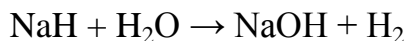


SALINE HYDRIDES

The instability of the hydride ion compared to the halide ions can be seen by comparison of the ΔH_f for alkali metal hydrides and chlorides.

Cation	ΔH_f MH / kJmol^{-1}	ΔH_f MCl / kJmol^{-1}
Li	-90.5	-409
Na	-56.3	-411
K	-57.7	-436
Rb	-52.3	-430
Cs	-54.2	-433

Saline hydrides are formed by the group 1 and 2 metals when heated with dihydrogen (H_2). They are white, high melting point solids that react immediately with protic solvents, for example:

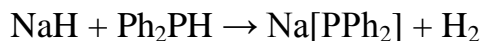


(Their moisture sensitivity means that reaction conditions must be water-free.)

Evidence for the ionic nature of these hydrides is:

- 1) molten salts show ionic conductivity.
- 2) X-ray crystal data gives reasonable radius ratios expected for ionic compounds.
- 3) Observed and calculated Lattice Energies (from Born-Haber cycles etc.) are in good agreement (i.e. show little covalency).

NaH is capable of deprotonating a range of even weak Brønsted acids to give the corresponding sodium derivatives.



Sodium hydride is sold by many chemical suppliers as a mixture of 60% sodium hydride (w/w) in mineral oil. Such a dispersion is safer to handle and weigh than pure NaH. The compound can be used in this form but the pure grey solid can be prepared by rinsing the oil with pentane or tetrahydrofuran, THF, care being taken because the washings will contain traces of NaH that can ignite in air. Reactions involving NaH require an inert atmosphere, such as nitrogen or argon gas. Typically NaH is used as a suspension in THF, a solvent that resists deprotonation but solvates many organosodium compounds.

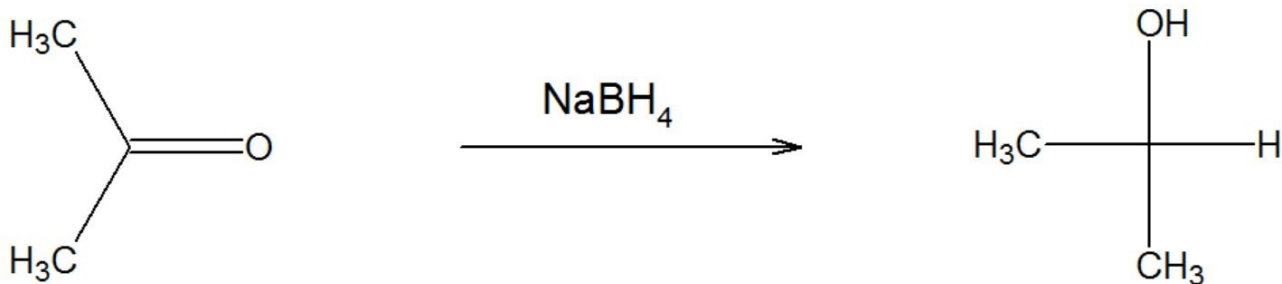
Hydride reducing agents

LiH and Al_2Cl_6 gives [lithium aluminium hydride](#) (lithal LiAlH_4), NaH reacts with $\text{B}(\text{OCH}_3)_3$ to give [sodium borohydride](#) (NaBH_4). These find wide scope and utility in organic chemistry as reducing agents.

LiAlH_4 is commonly used for the reduction of esters and carboxylic acids to primary alcohols; previously this was a difficult conversion that used sodium metal in boiling ethanol (the Bouveault-Blanc reduction). The solid is dangerously reactive toward water, releasing gaseous hydrogen (H_2). Some related derivatives have been discussed for hydrogen storage.

NaBH_4 is used in large amounts for the production of sodium dithionite from sulfur dioxide: Sodium dithionite is used as a bleaching agent for wood pulp and in the dyeing industry. NaBH_4 consists of the tetrahedral BH_4^- anion in the crystalline form and is found to exist as three polymorphs: α , β and γ . The stable phase at room temperature and pressure is α - NaBH_4 , which is cubic and adopts an [NaCl-type structure](#). Millions of kilograms are produced annually, far exceeding the production levels of any other hydride reducing agent.

NaBH_4 will reduce many organic carbonyls, depending on the precise conditions. Most typically, it is used in the laboratory for converting ketones and aldehydes to alcohols. For example, reduction of acetone (propanone) to give propan-2-ol.



Molecular hydrides - covalent hydrides and organic compounds

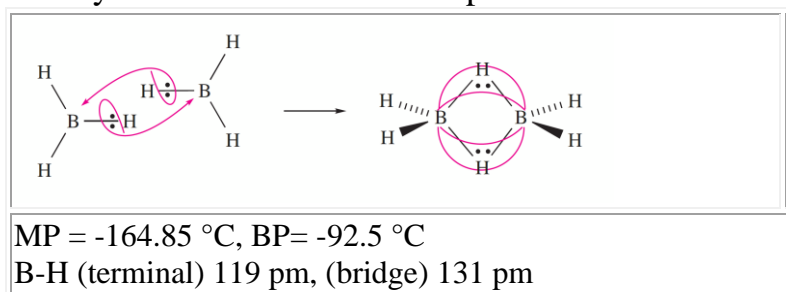
Hydrogen forms a vast number of compounds with carbon, (the hydrocarbons), and an even larger array with heteroatoms that, because of their general association with living things, are called organic compounds. The study of their properties is covered in organic chemistry and their study in the context of living organisms is covered in biochemistry. By some definitions, "organic" compounds are only required to contain carbon. However, most of them also contain hydrogen, and because it is the carbon-hydrogen bond which

gives this class of compounds most of its particular chemical characteristics, carbon-hydrogen bonds are required in some definitions of the word "organic" in chemistry. Millions of hydrocarbons are known, and they are usually formed by complicated synthetic pathways, which seldom involve direct reaction with elementary hydrogen.

Most molecular hydrides are volatile and many have simple structures that can be predicted by the VSEPR model. There are a large number of B hydrides known (boranes) and although the simplest BH_3 has been found in the gas phase it readily dimerises to give B_2H_6 .

In inorganic chemistry, hydrides can serve as bridging ligands that link two metal centers in a coordination complex. This function is particularly common in group 13 elements, especially in boranes (boron hydrides) and aluminium complexes, as well as in clustered carboranes, (composed of boron, carbon and hydrogen atoms). The bonding of the bridging hydrogens in many of the boranes is explained in terms of 3 centre - 2 electron bonds.

Diborane is a colourless and highly unstable gas at room temperature with a repulsively sweet odour. Diborane mixes well with air, easily forming explosive mixtures. Diborane will ignite spontaneously in moist air at room temperature.



Metallic (interstitial) hydrides

Many transition metal elements form metallic (interstitial) hydrides, in which H_2 molecules (and H atoms) can occupy the holes in the metal's crystal structure. They are traditionally termed 'compounds', even though they do not strictly conform to the definition of a compound; more closely resembling common alloys such as steel. These systems are usually non-stoichiometric, with variable amounts of hydrogen atoms in the lattice.

Palladium is unique in its ability to reversibly absorb large amounts of H_2 or D_2 (up to 900 times its own volume of hydrogen, but no other gases, at room temperature) to form palladium hydride. Structural studies show that the absorbed H fits into octahedral holes in

the cubic close packed Pd lattice with a non-stoichiometric formula approximating to PdH_{0.6} for the β-form. This material has been considered as a means to carry hydrogen for vehicular fuel cells. Interstitial hydrides show some promise as a way for safe hydrogen storage. During the last 25 years many interstitial hydrides have been developed that readily absorb and discharge hydrogen at room temperature and atmospheric pressure. At this stage their application is still limited, as they are capable of storing only about 2 weight percent of hydrogen, insufficient for automotive applications.

Source :

http://wwwchem.uwimona.edu.jm:1104/courses/CHEM1902/IC10K_MG_hydrogen.html