



Hydride donating abilities of the tetracoordinated boron hydrides

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ABSTRACT

The hydride donating ability (HDA), determined as Gibbs free energy ($\Delta G^\circ_{\text{H}}$) for the reaction of H^- dissociation, was assessed via the DFT/M06/6-311++G (d,p) calculations for 90 tetracoordinated borohydrides $\text{Li}[\text{L}_3\text{B-H}]$ taking into account the solvent effects via the optimization in MeCN and CH_2Cl_2 under SMD model. Obtained this way, the HDA^{MeCN} values vary from 118.2 to 13.4 kcal/mol and correlate well with the Lewis acidity parameters (AN, HA and FA) of parent trigonal boranes (L_3B). These data show numerically how the variation of the substituents at the boron atom allows the fine-tuning the B–H bond reactivity (reduction power) in the reactions involving hydride transfer as well as the selectivity of the reduction processes. The analysis of the data obtained shows that by varying the number of substituents and their nature, it is possible not only to change the properties of neutral trisubstituted boranes from highly electrophilic (represented by halogenide- and pseudohalogenide-boranes) to highly nucleophilic (exemplified by alkoxy-an amidoboranes), but also to repolarize the boron-bound hydrogen and make the proton transfer process more favourable than the hydride transfer.

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1. Introduction

After its discovery in 1942, sodium borohydride (NaBH_4) has rapidly become recognised as an extremely convenient reductant [1–3]. Nowadays the diverse boron hydrides derivatives are widely used as selective reducing agents in fine organic synthesis [3–5]. The reactivity of borohydrides is connected with their ability to act as an H^- donor [6] that can be increased by B–H bond activation. The reactivity of tetra-coordinated borohydrides in reduction processes is substantially determined by the coordination environment of the boron atom. As has been shown by H. C. Brown [2,3], the modification of parent tetrahydroborate MBH_4 provides an effective tool for the fine-tuning its reactivity towards the reactions with hydride transfer as well as the selectivity and stereospecificity of reduction.

As a general rule, the electron withdrawing groups (EWG) increase the electron deficiency (Lewis acidity) of a boron atom, whereas the electron donating groups (EDG) stabilize planar configuration of tricoordinated boranes due to the donation of electron density from the substituents to the empty $2p_z$ orbital of

boron atom [7]. However, the stability of tetracoordinated boron hydrides $[\text{R}_3\text{BH}]^-$ could not be explained solely on the base of electron withdrawing or electron donating ability of the substituent groups [8].

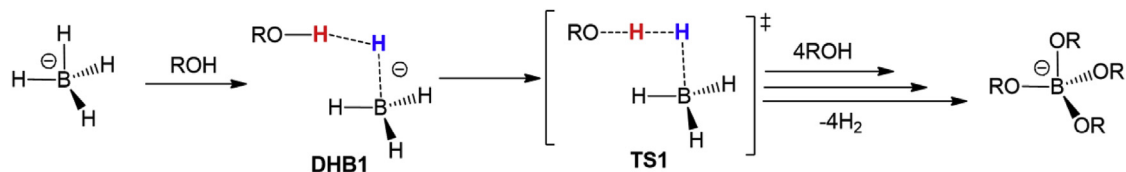
In our recent study [9] we have revealed that the ability of alkoxyborohydrides to transfer hydride increases upon the consecutive substitution of H^- by RO^- at the boron atom. This results in a significant facilitation of the cascade BH_4^- alcoholysis, which energetic profile has a descending sawtooth shape (Scheme 1 and Fig. 1).

In a series of papers on the mechanistic investigations of transition metal tetrahydroborates alcoholysis, we have revealed the importance of the B–H bond activation in order to promote the H_2 release from borohydrides during the alcoholysis of these complexes [10–13]. Thus, in ruthenium hydrido-tetrahydroborate complexes the coordination to Ru(II) atom activates B–H bond and facilitates its cleavage via the hydride transfer within the (3c-2e) Ru–H–B bond [11,13].

Thermodynamic hydricity, i.e. hydride donating ability (HDA), determined as Gibbs free energy ($\Delta G^\circ_{\text{H}}$) for the reaction in Scheme 2 is a very important characteristic of transition metal hydrides that describes their reactivity and is used for the rational design of catalytic reactions [14,15]. For that reason, the hydride donating ability (HDA) of borohydrides can also be considered as a measure

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Scheme 1. The general mechanism of BH_4^- alcoholysis.

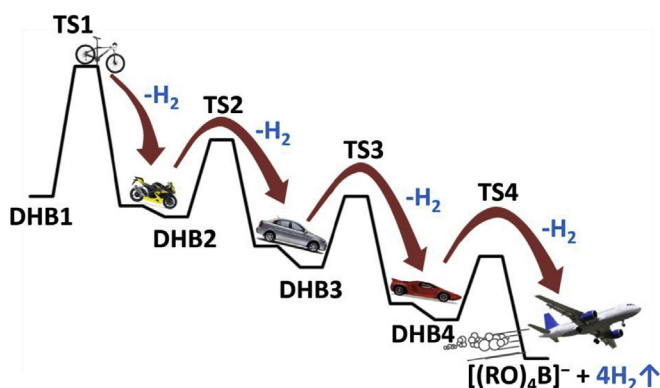
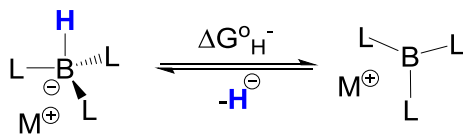


Fig. 1. The general view of BH_4^- alcoholysis.



Scheme 2. Hydride transfer from tetracoordinated boron hydrides.

of their reactivity [16].

However, as it was shown recently by Haiden and Lathem [16], the experimental examination of the hydride donating ability (HDA) of main group hydrides is problematic due to their instability in polar media. Moreover, these compounds have low E–H bond polarizability in comparison with transition metal hydrides and thus the hydride cannot be torn away even in the presence of excess strong Lewis acid. Therefore, the computational methods become extremely helpful in prediction their properties.

Since HDA is a Gibbs free energy ($\Delta G_{\text{H}}^\circ$) of hydride transfer reaction in a chosen media, the lowest HDA value corresponds to the easiest ability of borohydride for hydride transfer to the substrate. Moreover, HDA values are strongly solvent-dependent, in this way switching solvents offers a strategy for changing the Gibbs free energy of hydride transfer ($\Delta G_{\text{H}}^\circ$ or HDA) [14]. Hence, in this work, we performed the evaluation of HDA for various substituted tetracoordinated borohydrides in the media of different polarity to pinpoint the ways of B–H bond activation and enhancing the borohydrides reducing power. The HDA values for some boranes were previously calculated by Haiden and Lathem [16], but that study was mainly focused on the well-known boron species used for H_2 activation or as reducing agents. Some of those compounds are very reactive species, so their reactivity could not be quantified experimentally. Moreover, the analysis of general trends as well as the analysis of substituents impact was not performed. With this objective in mind, we present in this paper the analysis of the hydride donating ability in MeCN (HDA^{MeCN}) and dichloromethane (HDA^{DCM}) for 90 tetracoordinated borohydrides. Acetonitrile (MeCN; $\epsilon = 35.7$) was chosen as a solvent for optimization because

the large amount of data on reduction potentials, pK_a values and experimental hydride donating ability (HDA) of transition metal hydride complexes were determined in MeCN [14,15]. Dichloromethane (CH_2Cl_2 , DCM; $\epsilon = 8.9$) was used previously as solvent a solvent for spectroscopic studies of borohydrides [17–22] and mechanisms of catalytic dehydrocoupling of amine-boranes [23,24]. It was also used for hydroboration catalysed by boron Lewis acids [25]. Thus, these two solvents were chosen to estimate the effect of the solvent polarity and in order to compare the hydride donating ability (HDA) values obtained in this work with the published data. Within the main text, we discuss mostly the data obtained in acetonitrile, whereas the comprehensive set of data can be found in the Supporting Information.

2. Computational details

All calculations were performed without symmetry constraints using the M06 hybrid functional [26] implemented in Gaussian09 (Revision D.01) [27] software package, using 6-311++G (d,p) [28] basis set. The calculations were carried out with ultrafine integration grid and very tight SCF option in order to improve the accuracy of the optimization procedure. Vibrational frequencies were calculated for all optimized complexes at the same level of theory to confirm a character of local minima on the potential energy surface.

The inclusion of nonspecific solvent effects in the calculations was performed by using the SMD method [29]. The geometries of all species were optimized in a vacuum and then re-optimized in 1,4-dioxane ($\epsilon = 2.2$), tetrahydrofuran (THF) ($\epsilon = 7.4$), dichloromethane (CH_2Cl_2) ($\epsilon = 8.9$), acetonitrile (MeCN) ($\epsilon = 35.7$), water (H_2O) ($\epsilon = 78.4$) by SMD method.

Electrostatic potentials were calculated by Gaussian09 (Revision D.01) [27]. The exact values of MEP extremes at the 0.001 au electron density isosurface were calculated by Multiwfn 3.4 software [30,31] using the Gaussian formatted checkpoint file. The graphical visualization of MEP maps calculated for the 0.001 au electron density and generated as cube file was implemented using Chemcraft 1.8 [32] (as the R-G-B projection on 1.2 times vdW radii surface).

3. Results and discussion

3.1. Lewis acidity of tricoordinated boranes

Lewis acidity of tricoordinated boranes can be considered as a reverse measure of tetracoordinated borohydrides reactivity. There are several approaches to estimate this property. The acceptor numbers (AN) [33] were determined experimentally according to Guttman-Beckett method, which is based on the change of the ^{31}P NMR chemical shift of Et_3PO upon its complexation with Lewis acid [34]. The ion affinities (hydride affinity (HA) [35] and fluoride affinity (FA) [36]) were determined by *ab initio* calculations or experimentally as the enthalpies of the complexation of Lewis acid with the chosen ion (H^- and F^- , respectively). In order to validate our results and get comprehensive understanding of the

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