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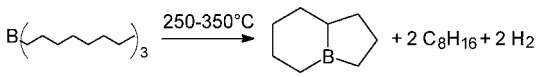
C–H Activation by Direct Borane – Hydrocarbon Dehydrogenation: Kinetic and Thermodynamic Aspects**

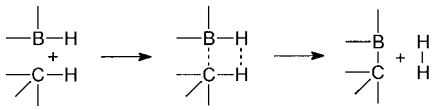
Bernd Goldfuss,* Paul Knochel,* Lars O. Bromm, Kolja Knapp

Dedicated to Prof. Manfred Regitz on the occasion of his 65th birthday

Selective C–H activations and functionalizations of hydrocarbons are challenging chemical processes with enormous synthetic potential.[1] Transition metal catalyzed[2, 3] and metal-free[4] C–H activations are being studied intensively.[5] Allylic C–H activations with organoborane reagents have been established as useful methods in organic synthesis.[6] Köster and Rotermund discovered in 1960 that the pyrolysis of triorganoboranes (e.g. tri-*n*-octylborane) yielded bicycloorganoborane, alkene, and molecular hydrogen (Scheme 1).[7] After further studies Köster et al. proposed a four-center mechanism for the observed cleavage of C–H and the formation of C–B bonds (Scheme 2).[8]



Scheme 1. Pyrolysis of tri-*n*-octylborane.



Scheme 2. The four-center mechanism of borane – hydrocarbon dehydrogenation reactions proposed by Köster.

Recently, similar intramolecular C–H activations of *tert*-butyl and phenyl groups in organoboranes in solution were reported[6e] without transition metal catalysts.[3] To analyze the factors influencing the reactivity and selectivity of these *direct*, uncatalyzed borane – hydrocarbon dehydrogenations, we have studied the kinetic and thermodynamic aspects by theoretical methods.

[*] Dr. B. Goldfuss,
Organisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
www.uni-heidelberg.de/institute/fak12/OC/goldfuss
Fax: (+49) 6221-54-4205
E-mail: Bernd.Goldfuss@urz.uni-heidelberg.de
Prof. Dr. P. Knochel, Dipl.-Chem. L. O. Bromm,
Dipl.-Chem. K. Knapp
Ludwig-Maximilians-Universität
Butenandtstrasse 5 – 13, 81377 München (Germany)
Fax: (+49) 89-2180-7680
E-mail: knoch@cup.uni-muenchen.de

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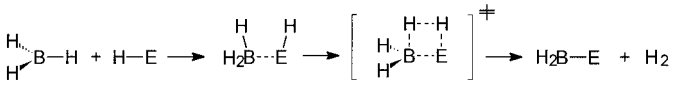
While reactions of borane **1** with ammonia (**2b**) and water (**2c**) are well known, there are no reports on the analogous direct borane–methane (**2a**) dehydrogenation reaction (Scheme 3).[9] With borane both ammonia and water



E= CH_3	**1** (D_{3h})	**2a** (T_d)	**3a** (C_s)	**4a** (C_s)	**5a** (C_s)	**6** ($D_{\infty h}$)
E= NH_2		**2b** (C_{3v})	**3b** (C_{3v})	**4b** (C_s)	**5b** (C_{2v})	
E= OH		**2c** (C_{2v})	**3c** (C_s)	**4c** (C_1)	**5c** (C_s)	

Scheme 3. Reactions of borane with methane, ammonia, and water (Tables 1 and 2).

form stabile adduct complexes[10] (see the adduct formation energies E_{ad} of **3b** and **3c** calculated at the B3LYP/6-311++G**[11, 12] level, Tables 1 and 2).[13] The subsequent elimination of hydrogen (**6**) via the transition structures **4b** and **4c** (activation energy, E_a Table 2)[14] yield the exothermic and exergonic products **5b** and **5c** (total reaction energy E_r, Table 2, Scheme 3). Methane (**2a**) and borane form only a weakly bound van der Waals complex **3a** (see E_{ad} in Table 2). However, relatively small activation barriers relative to the educts E_a(Ed), are computed for the hydrogen elimination between methane and borane via the transition structure **4a** (Figure 1) ($\Delta E^{\neq} = 23.5$ kcal mol^{-1}, $\Delta H^{\neq} = 21.8$ kcal mol^{-1}, $\Delta G^{\neq} = 30.5$ kcal mol^{-1}, Table 2).[15] The attack of the electrophilic boron atom occurs at the C–H bond and induces the elimination of H_2 from the transition **4a** (Figure 1).[16] The analogy to the four-center mechanism proposed by Köster (Scheme 2) is apparent. While ammonia and water yield products (**5b** and **5c**) in strongly exothermic and exergonic reactions the formation of methylborane **5a** is slightly endothermic and endergonic (see E_r in Table 2).[17]

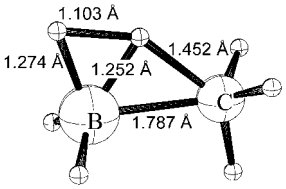


Figure 1. The transition structure **4a** of the methane–borane dehydrogenation optimized at the B3LYP/6-311++G** level.

Activation of C–H bonds through direct, intramolecular dehydrogenation reactions has been observed for *tert*-butyl groups and also for phenyl moieties in organoborane compounds.[6e] From benzene and borane a weakly bound van der Waals complex is formed (E_{ad} in Table 3).[18] The transition structure for the benzene–borane dehydrogenation (Figure 2)[19] is similar to that of the methane–borane dehydrogenation (Figure 1), however smaller activation barriers (E_a(Ed) values for X = H in Table 3) and an exothermic energy of reaction (E_r) are predicted.[20] The influence of electronic effects on the dehydrogenations of arenes is clearly demonstrated in monosubstituted benzene derivatives, in which the borane attacks the *para* position (Scheme 4, Table 3). The lowest activation energy barriers (E_a) and the most exothermic energies of reaction (E_r) are found for electron-donating substituents (e.g. X = NMe_2, OMe). In contrast, electron-withdrawing substituents in the *para* position cause increased activation barriers and less exothermic reactions. There is a good correlation between Hammett σ_p values of the *para* substituents X and electronic activation energies (Figure 3).[21] In transition structures with electron-donating substituents, the H–H bonds of the leaving dihydrogen units are shorter than in the transition structures with electron-withdrawing-substituents (e.g. NMe_2: 1.093 Å versus NO_2: 1.147 Å, Table 4).

Table 1. Electronic,[a] enthalpic,[b] and Gibbs' free energies[b] [a.u.] for the starting materials, first-formed adducts, transition structures, and products of the reactions between BH_3 and H-E (Scheme 3).

E	**1**	**2**	**3**	**4**[c]	**5**	**6**
CH_3 (**a**)	– 26.59500	– 40.48940	– 67.08341	– 67.04689 (1139)	– 65.91272	– 1.16951
	– 26.59117	– 40.48559	– 67.07597	– 67.04205	– 65.90789	– 1.16620
	– 26.61254	– 40.50672	– 67.11258	– 67.07064	– 65.93604	– 1.18100
NH_2 (**b**)		– 56.54846	– 83.18046	– 83.12560 (1442)	– 82.02631	
		– 56.54464	– 83.17569	– 83.12101	– 82.02214	
		– 56.56649	– 83.20290	– 83.14887	– 82.04806	
OH (**c**)		– 76.43726	– 103.04509	– 103.01126 (1421)	– 101.91276	
		– 76.43348	– 103.03992	– 103.00696	– 101.90877	
		– 76.45490	– 103.06898	– 103.03432	– 101.93494	

[a] B3LYP/6-311++G** optimized structures, unscaled zero-point energy corrections are included. [b] $T = 298.15$ K, $p = 1$ atm. [c] Transition structures with imaginary frequency in parenthesis [cm^{-1}].

Table 2. Relative electronic,[a] enthalpic,[b] and Gibbs' free energies[b] [kcal mol^{-1}] of adduct formations of **3** (E_{ad}), energy barriers of dehydrogenations relative to **3** E_a(vdW), and relative to the starting materials **1** and **2** E_a(Ed), and the total reaction energies relative to the starting materials E_r (Table 1, Scheme 3).

E	E_{ad}	E_a(vdW)	E_a(Ed)	E_r
CH_3 (**a**)	0.6 (– 0.1),[c] 0.5, 4.2	22.9, 21.3, 26.3	23.5, 21.8, 30.5	1.4, 1.7, 1.4
CH_3 (**a**)[d]	– 0.1 (– 1.2),[c] – 0.4, 4.3	22.2, 20.8, 24.8	22.1, 20.4, 29.1	0.0, 0.3, 0.1
NH_2 (**b**)	– 23.2, – 25.0, – 15.0	34.4, 34.3, 33.9	11.2, 9.3, 18.9	– 32.9, – 33.0, – 31.4
OH (**c**)	– 8.0, – 9.6, – 1.0	21.2, 20.7, 21.8	13.2, 11.1, 20.8	– 31.4, – 31.6, – 30.4

[a] B3LYP/6-311++G** optimized structures, unscaled zero-point energies are included. [b] $T = 298.15$ K, $p = 1$ atm. [c] No zero-point energy correction. [d] MP2(fc)/6-311++G** optimized structures, unscaled zero-point energies are included.

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Table 3. Hammett parameter σ_p of the substituents X and the relative electronic,[a] enthalpic,[b] and Gibbs' free energies,[b] [kcal mol^{-1}] of adduct formation (E_{ad}), activation barriers (E_a), and total reaction energies (E_r) for the reaction shown in Scheme 4.

X	σ_p(X)[c]	E_{ad}[d]	E_a(vdW)[e]	E_a(Ed)[f]	E_r[g]
NMe_2	−0.63	−1.8 (−3.8), −2.5, 6.7	17.4, 17.0, 18.0	15.6, 14.5, 24.7	−9.8, −9.5, −6.6
OMe	−0.28	−0.8 (−2.7), −0.9, 7.1	17.5, 16.5, 19.2	16.7, 15.5, 26.3	−7.8, −7.2, −5.1
*t*Bu	−0.15	−0.3 (−2.1), −0.4, 7.3	17.4, 16.3, 19.4	17.1, 15.9, 26.7	−6.3, −5.7, −3.7
Me	−0.14	−0.4 (−2.1), 0.1, 5.4	17.6, 16.4, 20.3	17.1, 16.5, 25.7	−6.4, −5.8, −3.8
H[h]	0.0	−0.2 (−1.7), −0.2, 5.6	17.8, 16.6, 20.0	17.6, 16.4, 25.6	−5.6, −4.9, −4.0
F	+0.15	−0.1 (−1.8), −0.2, 6.7	17.9, 16.7, 20.2	17.8, 16.5, 26.9	−6.3, −5.6, −3.6
Cl	+0.24	−0.1 (−1.5), 0.0, 6.7	17.9, 16.7, 20.3	17.8, 16.6, 27.0	−5.9, −5.2, −3.2
Br	+0.26	0.0 (−1.5), 0.0, 6.8	17.8, 16.7, 20.2	17.9, 16.7, 27.0	−5.8, −5.1, −3.1
COMe	+0.47	0.1 (−1.2), 0.3, 6.4	18.0, 16.7, 21.2	18.1, 17.0, 27.7	−4.6, −3.9, −2.0
CF_3	+0.53	0.3 (−1.0), 1.0, 5.4	18.2, 16.9, 21.3	18.5, 17.9, 26.7	−4.5, −3.8, −1.8
CN	+0.70	0.4 (−0.9), 0.5, 6.6	18.2, 16.9, 21.2	18.6, 17.4, 27.8	−4.4, −3.8, −1.8
NO_2	+0.81	0.5 (−0.7), 0.7, 6.5	18.4, 17.1, 21.5	18.9, 17.8, 28.1	−3.9, −3.2, −1.4

[a] B3LYP/6-311++G** optimized structures, unscaled zero-point energies are included. [b] $T = 298.15$ K, $p = 1$ atm. [c] Hammett values.[21] [d] Electronic energies of adduct formation, in parentheses are the values without zero-point energy correction. [e] Activation barrier relative to van der Waals complexes. [f] Activation barrier relative to isolated starting materials molecules. [g] Energy of reaction relative to isolated starting materials molecules. [h] See Figure 2.

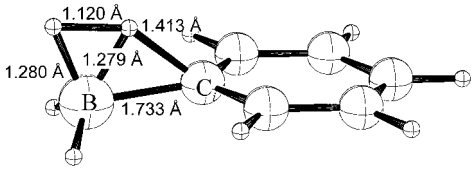
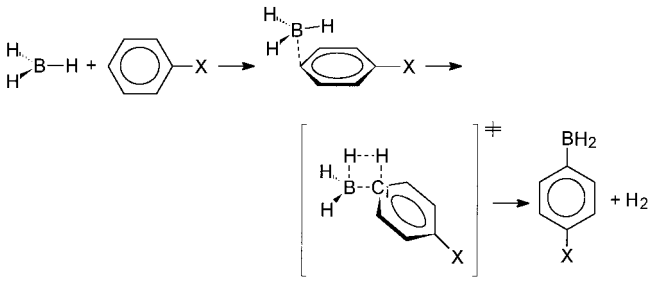


Figure 2. The transition structure of the benzene–borane dehydrogenation optimized at the B3LYP/6-311++G** level.



Scheme 4. Dehydrogenation between BH_3 and monosubstituted benzene derivatives.

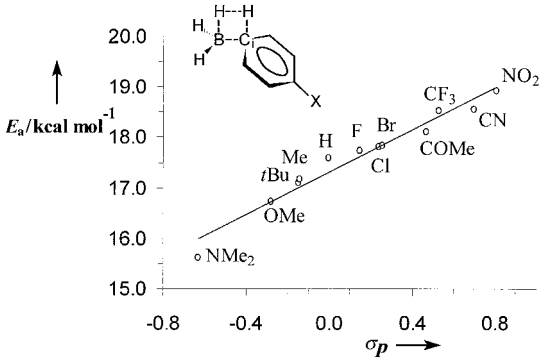


Figure 3. Correlation of the electronic activation energies (E_a) and the Hammett σ_p values for dehydrogenations between borane and monosubstituted benzene derivatives (correlation coefficient: 0.96, $y = 2.1x + 17.3$; Table 3, Scheme 4).

Analysis of the B–C_{ipso} bond lengths and of the C_{ipso} partial charges explains the decrease of the activation barriers with increasingly stronger electron-donating substituents X (Table 4): more negative partial charges at C_{ipso} (e.g. −0.34 for NMe_2 versus −0.26 for NO_2) result in more stable bonds to the electrophilic boron center,[22] which lead to shorter B–C_{ipso} bonds (1.710 Å for NMe_2 versus 1.747 for NO_2, Table 4).

Table 4. Selected bond lengths (B–C_i, C_i–H, H–H [Å]) and natural bond orbital (NBO) partial charges q [a.u.] of the transition structures in borane–arene dehydrogenations (Scheme 4).[a]

X	B–C_i	C_i–H	H–H[c]	$q(C_i)$[d]	$q(H_{C_i})$[d]
NMe_2	1.710	1.431	1.093	−0.341	+0.341
OMe	1.721	1.421	1.106	−0.324	+0.344
*t*Bu	1.727	1.417	1.114	−0.297	+0.345
Me	1.728	1.417	1.114	−0.299	+0.345
H[b]	1.733	1.413	1.120	−0.290	+0.346
F	1.733	1.409	1.121	−0.310	+0.347
Cl	1.735	1.406	1.126	−0.294	+0.348
Br	1.735	1.405	1.127	−0.287	+0.348
COMe	1.739	1.403	1.134	−0.268	+0.347
CF_3	1.743	1.399	1.138	−0.274	+0.348
CN	1.744	1.396	1.142	−0.267	+0.349
NO_2	1.747	1.392	1.147	−0.260	+0.350

[a] B3LYP/6-311++G** optimized structures. [b] See Figure 2. [c] Bond lengths in the leaving H_2 molecule. [d] B3LYP/6-31G**//B3LYP/6-31G**.

In conclusion, relatively small activation barriers (≤ 30 kcal mol^{-1}) are predicted for dehydrogenation reactions between borane and hydrocarbons that occur via four-center transition states. Even lower activation barriers and more exothermic reactions should result for donor-substituted arenes. These different reactivities, which can be tuned by the substituents, could provide the basis for selective and directed functionalizations of hydrocarbons.

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Multilevel Molecular Electronic Species: Electrochemical Reduction of a [2 × 2] Co^{II}_4 Grid-Type Complex by 11 Electrons in 10 Reversible Steps**

Mario Ruben, Esther Breuning, Jean-Paul Gisselbrecht,* and Jean-Marie Lehn*

The search for high-density information storage devices has stimulated an increasing interest in molecules exhibiting multistable behavior.[1] Multistability can be achieved by several means by exploiting changes in intrinsic molecular properties such as spin state,[2] conformation,[3] or redox state.[4] For instance, fullerenes and nanotubes have attracted wide interest in view of their potential in the design of new materials and electronic devices based on their unusual electrochemical behavior (reversible single-electron reductions and semiconducting properties).[5] Multicenter transition metal complexes with different redox states are very attractive candidates for the design of multilevel electronic systems. Thus, for instance, polynuclear metal complexes of polypyridine ligands present several reversible multielectron steps.[6]

We have described recently a new class of polypyridine-derived, multinuclear metal complexes of the [2 × 2] M^{II}_4 grid-type (M = transition metal),[7, 8] which have been found to present a range of interesting structural[7] and physicochem-

[*] Prof. Dr. J.-M. Lehn, Dr. M. Ruben, E. Breuning
Laboratoire de Chimie Supramoléculaire
ISIS-Université Louis Pasteur
4, rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33) 388-411020
E-mail: lehn@chimie.u-strasbg.fr
Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide
UMR 7512,CNRS-Université Louis Pasteur
4, rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33) 388-611553
E-mail: gissel@chimie.u-strasbg.fr

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