal/mol can be predicted from eq 2. Of the remaining third-row elements, Ta and Re possess large promotion energies (27.9 and 33.6 kcal/mol, respectively)[29] and predicted high-spin ground states for their hydrides, while Hf does not form a stable negative ion[41] and therefore eq 2 is inapplicable.

Thus far, we have considered only periodic behavior by row. The predicted bond energies in Table IV serve to complete several transition-metal columns and thereby permit an examination of the vertical trends in M–H bond strengths. Perhaps the most striking finding here is the large increase in MH bond energies between the first and second row for the group 8 elements. This is, of course, merely a consequence of the large increases in the atomic electron affinities from which the bond energy estimates are derived.[18] For instance, the bond energy (electron affinity) almost doubles between FeH and RuH and a 27% increase occurs between CoH and RhH. A much smaller change obtains between RuH and OsH (1.6 kcal/mol) while for the cobalt group a second substantial increase is evident between the second and third row (10 kcal/mol). In contrast, the group 6 MH bond strengths and atomic electron affinities are all quite similar, and the spread among values for the noble metals is only half that of the group 8 elements. As pointed out by Lineberger and co-workers,[39] the observed differences between the second- and third-row transition elements with respect to s-electron binding energies are likely to arise from nuclear shielding effects of the filled 4f shell in the third transition series. Such effects are not well-characterized at present, but it is evident from the data in Tables III and IV that the columnar trends in the [$d^n s^2 \rightarrow d^{n+1}s^1$] promotion energies generally parallel those for the atomic electron affinities (and MH bond strengths). For example, the $d^{n+1}s^1$ atomic configuration is strongly favored for both Ru and Rh (PE – –21.4 and –36.3 kcal/mol, respectively). Accordingly, RuH and RhH possess high bond-dissociation energies. The promotion energies and ground-state configurations for the corresponding first- and third-row elements (Fe and Os; Co and Ir) more closely resemble one another, and the atomic electron affinities and MH bond

energies are directly related in proportion. This may be attributed to an increased stability of the 6s orbital relative to the 5d orbital in the third transition series which may have its origin in differential 4f shielding.

As an added note, a rough linear correlation between atomic electron affinity and MH bond strength[42] also exists for the alkali metals; however, in this case a different correlation line is defined (slope – 4.4; intercept = –8.1, R = 0.96). Here an analogy between the s^2 configuration of the atomic anions and the σ^2 covalent term of the hydrides may be drawn. However, the correlation is probably fortuitous since the alkali hydrides are largely ionic ($M^+ H^-$).[40] Insufficient data exist to permit identification of analogous column-wise correlations between electron affinity and diatomic hydride bond energy for the main-group elements. Correlation fails for the halogens, where the bond energies and electron affinities are well established.[26]

Conclusion

An analysis of recently determined diatomic metal–hydride bond energies and metal atom electron affinities has led to the discovery of a new periodic property correlation for transition-series elements. The following trends have emerged: (1) Diatomic transition-metal hydride gas-phase acidity is generally constant and equal to 341 ± 5 kcal/mol. (2) A simple linear relationship between metal atom electron affinity and metal–hydrogen bond-dissociation energy exists: D[M–H] = EA(M) + 27.5 (kcal/mol). (3) For metals of the first and third transition series, MH bond strengths inversely parallel the corresponding atomic promotion energies, ΔE[$d^n s^2 \rightarrow d^{n+1}s^1$], with the exception of the early metal hydrides. A simple qualitative model which equates the atomic metal anion electron configuration with the electron configurations for the corresponding low-spin diatomic hydride has been developed to rationalize the correlation between electron and H-atom binding energies. The correlation is expected to hold for elements which possess small or negative promotion energies and a bound atomic anion with an s^2 electron configuration. New MH bond energies are predicted from the correlation for second- and third-row transition-metal monohydrides for which neither experimental nor theoretical data are currently available.

Note Added in Proof. While this manuscript was in press, a related analysis of transition-metal hydrogen bonds in terms of Mulliken electronegativities appeared.[43] I thank Professor Pearson for a reprint of his review.

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