

The Transition-Metal-Hydrogen Bond

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I. Introduction

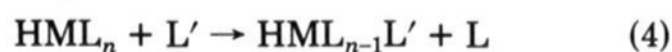
There is great current interest in the transition-metal hydrides, both because of their unusual reactivity and because of their potential as homogeneous catalysts for hydrogenation and other reactions of organic substrates. Though several thousand such hydrides have been synthesized and their properties studied, there is still a dearth of basic information on metal-hydrogen bond energies.¹ This paper is an attempt at drawing together the available data and at making extrapolations useful in future work on hydrides.

Actually there are three bond energies of interest. Writing HML_n for a general transition-metal hydride, where L represents other ligands on the metal



We have the homolytic bond energy, and the two possible heterolytic bond energies.

The first of these is important in determining the thermal stability of the hydride toward hydrogen gas evolution. It also determines, in a reverse sense, the ability of the fragment ML_n to cleave a hydrogen molecule to form the hydride. Also of considerable importance, the ease of reaction 1 determines the stability of the hydride to free-radical attack, with hydrogen atom abstraction. Such a free-radical attack can lead to very rapid substitution reactions of L for L', as Brown has ably demonstrated.²



free radical chain path

Reaction 2 is important in determining the power of the metal hydride on a reducing agent, by way of hydride ion transfer. This leads to reactions such as the reduction of suitable ketones. It also determines the stability of the compound towards hydrogen gas evolution in the presence of protons, or proton donors.



Ralph G. Pearson was born in Chicago and received the Ph.D. degree from Northwestern University in 1943. After service in the Air Force during World War II, he returned to Northwestern and began his work on organic and inorganic reaction mechanisms. He has written several well-known books, including "Kinetics and Mechanism", with A. A. Frost and (later) J. W. Moore, "Mechanisms of Inorganic Reactions", with F. Basolo, "Some Aspects of Crystal Field Theory", with D. S. McClure and T. M. Dunn, "Hard and Soft Acids and Bases", and "Symmetry Rules for Chemical Reactions". In 1976 he moved to the University of California, Santa Barbara, where he is Professor of Chemistry. His current research interest is in the properties and reactions of transition-metal hydrides.

Reaction 3, in which the metal hydride acts on a Brønsted acid, is a fascinating and originally unexpected reaction. The reaction is often critical in determining the species which are actually present in solution. The anion ML_n^- is usually a good reducing agent, but by way of electron-transfer mechanisms. The anion is usually a good nucleophile, especially when strongly basic. Also reaction 3 is very important, in the reverse direction, by making it possible to easily synthesize a large number of new hydrides. Many neutral organometallic compounds can be protonated to form cationic hydrides, as originally shown by Wilkinson.



II. Diatomic Hydrides

The simplest systems with metal-hydrogen bonds would be the diatomic MH molecules. These are transient species, usually formed in the gas phase and studied spectroscopically. Some homolytic bond energies, D_0 , are known, but it is instructive to first examine bonds to hydrogen formed by the representative elements. It is found that average E-H bond energies, such as those tabulated by Pauling,³ are large when E is an electronegative element and small when E is of low electronegativity. For example D_0 is 135 kcal/mol for

TABLE I. Some Properties of the Transition Metals

metal	χ , ^a eV	Δ , ^b kcal	D_0 , MH, ^c kcal	$\Delta H_{\text{vap}}/6$, ^h kJ	
Ti	d ² s ²	3.51	18.7	37	78
V	d ³ s ²	3.64	6.0		100
Cr	d ⁵ s ¹	3.76	0	42 ^d	78
Mn	d ⁵ s ²	3.72	48.8	36 ^e	47
Fe	d ⁶ s ²	4.03	19.8	39 ^f	81
Co	d ⁷ s ²	4.26	10.0	45 ^g	71
Ni	d ⁸ s ²	4.44	0.6	68	72
Cu	d ¹⁰ s ¹	4.48	0	66	56
Zr	d ² s ²	3.63	13.9		102
Nb	d ⁴ s ¹	3.88	0		141
Mo	d ⁵ s ¹	3.92	0		129
Tc	d ⁵ s ²	4.00	30.1		113
Ru	d ⁷ s ¹	4.24	0		107
Rh	d ⁸ s ¹	4.30	0		93
Pd	d ¹⁰ s ⁰	4.44	18.8		63
Ag	d ¹⁰ s ¹	4.44	0	53	47
Hf	d ² s ²	3.50	40.3		103
Ta	d ³ s ²	4.25	27.9		152
W	d ⁴ s ²	4.19	8.4		165
Re	d ⁵ s ²	4.01	33.6		128
Os	d ⁶ s ²	4.90	14.7		132
Ir	d ⁷ s ²	5.35	8.1		111
Pt	d ⁹ s ¹	5.70	0	80	94
Au	d ¹⁰ s ¹	5.80	0	74	61

^a Ionization potentials and ground-state configuration from Moore, C. E. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1970, NSRDS-NBS 34. Electron affinities from Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* 1975, 4, 539. ^b C. E. Moore, *Natl. Bur. Stand. Circ. (U.S.)*, 1949, 1952, 1958, 467. ^c From Connor, J. A. *Top. Curr. Chem.* 1977, 71, 101, except as noted. ^d Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* 1983, 105, 6352. ^e Reference 7. ^f Dendramis, A.; VanZee, R. J.; Weltner, Jr., W. *Astrophys. J.* 1979, 231, 632. ^g Kant, A.; Moon, K. A. *High Temp. Sci.* 1981, 14, 23. ^h Dasent, W. E. "Inorganic Energetics", 2nd ed.; Cambridge University Press: Cambridge, 1982, p 133.

HF and 42 kcal/mol for CsH.

For reasons that will become clear, we will use Mulliken electronegativities, defined as⁴

$$\chi = \frac{I + A}{2} \quad (6)$$

where I is the ionization potential of an atom and A is its electron affinity. The values of χ run from 10.41 eV for F to 2.18 for Cs. Mulliken electronegativities parallel the more common Allred-Rochow scale, except for H which has $\chi = 7.17$. This corresponds to 2.5 on the Allred-Rochow scale, instead of the usual 2.1. It has been shown by Parr that $-\chi$ is approximately equal to the chemical potential of the electrons in an atom or molecule.⁵

If D_0 , or mean bond energies for various E-H bonds are plotted against χ_E , there is a rough linear relationship. This enables us to estimate the expected value of D_0 for M-H bonds. Table I shows a number of properties of the transition metals. Sc, Y, and La have been omitted on the grounds that they behave more like representative elements. The values of χ_M range from 3.51 for Ti to 5.8 for Au. These lead to predicted values of D_0 of about 50 kcal for TiH, and 75 kcal for AuH.

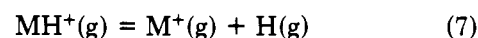
Such values of D_0 for MH molecules as are known are also listed in Table I. They are seen to be in the expected range, but there are substantial variations from one metal to the next, which do not follow the more regular χ_M trends. Some of the variations are easy to understand. They arise from the requirement of a promotion energy from the ground state of the atom to

the reactive valence state.⁶ For example, except for Cr and Cu, the first transition series has a (3d)^{*n*}(4s)² electron configuration. This is unfavorable for reaction with an H atom, but promotion to a (3d)^{*n*+1}(4s)¹ configuration would be very favorable.

Table I shows the ground-state configuration of the free metal atoms, and also the promotion energy, Δ , to the valence state postulated. When Δ is large the bond energy is reduced, as in Mn and Fe. Cr, Cu, and Ni have 0 or small values of Δ , and D_0 is larger.

Accurate ab initio calculations have shown that MnH uses a different valence state.⁷ Since Δ is very large, it is more favorable to form two s-p hybrid orbitals on Mn, each containing one electron. One of these is used to form the Mn-H bond. While excitation to a 4p orbital requires more energy than to a 3d, the s-p hybrid is a better bonding orbital because of larger overlap.

Evidence for the importance of the promotion energy concept comes from some D_0 values for MH⁺ molecules.⁹ The reaction is



Mn⁺ and Fe⁺ have the (3d)^{*n*}(4s)¹ valence-state configuration, and have D_0 values of 53 and 58 kcal. Cr⁺, Co⁺, and Ni⁺ have (3d)^{*n*+1} configurations and must be promoted. The D_0 values of 35, 52, and 43 kcal reflect the magnitude of the promotion energies in each case.

It would be useful to have even an approximate method to fill in the missing values in Table I. An equation (8) for single bond energies between atoms A and

$$D_{AB} = (D_{AA}D_{BB})^{1/2} + 103(1 - e^{-0.291(\chi_A - \chi_B)^2}) \quad (8)$$

B has recently been given by Matcha.¹⁰ It is an improved version of one originally used by Pauling.³ The χ 's are now the Pauling electronegativities.

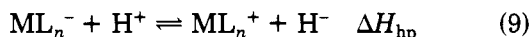
The difficulty with using (8) is that single bond energies, D_{AA} , for transition metals are not known, except for Cu₂, Ag₂, and Au₂. For these metals, using $D_{BB} = 103$ kcal/mol for H₂, eq 8 gives values about 10% higher than those shown in the table. Bond energies are known for a number of other M₂ molecules, but these are usually for multiple bonds.¹² With incomplete d shells, a molecule like Cr₂ could have as high as a sextuple bond. Only three of these are expected to be of any considerable strength, however. The strongest bond known is in Nb₂ and is 120 kcal/mol.¹¹

Instead of dissociation energies for M₂ molecules, many of which are unknown, Table I contains the heats of atomization of all the transition metals, divided by 6. This number is often used to estimate the strength of metal-metal bonds. The values usually follow trends in D_0 for M₂ molecules very well.

Though we still have the problem of multiple bonding we may at least assume that the potential bond multiplicity is the same in any triad. It may be seen that the mean metal-metal bond strength is always greatest in the third transition series. The second series is variable, at the beginning, Ti, Zr, and Hf, for example, the mean bond strength is almost as large as for the third series. At the end of the series, for Pd and Ag at least, the bond strength is anomalously low. This should relate to the weak bond in AgH compared to CuH and AuH. If this is so, we may expect PdH to have a weaker bond than NiH, and much weaker than PtH.

III. The Hydridic-Protonic Preference

In considering the two possible heterolytic dissociations, eq 2 and 3, it is convenient to first decide which mode is more likely for a given hydride. The hydridic-protonic preference may be defined as ΔH_{hp} , the enthalpy change in kcal/mol at 25 °C, for the equilibrium



A negative value for ΔH_{hp} means that hydride dissociation is energetically easier than proton dissociation. A positive value means the reverse.

For diatomic hydride molecules, HE, the value of ΔH_{hp} is easily calculated in the gas phase

$$\Delta H_{\text{hp}} = -46.1(\chi_{\text{H}} - \chi_{\text{E}}) \quad (10)$$

where the Mulliken electronegativities must be used. From the chemical potential point of view, $(\chi_{\text{H}} - \chi_{\text{E}})$ is the driving force for electron transfer from the element E to H.¹² Only F, O, Cl, N, and Br have χ_{E} larger than χ_{H} . In the gas phase these have a positive value for ΔH_{hp} , and their hydrides are protonic. Also their bond polarities are E^-H^+ . The dipole moment of HE is more complex, however, since the nonbonding electrons of E can be polarized. All other elements, including the transition metals, are hydridic in the gas phase and have E^+H^- polarity.

These values of ΔH_{hp} are of little practical value since in the gas phase nonionic, or homolytic, bond dissociation would actually occur. It is necessary to evaluate reaction 9 in solution. The best solvent to consider is water, even though water is not a good solvent for most transition-metal hydrides. But for water we have the greatest amount of information on solvation energies. If necessary, estimates can be made for conversion to other solvents.¹³ In most cases this will mean a moderate shift towards the gas-phase values.

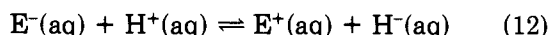
In water at 25 °C there are a number of individual ionic heats of hydration available.¹⁴ We also have a simple empirical equation for estimating heats of hydration for ions,¹⁵

$$-\Delta H_{\text{hyd}} = \frac{167q^2}{R + \delta} \text{ kcal/mol} \quad (11)$$

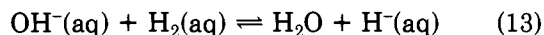
where q is the charge on the ion in electronic units, R is the crystallographic radius of the ion in Angstroms, and δ is a parameter. For monatomic ions of the representative elements, $\delta \approx 0.8$ for cations and $\delta = 0$ for anions. For the transition metals δ is smaller for cations, about 0.6 or less.

If instead of a monatomic ion, we have a complex ion, such as $\text{Co}(\text{NH}_3)_6^{3+}$, then δ can be set equal to 0. The value of R becomes the crystallographic radius of the large complex ion, and (11) is simply the Born equation for the hydration enthalpy of the ion.¹³

Consider the solution equilibrium corresponding to (9) for diatomic hydrides.



We will use a value of $-\Delta H_{\text{hyd}} = 267$ kcal for the proton¹⁴ and 108 kcal for the hydride ion. The latter figure comes from the ionic radius of H^- in crystals. It also agrees with experimental data on the exchange reaction in aqueous solution¹⁶



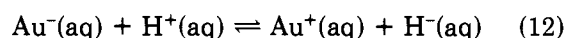
The rapid reverse of reaction 13 means that hydride ion is unstable in aqueous solution. This does not affect our calculations, however. Also there is some evidence that H^- does dissociate reversibly from transition-metal hydrides in nonprotic solvents.¹⁷

We can calculate ΔH_{hp} for reaction 12.

$$\Delta H_{\text{hp}} = 46.1(\chi_{\text{E}} - \chi_{\text{H}}) + 267 - 108 + (\Delta H_{\text{E}^-} - \Delta H_{\text{E}^+}) \quad (14)$$

If we assume that the ionic radius of E^- will be about 0.8 Å greater than for E^+ , then the last term in (14) will be 0, or close to it. The hydridic-protonic preference number will now be 0 when $\chi_{\text{E}} = 3.7$. This number should not be taken too seriously, but it does make all of the representative metals definitely hydridic, and all of the non-metals definitely protonic.

The value $\chi = 3.7$ also suggests that the transition metals will be in a borderline situation. But this must be modified by recalling that δ for the transition-metal cations is less than 0.8. Actually there is a crystallographic value for Au^- available and estimates have been made for some other monatomic metal anions.¹⁸ The value of R for Au^- is 2.0 Å, and it is likely that R for all of the transition-metal anions is in the range 1.9–2.2 Å. We can, accordingly, calculate the heat of reaction 12 for CuH , AgH , and AuH . For example,

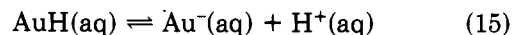


$$\Delta H_{\text{hp}} = 46.1(5.8 - 7.17) + 159 + 84 - 154 = +26 \text{ kcal} \quad (14)$$

The experimental heats of hydration are used for the metal cations, and eq 12 with $R = 2.0$ and $\delta = 0$ is used for the anions. This gives $-\Delta H_{\text{hyd}} = 154$ kcal for Au^+ and 84 kcal for Au^- . For CuH the value of ΔH_{hp} is -20 kcal, and for AgH about 0.

If we now go to the beginning elements of the three transition series, we see for Hf that χ is only 3.5 (Table I). Even though there will be a smaller heat of hydration for Hf^+ than for Au^+ , the change will be much too small to compensate for the change in χ of 2.3 eV. Similar, but smaller effects will be seen for Ti compared to Cu and Zr compared to Ag^+ . We conclude that these early transition-metal hydrides will be hydridic.

The value of ΔH_{hp} of +26 kcal for AuH means that it is more likely to act as an acid than as a hydride donor. But this does not mean that it will dissociate appreciably in solution. To estimate the pK_a it is necessary to also use D_0 , the homolytic bond energy.



$$\Delta H = 74 + 314 - 53 - 267 - 84 + 5 = -11 \text{ kcal}$$

The 74 kcal is D_0 for AuH , the ionization potential of H is 314 kcal, and the electron affinity of Au is 53 kcal. The 5 kcal is a rough estimate of the heat of hydration of AuH .

The value of ΔS° for (15) may be estimated as -20 eu.¹³ The final calculation then gives $\Delta G^\circ = 5$ kcal for (15). This corresponds to a pK_a value of -4, which suggests that AuH should be a fairly strong acid. The acid strength is due largely to the large electron affinity of gold. Ir and Pt also have large values for A , and we expect IrH and PtH to be protonic.

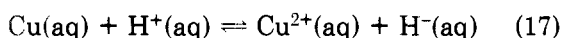
A similar calculation for AgH gives an estimated pK_a of -2 . Silver hydride is an unusual case. Since it has a hydridic-protonic preference of 0, it can act as both a strong proton donor and a strong hydride ion donor. AgH, and CuH, have been made in solution, and their behavior is essentially hydridic.¹⁹ For example, the reversible reaction



leads to H_2 - D_2O exchange. The reverse reaction is typical hydride behavior.

AuH has not been made in water. While Au^- is stable in the solid state and in certain other environments,¹⁸ it would not be stable in water. In fact all M^- species in water would be powerful reducing agents, and evolve H_2 .

The cationic hydrides CuH^+ , AgH^+ , FeH^+ , and CrH^{2+} have been made in water by adding H atoms to the metal ions. They show typical hydridic behavior. This seems inconsistent since the positive charge should enhance proton acidity. A calculation shows that solvation energies reverse the expected behavior.



$$\Delta H_{\text{hp}} = 318 + 267 + 5 - 108 - 516 = -34 \text{ kcal}$$

The gas-phase value is 318 kcal, very protonic, but the large heat of hydration of Cu^{2+} , -516 kcal, more than offsets this. A similar calculation can be made to show that HS^- , like H_2S , is protonic in solution, in spite of the negative charge.

Apparently CrH^{2+} , which is really $\text{Cr}(\text{H}_2\text{O})_5\text{H}^{2+}$, is unstable in solution. But related complex ions, such as $\text{Rh}(\text{NH}_3)_5\text{H}^{2+}$, are known and are stable.²¹ They show no acid properties in solution. Net positive or negative charges on a complex metal hydride are not reliable guides to hydridic or protonic behavior. As we shall see, changing the nature of the other ligands, L, does have a predictable effect. As far as the metal goes, low values of χ cause hydridic behavior, and large values of χ lead to protonic behavior. A large value of the electron affinity is very favorable for acidity.

IV. Bond Energies in HML_n

In order to obtain hydrides stable in aqueous solution, or similar media, it is necessary to surround the metal atom with suitable ligands, leaving room in the first coordination sphere for one or more hydrogen atoms. As a first approximation the homolytic bond energies for the M-H bond would still be in the 50-75 kcal range.

Two changes would be expected, however. The first is that the promotion energies to the valence state found for metal atoms would no longer play a role. The radical $\text{ML}_n\cdot$ would normally be in the same valence state as HML_n . This would increase some bond energies, compared to the diatomic hydrides, e.g., Fe, Co, and Mn. The second effect that the ligands might have would be to delocalize the odd electron of the broken M-H bonds, by spreading it over the ligands. This could happen best for π -accepting ligands such as CO. The net effect would be to lower M-H bond energies by stabilizing the radical.

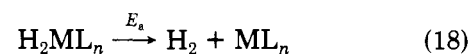
Table II summarizes the available data on metal-hydrogen bond strengths in complexes. Some of the

TABLE II. Mean Metal-Hydrogen Bond Energies in Transition-Metal Complexes

complex	\bar{D}_0 , kcal	ref
$\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	59	64
$\text{H}_2\text{IrBr}(\text{CO})(\text{PPh}_3)_2$	56	64
$\text{H}_2\text{IrI}(\text{CO})(\text{PPh}_3)_2$	54	64
$\text{HMn}(\text{CO})_5$	65	28, 72
$\text{HCo}(\text{CO})_4$	57	a
$\text{H}_2\text{Mo}(\text{Cp})_2$	60	b
$\text{H}_2\text{W}(\text{Cp})_2$	73	b
$\text{H}_3\text{Ru}_3(\text{COCH}_3)(\text{CO})_9$	65	c
$\text{H}_3\text{Pt}_2(\text{dppm})_2(\text{PPh}_3)^+$	59	d
$\text{HCo}(\text{CN})_5^{3-}$	58	19
$\text{H}_2\text{RhCl}(\text{PAR}_3)_3$	58	h
$\text{H}_2\text{Fe}(\text{CO})_4$	<65	e
$\text{H}_2\text{Ir}(\text{CO})_2(\text{PMePh}_2)_2^+$	<62	b
$\text{H}_2\text{Co}[\text{P}(\text{OCH}_3)_3]_4^+$	<62	g

^a Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363. ^b Calado, J. C. G.; Dias, A. R.; Martinho-Simoes, J. A.; Ribiero da Silva, M. A. V. *J. Organomet. Chem.* **1979**, *174*, 77. ^c Bavaro, L. M.; Montagero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977. ^d Hill, R. H.; Puddephat, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 5797. dppm = bis(diphenylphosphino)methane. ^e Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500. ^f Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 3000. ^g Muettterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978. ^h Drago, R. S.; Miller, J. G.; Hoselton, M. A.; Farris, R. D.; Desmond, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 444. Ar = *p*-tolyl.

data comes from standard thermochemical methods. Some comes from activation energies for reductive elimination of H_2 from hydrides.



$$\bar{D}_0 \leq \frac{103 + E_a}{2} \text{ kcal/mol}$$

In these cases only an upper limit can be set on the mean M-H bond energy. The activation energy for the reverse of (18) is not expected to be large.²²

The data, though sparse, are in line with expectations. Since the ligands change as well as the metal, it is not clear that bond strengths increase with the electro-negativity of the metal, as might be predicted. It does appear that the third transition series forms stronger bonds, particularly if some circumstantial evidence is admitted. For example, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ will not add H_2 to any extent, whereas the iridium analogue does. Also $\text{Pt}(\text{PR}_3)_2$ will add H_2 , while $\text{Pd}(\text{PR}_3)_2$ will not.²³

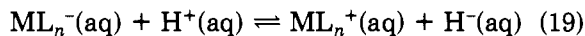
Some additional inferences may be drawn from the thermal stabilities of other metal hydrides. For example, $\text{HRe}(\text{CO})_5$ is more stable, and $\text{HTc}(\text{CO})_5$ much less stable, than $\text{HMn}(\text{CO})_5$.²⁴ $\text{H}_2\text{Os}(\text{CO})_4$ is much more stable, and $\text{H}_2\text{Ru}(\text{CO})_4$ much less stable, than $\text{H}_2\text{Fe}(\text{CO})_4$. The order of stability is $\text{HCo}(\text{CO})_4 > \text{HIr}(\text{CO})_4 > \text{HRh}(\text{CO})_4$.²⁵ Conclusions drawn from such data are suspect, however, since the mechanism for decomposition can be complex. The rates may have little to do with the strength of the metal-hydrogen bond.

Polynuclear hydrides, such as $\text{H}_2\text{Ru}_4(\text{CO})_{13}$, are usually very stable. This may be deceiving in that the stability may result from the nonavailability of an easy mechanism for H_2 loss. This is the case for $\text{H}_2\text{Fe}_3(\text{CO})_{11}$, where one hydrogen exists as a proton in solution, or is coordinated to an oxygen atom in the solid state.²⁶ There are two polynuclear hydrides in Table II. At least one H atom is bridging between two metal atoms in these two cases, yet the mean bond energies seem normal.

The ultimate in a bond between a hydrogen atom and several metal atoms would be H₂ dissociatively adsorbed on a metal surface. From heats of adsorption it is possible to calculate mean bond energies.²⁷ The values are very similar to those in the tables. Cu, Ag, and Au give low bond energies when estimated in this way. Since the electronic structure of the bulk metal plays a key role in these heats, it seems safest not to use such data to make predictions for simple metal hydrides.

V. Hydridic-Protonic Preference for HML_n

We wish to know ΔH_{hp} , the enthalpy change for the reaction



To a good approximation we can assume that the Born heats of hydration of ML_n^- and ML_n^+ cancel each other. This gives the very simple result

$$\Delta H_{\text{hp}} = 46.1(\chi_{\text{R}} - \chi_{\text{H}}) + 159 \quad (20)$$

where χ_{R} is one-half the sum of the ionization potential and electron affinity of the radical ML_n . These data are not available (with one exception), but they can at least be estimated. The first approximation would set χ_{R} equal to χ_{M} for the metal. The second approximation would be a correction for the effect of the ligands.

A set of CO ligands would be expected to increase the values of both I and A , since the electrons are stabilized by delocalization. A set of H₂O or NH₃ ligands would decrease I and A , since the polar ligands would favor the creation of positive charge on the metal. There are data to test this idea for $\text{Mn}(\text{CO})_5$. The ionization potential is 8.32 eV,²⁸ and the electron affinity is 2 eV.²⁹ This gives $\chi_{\text{R}} = 5.16$, compared to $\chi_{\text{M}} = 3.72$ for manganese. This is probably close to a maximum effect for raising χ_{R} , compared to χ_{M} . The value of ΔH_{hp} for $\text{HMn}(\text{CO})_5$ is now calculated to be 66 kcal, which makes this hydride strongly protonic, as expected.

The effect of water ligands is implicit in the calculations made earlier on the effect of hydration on AuH. The difference in ΔH_{hyd} of 70 kcal, between Au⁺ and Au⁻, is equivalent to a lowering of χ_{R} by 1.5 eV, compared to χ_{Au} . The radical R in this case is the (non-existent) Au(H₂O)_n species. This is also a maximum effect as far as the metal goes. Some ligands might give a greater lowering of χ_{R} .

Changing the charge on HML_n will change the electronegativities of the resulting radical. A positive charge will increase χ_{R} , and a negative charge will decrease it. But for HML_n⁺ and HML_n⁻, eq 20 is no longer valid. Corrections for solvation energies must now be made. Approximate calculations for $\text{HMn}(\text{CO})_5^+$ and $\text{HFe}(\text{C}-\text{O})_4^-$ show that both are strongly protonic. Recall that $\text{HCr}(\text{H}_2\text{O})_5^{2+}$ was hydridic. The nature of the ligands is more important than the charges in determining ΔH_{hp} .

VI. Brønsted Acidity

Of the three dissociation modes for HML_n, the easiest to measure is proton dissociation, eq 3. Standard methods for determining pK_{a} values can be used in many cases. Though the number of compounds for which data exist is still small, enough have been done to start drawing useful conclusions. Table III lists the data available in water and in methanol. Some further

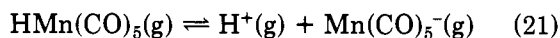
TABLE III. Brønsted Acidity of Transition-Metal Hydrides

hydride	pK_{a}	ref
Water, 25 °C		
HCo(CO) ₄	strong acid	a
HCo(CO) ₃ (PPh ₃)	7.0	b
HCo(CO) ₃ (P(OPh) ₃)	5.0	b
HMn(CO) ₅	7.1	31
H ₂ Fe(CO) ₄	4.4 = pK_1 ~14 = pK_2	c
HFe(NO)(CO) ₃	~5.1	61
HV(CO) ₆	strong	44
HV(CO) ₅ (PPh ₃)	6.8	44
HM(PF ₃) ₄ , (M = Co, Rh, Ir)	strong	39
HRe(CO) ₅	very weak	d
HCo(dmgh) ₂ (PBu ₃)	10.5	e
HRh(dmgh) ₂ (PPh ₃)	9.5	b
HCo(CN) ₅ ⁻	~20	g
Methanol, 25 °C		
H ₄ Ru ₄ (CO) ₁₂	11.9	50
H ₄ FeRu ₃ (CO) ₁₂	13.4	50
H ₂ Ru ₄ (CO) ₁₃	14.7	50
H ₂ FeRu ₃ (CO) ₁₂	14.3	50
H ₂ Os(CO) ₄	14.7	50
H ₂ Os ₄ (CO) ₁₂	12.0	50
H ₂ Os ₃ (CO) ₁₂	14.5	50
H ₂ Fe(CO) ₄	6.8	50
H ₄ Ru ₄ (CO) ₁₁ P(OMe) ₃	13.6	50
HCr(Cp)(CO) ₃	6.4	h
HMo(Cp)(CO) ₃	7.2	h
HW(Cp)(CO) ₃	9.0	h
HNi(dppe) ₂ ⁺	2.6	j
HNi[P(OCH ₃) ₃] ₄ ⁺	1.5	59
HPd[P(OCH ₃) ₃] ₄ ⁺	0.7	i
HPt[P(OCH ₃) ₃] ₄ ⁺	10.2	i
HIr(CO)Cl(PPh ₃) ₂ ⁺	2.1	62
HRh(CO)Cl(PPh ₃) ₂ ⁺	1.8	62
HRh(dppe)(CH ₃ OH) ₂ ²⁺	1.0	k
HIr(CO)Br(PPh ₃) ₂ ⁺	2.6	62
HIr(CO)I(PPh ₃) ₂ ⁺	2.8	62

^aHieber, W.; Hübel, W. *Z. Electrochem.* 1953, 57, 235. ^bHieber, W.; Lindner, E. *Chem. Ber.* 1961, 94, 1417. ^cKrumholz, P.; Stetlin, H. M. *J. Am. Chem. Soc.* 1949, 71, 3035. ^dBeck, W.; Hieber, W.; Brown, G. *Z. Inorg. Allg. Chem.* 1961, 308, 23. ^eSchrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* 1971, 93, 1505. dmgh = monoanion of dimethylglyoxime. 50% H₂O-CH₃OH. ^fRamasami, R.; Espenson, J. H. *Inorg. Chem.* 1980, 19, 1846. 50% H₂O-CH₃OH. ^gVenerable, G. D., II; Halpern, J. *J. Am. Chem. Soc.* 1971, 93, 2176. ^hPearson, R. G.; Amman, C., unpublished results. Measurements in 70% CH₃OH-30% H₂O v/v extrapolated to 100% CH₃OH using factor for H₂Fe(CO)₄. See Pearson, R. G.; Mauer-mann, H. *J. Am. Chem. Soc.* 1982, 104, 500. ⁱPearson, R. G.; Rebo, P., unpublished results. ^jTolman, C. A. *Inorg. Chem.* 1972, 11, 3128. ^kHalpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* 1977, 99, 8055.

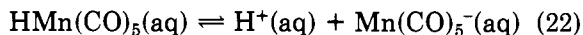
information is available in acetonitrile, which seems to be a very useful solvent for metal hydrides.³⁰

Stevens and Beauchamp have also determined the gas-phase proton affinities of $\text{Mn}(\text{CO})_5^-$, $\text{Co}(\text{CO})_4^-$, and $\text{HFe}(\text{CO})_4^-$.²⁹



$$\Delta H = 318 \text{ kcal/mol}$$

Corresponding values are 319 kcal for H₂Fe(CO)₄, and ≤314 kcal for HCo(CO)₄. Since pK_{a} 's are known in water for HMn(CO)₅ and H₂Fe(CO)₄, this enables a calculation of the heats of hydration of the anions.



$$\Delta H = 4 = 318 - 267 + 5 + \Delta H_{\text{R}}^-$$

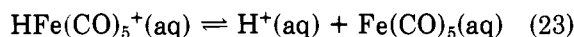
A value of -20 eu for ΔS° is assumed; and 5 kcal is again a rough value for the heat of hydration of the

neutral hydride molecule. The value of ΔH_{R^-} is found to be -56 kcal. Using eq 11 with $\delta = 0$, the Born equation, the value of R is calculated as 2.98 Å. This agrees very well with the crystallographic radius of $Mn(CO)_5^-$.³² For $HFe(CO)_4^-$ a similar calculation gives $R = 2.93$ Å.

The proton affinities and the dissociation energies for the M-H bond in Table II allows limits to be calculated for the electron affinities of $Co(CO)_4$, ≥ 2.5 eV, and $HFe(CO)_4$, ≤ 2.6 eV. The importance of large values of A in determining the acidity of carbonyl hydrides was first pointed out by Imyanitov.³³

Table III gives information on the effect of overall charge, changes in the ligands, changes in the metal, and changes in the nuclearity. The effect of overall charge is normal for Brønsted acids. It is much more difficult to remove the second proton from these hydrides than the first. The magnitude of the effect is about 10 p K_a units for $HFe(CO)_4^-$. Positively charged acids are much more acidic than similar neutral ones. For example, $HNi[P(OCH_3)_3]_4^+$ has a p K_a of 1.5 in methanol, whereas the isoelectronic $HCo[P(CH_3)_3]_4$ requires LiH to remove the proton.³⁴

Stevens and Beauchamp have measured proton affinities in the gas phase for a number of neutral metal complexes.³⁵ By estimating solvation energies, these may be converted to aqueous solution. For $Fe(CO)_5$ the proton affinity is 204 kcal. In solution



$$\Delta H = 204 - 267 + 57 - 5 = -11 \text{ kcal}$$

leading to a p K_a of about -8 . This agrees with the observation that $HFe(CO)_5^+$ can only be formed in very strong acid solution.³⁶

In all cases where analogous compounds have been compared, the third transition series has been found to give the least acidic hydrides. In addition to the data shown in Table III, it may also be mentioned that $HRe(Cp)(CO)_2(PPh_3)^+$ is less acidic than $HMn(Cp)(CO)_2(PPh_3)^+$,³⁷ and $HPt(PEt_3)_3^+$ is less acid than the Ni and Pd analogues.³⁸ The order of decreasing acidity is $HRh(CO)_4 > HCo(CO)_4 > HIr(CO)_4$,²⁵ and $HRh(PF_3)_4 > HCo(PF_3)_4 > HIr(PF_3)_4$.³⁹

The second transition series seems to be less acid than the first for the metals to the left in the periodic table. $HMo(Cp)(CO)_3$ is less acid than $HCr(Cp)(CO)_3$ (Table III), and also $HNb(Cp)(CO)_3^+$ is less acid than $HV(Cp)(CO)_3^+$.³⁷ But the pattern is changed to the right of the periodic table where complexes of Pd and Rh are less basic than the Ni and Co analogues. The position of Ru compared to Fe seems to be variable, some evidence showing that Ru is more basic,³⁵ and some that Fe is more basic.⁴⁰ The great thermal instability of $H_2Ru(CO)_4$ suggests that it may be more acid than $H_2Fe(CO)_4$ (vide infra).

The low acidity of the third series is somewhat unexpected, in view of the earlier conclusion that AuH, PtH, and IrH were the most acidic of the diatomic metal hydrides, in spite of large M-H bond strengths. The acidity, however, arose from the very large electron affinities of the metals, stabilizing M^- . This advantage must vanish in the anions ML_n^- . It resides in the very stable $6s$ orbital of the free atoms. This orbital is used to bond all of the ligands, as well as the H atom, and its effect is diffused. The electron affinity now resides

chiefly in the delocalization afforded by the ligands themselves.

For carbonyl ligands there is a good experimental assay of the effectiveness of this delocalization. The force constant for the C-O vibration in metal carbonyls is a good measure of the amount of $d-\pi^*$ back-bonding from the metal to the ligand.⁴¹ An examination of these constants shows that π -bonding is nearly constant for the three transition series, being a function of the number of d electrons, and the number and position of the CO ligands.⁴²

This leads one to expect that the electron affinities in the third transition series will not be much different from those of series one and two. Solvation energies of the anions, ML_n^- , will also not be much different, since atomic sizes vary little among the transition metals. We must conclude that it is the greater value of the M-H bond strengths which accounts for the higher p K_a values of the third series in general.

From the order in $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$, it appears that acidity increases in going from left to right in a given transition series. Also $HNi[P(OCH_3)_3]_4^+$ is a stronger acid than $H_2Co[P(OCH_3)_3]_4^+$, and $HMn(Cp)(CO)_2PR_3^+$ is more acid than $HV(Cp)(CO)_3PR_3^+$,³⁷ in agreement with the generalization. The ordering is not the expected one from bond strengths, since these increase in going from left to right, according to the limited data of Table II, and the order expected on the basis of increasing electronegativities of the metals.

The order does follow that of the electron affinities of $Mn(CO)_5$, $HFe(CO)_4$, and $Co(CO)_4$ given earlier. These can be rationalized in terms of the total gain in π -bonding energies upon forming the corresponding anions. For example, $Mn(CO)_5^-$ has the D_{3h} structure which gives maximum π -bonding for eight d electrons.³² $Co(CO)_4^-$ has the T_d structure, which allows all ten d electrons to enter into π -bonding.

It would not be expected that other ligands would give as large an effect, and it must be concluded that the left-to-right increase in acidity would not be invariant. In fact, it is already known that $HFe(Cp)(CO)_2$ is a much weaker acid than $HMo(Cp)(CO)_3$, and therefore weaker than $HCr(Cp)(CO)_3$.⁴³

The π -bonding hypothesis also explains why $HV(C-O)_6$ is a strong acid. The anion has the octahedral structure which gives maximum π -bonding for six d electrons. Addition of a proton to $V(CO)_6^-$ would be very unfavorable, and indeed the neutral hydride has not been isolated.⁴⁸

The hydrides of Ti, Zr, and Hf show no acid properties and they behave as typical hydride ion donors.⁴⁵ This may be related to the fact that the metals do not bond ligands like CO well, because they have so few d electrons. On the basis of chemical evidence, the best hydride donors are found to the left in the periodic table.⁴⁶ In general hydrides which are good proton donors are poor hydride donors.⁴⁷ However there could be examples, like AgH, which can function as both.

If delocalization of electrons in the anion is of such great importance, it would be expected that polynuclear metal hydrides would be more acid than mononuclear ones. This conclusion is based simply on size considerations. Hieber showed that the order of decreasing acid strength was indeed $H_2Fe_3(CO)_{11} > H_2Fe_2(CO)_8 >$

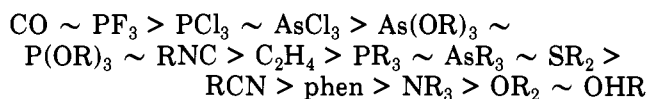
$\text{H}_2\text{Fe}(\text{CO})_4$.⁴⁸ Also Kaesz has remarked that $\text{H}_3\text{Re}_3(\text{C}-\text{O})_{12}$ is more acid than $\text{HRe}(\text{CO})_5$.⁴⁹ Table III shows that $\text{H}_4\text{Os}_4(\text{CO})_{12}$ is more acid than $\text{H}_2\text{Os}(\text{CO})_4$. But $\text{H}_2\text{Os}_3(\text{CO})_{12}$ is not more acid than the mononuclear hydride. The hydrogen atoms in the latter compound are both terminal, whereas the more acid polynuclear compounds have bridging hydrogen atoms.

The acid strength of the $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ is quite small, and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ also is of low acidity. It is hard to believe that $\text{H}_2\text{Ru}(\text{CO})_4$ is less acid than these polynuclear analogues. Large structural changes accompany the deprotonation of polynuclear hydrides in some cases.⁵⁰ Some neutral hydrides, or anions, may have very stable structures, and would resist losing, or gaining, protons.

VII. Influence of the Ligands on Acidity

The pK_a of metal hydrides can be changed as much, or more, by changing the ligands, L, in HML_n , as by changing the metal. It is already apparent that CO is at the head of the list in favoring protonic behavior, though PF_3 may be nearly equal. The best way to rate other neutral ligands is to examine the effect that they have on C–O stretching frequencies, when both CO and L are attached to the same metal atom.⁵¹ Strong π -bonding by L will raise the CO frequencies by reducing bonding to the π^* orbital of CO.

This enables the ligands to be put in an order of decreasing π -bonding ability.⁵²



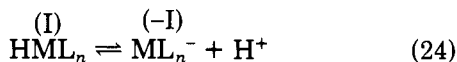
NO is not included because it can act as NO^+ , strongly π -bonding, or NO^- , only weakly π -bonding. If it acts as NO^+ , then it must add an electron to the metal and this can have an effect on the electronegativity. For example, the anion $\text{Cr}(\text{Cp})(\text{NO})_2^-$ has a very high-energy highest occupied molecular orbital.⁶⁹ Since in MO theory we have

$$-\epsilon_{\text{HOMO}} = \frac{I + A}{2} = \chi$$

the value of χ for the radical $\text{Cr}(\text{Cp})(\text{NO})_2$ is small. As expected, the compound $\text{HCr}(\text{Cp})(\text{NO})_2$ is nonacidic and acts as a hydride donor.⁷⁰

Ordering anionic ligands is more difficult because the charge can affect the force constants for C–O stretching by way of a σ inductive influence.⁵³ Some good π -accepting ligands can be identified as $(\text{CH}_3)_3\text{Sn}^-$, $(\text{C}_6\text{H}_5)_3\text{Sn}^-$, $(\text{C}_6\text{H}_5)_3\text{Si}^-$, Cl_3Si^- , Cp^- , CN^- , and similar anions where there clearly are empty π -type orbitals available.

For anions where π -acceptor properties are not important, a different approach seems to be useful. The ionization of a proton from a metal hydride is accompanied by a formal change in the oxidation state of M by 2 units (reductive elimination).



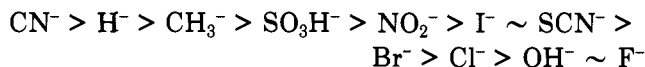
Actually the change is more than a formal one, since the structures of HML_n and ML_n^- are generally those expected for the indicated oxidation states. Even in metal carbonyl hydrides, ESCA studies show that the hydrogen is nearer to H^- than H^+ .⁵⁴

In every case, M in the hydride will be in the higher oxidation state and M in the anion in the lower oxidation state. Except for Au, Hg, Tl, and Pb, the higher oxidation state of a metal corresponds to a harder Lewis acid than the lower oxidation state.⁵⁵ We can then predict that hard bases will stabilize the HML_n form, and soft bases will stabilize ML_n^- .

An examination of the neutral ligands shows how well this simple HSAB principle works. The acid-strengthening ligands are all soft bases, and the acid-weakening ligands, such as amines and alcohols, are hard bases. The acid-strengthening, π -accepting, anions are also all soft.

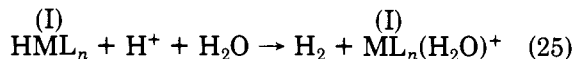
We can accordingly order the remaining anions by putting them in an order of decreasing softness. Unfortunately there is no one order which fits all purposes, though roughly the orders are all similar. A scale of absolute hardness for bases has recently been proposed, but it is appropriate for isolated gas-phase systems.¹²

A reasonable scale to use seems to be the trans effect series, appropriate for substitution reactions of Pt(II) complexes.⁵⁶ This series rates ligands according to the stabilization they afford for addition of a nucleophilic reagent (negative charge). The order for removal of a proton (positive charge) should be similar.



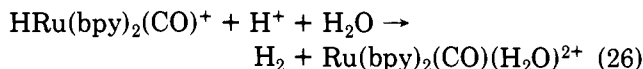
There is not enough information on pK_a values to check the lists for neutral ligands and for anions in detail. But there is enough information to show that they are reasonably accurate. From Table III we see that replacing a CO ligand with a phosphite reduces the acidity somewhat. Replacing with a phosphine has an even larger acid-weakening effect. The complex $\text{Ir}(\text{cod})\text{Cl}(\text{PPh}_3)$ is a base of about the same strength as $\text{IrCOCl}(\text{PPh}_3)_2$.⁵⁷ The cod ligand is 1,5-cyclooctadiene, so that two olefin groups are about equal to a CO plus a phosphine.

There is no direct evidence on the predicted base-strengthening effect of hard ligands.⁷¹ However there is some indirect evidence based upon hydridic behavior. Consider the hydride transfer reaction



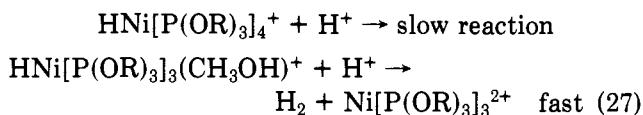
There is no decrease in the oxidation state of the metal and furthermore the net positive charge increases by 1 unit. The prediction is that hard ligands, L, will favor reaction 25.

This is borne out by the behavior of some bipyridine complexes



Reaction 26 has a half-life of 10 min at 25 °C and a pH of 5.1.⁵¹ The osmium analogue reacts in a similar fashion in acetonitrile with added acid. But the reaction of $\text{HOs}(\text{bpy})(\text{PPh}_3)_2(\text{CO})^+$ under the same conditions gives no hydrogen, even upon prolonged heating.⁵⁸

A similar result is seen in the complexes $\text{HNi}[\text{P}(\text{OR})_3]_4^+$ studied by Tolman.⁵⁹



Replacement of a soft phosphite ligand by a hard methanol greatly hastens the loss of hydrogen. To the degree that strong hydridic behavior indicates weak protonic behavior, these results support the conclusion that hard bases are acid weakening in metal hydrides.

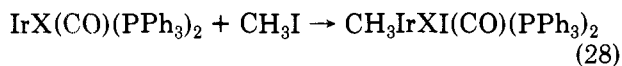
With regard to anionic ligands, comparisons must be made between complexes of the same total charge. Changes in the oxidation state of the metal do not seem to play an important part, except as they replace neutral ligands by anionic ones. Examples are known where ligands such as SiCl_3^- , SiPh_3^- , and GePh_3^- show the acid-strengthening influence expected.⁶⁰ The complex $\text{HFe}(\text{Cp})(\text{CO})(\text{SiCl}_3)_2$ has a $\text{p}K_a$ of 2.6 in CH_3CN , which makes it a very strong acid indeed. For comparison, HClO_4 has a $\text{p}K_a$ of 4.7 in CH_3CN , and $\text{HCr}(\text{Cp})(\text{CO})_3$ has a $\text{p}K_a$ of 13.3.³⁰

The cyclopentadienyl ion, Cp^- , is often found in hydrides which are moderately acidic. Since it is usually tridentate, it replaces ligands such as CO with a reduction in acidity. Thus $\text{HFe}(\text{Cp})(\text{CO})_2$ is a weaker acid than $\text{H}_2\text{Fe}(\text{CO})_4$.⁴³ $\text{H}_2\text{Os}(\text{CO})_4$ is a slightly stronger acid than $\text{HOs}(\text{CH}_3)(\text{CO})_6$,³⁰ and $\text{HFe}(\text{CN})(\text{CO})_4$ is more acidic than $\text{H}_2\text{Fe}(\text{CO})_4$.⁶¹

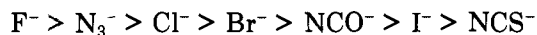
Table III shows that the series $\text{HIrX}(\text{CO})(\text{PPh}_3)_2$ where $\text{X} = \text{Cl}^-$, Br^- , I^- does not follow the predicted order. The effect is small, being only a factor of 6. A factor of 2 is found for the rhodium analogues.⁶² This order has often been found for oxidative-addition reactions of various kinds.²³ Together with the observation that phosphine complexes react more rapidly than phosphite analogues, it has led to the view that electron-donating ligands favor oxidative addition.

While this seems very reasonable in terms of increased electron density on the metal making it easier to remove electrons, it is the opposite to the conclusions of the HSAB principle. Hard ligands, which withhold electron density, favor the oxidation process, at least for the equilibrium situation. Rates could be affected differently, soft bases often showing higher rates.⁵⁵

In the most complete study of oxidative addition of an alkyl halide



the order of rates found for different X was⁶³

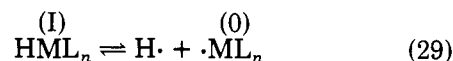


with hard F^- reacting 100 times faster than soft NCS^- . This is the order expected according to the HSAB view. Also in Table II it may be seen that the Ir-H bond strength in the dihydrides of Vaska's compound fell off in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, as expected. The equilibrium constants for oxidative addition of H_2 to $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ are in the order $\text{Cl}^- \gg \text{Br}^- > \text{I}^-$, and the rates are in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$.⁶⁴

VIII. Homolytic Bond Energies and Brønsted Activity

The previous remark about metal-hydrogen bond strengths and the influence of ligands suggests a general relation between homolytic bond strengths and Brønsted acidities. Since the addition of H_2 and of H^+ are both oxidative addition, both should be affected in the same direction, by changing either the metal or the ligands.

The same conclusion can be drawn even if the molecule has only a single hydrogen.



Homolytic breaking of a single M-H bond also is a reductive process on the metal. One would again predict that hard ligands would stabilize the oxidized form, the hydride, and soft ligands would favor the reduced form, the radical.

Alternatively, the electron delocalization concept may be used. Ligands, such as CO or $\text{P}(\text{OR})_3$, which stabilize the anion by π -delocalization, would also stabilize the radical to some lesser extent. There is evidence for structural rearrangement in the radical $\text{Mn}(\text{CO})_5$, compared to $\text{HMn}(\text{CO})_5$, for example.⁶⁵ Typically we would expect the effect on the bond strength to be about one-half the effect on the ΔH for acid dissociation.

In a qualitative sense there is no doubt that strong Brønsted acidity goes along with weak M-H bonds. $\text{HCo}(\text{CO})_4$ and $\text{H}_2\text{Fe}(\text{CO})_4$ evolve hydrogen even at 0 °C, whereas $\text{H}_2\text{Os}(\text{CO})_4$, $\text{H}_2\text{Os}_3(\text{CO})_{12}$, and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ are stable above 100 °C. The order of thermal stability, $\text{HCo}(\text{CO})_4 > \text{HIr}(\text{CO})_4 > \text{HRh}(\text{CO})_4$, is the same as the order of increasing acidity.²⁵ All three hydrides are strong acids and also very unstable. $\text{HCr}(\text{Cp})(\text{CO})_3$ is the least stable and $\text{HW}(\text{Cp})(\text{CO})_3$ the most stable, with $\text{HMo}(\text{Cp})(\text{CO})_3$ intermediate.⁶⁶ This follows the order of acid strength, with the chromium compound stable up to 60 °C, in line with its $\text{p}K_a$ compared to $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$.

Substitution of CO with a phosphite or phosphine in $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$ not only decreases the acid strength, but also increases the thermal stability. There is no information on the influence of a hard ligand such as pyridine. This is expected to have an even greater effect, both on decreasing the acidity, and on increasing thermal stability. However H_2 loss by reactions such as (26) would be enhanced.

Changing the metal in HML_n , keeping L_n as much the same as possible, should also produce changes in the same direction for both homolytic and protonic dissociation. However the situation is now less straightforward since the intrinsic M-H bond strength also plays a role. Intrinsic means free of both the influence of the ligands and the effect of promotion energy.

The only relevant quantitative data in Table II show that D_0 is 8 kcal greater for $\text{HMn}(\text{CO})_5$ than for $\text{HCo}(\text{CO})_4$. This is expected since $\text{HCo}(\text{CO})_4$ is the stronger acid, but the combined uncertainties in D_0 are greater than the difference. $\text{HMn}(\text{CO})_5$ is more stable to heat than $\text{HCo}(\text{CO})_4$, and undergoes ligand substitution more slowly.⁵⁶ This may simply mean that loss of CO is rate determining for both processes, in which case the metal-hydrogen bond strength may play only a minor role.

IX. Concluding Remarks

The most important conclusions of the preceding analysis are that soft, electron-delocalizing ligands attached to the metal both weaken the metal-hydrogen bond and increase the Brønsted acidity. Hard ligands increase the hydridic nature of the bond.

These conclusions seem to contradict some older rules, particularly of organic chemistry. These rules state that electronegative substituents increase acid strength by an inductive effect. Such electronegative groups are F, OR, and NR_2 , which are hard bases. But the rule applies only to substituents in a more remote position, such as fluorine in CF_3COOH .

If we focus on the C-H bond and on the substituents directly attached to carbon, we find exactly the same rules as for M-H bonds. CH_3L^+ is more acidic if L is PR_3 or R_2S than if it is NR_3 or R_2O .⁶⁸ Conversely, if we wish to remove H^- , or any anion, from a carbon atom, then we find that F, O, and N are the better substituents for stabilizing the resulting carbonium ion.

The transition-metal-hydrogen bond is very similar to the carbon-hydrogen bond. Both are of low polarity and can react as H^+ , H^\cdot , or H^- donors for that reason. The tendency to behave in one way or another depends on stabilization of the resulting anionic, radical, or cationic species. Extensive electronic and structural rearrangement usually accompanies this stabilization. Rates of removal of protons by bases is unusually slow, because of this rearrangement.^{30,50} The main difference is that the C-H bond is appreciably stronger, in part because χ for carbon is 6.27, larger than for any transition metal.

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