Hydrogen Transfer

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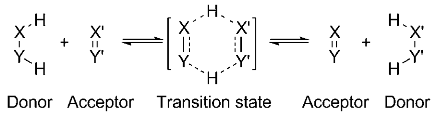
Transfer Hydrogenation of Imines with Ammonia–Borane: A Concerted Double-Hydrogen-Transfer Reaction**

*Xianghua Yang, Lili Zhao, Thomas Fox, Zhi-Xiang Wang, and Heinz Berke**

Ammonia–borane (H_3N-BH_3, AB) is considered a feasible material for chemical hydrogen storage owing to its ideally very high storage capacity (19.6 weight% H) and thus has attracted much attention.[1] Dehydrogenations of AB were accomplished either thermally or by transition metal catalysis.[2] Considering AB as a significantly polarized molecule, we reasoned that it could be dehydrogenated by direct reaction with a similarly polarized unsaturated compound by the rarely explored reaction mode of double H transfer (Scheme 1).



Scheme 1. Double H transfer as an elementary process. X, Y, X′, and Y′ are main group element or transition metal fragments.

In certain cases, double H transfers are the crucial step of multistep transition-metal-catalyzed transfer hydrogenations,[3,4] with separate processes for hydrogenation and dehydrogenation. In contrast to these catalyses, the true double H transfer reaction is an all-in-one transfer hydrogenation, with concerted hydrogenation and dehydrogenation reactions merged into one elementary step.

Such elementary double H transfer processes are rare to date. DFT calculations suggest that the prototypical homopolar reaction course of H_2 exchange between ethane and ethylene could principally proceed along the lines of Scheme 1.[3,5] Despite its principal character of a (4+2) symmetry-allowed concerted process, it was calculated to possess a very high barrier, thus making it difficult to realize this reaction. However, polar reagents are expected to have much lower barriers. For example, the aluminum-complex-catalyzed Meerwein–Ponndorf–Verley reduction[6] of carbonyl substrates to alcohols is thought to proceed along such a reaction path, and it can be carried out at room temperature.[7] The mechanistically related reductions of olefins and acetylenes with diimine proceed even below room temperature.[8] The ruthenium- or iridium-catalyzed multistep transfer hydrogenation reactions provide a powerful basis for the preparation of primary or secondary amines.[9] Furthermore, Noyori- and Shvo-type transfer hydrogenations are widely applied in organic chemistry.[10] All these catalytic reactions are thought to proceed in their essential H_2 transfer step as bifunctional activation processes with double H transfers. In recent studies, it was demonstrated that rhenium catalysts can promote multistep transfer hydrogenations of olefins using AB and dimethylamine borane as a polar hydrogen donor.[11] Herein, we investigate the direct reaction between imines and AB, and reach the conclusion that concerted polar double H transfers are involved.

N-benzylidene aniline (**1a**), as the simplest aromatic Schiff-base derivative, was selected as the reference compound for the reaction with AB. To avoid decomposition of the Lewis pair AB, only temperatures below 60 °C and concentrations lower than 0.2 M were applied.[12] For the reaction of **1a** with AB, very practical rates were obtained at 60 °C (Table 1, entries 1, 5, and 6). The transfer hydrogenation was found to proceed even at room temperature, but then much more slowly (Table 1, entry 4). As the thermal dehydrogenation of AB was nearly indetectable at room temperature, we can exclude the possible reaction pathway via thermal dehydrogenation of AB followed by imine hydrogenation. With the progression of the transfer hydrogenation, a trace amount of H_2 was always obtained. This side reaction can be considered as evidence for the generation of BH_2NH_2, which is presumed to be able to catalyze the dehydrogenation of AB.[13,14] However, it was only a minor competition reaction here, because 1 equiv of AB can hydrogenate 2 equiv of **1a** nearly quantitatively if given enough time (Table 1, entry 6). A scrambling experiment with AB and its doubly deuterated isotopologue A(D)B(D) was also carried out to see whether AB would decompose at such conditions. No reaction was noticed over several hours at 60 °C and several days at room temperature; therefore, transfer hydrogenation via Lewis acid (BH_3) or base mediation (NH_3) can be discounted.

After this initial test on the double H transfer to benzylidene aniline, an extended selection of imines was probed with a 1:1 ratio of imine to AB by applying various conditions given in Table 1 (entries 7–21). The reaction times for various *para*-substituted *N*-benzylidene anilines were found to vary between 0.5 h and several days. Alkyl imines turned out to be much slower (Table 1, entries 7–10), and in

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[*] X. Yang, Dr. T. Fox, Prof. Dr. H. Berke
Institute of Inorganic Chemistry, University of Zürich
Winterthurstrasse 190, 8057 Zürich (Switzerland)
Fax: (+41) 1-635-6802
E-mail: hberke@aci.uzh.ch

L. Zhao, Prof. Dr. Z.-X. Wang
College of Chemistry and Chemical Engineering
Graduate University of Chinese Academy of Sciences (China)

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Table 1: Reactions of AB with various imines in THF.[a]

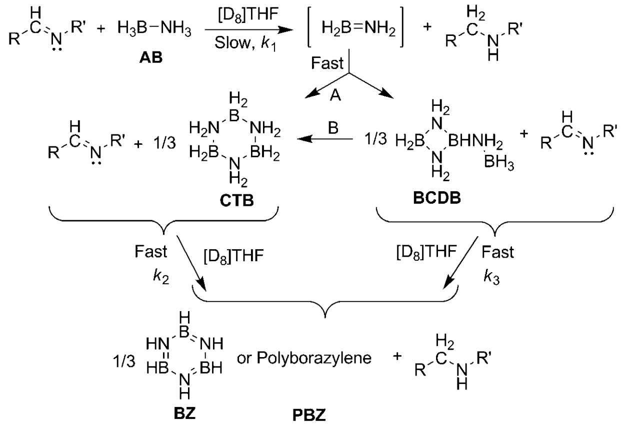
Entry	R/R' of imine or amine	T [°C]	t	Yield [%][b]
1	**1a/b**: Ph/Ph	60	7 h	99 (>99)[c]
2		50	14 h	(>99)
3		40	2 d	(>99)
4		RT	5 d	(84[d])
5[e]		60	3 h	(>99)
6[f]		60	24 h	(93[g])
7	**2a/b**: Ph/Bn[h]	60	3 d	99 (>99)
8	**3a/b**: Ph/*t*Bu	60	4 d	45 (46)
9	**4a/b**: Cy/*t*Bu	60	3 d	97 (99)
10	**5a/b**: Ph/$CHPh_2$	60	1 d	99 (>99)
11	**6a/b**: Ph_2/H	60	14 h	98 (>99)
12	**7a/b**: *p*-$MeOC_6H_4$/Ph	60	8 h	99 (>99)
13	**8a/b**: *p*-ClC_6H_4/Ph	60	5 h	99 (>99)
14	**9a/b**: *p*-$O_2NC_6H_4$/Ph	60	3 h	99 (>99)
15	**10a/b**: Ph/*p*-C_6H_4OMe	60	1 d	99 (>99)
16	**11a/b**: Ph/*p*-C_6H_4Cl	60	4 h	99 (>99)
17	**12a/b**: Ph/*p*-$C_6H_4NO_2$	60	0.5 h	99 (>99)
18	**13a/b**: *p*-ClC_6H_4/*p*-C_6H_4OMe	60	20 h	98 (>99)
19	**14a/b**: *p*-ClC_6H_4/*p*-ClC_6H_4	60	4 h	99 (>99)
20	**15a/b**: *p*-$MeOC_6H_4$/*p*-C_6H_4Cl	60	5 h	99 (>99)
21	**16a/b**: *p*-C_6H_4OMe/*p*-C_6H_4OMe	60	20 h	99 (>99)

[a] 0.1 mmol AB react with 0.1 mmol imine, unless stated otherwise. [b] GC-MS yield (NMR yields in brackets) based on the initial amount of imine. [c] Yield of isolated product 92%. [d] 100% could be obtained with a longer reaction time. [e] Amount of AB: 0.2 mmol. [f] Amount of **1a**: 0.2 mmol. [g] Better results can be obtained with longer reaction times. [h] Bn = benzyl.

particular *N*-(*tert*-butyl)benzylimine (Table 1, entry 8). It will be shown below that this behavior is due to the electron-donating rather than the stereochemical properties of the *tert*-butyl group.

Although the imines are all uniquely transformed to amines, many dehydrogenation products of AB were observed. According to the ^{11}B NMR spectra (see the Supporting Information), AB was converted into *B*-(cyclodiborazanyl)aminoborohydride (BCDB), borazine (BZ), poly(borazylene) (PBZ), and cyclotriborazane (CTB). After long reaction times (2 days at 60 °C with 0.1 mmol AB and 0.5 mmol **1a**), both BCDB and CTB had disappeared completely, thus indicating they are intermediates on the way from AB to BZ and PBZ.

Other possible products, such as $[NH_3BH_2NH_3]BH_4$ and cyclodiborazane, were not observed even at room temperature. The reaction course of AB and **1a** was further studied tracing the boron-containing products. First, BZ and CTB were employed to react with **1a**. Although BZ turned out to be stable towards **1a**, CTB was found to hydrogenate **1a** much faster than AB, and the dehydrogenation product was almost exclusively BZ. Although clearly identified in the ^{11}B NMR spectrum, we were not able to separate these boron-containing products. In accordance with earlier conclusions on other AB dehydrogenations, the appearance of CTB and BCDB witnesses the primary intermediacy of the very reactive $[H_2B{=}NH_2]$ molecule, which decayed in fast subsequent reaction steps. It remains an open question as to whether CTB was formed by direct cyclization of $[H_2B{=}NH_2]$ (path **A**, Scheme 2) or via isomerization of BCDB (path **B**, Scheme 2).[12,14]

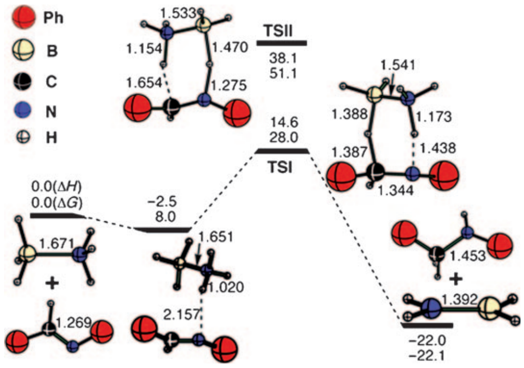


Scheme 2. Proposed overall reaction route.

As illustrated in Scheme 2, the overall reaction rate from AB to BZ and PBZ may be described by k_1, k_2, and k_3, which are potentially the double H transfer steps. Under pseudo-first-order conditions with an excess of **1a**, k_1 and k_2 were determined in reactions with AB and CTB, respectively. As BCDB could not be prepared in pure form, k_3 could not be determined. BCDB was anticipated to be a comparable hydrogen donor to CTB and therefore its reaction rate with **1a** was assumed to be close to k_2. In separate experiments under comparable conditions, k_2 was six times faster than k_1; therefore, k_1 of the AB dehydrogenation is rate-determining. In conjunction with the kinetically silent consumption of **1a** via the reactions with CTB and BCDB, the order of the reaction is one-half in **1a** and one in AB, as established by curve-fitting in appropriate kinetic experiments (Supporting Information, S4).

These facts would be in agreement with a mechanistic picture featuring the k_1, k_2, and k_3 steps as double H transfers, which poses the important question as to whether these polar transfers are proceeding in a concerted or stepwise pathway.[3,4] We tried to gain insights by DFT calculations using the Gaussian 03 program[15] (Supporting Information, S5).

The quantum mechanics calculations carried out at the M05-2X/6-311++G** level indicate the double-H-transfer pathway for the reaction of AB with **1a**.[16] A thermodynamically and kinetically feasible concerted reaction path resulted (Scheme 3). Two six-membered cyclic double-H-transfer transition states (**TS I** and **TS II**) were approached with different AB orientations with respect to the imine C=N bond. As expected, the reaction path via **TS I** with B−H···C and N−H···N transfers is energetically highly favored over the alternative **TS II** with N−H···C and B−H···N transfers (by ca. 23 kcal mol^{-1}). In **TS I**, the transferred H atoms on the boron and nitrogen of AB have opposite polarization with respect to the attacked carbon and nitrogen atoms, respectively. From a charge point of view, this naturally copes with the low energy pathway, whilst the opposite orientation in **TS II** would have the transferred hydrogen atoms attacked at evenly charged centers, thus disfavoring the pathway. Moreover, an initial N−H···N hydrogen bonding in the reaction path via **TS I** would help to pre-organize **TS I** in the right orientation but



Scheme 3. DFT calculations for the reaction of AB with benzylidene aniline **1a** leading to aminoborane and *N*-benzylaniline **1b**. The bond lengths [Å] were obtained at the M05-2X/6-311++G**level. The ΔH and ΔG values (kcal mol^{-1}) in THF at 298 K and 1 atm were corrected with the M05-2X/6-311++G** gas-phase harmonic frequencies.

not **TSII**. Stepwise reaction paths were also considered with the assumption that the relative energies of the first H transfer is the energetically decisive step.[17] All such possible reaction channels are predicted to be endergonic. The most energetically favored was 44.9 kcal mol^{-1} higher in free energy than the reactants (Supporting Information, S5), which is 16.9 kcal mol^{-1} higher than the transition state (**TSI**). This undoubtedly verifies the favorable concerted double-H-transfer mechanism. Note that the concerted reaction path for the hydrogen transfer between ethane and ethylene has been computed to be more favorable than the stepwise pathway.[3] The concerted pathway was reconfirmed by the MP2/6-311++G** calculations, which gave similar geometric and energetic results (Supporting Information, S5).

To further support the understanding of the regioselectivity of this reaction suggested by the calculations, deuterium labeling studies were carried out. Deuterated AB's (BD_3NH_3 (AB(D)), BH_3ND_3 (A(D)B)and BD_3ND_3 (A(D)B(D))) were employed to react with **1a**. The in situ ^{1}H and ^{13}C NMR spectra proved stereocontrolled reaction courses. A product deuterated at the carbon end of the C=N bond was obtained from an experiment with AB(D) and **1b** and showed a triplet ($J_{C,D}=20$ Hz) for the CHD group in the ^{13}C NMR spectrum at the same chemical shift as the CH_2 group of **1b**. A doublet at $\delta = 4.23$ ppm in the ^{2}H NMR spectrum further confirmed the presence of the CHD unit. In the related experiment with A(D)B and the imine, absence of the N–H signal in the ^{1}H NMR spectrum and appearance of a N–D signal in the ^{2}H NMR spectrum indicated the exclusive formation of an N−D bond. Both of these results are supportive of the **TSI** geometry of Scheme 3. In the case of A(D)B(D), both the CH and N positions of the amine were fully deuterated, as verified by ^{2}H NMR spectroscopy.

Further to these deuterium labeling studies, primary deuterium kinetic isotope effects (DKIE) were investigated. Considering the manifold dehydrogenation products of AB, all the reactions were carried out with in situ NMR measurements under approximate pseudo-first-order conditions for AB with the imines in excess (0.5 mmol of **1a** reacting with 0.1 mmol of AB). According to the kinetic conversion chart based on ^{11}B NMR (Figure 1), the rate constants k were simulated and the DKIE values obtained [Eq. (1)].

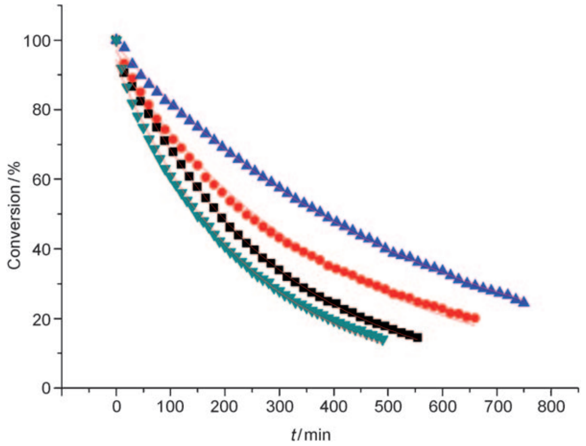


Figure 1. Conversion chart of the reaction of 0.5 mmol benzylidene aniline **1a** with 0.1 mmol AB, AB(D), A(D)B or A(D)B(D) followed by ^{11}B NMR in [D$_8$]THF at 60 °C, determined by intensities of AB on the ^{11}B NMR spectra with 15 min intervals. Black squares: reactions with AB, red circles: A(D)B(D), green triangles: AB(D), blue triangles: A(D)B. Simulated reaction constants: $k_{AB}=0.00350$, $k_{AB(D)}=0.00404$, $k_{A(D)B}=0.00181$, $k_{A(D)B(D)}=0.00251$.

$$k_{AB}/k_{AB(D)} = 0.87,\ k_{AB}/k_{A(D)B} = 1.93,\ k_{AB}/k_{A(D)B(D)} = 1.39 \qquad (1)$$

For the reaction of **1a** with AB(D), an inverse DKIE [Eq. (1), DKIE = 0.87] was obtained, which speaks for the formation of a stronger bond with a steeper potential energy curve in the presumably late transition state.[18] Together with the given size of the isotope effect, this effect could be rationalized on the basis of the transfer of the hydridic H_B atom having a flatter ground state potential curve. The H−C bond developed in the late transition state is expected to cause a steeper potential energy curve.

In the case of the reaction with A(D)B, a normal DKIE [Eq. (1), DKIE = 1.93] was observed, which indicates that breakage of the N−H bond participates in the rate-determining step and that both the broken and the installed bonds have approximately the same strengths.[18] For the double DKIE reaction of A(D)B(D) with the imine, a DKIE smaller than A(D)B was observed [Eq. (1), DKIE = 1.39]. This value would constitute an average with approximate cancellation of the kinetic effects of the two monodeuterated cases. The calculated DKIE for AB(D) and A(D)B are 0.82 and 1.84, respectively, which is in good agreement with the experimental values (0.87 and 1.93, respectively). However, the predicted DKIE value of A(D)B(D) (2.80) is somewhat higher than the experimental value (1.39), which may be due to the use of a harmonic model for the frequency calculations. The averaging of the experimental double DKIE values of double H transfers is presently not fully understood on a quantum mechanical basis of the single DKIE values.[19] According to the sizes of the single DKIE values, we may conclude that both H transfers participate in the rate-determining step. This participation makes a concerted mechanism quite plausible, because if it proceeds via a stepwise mechanism, the reaction rate should at least not be affected by one of the deuterium labeling reactions.

The Hammett correlation was then also checked for the reactions of AB with the *para*-H-, methoxy-, chloro-, or nitro-substituted *N*-benzylidene anilines **1a**–**12a**. The initial rate constants k were calculated from the conversion charts. Hammett correlations (Figure 2) from plotting $\log k$ versus substitutent constants σ[20] gave different slopes for substrates substituted on the *C*- or *N*-phenyl groups of the imine. The slope of the Hammett plot (ρ) represents the sensitivity constant, indicating the susceptibility of the reaction to substituents. From Figure 2, $\rho = 1.61$ was obtained for the reactions with imines substituted at the *para* position of the nitrogen end, and $\rho = 0.69$ for those substituents at the carbon end. A positive ρ value means that negative charge is built up during the transition state, and a value of ρ that is larger than unity means that the reaction is very sensitive to substituents.[18,20] Negative charge buildup during the reaction means increased electron density in the transition state, which seems realistic for a concerted mechanism and thus supportive for a simultaneous double H transfer. If the two H atoms were transferred sequentially, the charges generated on the B–H$^-$–C side and that of the N–H$^+$–N side should be of different signs, which would result in one positive ρ and the other negative.

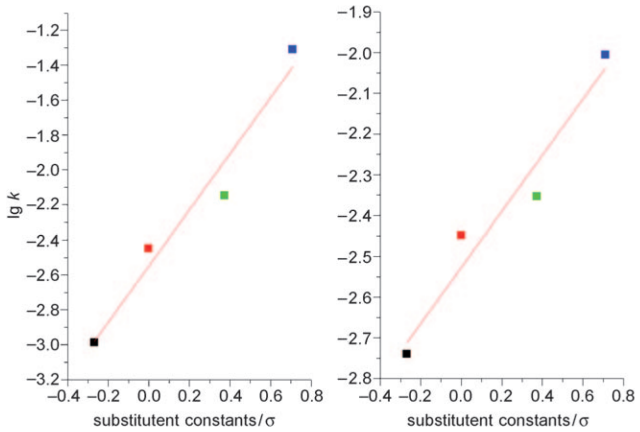


Figure 2. Hammett plots for the reactions of 0.1 mmol AB with 0.5 mmol *para*-substituted diaryl imines extracted from kinetic ^{11}B NMR spectra in [D$_8$]THF at 60 °C. Left, with a $\rho = 1.61$: reactions with the *para* substitutent at the aniline side; right, with $\rho = 0.69$: *para* substitution at the benzylidene side. Black: *p*-MeO, red: *p*-H, green: *p*-Cl, blue: *p*-NO$_2$ groups.

In conclusion, metal-free transfer hydrogenations of imines with ammonia–borane were observed to proceed under mild conditions. Based on DKIE determinations, Hammett correlations and ab initio calculations, the reaction courses are proposed to follow the profile of concerted double H transfers. The adaptability and generality of this type of reaction applying to other unsaturated compounds with the goal of the development of respective catalytic reactions is currently under investigation in our group.

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