JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

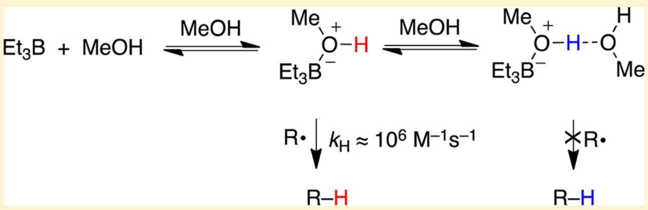
Role of Equilibrium Associations on the Hydrogen Atom Transfer from the Triethylborane–Methanol Complex

Guillaume Povie, Mattia Marzorati, Peter Bigler, and Philippe Renaud*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

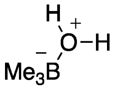
Supporting Information

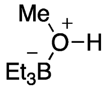
ABSTRACT: The triethylborane–methanol system used in radical deoxygenation and dehalogenation processes has been investigated. Unambiguous evidence for the formation of a complex between triethylborane and methanol is provided. It was shown that the complexation process is exothermic ($\Delta H° \approx -7.6$ kcal mol^{-1}) while being entropically disfavored ($\Delta S° \approx -24$ cal mol^{-1} K^{-1}). This study demonstrates that only very small quantities of complex (1–2%) are present in most of the reported conditions used in dehalogenation and deoxygenation processes. Recalculating the rate constant for the hydrogen transfer to a secondary alkyl radical with this concentration suggests a value in the 10^6 M^{-1} s^{-1} range for the complex itself, indicating a much more important activation of the O–H bond than previously thought. The importance of solvent effects is also highlighted. The formation of a larger amount of complex by the addition of methanol is accompanied by its deactivation via hydrogen bonding. These observations open new opportunitites for the future preparation of more effective hydrogen atom donors involving borane complexes.

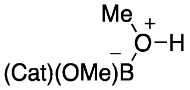


INTRODUCTION

In 2005, Wood and co-workers reported the reduction of alkyl radicals in the presence of trimethylborane (Me_3B) and water.[1] Surprisingly, deuteration experiments showed the unprecedented role of water as a source of hydrogen atoms.[1−3] Since its bond dissociation energy is far too high to allow hydrogen abstraction (BDE around 118 kcal mol^{-1}), the formation of a Lewis acid–base complex **A** between trimethylborane and water was proposed to activate the O–H bond. Several applications of the system on reductive addition,[4] deoxygenation,[1,5] deiodination,[6] and cyclization[7] radical reactions were reported, and similar behavior was observed using different primary trialkylboranes and water (deuterium oxide) or methanol as hydrogen (deuterium) sources. The mechanism is supported by the inhibition of the process when stronger Lewis bases, such as pyridine, are added to the reaction.[2] Computational studies confirmed the original proposal showing a very large effect of the complexation with trimethylborane on the activation barrier and on the exothermicity of the hydrogen atom abstraction from water.[1,8] For an equimolar mixture of triethylborane and water, Newcomb and Jin measured a rate constant of 2×10^4 M^{-1} s^{-1} (293 K) for the reduction of a secondary radical, 5 times faster than in anhydrous conditions.[2] Disclosing the Arrhenius parameters for the hydrogen atom transfer from the triethylborane–methanol complex **B**, they underlined the possibility of a partial complexation: "The pre-exponential factor in the Arrhenius function is quite small, indicating either a highly organized transition state [...] or an entropically unfavorable prior equilibration before [...] the hydrogen atom transfer step".[9] At the same time, our group reported the radical reduction of *B*-alkylcatecholborane in the presence of methanol and, also supported by deuteration experiments, postulated complex **C** between methanol and methoxycatecholborane to explain the reduction of the O–H BDE.[10]


A

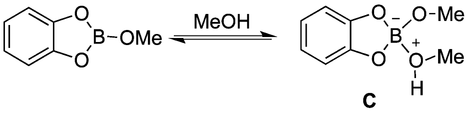

B


C [Cat = benzene-1,2-bis(oxyl)]

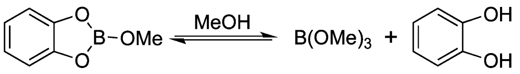
The ability of the boron atom to form stable trivalent compounds represents a rare exception to the octet rule among the elements of the first period. This electron deficiency results in a strong Lewis acidic character, and considerable interest has been devoted to rationalize and quantify this property.[11−15] From the early work of Brown[16,17] on trialkylborane–amine complexes to the recent concept of frustrated Lewis pairs,[18] careful analysis of the association process has always been a key point to understand new reactivities. Although complexation of triorganylboranes with a variety of bases is reported, little is known about the equilibrium association with alcohols.[19−22] ^{11}B NMR is a reliable tool to study the environment of the boron atom since formation of a tetra-coordinated boronate induces a large upfield shift relative to the parent tricoordinated compound.[23,24] In addition, the rate of exchange between free and complexed species is fast enough on the NMR time scale to result in only one weighted average signal.[25] For example, the ^{11}B NMR signal of triphenylborane shifts

Received: December 4, 2012
Published: January 19, 2013

from 68 ppm in pure benzene to 39 ppm in the presence of 3 equiv of methanol.[22] A similar behavior was therefore expected for the different complexes **A**, **B**, and **C** mentioned above. We recently disclosed a study of the catecholborane−methanol system, but no complex **C** according to eq 1 was detected.[26]



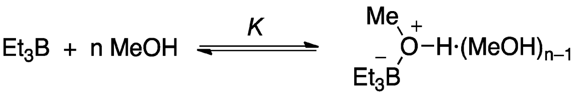
(1)



(2)

Instead, a transesterification process affording trimethylborate and catechol was observed (eq 2), and catechol was unambiguously identified as the effective source of the hydrogen atom.

For comparison, we have studied the triethylborane−methanol system (eq 3). We could show that the efficiency of methanol activation toward hydrogen atom transfer has been underestimated, opening new perspectives for the future preparation of more effective hydrogen atom donors involving borane complexes.



$$Et_3B + n\,MeOH \xrightleftharpoons{K} \underset{\overset{-}{Et_3B}}{\overset{Me\;+}{O}}{-}H{\cdot}(MeOH)_{n-1} \qquad (3)$$

RESULTS AND DISCUSSION

We have limited our investigation to the system involving triethylborane and methanol (eq 3) that was more convenient to investigate than the trimethylborane−water system originally reported by Wood.[1] Since methanol and water give very similar results,[2] we believe that our conclusions will also be valid for both systems.

^{11}B and ^{1}H NMR Spectra. In the absence of covalent interactions, boron chemical shifts are barely sensitive to solvent effects. Et_3B displays similar chemical shifts δ_{Et_3B} (relative to BF_3−Et_2O) in C_6D_6 (86.9 ppm), $CDCl_3$ (86 ppm),[27] Et_2O (87.3 ppm),[28] and more surprisingly in THF (80.7 ppm),[29] which indicates only little coordination with the latter. Recording the ^{11}B NMR spectra of Et_3B in C_6D_6 with increasing amounts of methanol shows a significant upfield shift of the boron peak, up to 27 ppm in pure methanol (Figure 1).[30] The ^{1}H NMR spectrum changes considerably due to a marked upfield shift of the CH_2 protons with increasing amounts of methanol (Figure 2). This upfield shift illustrates the strong shielding effect of the neighboring boron atom. These early spectrometric results suggested the formation of a new species assigned to the boronate complex **B**. We decided to focus next on the determination of constant K (eq 4) characterizing equilibrium 3.

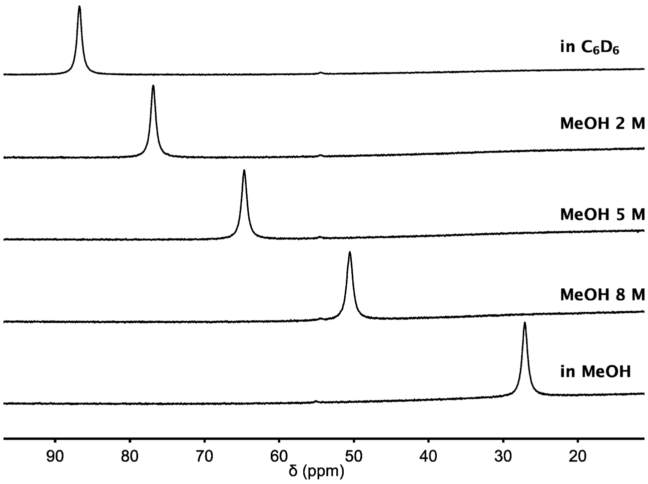


Figure 1. ^{11}B NMR spectra of Et_3B in C_6D_6 in the presence of methanol (reference $BF_3{\cdot}OEt$ = 0 ppm): (A) 0 M, (B) 2 M, (C) 5 M, (D) 8 M, (E) Et_3B in methanol.

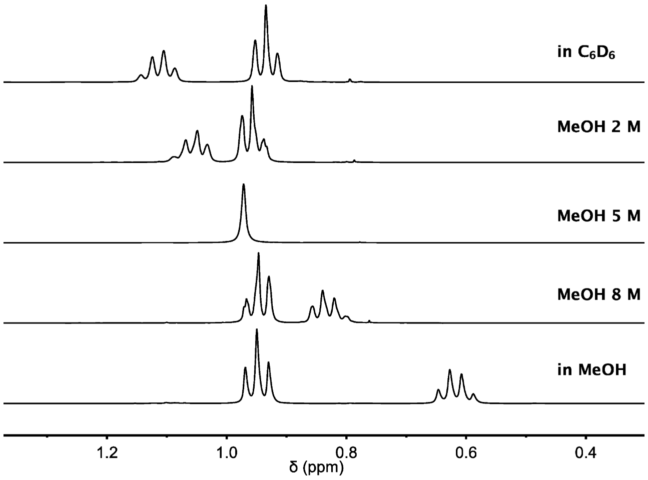


Figure 2. ^{1}H NMR spectra of Et_3B in C_6D_6 in the presence of methanol (reference Me_4Si = 0 ppm): (A) 0 M, (B) 2 M, (C) 5 M, (D) 8 M, (E) Et_3B in methanol.

^{11}B Chemical Shift of the Triethylborane−Methanol Complex B. For equilibrium 3, the observed chemical shift (δ_{obs}) can be rationalized following eq 5, where X_{Et_3B}, X_B, δ_{Et_3B}, and δ_B are the respective molar fractions and chemical shifts of each species. Equation 6 is then given using $\Delta\delta = \delta_{Et_3B} - \delta_{obs}$ and $\Delta\delta_{max} = \delta_{Et_3B} - \delta_B$. Introduced into 4, eq 7 is obtained, which allows the determination of the stoichiometry in methanol (n) and the equilibrium constant (K). Analytical treatment of the data proved to be difficult since different parameters had to be evaluated. First, we concentrated on the stoichiometry of the reaction. Although a covalent representation of complex **B** involves only one molecule of methanol, the second coordination sphere has to be taken into account. For instance, triphenylborane has been described to associate with three molecules of methanol at room temperature.[22] Consequently, the different oligomeric forms of the alcohol in solution are also important, and the self-association of methanol should not be neglected. Assuming even a 1:1 stoichiometry, the determination of the equilibrium constant is still not straightforward. Many methods have been reported to determine K using eq 7 or its equivalencies, and most of them are based on the simultaneous determination of K and $\Delta\delta_{max}$ by extrapolation from a graphic plot.[31] The problem arises from the determination of small equilibrium constants ($<10\ M^{-1}$), where the error on $\Delta\delta_{max}$ becomes too large. Indeed, applying classical methods such as the Benesi−Hildebrand treatment[31] leads to weak equilibrium constants ($K \approx 10^{-1}\ M^{-1}$) thus incoherent chemical shift values for the complex **B**.

$$K = \frac{[\mathrm{B}]}{[\mathrm{Et_3B}][\mathrm{MeOH}]^n} \tag{4}$$

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{Et_3B}} X_{\mathrm{Et_3B}} + \delta_{\mathrm{B}} X_{\mathrm{B}} \tag{5}$$

$$\frac{X_{\mathrm{B}}}{X_{\mathrm{Et_3B}}} = \frac{[\mathrm{B}]}{[\mathrm{Et_3B}]} = \frac{\Delta\delta}{\Delta\delta_{\mathrm{max}} - \Delta\delta} \tag{6}$$

$$\frac{\Delta\delta}{\Delta\delta_{\mathrm{max}} - \Delta\delta} = K[\mathrm{MeOH}]^n \tag{7}$$

Alternatively and more promising, the chemical shift of complex **B** can be measured directly either by its quantitative formation or by slowing down the exchange process in a low-temperature experiment to such a degree that separated signals for both species can be observed.[32] With $\Delta\delta_{\mathrm{max}}$ measured in such a way, a plot of $\Delta\delta/(\Delta\delta_{\mathrm{max}} - \Delta\delta)$ versus the concentration of methanol according to eq 7 allows the determination of K. Therefore, the ^{11}B NMR spectra of a 0.3 M solution of $\mathrm{Et_3B}$ in pure methanol were recorded at different temperatures from 350 to 199 K. At any temperature, only one coalescent signal was observed, the shift (and line width) of which was strongly dependent (Figure 3, Supporting Information). This behavior suggests fast exchange between trivalent and tetravalent species even at low temperature with only one coalescent signal throughout. Most interesting is the flattening of the curve at low temperatures, tending to a minimum value around 11 ppm. The possibility of an entropically disfavored equilibrium was already mentioned by Newcomb and should result from the highest level of organization of complex **B**. At low temperatures, the formation of the tetravalent species is favored, shifting upfield the observed resonance frequency. Eventually, complex **B** is almost the sole compound present at 199 K, and the observed chemical shift can be attributed to δ_{B} (ca. 11 ppm).[33] This is further corroborated by the increasing line widths of the boron signal with decreasing temperature. Relaxation of the ^{11}B is governed by quadrupolar relaxation, the degree of which is highly dependent on the intensity of electric field gradients acting at the nucleus position. Lower coordination symmetry as expected for complex **B** compared to $\mathrm{Et_3B}$ results in stronger electric field gradients, thus more efficient quadrupolar relaxation causing line broadening. Therefore, increasing line widths with decreasing temperatures may indicate an increasing amount of the less symmetric complex **B**.

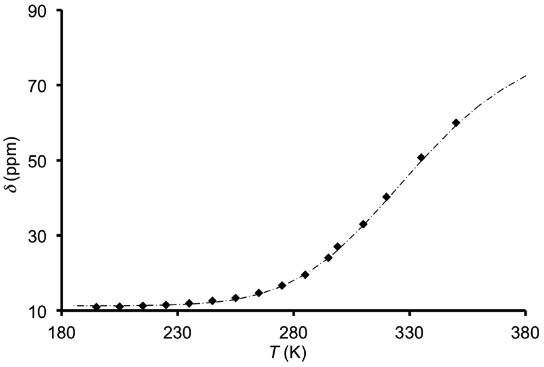


Figure 3. Temperature dependence of the ^{11}B chemical shift of $\mathrm{Et_3B}$ (0.3 M) in methanol solution (reference $\mathrm{BF_3 \cdot OEt}$ = 0 ppm).

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{B}} + \frac{\Delta\delta_{\mathrm{max}}}{1 + e^{-\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}} \tag{8}$$

Figure 3 shows the plot of δ_{obs} versus T (K) fitted by a sigmoid curve. Equation 8 represents the Van't Hoff equation where K has been calculated according to eq 4 and the entropic term (ΔS°), the stoichiometry (n), and the concentration of methanol have been merged in T_0 (see Supporting Information for the detail of the calculation). Curve fitting treatment of the experimental data according to eq 8 where $\delta_{\mathrm{Et_3B}}$ is set at its experimental value (86.9 ppm) and using ΔH°, T_0, and δ_{B} as variable parameters shows an excellent correlation. An almost identical result was obtained when the calculations were performed using $\delta_{\mathrm{Et_3B}}$ as a variable. In this case, the value computed for $\delta_{\mathrm{Et_3B}}$ (85.6 ppm) is found very close to the experimental one. The model yields values for ΔH° (−8.1 kcal mol^{-1}), T_0 (333 K), and a shift value δ_{B} (11.2 ppm), which falls in the expected range for a trialkylboronate complex (0 ± 20 ppm).[34,35] This chemical shift did not require such a sophisticated model to be determined, but the mathematical analysis of its temperature dependence validates the corresponding (related) process to obey the Van't Hoff law. The value for T_0 has no direct physical meaning, and the enthalpy of the reaction will be discussed in more detail later.

Determination of the Equilibrium Constant and of Thermodynamic Parameters (Van't Hoff Equation). A plot of $\log(\Delta\delta/(\Delta\delta_{\mathrm{max}} - \Delta\delta))$ versus $\log[\mathrm{MeOH}]$ according to eq 9 gives theoretically a straight line, the slope indicating the stoichiometry n. The results obtained from the series of experiments at room temperature varying the concentration of methanol from 0.08 to 8 M are shown in Figure 4. Since the quantity of complex **B** is always very small relative to methanol, the concentration of methanol at the equilibrium is approximated to the initial value: $[\mathrm{MeOH}] = [\mathrm{MeOH}]_0$. If the self-association of methanol is neglected, the plot shows roughly the formation of a 1:1 complex (n = 1.39) which physically represents the ability of triethylborane to complex rather unselectively monomeric and oligomeric forms of methanol. The same stoichiometry ($1 < n < 1.4$) was found when the experiment was repeated at four different temperatures up to 350 K. However, the apparent deviation from linearity and the exact values for n highlight the limitation of this simple model.

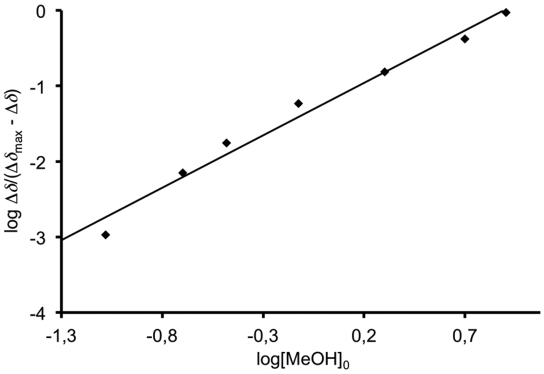


Figure 4. (a) $\mathrm{Log}(\Delta\delta/(\Delta\delta_{\mathrm{max}} - \Delta\delta))$ versus $\log[\mathrm{MeOH}]_0$ neglecting the self-association of methanol.

$$\log \frac{\Delta\delta}{\Delta\delta_{\max} - \Delta\delta} = \log \frac{[\mathrm{B}]}{[\mathrm{Et_3B}]} = n\log[\mathrm{MeOH}] + \log K \tag{9}$$

Assuming a 1:1 association model, the equilibrium constant at a given temperature (K_T) could be determined by plotting $\Delta\delta/(\Delta\delta_{\max} - \Delta\delta)$ versus the concentration of methanol according to eq 7. The graphical determinations of $K_{T(K)}$ are shown in Figure 5. Very good correlation is observed up to a 5 M concentration of methanol; above this value, slight deviations from linearity are observed (see Supporting Information).

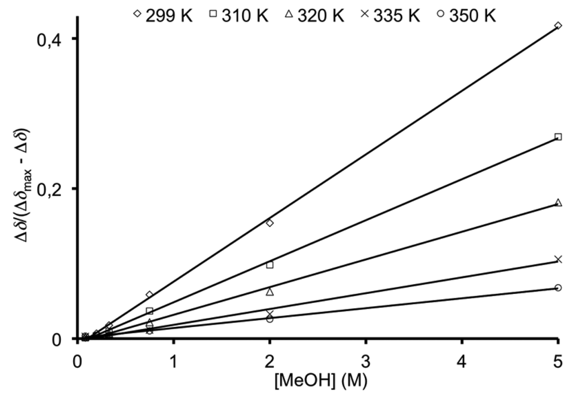


Figure 5. $\Delta\delta/(\Delta\delta_{\max} - \Delta\delta)$ versus [MeOH] and temperature dependence of the equilibrium constant K_T.

The temperature-dependent values of K_T shown in Table 1 allow an evaluation of the thermodynamic parameters of the reaction according to eqs 11 and 12. Since the mole number changes during the reaction, the pre-exponential factors for the formation and for the dissociation of the complex (A_1 and A_{-1}) have to be taken into account to ensure homogeneity of the units.[36] The slope of the plot of $\log(K_T)$ versus $1000/2.3RT$ according to eq 12 yields $\Delta H° \approx -7.6$ kcal mol^{-1} (Figure 6), consistent with the value determined above in pure methanol by curve fitting analysis (-8.1 kcal mol^{-1}). Using calculated values for A_1 (2.2×10^{11} M^{-1} s^{-1}) and A_{-1} (6.3×10^{12} s^{-1}) according to the collision theory and the absolute rate theory, respectively, $\Delta S° \approx -24$ cal mol^{-1} K^{-1} can be evaluated from the intercept. As mentioned before, this model neglects solvation effects that are likely to be important in this system (vide infra). As a consequence, these thermodynamic parameters do not solely apply to the formation of the complex itself, but also to the self-association of methanol and to the possible coordination of the complex with the methanol in solution. Nonetheless, the negative signs for the enthalpy and for the entropy of the reaction are believed to be reliable and to be a quantitative measure, suggesting the presence of complex **B** in solution.

$$K_T = \frac{k_1}{k_{-1}} = \frac{A_1 e^{-\Delta G_1^{\ddagger}/RT}}{A_{-1} e^{-\Delta G_{-1}^{\ddagger}/RT}} \tag{11}$$

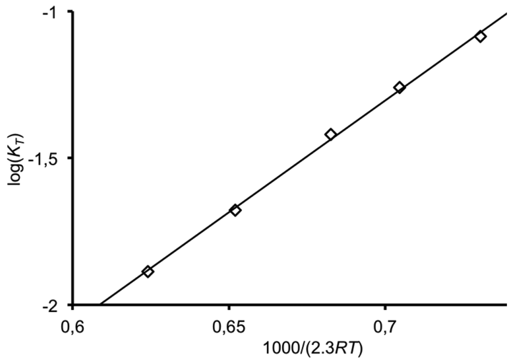


Figure 6. $\log(K_T)$ versus $1000/2.3RT$ between 299 and 350 K (Van't Hoff plot for the formation of complex **B**).

$$\log(K_T) = -\frac{\Delta H°}{2.3RT} + \frac{\Delta S°}{2.3R} + \log\left(\frac{A_1}{A_{-1}}\right) \tag{12}$$

Self-Association of Methanol. Many quantitative models for the self-association of alcohol in apolar media have been proposed, depending on which species are assumed.[37−42] The concentration of monomeric methanol $[\mathrm{MeOH}]_{\mathrm{free}}$ as a function of total alcohol was calculated using the equilibrium constants for the formation of dimers, trimers, and tetramers in CCl_4 (294 K) as reported by Saunders.[43] Using the recalculated concentration of free methanol, a plot according to eq 6 correlates with a 1:3 association model ($n = 3.02$, Figure 7).

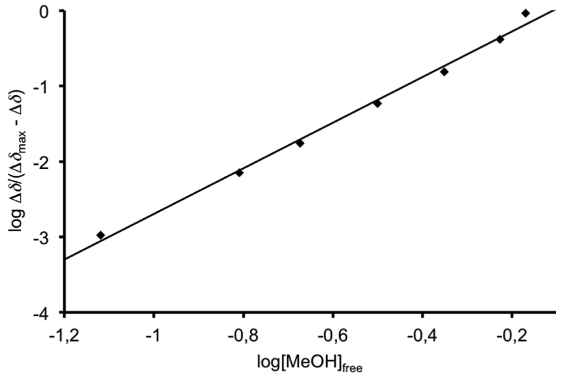


Figure 7. $\log(\Delta\delta/(\Delta\delta_{\max} - \Delta\delta))$ versus $\log[\mathrm{MeOH}]_{\mathrm{free}}$ calculated using Saunders's self-association model.

Following Saunders' model, tetrameric methanol is the predominant species in solution at 294 K. With Et_3B dissolved in methanol and after substitution of one component in tetrameric methanol, the complex $Et_3B(MeOH)_3$ will most probably be formed. The resulting species could be represented by a molecule of Et_3B substituting one molecule of methanol to form $Et_3B(MeOH)_3$. The same behavior has also been reported for the triphenylborane/methanol association.[22]

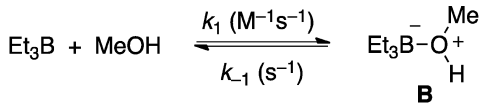
This short discussion on the stoichiometry of the complexation mainly shows that the OH group of complex **B** retains its ability to form hydrogen bonds with the methanol in solution

Table 1. Equilibrium Constant at Different Temperatures[a]

T (K)	299	310	320	335	350
K_T (M^{-1})	$8.2(3) \times 10^{-2}$	$5.5(2) \times 10^{-2}$	$3.8(2) \times 10^{-2}$	$2.1(2) \times 10^{-2}$	$1.3(1) \times 10^{-2}$

[a] Standard deviations (in parentheses) are in units of the last significant figure.

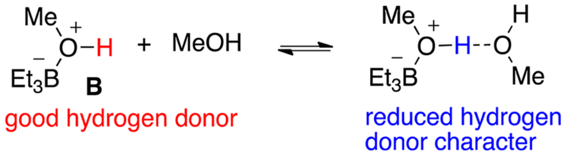
(equilibrium 10). This raises the question of the actual species relevant in the hydrogen atom transfer process. As comparable



$$Et_3B + MeOH \underset{k_{-1}\ (s^{-1})}{\overset{k_1\ (M^{-1}s^{-1})}{\rightleftharpoons}} Et_3\overset{-}{B}{-}\overset{+}{O}(Me)H \tag{10}$$

hydroxylic hydrogen donors, phenols exhibit a much lower rate of hydrogen atom transfer in hydrogen bond accepting (HBA) solvents compared to apolar media.[44−47] This kinetic solvent effect is attributed to the formation of hydrogen bonds between the phenolic hydroxyl groups and the lone pairs of the solvent, which dramatically increase the O−H bond dissociation energy. In accordance with this behavior, Zipse computed a higher activation barrier for the hydrogen atom transfer from the trimethylborane−water complex if hydrogen bonded to a second molecule of water.[8] Similarly, hydrogen bonding with THF was shown recently to decrease the reactivity of the titanocene−water complex toward hydrogen abstraction.[48] Thus, complex **B** is expected to have a different behavior depending upon its hydrogen bonding environment (Scheme 1). In diluted solutions (<0.3 M in methanol), complex **B** is expected to be uninvolved in hydrogen bonds.[49] Under the conditions used for the kinetic experiments by Jin and Newcomb (maximum of 0.3 M in Et_3B−MeOH at 292 K), only 1−2% of Et_3B is complexed according to our model. Recalculating the rate constant for the hydrogen transfer to a secondary alkyl radical with this concentration suggests a value in the 10^6 M^{-1} s^{-1} range for the complex itself, indicating a much stronger activation of the O−H bond than previously thought. On the basis of this observation, the reduction in pure methanol (with around 65% of Et_3B complexed at 299 K) is expected to be very fast at first glance. However, under these conditions, complex **B** is mainly involved in hydrogen bonds and its hydrogen donor properties are strongly decreased. This explains why efficient carbon−carbon bond formation under iodine atom transfer conditions can be run in aqueous/alcoholic media in the presence of triethylborane.[50−54]

Scheme 1. Effect of Methanol Concentration on Hydrogen Abstraction from Complex B



■ CONCLUSIONS

Unambiguous evidence for the formation of complex **B** between triethylborane and methanol is provided. Although solvation effects complicate an exact interpretation of the thermodynamic parameters, it was shown that the complexation process is exothermic ($\Delta H° \approx -7.6$ kcal mol^{-1}) while being entropically disfavored ($\Delta S° \approx -24$ cal mol^{-1} K^{-1}) as previously anticipated. The study shows that only very small quantities of complex **B** are present in most of the reported conditions used in dehalogenation and deoxygenation processes. According to these results, the activation of the O−H bond appears to be particularly important, resulting in the formation of a potent hydrogen donor. This species is also believed to be sensitive to solvent effects. The formation of a larger amount of complex by the addition of methanol is accompanied by its deactivation via hydrogen bonding. These two competing processes might be general for all kinds of activation of the O−H bond of water and alcohols by Lewis acids. These findings suggest that borane−alcohol complexes could act as effective hydrogen atom donors at low temperature (−80 °C), as already proposed by Newcomb.[2,9] At high temperature (≥50 °C), these systems are expected to be much less efficient. Interestingly, since the rate constant reported here for the Et_3B−MeOH complex is close to the one of Bu_3SnH (the most used and flexible hydrogen atom donor in radical processes), the design of new and highly reactive reagents involving intramolecular borane−alcohol complex is expected to be possible.

■ EXPERIMENTAL SECTION

The NMR experiments were performed at a resonance frequency of 400.13 MHz for ^1H nuclei and 128.38 MHz for ^{11}B nuclei. The ^1H NMR spectra were recorded using the "zg30" pulse sequence. Typically, 16 transients, a spectral width of 4401.4 Hz, 32 K data points, an acquisition time of 3.72 s, and a relaxation delay of 6 s were used to acquire the ^1H NMR spectra. The ^{11}B NMR spectra were recorded using a 1D sequence with power-gated ^1H decoupling. Typically, 16 transients, a spectral width of 30 864.2 Hz, 64 K data points, an acquisition time of 1.06 s, and a relaxation delay of 0.1 s were used to acquire the ^{11}B NMR spectra. The free induction decays (FIDs) were exponentially weighted with a line-broadening factor of 5.0 Hz, Fourier transformed, phase and baseline corrected to obtain the ^{11}B NMR spectra. ^{11}B NMR spectra were calibrated using $Et_2O{\cdot}BF_3$ (0.0 ppm) as an external reference.

C_6D_6 was degassed by four freeze−pump−thaw (N_2) cycles and then stored on 4 Å molecular sieves in a glovebox under argon. Commercial anhydrous methanol was used without further purification. For the determination of δ_B, a series of ^{11}B spectra of a 0.3 M solution of Et_3B in methanol (0.48 mL of Et_3B, 3 mmol in 9.52 mL of MeOH) were recorded at different temperatures (195−350 K). For the determination of the equilibrium constant, a series of ^{11}B spectra of Et_3B in C_6D_6 in the presence of different amounts of methanol (0.083−8 M) were recorded. The series of experiments varying the concentration of methanol were carried out at five different temperatures (299−350 K). The samples were prepared in a glovebox by mixing fresh stock solutions (A and B or C) completed to 0.6 mL with C_6D_6. They were then immediately frozen at −78 °C under nitrogen and glass-sealed under vacuum. Solution A: 0.58 mL of Et_3B, 4 mmol in 3.42 mL of C_6D_6, 1 M. Solution B: 0.97 mL of MeOH in 1.03 mL of C_6D_6, 12 M. Solution C: 0.04 mL of MeOH in 1.96 mL of C_6D_6. The curve fitting analysis was performed using the freeware plot version 0.997.[55]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the calculations and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: philippe.renaud@ioc.unibe.ch.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Swiss National Science Foundation (Grant 20020_135087) and the University of Bern for financial support. We are grateful to BASF Corporation for generous gift of Et_3B. We thank Professor Martin Newcomb for useful comments and discussions.

■ REFERENCES

(1) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513.
(2) Jin, J.; Newcomb, M. *J. Org. Chem.* **2007**, *72*, 5098.
(3) Allais, F.; Boivin, J.; Nguyen, V. T. *Beilstein J. Org. Chem.* **2007**, *3*, 46.
(4) Boivin, J.; Nguyen, V. T. *Beilstein J. Org. Chem.* **2007**, *3*, 47.
(5) Boivin, J.; Nguyen, V. T. *Beilstein J. Org. Chem.* **2007**, *3*, 45.
(6) Medeiros, M. R.; Schacherer, L. N.; Spiegel, D. A.; Wood, J. L. *Org. Lett.* **2007**, *9*, 4427.
(7) Davy, J. A.; Mason, J. W.; Moreau, B.; Wulff, J. E. *J. Org. Chem.* **2012**, *77*, 6332.
(8) Tantawya, W.; Zipse, H. *Eur. J. Org. Chem.* **2007**, 5817.
(9) Jin, J.; Newcomb, M. *J. Org. Chem.* **2008**, *73*, 4740.
(10) Pozzi, D.; Scanlan, E. M.; Renaud, P. *J. Am. Chem. Soc.* **2005**, *127*, 14204.
(11) Lappert, M. F. *Chem. Rev.* **1956**, *56*, 959.
(12) Coyle, T. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 4138.
(13) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polym. Commun.* **1996**, *37*, 4629.
(14) Vianello, R.; Maksic, Z. B. *Inorg. Chem.* **2005**, *44*, 1095.
(15) Plumley, J. A.; Evanseck, J. D. *J. Phys. Chem. A* **2009**, *113*, 5985.
(16) Brown, H. C. *J. Am. Chem. Soc.* **1945**, *67*, 374.
(17) Brown, H. C. *J. Am. Chem. Soc.* **1945**, *67*, 378.
(18) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
(19) Chen, K.; Gunderson, K. G.; Hardtmann, G. E.; Prasad, K.; Repic, O.; Shapiro, M. J. *Chem. Lett.* **1987**, 1923.
(20) Drewitt, M. J.; Niedermann, M.; Kumar, R.; Baird, M. C. *Inorg. Chim. Acta* **2002**, *335*, 43.
(21) Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581.
(22) Domaille, P. J.; Druliner, J. D.; Gosser, L. W.; Read, J. M.; Schmelzer, E. R.; Stevens, W. R. *J. Org. Chem.* **1985**, *50*, 189.
(23) Phillips, W. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 4496.
(24) Hermanek, S. *Chem. Rev.* **1992**, *92*, 325.
(25) Pizer, R. D.; Tihal, C. *Polyhedron* **1996**, *15*, 3411.
(26) Povie, G.; Villa, G.; Ford, L.; Pozzi, D.; Schiesser, C. H.; Renaud, P. *Chem. Commun.* **2010**, *46*, 803.
(27) Ramachandran, P. V.; Biswas, D. *Org. Lett.* **2007**, *9*, 3025.
(28) Bremer, M.; Nöth, H.; Warchhold, M. *Eur. J. Inorg. Chem.* **2003**, 111.
(29) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *Inorg. Chem.* **1965**, *4*, 1649.
(30) Under the same conditions, the signal of Et_2BOMe (54.4 ppm in C_6D_6) remains almost unaffected (53.2 ppm in MeOH), indicating no significant interactions between MeOH and the considerably less Lewis acidic borinic ester derivative.
(31) Fielding, L. *Tetrahedron* **2000**, *56*, 6151.
(32) This method is only applicable if K is not too small. Otherwise, the concentration of **B** is too low, thus its lifetime in the exchange process is, in contrast to the lifetime of Et_3B, very short, resulting in severe broadening of the already weak signal. This makes its detection difficult or even impossible.
(33) If no change in the covalent structure of the boron atom occurred (e.g., formation of tetra-coordinated complex), the chemical shift of a given boron derivative is constant over a large range of temperature. For instance, the chemical shift of Et_3B in C_6D_6 was found at 86.6 ± 0.3 ppm from 298 to 350 K. The chemical shift of Et_2BOMe, detected as traces (< 1%) in most of the samples, is found at 51.0 ppm at 239 K instead of 53.2 ppm at 299 K. For similar examples with tetrahedral boron-ate complexes at different temperatures, see: Thompson, R. J.; Davis, J. C. *Inorg. Chem.* **1965**, *4*, 1464.
(34) Landesman, H.; Williams, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 2663.
(35) Cole, T. E.; http://www.chemistry.sdsu.edu/research/BNMR/#summary, San Diego State University, 2010.
(36) Keleti, T. *Biochem. J.* **1983**, *209*, 277.
(37) Shekaari, H.; Modarress, H.; Hadipour, N. *J. Phys. Chem. A* **2003**, *107*, 1891.
(38) Fletcher, A. N.; Heller, C. A. *J. Phys. Chem.* **1967**, *71*, 3742.
(39) Frange, B.; Abboud, J. L. M.; Benamou, C.; Bellon, L. *J. Org. Chem.* **1982**, *47*, 4553.
(40) Tucker, E. E.; Farnham, S. B.; Christian, S. D. *J. Phys. Chem.* **1969**, *73*, 3820.
(41) Anderson, B. D.; Rytting, J. H.; Lindenbaum, S.; Higuchi, T. *J. Phys. Chem.* **1975**, *79*, 2340.
(42) Duboc, C. *Spectrochim. Acta* **1974**, 441.
(43) Saunders, M.; Hyne, J. *J. Chem. Phys.* **1958**, *29*, 1319.
(44) Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469.
(45) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2004**, *69*, 5888.
(46) Nielsen, M. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2006**, *128*, 1172.
(47) Litwinienko, G.; Ingold, K. U. *Acc. Chem. Res.* **2007**, *40*, 222.
(48) Gansäuer, A.; Behlendorf, M.; Cangönül, A.; Kube, C.; Cuerva, J. M.; Friedrich, J.; van Gastel, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3266.
(49) From Saunders model, a 0.33 M MeOH solution in CCl_4 implies 0.21 M of monomeric alcohol at ambient temperature.
(50) Yorimitsu, H.; Nakamura, T.; Shinokubo, H.; Oshima, K.; Omoto, K.; Fujimoto, H. *J. Am. Chem. Soc.* **2000**, *122*, 11041.
(51) Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K.; Omoto, K.; Fujimoto, H. *J. Org. Chem.* **2001**, *66*, 7776.
(52) Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Synlett* **2002**, *5*, 674.
(53) Panchaud, P.; Renaud, P. *J. Org. Chem.* **2004**, *69*, 3205.
(54) During this study, we also observed that triethylborane is stable for several days in MeOH solution when a good reducing ability of the complex would lead to the rapid formation of ethane and methyl diethylborinic ester (Et_2BOMe) upon initiation with air.
(55) Wesemann, M.; Thijsse, B. J. *Plot*, version 0.997; http://plot.micw.eu.