

2.6: Hydrides

The combination of hydrogen with another element produces a hydride, E_xH_y . The formal charge or oxidation state of the hydrogen in these compounds is dependant on the relative electronegativity of the element in question.

Ionic hydrides

Hydrogen compounds with highly electropositive metals, i.e., those in which the metal has an electronegativity of less than 1.2, are ionic with the hydrogen having a s^2 configuration (H^-). Typical ionic metal hydrides are those of the Group 1 (IA) metals and the heavier Group 2 (IIA) metals.

The ionic radius of the hydride ion is in between that of fluoride and chloride and the same as oxide (Table 2.6.2.2). As a consequence, in the solid state the hydride ion replicates that of a halide ion (e.g., Cl^-), and as such similar solid state structures are observed (Table 2.6.2.3).

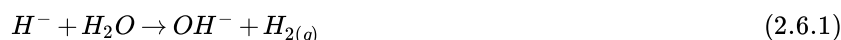
Table 2.6.2.2: Selected ionic radii.

Ion	Ionic Radius (Å)
H^-	1.40
F^-	1.36
Cl^-	1.81
O^{2-}	1.40

Table 2.6.2.3: Lattice parameters (Å) for hydrides, and halides of the Group 1 metal salts with cubic rock salt structures.

Metal	Hydride	Fluoride	Chloride
Li	4.085	4.0173	5.129
Na	4.880	4.620	5.640
K	5.700	5.347	6.292
Rb	6.037	5.640	6.581
Cs	6.376	6.008	7.020

Unlike the halide ions that are soluble in water, the hydride ion reacts with water, (2.32), and consequently NaH and CaH_2 are commonly used as drying agents. The liberation of hydrogen was used as a commercial source of hydrogen for small-scale applications.



WARNING

Group 1 and 2 metal hydrides can ignite in air, especially upon contact with water to release hydrogen, which is also flammable. Hydrolysis converts the hydride into the analogous hydroxide, which are caustic bases. In practice, most ionic hydrides are dispensed as a dispersion in oil, which can be safely handled in air.

Covalent Hydrides

The most common binary compounds of hydrogen are those in which hydrogen bonds have covalent bond character. The E-H bond is usually polar ranging from those in which the hydrogen is polarized positively (e.g., those with non-metals such as F, O, S, and C) to where it is negative (e.g., those with metals and metalloids such as B, Al, etc). Magnesium hydride is intermediate between covalent and ionic since it has a polymeric solid similar to AlH_3 , but reacts rapidly with water like ionic hydrides. Table 2.6.2.4 lists the important covalent hydrides of p-block elements. It should be noted that all organic hydrocarbons can be thought of as simply the hydrides of carbon!

Group 13	Group 14	Group 15	Group 16	Group 17
B_2H_6	C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2}	NH_3 , N_2H_4	H_2O , H_2O_2	HF
$(AlH_3)_n$	Si_nH_{2n+2}	PH_3 , P_2H_4	H_2S , H_2S_n	HCl
Ga_2H_6	Ge_nH_{2n+2}	AsH_3	H_2Se	HBr
	SnH_4	SbH_3	H_2Te	HI

The elements of Group 14 to 17 all form hydrides with normal covalent bonds in which the hydrogen is bonded by a single bond to the element in question. In contrast, the elements of Group 13 (as typified by boron) all exhibit a second type of covalent bond: the electron deficient **hydrogen bridged bond**. In this type of bond the hydrogen nucleus is embedded in a molecular orbital that covers more than two atoms to create a multi-center two-electron bond. Diborane (Figure 2.6.2.13) represents the archetypal compound containing the hydrogen bridge bond. Hydrides are not limited to terminal (E-H) or those bridging two atoms (E-H-E), but are also known where the hydrogen bridges (or caps) more than two atoms, i.e., Figure 2.6.2.14.

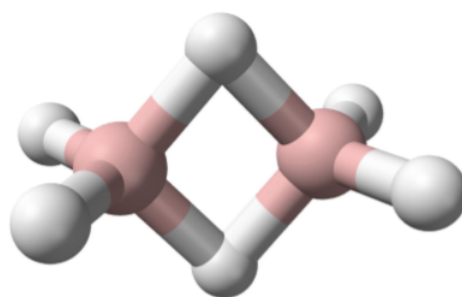


Figure 2.6.13: Structure of diborane (B_2H_6); where pink = boron; white = hydrogen.

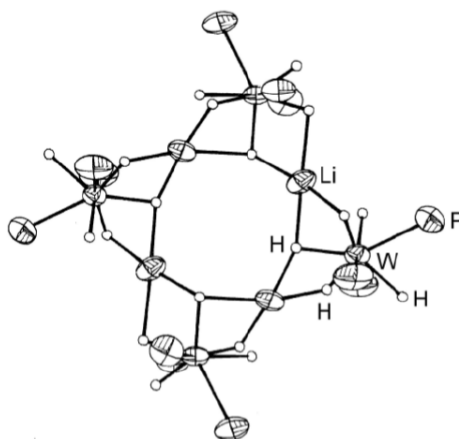


Figure 2.6.14: The structure of $\{[(Me_3P)_3WH_5]Li^+\}_4$ showing the presence of terminal, bridging, and trifurcated hydrides. The methyl groups have been omitted for clarity. Adapted from A. R. Barron, M. B. Hursthouse, M. Motevalli, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1986, 81.

Synthesis of covalent hydrides

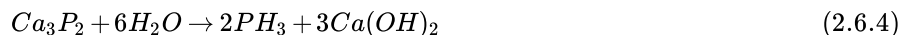
Covalent hydrides can be made by a range of synthetic routes. The simplest is direct combination of the elements (in a similar manner to that used with ionic hydrides).



The use of a hydride as a reagent to reduce a halide or oxide of the desired element



Metal phosphides, carbides, silicides, and borides result in the formation of the hydride.



Hydride compounds can be interconverted in the presence of a catalyst, heat, or an electrical discharge. This is the basis of catalytic cracking of petroleum mixtures.

Interstitial hydrides

Many transition metal, lanthanides and actinides absorb hydrogen to give a metallic hydride which retain the properties of a metal, although the presence of hydrogen does result in embrittlement of the metal. As such these hydrides are best considered as alloys since they do not have defined stoichiometries. For example, vanadium absorbs hydrogen to form an alloy with a maximum hydrogen content of $VH_{1.6}$. In a similar manner palladium forms $PdH_{0.6}$. The hydrogen atoms are present in interstitial sites in the metal's lattice; hence *interstitial hydride*. Interstitial hydrides show certain promise as a way for safe hydrogen storage.

Bibliography

- A. R. Barron, M. B. Hursthouse, M. Motevalli, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1986, 81.

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