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Chemical tuning of the thermal decomposition temperature of inorganic hydrides: Computational aspects

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Abstract

We show that chosen computationally-derived molecular features along several atomic descriptors of the metallic center, as well as the value of the standard redox potential of the metal center, E^0, allow for the semiquantitative estimate of the ease of metal–hydrogen bond rupture for binary and multinary hydrides. Utility of E^0 is illustrated for Group 2 hydrides, and further extended to complex systems such as amido- (NH_2^-), imido- (NH^{2-}) and methyl anion (CH_3^-) model complexes of metal cations bound to tetrahydridoborate anion (BH_4^-). Such considerations may be utilized for the tuning of the thermal decomposition temperature, T_{dec}, of the chemical hydrogen store, and for the design of the *low-temperature* hydrogen fuel source, via deliberate choice of chemical elements constituting the hydrogen storage material.

Keywords: Hydrogen storage materials; Electrochemical reactions; Thermal analysis; Quantum mechanical computations; Population analysis

1. Main text

For a chemist, the reactions taking part in decomposition and recharging of a hydrogen store, are the reduction–oxidation (redox) reactions:

$$M + \frac{n}{2}H_2 \rightarrow M^{n+}H_n \quad \text{(oxidative addition)} \tag{1a}$$

$$M^{n+}H_n \rightarrow M + \tfrac{1}{2}nH_2 \quad \text{(reductive elimination)} \tag{1b}$$

where M stands for an element, a lower binary hydride, a ternary one, or even a more complex entity.

Using the established formalism of the redox reaction, we have recently shown that the thermal decomposition temperature, T_{dec}, is nicely correlated with the standard redox potential for the metal cation/metal redox couple, E^0, and with the standard enthalpy of decompositon, ΔH^0, for a vast family of binaries, and for an impressively large span of the T_{dec} values ($> 850\,^\circ C$) [1]. We have also argued that tuning of the T_{dec} value is further possible via deliberate choice of the stoichiometric ratio and of Lewis acid/base character of the chemical elements constituting the multinary hydrides [1]. Thus, evidence was delivered that the kinetic aspects of thermal decomposition are in fact often interrelated with the thermodynamic parameters for this process, as long as a broad stability range is considered. Large thermodynamic stability of a hydride *typically* pushes up the energy barrier for dihydrogen evolution from a material, and pulls down the energy barrier for H_2 reabsorption, while the latter two are also correlated with each other.

The particularly useful T_{dec} versus E^0 relationship, vividly illustrated below for the homologic Ba, Sr, Ca, Mg, Be binary hydride series [2], will now be supplemented by DFT quantum mechanical computations for MH_2 molecules.

Table 1 shows chosen *computed molecular parameters* (the equilibrium M–H bond distance, R_0; the energy of HOMO and LUMO orbitals, E_{HOMO} and E_{LUMO}, and the HOMO/LUMO gap, ΔE_{HL}; the Mulliken charge on H and M atoms, q(H) and q(M); the force constants for the symmetric and asymmetric stretching mode, $f(\sigma_g)$ and $f(\sigma_u)$), *experimental atomic parameters* describing M or M^{2+} (configuration energy, CE(M) [3]; Mulliken electronegativity, $\mu(M^{2+})$, and Pearson hardness $\eta(M^{2+})$ [4]; ionic radius, $R(M^{2+})$; softness

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Table 1
Comparison of chosen (experimental and theoretical) atomic, molecular and condensed-phase parameters, which might serve as predictors of the T_{dec} value for the solid dihydrides of Group 2 elements

Parameter	BaH_2	SrH_2	CaH_2	MgH_2	BeH_2
Molecular					
R_0(M–H)[a](Å)	2.528	2.308	2.121	1.704	1.327
E_{HOMO}[a] (au)	−0.182	−0.202	−0.221	−0.259	−0.319
E_{LUMO}[a] (au)	−0.063	−0.058	−0.046	−0.033	−0.040
ΔE_{HL}[a] (au)	0.119	0.144	0.175	0.226	0.279
q(H)[a] (e)	−0.502	−0.390	−0.360	−0.268	−0.148
q(M)[a] (e)	+1.004	+0.780	+0.720	+0.536	+0.296
$f(\sigma_g)$[a] (mDyne $Å^{-1}$)	0.545	0.691	0.899	1.536	2.476
$f(\sigma_u)$[a] (mDyne $Å^{-1}$)	0.637	0.768	0.920	1.712	3.617
Atomic					
CE(M)[b] (eV)	5.21	5.70	6.11	7.65	9.32
$\mu(M^{2+})$[c] (eV)	22.8	27.3	31.6	47.6	86.1
$\eta(M^{2+})$[c] (eV)	12.8	16.3	19.7	32.5	67.8
$R(M^{2+})$[e] (Å)	1.35	1.13	0.99	0.65	0.31
σ(M)[d] (eV^{-1})	0.51	0.48	0.45	0.38	0.30
E_{bind}(ns)[e] (eV)	?	6.6	7.0	9.0	10.0
Solution					
$E^0(M^{2+}/M^0)$[e] (V)	−2.92	−2.89	−2.84	−2.36	−1.97
Solid state					
$T_{dec}(MH_{2(s)})$[f] (°C)	675	675	600	327	250
$\Delta H^0_{dec}(MH_{2(s)})$[f] (kJ mol^{-1})	177	180.3	181.5	75.2	18.9

For detailed description, see text.

[a] Our computations for linear MH_2 molecules.

[b] From ref. [3].

[c] Values from ref. [4], based on experimental data.

[d] Values from ref. [2a].

[e] Values from http://www.webelements.com; E^0 values for acidic aqueous solutions.

[f] From ref. [1].

of M, σ(M); and binding energy of valence ns electrons of a metal M, E_{bind}(ns)), the value of standard redox potential for the M^{2+}/M^0 redox pair in the acidic aqueous *solution*, $E^0(M^{2+}/M^0)$, and two important parameters describing the thermodynamic and kinetic stability of a hydride in a *solid state* (temperature of the thermal decomposition, T_{dec}; and enthalpy of decomposition, ΔH_{dec}).

As it may be seen from Table 1, the T_{dec} value correlates *monotonically* with all molecular and atomic parameters, except for E_{LUMO}. The following simple picture may now be built on the basis of quantum mechanical computations: along with an increasing electronegativity and hardness of a metal, M, and its cation, M^{2+} (in direction from Ba to Be), the energy of the valence orbitals of M decreases and orbitals become more contracted; this causes the increase of affinity of M^{2+} towards electron attachment, i.e. the increase of a corresponding E^0 value, and a substantial charge withdrawal by M^{2+} from hydride anion in a MH_2 molecule; thus the ionicity of the M–H bonds, as well as a factual negative charge on the H center (and its electronic polarizability) decrease. The stronger binding of 1s electrons to the H nucleus for Be than for Ba is also revealed by the decreasing energy of HOMO orbital (which is in fact centered mainly on H atoms) in MH_2 molecules. In consequence, one could view the situation that H^- starts to resemble H^0 more-and-more as the metal's electronegativity increases; analogous thing happens in the MH_2 solids, which are – however – characterized by larger ionicity of the MH bonds [5] and dramatically increased thermodynamic stability [6], than in the corresponding molecules. In consequence (since in the course of the reaction described by Eq. (1b), the M–H bonds need to be broken – or at least significantly elongated), the energy barrier for H_2 evolution in a solid, $\Delta E^{\#}$, decreases [7], and T_{dec} also thereby decreases [8]. Thus, simple theoretical arguments whose origins are in molecular orbital (MO) theory [9], help to explain the monotonic T_{dec} versus E^0 relationship [1].

The validity of the screenplay outlined above allows the use of many simple molecular or even atomic parameters as valuable signatures of the ease of metal–hydrogen bond rupture for many molecular and solid binary hydrides [10].In many cases, E^0 helps to predict T_{dec} quantitatively with sufficient reliability. And what about the multinary materials? Let us now explore the systems which contain the tetrahydridoborate (i.e. borohydride) anion as source of hydrogen, and a variety of main group, transition and post-transition metal centers, ligated by isoelectronic Lewis bases, L, of relatively similar strength (L = NH_2^-, NH^{2-} or CH_3^-) to equilibrate the total charge of this species to −1.

Fig. 1 presents the graph of the bridging BH bond length (and not for the terminal BH bonds) plotted versus the E^0

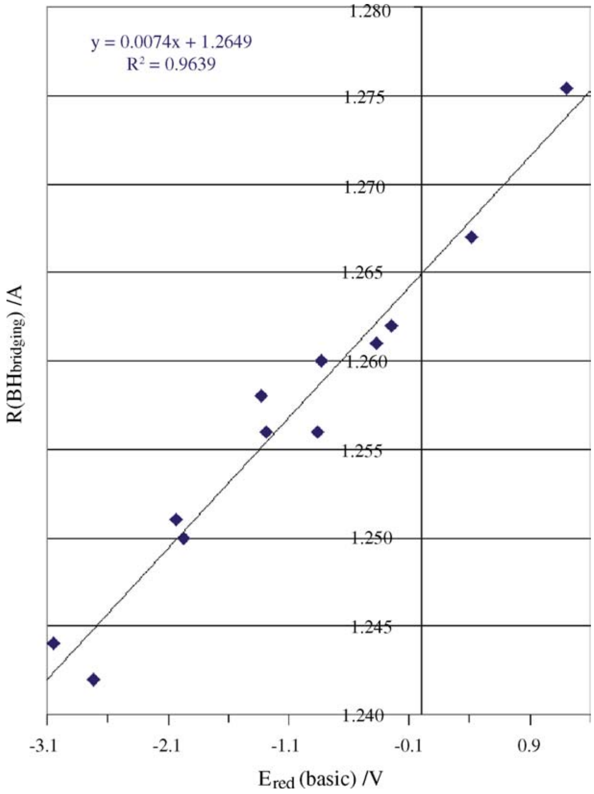

Fig. 1. Illustration of the relationship between the value of the longest *computed* BH bond length and the *experimental* value of the standard redox potential (in basic aqueous solution) of the metallic center entering the molecular complex, E^0 (see text and Supplementary Material for details). The progressive elongation of the bridging BH bond is seen as the metal cation becomes stronger and stronger oxidant, as compared to the computed BH bond length in a free BH_4^- anion (1.241 Å). Chosen cations are explicitly listed which belong to the molecules studied.

value for the metal center (i.e. for the most typical redox pair associated with the oxidation state studied here). The numerical data is given in Table S1 in Supplementary data.

It turns out that as the redox potential of the metal center increases, the bridging BH bond length of the attached $BH_4{}^-$ anion becomes progressively longer. This result agrees with simple chemical intuition of the redox reaction associated with the liberation of H_2:

$$[M^{n+}L_n]HBH_3{}^- \rightarrow [M^{(n-1)+}L_n]^- + \tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,B_2H_6, \quad (2)$$

since the value of the bridging BH bond length informs of the early stage of the BH bond rupture reaction. As the metal center becomes a better electron acceptor, the charge density is transferred from $BH_4{}^-$ anion onto the $[M^{n+}L_n]$ one, and the bridging BH bond which participates in the three-center $M\cdots H\cdots B$ bonding, becomes weaker and more ionic [11]. It thus appears that E^0 can serve as a valuable predictor of the bond length of the bridging BH bond for a large family of systems, despite the fascinating variety of transition metal borohydride chemistry. We expect that the most potent oxidizers should release H_2 most easily [12] (although most probably irreversibly), in agreement with our earlier observations [1].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.jallcom.2005.01.135.

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[5] All ionic solids (including halides and hydrides of Group 1 and Group 2 metals) all typically more ionic than the corresponding molecules, due to the necessity to form more MH bonds in the solid than in the molecule (requirement of extended net propagation in 3D), or – alternatively – due to energetically advantageous Madelung stabilization via non-additive polarization. This is also revealed in the increase of MH bond length (weakening of the MH bond) in the solids as compared to molecules (see Supplementary data for details). Still, the trend of ionicity of the MH bond decreasing in the direction from Ba to Be, seen for the MH_2 molecules, is preserved for solids, as well (exceptionally, relativistic effects may slightly change the ranking for the heaviest elements – say, Ba vs. Sr or W vs. Mo – in certain families of hydrides).

[6] Remarkably, even the most thermally and thermodynamically stable Group 2 hydrides in the solid state are not thermodynamically stable in the gas phase with respect to the H_2 evolution. Similar behaviour is seen for other hydrides, e.g. ΔH_{dec} ($LiH_{(s)}$) = +90.5 kJ mol^{-1}, ΔG_{dec} ($LiH_{(s)}$) = +68.3 kJ mol^{-1}, while ΔH_{dec} ($LiH_{(g)}$) = -140.6 kJ mol^{-1}, ΔG_{dec} ($LiH_{(g)}$) = -119.7 kJ mol^{-1}. Large values of sublimation enthalpy of the metal hydrides (or – alternatively – substantial increase of ionicity of the MH bonds in the solid state) accounts for this vast stability difference. In case of BeH_2, $\Delta H^0_{dec}(MH_2)$ is +125.5 kJ mol^{-1} in the gas phase and -18.9 kJ mol^{-1} in the solid phase. Numerical data is taken from NIST and knovel databases on the world wide web, and from Ref. [1].

[7] Importantly, the increased covalence o the MH bond in the MH_2 molecules – as one goes up Group 2 – is seen in the increase of the force constants for the MH stretching modes, and in the increased value of

the HOMO/LUMO energy gap. This is a seeming paradox, since for many molecules large values of force constants for stretching modes, and of the energy gap, are usually informative of the large bond dissociation energies, and of increased difficulty in transferring charge between anion and cation present in the system. In case of hydrides, however, this is not the case, as large force constants tend to indicate rather the presumed vicinity (in terms of interatomic distance) of the excited charge-transfer states (electron density is transferred from hydride anion to metal center), and – in consequence – the increased ease of the MH bond rupture (this is probably due to large anharmonicity of the M—H oscillators, as electronic structure of these species greatly changes with the MH bond elongation). In addition, upon propagation into solid, smaller and more covalent MH_2 molecules give rise to much larger overlap of MOs, and thus to larger band widths (both for occupied and unoccupied bands) in the electronic structure of corresponding solids. This helps to reduce the HOMO/LUMO gap for light hydrides, and eventually even reverse the ranking of the values of indirect dielectric band gaps for solid semiconductors as compared to their parent molecules.

[8] The discussed covalence increase of the M—H bond may be interpreted in the terms of the solid state theory as a gradual introduction of holes to the hydride band by relatively electronegative metal cations. Similar correlation of the ionic character of the M—H bond, has been first attempted for much more limited set of compounds (for the BH bond only) half century ago:
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[10] This is of value, as readily accessible microscopic parameters could serve as qualitative or even semi–quantitative predictors of a statistical value of a macroscopic feature (here: temperature of thermal decomposition) of an analogous solid. Novel families of species might be designed at low cost (theoretical computations at molecular level) thus indicating promising candidates in the solid state for novel low-temperature sources of H_2.

[11] For these species, which contain the most potent oxidizers in the set of metal cations studied (and for many other not shown here, which exhibit the longest bridging BH bonds), the most negative difference of the Mulliken charge on the bridging H atom vs. the B atom, has also been computed. This result agrees with what is known for most chemical bonds: they become increasingly ionic upon elongation, and in rather large range of internuclear distances.

[12] Exceptions from this rule are very important. e.g., it turns out from our more advanced DFT computations, that moderate oxidants could stretch the bridging BH bond equally well – or even more – than the most potent ones. This, however, requires, that the empty or partially filled orbital, to which 1s electron density of bridging H^- is attached, is not equivalent with the orbital to which the electron is transferred at the final stage of reduction of the metal center, or if substantial reorganization takes place in the course of the reaction (M. Kijeńska, S. Ostrowski, J. Dobrowolski, W. Grochala, unpublished results).