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Article

Simultaneous Two-Hydrogen Transfer as a Mechanism for Efficient CO_2 Reduction

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Two-hydrogen transfer (simultaneous protic and hydridic hydrogen transfer) is examined as a potentially efficient mechanism for the selective reduction of CO_2 to methanol. High-level ab initio CCSD(T) coupled-cluster theory simulations of ammonia−borane (AB), which contains both protic and hydridic hydrogen, show the effectiveness of this mechanism. AB demonstrates how simultaneous two-hydrogen transfer is kinetically efficient because (1) two-hydrogen transfer avoids high-energy single-electron-reduced intermediates, (2) the CO_2's HOMO is protonated while the LUMO is concurrently reduced by a hydride, and (3) complementary charge polarities around the six-membered-ring transition-state structures stabilize the transition states. This study suggests that an effective mechanism for the reduction of CO_2 to methanol proceeds through three two-hydrogen-transfer steps and that suitable catalysts should be developed that exploit two-hydrogen transfer without the use of AB.

Introduction

Carbon monoxide (CO) dehydrogenase (for instance, in *Carboxydothermus hydrogenoformans* bacteria) is a well-known biological system that utilizes simultaneous acid−base coordination to reduce carbon dioxide (CO_2). In this enzyme, nickel serves as a Lewis base, while iron serves as a Lewis acid, which act in concert to stabilize and promote two-electron transfer to CO_2.[1,2] The key to this mechanism's effectiveness is the exploitation of CO_2's amphoteric nature; both acid and base functionalities are simultaneously reacted to avoid high-energy intermediates and thus allow for competitive kinetics. Following nature's lead, a key to efficient CO_2 reduction is to exploit the amphoteric reactivity of CO_2 through concurrent acid−base reactions. In this contribution, we show how species containing $H^{\delta+}$ (protic) and $H^{\delta-}$ (hydridic) hydrogens could prove to be effective for CO_2 reduction. Specifically, we utilize ammonia−borane (AB) to demonstrate an efficient, concerted acid−base mechanism for CO_2 reduction where AB acts as a simultaneous two-hydrogen-transfer reagent[3] to reduce CO_2 to formic acid (HCOOH). Although this process utilizes a sacrificial reagent, the two-hydrogen-transfer mechanism exemplifies how high product selectivity might be achieved by analogous mechanisms that avoid single-electron- or single-hydrogen-transfer reduction steps.[4] CCSD(T) quantum chemical simulations are employed to determine the feasibility of this mechanism. Finally, we highlight how the simultaneous two-hydrogen-transfer mechanism could be developed to selectively reduce CO_2 to methanol (CH_3OH). *We propose that careful exploitation of the mechanism exemplified here by AB will allow for the development of catalysts that efficiently reduce CO_2 to CH_3OH without the use of stoichiometric AB.*

Previous studies of AB[5−8] have revealed its unique electronic character[9] and its unusual chemical reactivity. Although isoelectronic to ethane, AB's B−N bond essentially consists of a nitrogen lone pair donating into an empty boron p orbital, resulting in a relatively weak dipolar (or dative) bond. The electronegativity difference between nitrogen and boron leads to acidic hydrogens bound to nitrogen and hydridic hydrogens bound to boron. Moreover, simultaneous transfer of both protic and hydridic hydrogens from AB has been shown to be possible.[5−8] Consequently, a molecule possessing both a highest occupied molecular orbital (HOMO) able to accept $H^{\delta+}$ and a lowest unoccupied molecular orbital (LUMO) capable of accepting $H^{\delta-}$ might be reduced by a similar process.

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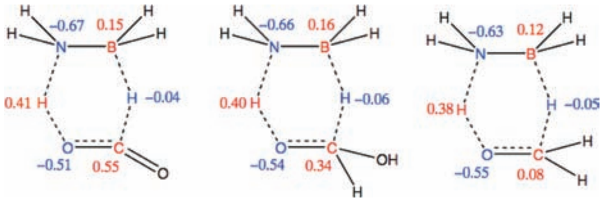
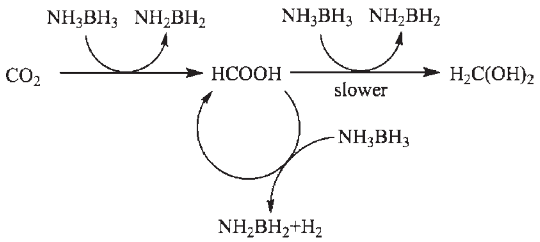


Figure 1. Chemical mechanism of two-hydrogen transfer: concerted addition across polarized C=O double bonds in (from left to right) CO_2, HCOOH, and formaldehyde. Complementary charge polarities (Mulliken atomic charges) around the six-membered ring make two-hydrogen transfer kinetically reasonable. Note that the second reaction, reduction of HCOOH, has a higher barrier than catalytic decomposition of AB by HCOOH.

Scheme 1. Proposed Mechanism of CO_2 Reduction by Simultaneous Two-Hydrogen Transfer and Subsequent AB Decomposition by HCOOH-Catalyzed Dehydrogenation[a]



[a] Substitution of AB for a reagent not sensitive to the decomposition reaction would favor the formation of more reduced products such as $CH_2(OH)_2$ or CH_3OH.

Recently, AB was shown to efficiently reduce imines by simultaneous two-hydrogen transfer.[1a] This process exhibited high yields under moderate reaction conditions, suggesting that two-hydrogen transfer may be an ideal mechanism for the selective reduction of particular amphoteric species. CO_2, with its basic oxygen atoms neighboring its acidic carbon, is another molecule that may be efficiently reduced by a similar mechanism.

Reduction of CO_2 by Two-Hydrogen Transfer

The first step in the reduction of CO_2 by concerted two-hydrogen transfer from AB to CO_2 yields HCOOH. The calculated Mulliken atomic charges at the transition state (TS) for this reaction are shown in Figure 1. In tetrahydrofuran (THF), this reaction involves a free-energy barrier lying 24.2 kcal/mol above the AB−CO_2 adduct, thus making the reaction feasible under mild conditions. A second two-hydrogen transfer from AB to CO_2 would yield methanediol [$CH_2(OH)_2$], and a third two-hydrogen transfer will lead to CH_3OH. With AB, however, the second step is not favorable because of the relatively facile acid-catalyzed decomposition of AB into NH_2BH_2 and H_2[10,11] (see Scheme 1 and Figure 2). However, two-hydrogen transfer is considerably more favorable than one-hydrogen transfer because it avoids high-energy radical intermediates. The calculated energetics of this reaction and competing reactions are listed in Table 1. In addition, we investigated many additional possible reactions between AB and CO_2, although because these other reactions all have significantly higher barriers, they are not kinetically competitive pathways. Furthermore, despite the fact that the reduction of CO_2 to HCOOH is slightly endothermic, oligomerization of the byproduct NH_2BH_2 is rapid and exothermic (e.g., dimerization of NH_2BH_2 > 15 kcal/mol downhill), preventing significant reverse reaction whenever NH_2BH_2 is formed.[6]

The reaction of AB and CO_2 by simultaneous two-hydrogen transfer demonstrates a mechanism for the reduction of CO_2 through six-centered moieties involving $O^{\delta-}$, $C^{\delta+}$, $H^{\delta-}$, $B^{\delta+}$, $N^{\delta-}$, and $H^{\delta+}$ that have complementary charges (see Figure 1). The reduction step effectively adds a proton to one oxygen of CO_2 (a Lewis base) with concurrent transfer of a hydride to the CO_2 carbon (a Lewis acid). The six-centered AB−CO_2 reduction TS exploits the intrinsic polarities of CO_2 and AB and would also allow for the reduction of HCOOH and formaldehyde.[3] Similar reactivity has been noted in transfer hydrogenation catalysis, which can undergo outer-sphere concerted two-hydrogen transfer;[12] however, similar concerted mechanisms have not yet been demonstrated for CO_2 reduction.

The proposed two-hydrogen-transfer mechanism for the reduction of CO_2 by AB could also be described as synchronous acid−base reactions, concerted $H^{\delta+}$ and $H^{\delta-}$ transfer, or simultaneous attachment of a proton to the HOMO of CO_2 and filling of CO_2's LUMO by the hydride.[5,7] While these descriptions highlight different aspects of the reactivity, they are fundamentally equivalent in that the mechanism relies on both the geometric and energetic positions of the HOMO and LUMO to facilitate simultaneous protic and hydridic hydrogen transfer. This is illustrated in Figure 3, which shows how the HOMO and LUMO are involved in this transformation and demonstrates this unusual chemistry. We note that at no point along the reaction coordinate is the HOMO separated from the hydrogen. Thus, this reactivity is distinct from geometrically separated proton−electron transfers that characterize electrochemical and enzymatic methods for CO_2 reduction.[1,2,13] Instead, AB's two hydrogens are transferred in concert to atoms of different electronegativities, thus altogether avoiding the high-energy intermediates of single-electron (or one-hydrogen)-reduced CO_2. In addition, because transferring two hydrogens simultaneously necessarily entails dual acid−base reactions, this mechanism allows for excellent product selectivity. Furthermore, because the CO_2 reduction products HCOOH and formaldehyde are also amphoteric molecules, the reduction of CO_2 by three two-hydrogen transfers [assuming dehydration of $CH_2(OH)_2$ to formaldehyde] would result in the selective production of CH_3OH.

Chemistry of NH_3 and BH_3 with HCOOH

Although we focus here on two-hydrogen transfer, the weak N−B dipolar bond of AB[9] leads to some dissociation, so the reactivities of NH_3 and BH_3 are also investigated to determine whether side reactions beyond those considered in Scheme 1 are competitive (see SI1 for a comprehensive comparison). In the gas phase, the calculated 0 K N−B bond

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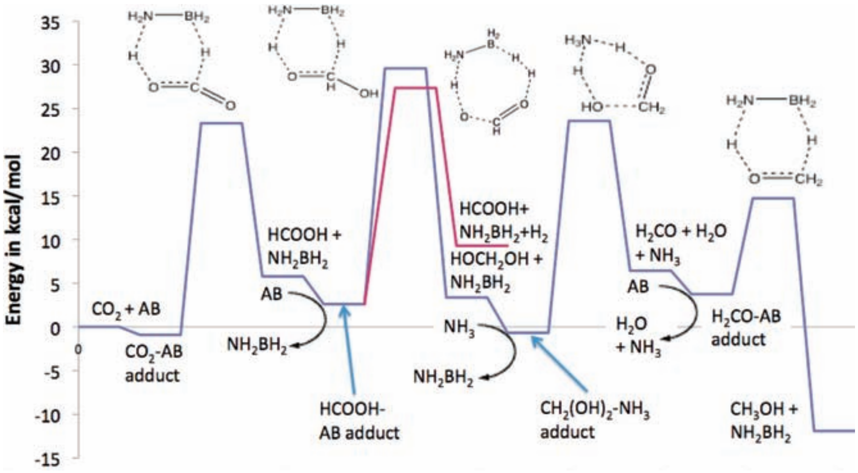


Figure 2. Potential energy surface ($\Delta G^{298\text{ K}}$) for the reduction of CO_2 to CH_3OH by AB, including catalytic decomposition of AB by HCOOH. The lower barrier for decomposition of AB by HCOOH means the reduction of CO_2 will not rapidly continue to $CH_2(OH)_2$ or CH_3OH. Exothermic oligomerization of NH_2BH_2[4] entails that steps producing NH_2BH_2 are irreversible.

Table 1. Elementary Reactions and TS Energies (in kcal/mol) for the Reduction of CO_2 by AB and BH_3 Predicted Using CCSD(T)[a]

	ΔE(0 K)	ΔH(298 K)	ΔG(298 K) in THF
AB + CO_2 → AB−CO_2 adduct	−3.7	−3.7	−0.9
AB−CO_2 adduct to HCOOH + NH_2BH_2 TS	24.6	23.3	24.2
AB−CO_2 adduct → HCOOH + NH_2BH_2	6.7[b]	6.6[b]	6.7[b]
AB + HCOOH → AB−HCOOH adduct	−9.7	−9.4	−3.2
AB−HCOOH adduct to $CH_2(OH)_2$ + NH_2BH_2 TS	28.9	27.9	27
AB−HCOOH adduct to HCOOH + NH_2BH_2 + H_2 TS	22.8	22	24.7
AB + CH_2O → AB−H_2CO adduct	−7.7	−7.7	−2.7
AB−CH_2O adduct to CH_3OH + NH_2BH_2 TS	10.6	9.3	11
BH_3 + HCOOH → $HCOHOBH_3$	−19.6	−21.1	−18.9
$HCOHOBH_3$ to $HCOOBH_2$ + H_2 TS	4.7	4.3	6.9
AB + $HCOOBH_2$ → AB−$HCOOBH_2$ adduct	−17.3	−18.3	−12.3
AB−$HCOOBH_2$ adduct to $HCOHOBH_3$ TS	18.7	18.6	19.8

[a] MP2 frequency calculations and solvent corrections[23] are applied to obtain ΔH and ΔG at 298 K. [b] Although this reaction is endothermic, dimerization of NH_2BH_2 is exothermic by more than 15 kcal/mol (ΔE),[6] so this reaction is essentially irreversible.

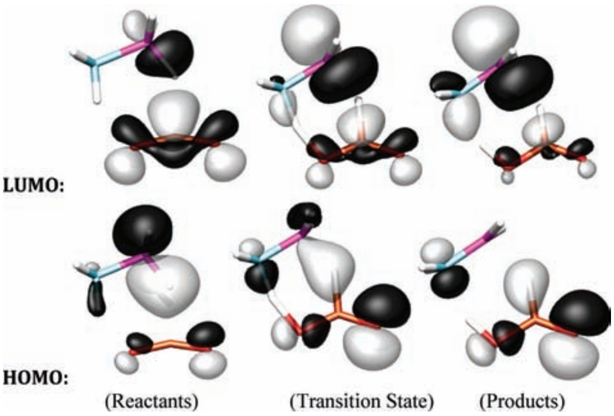
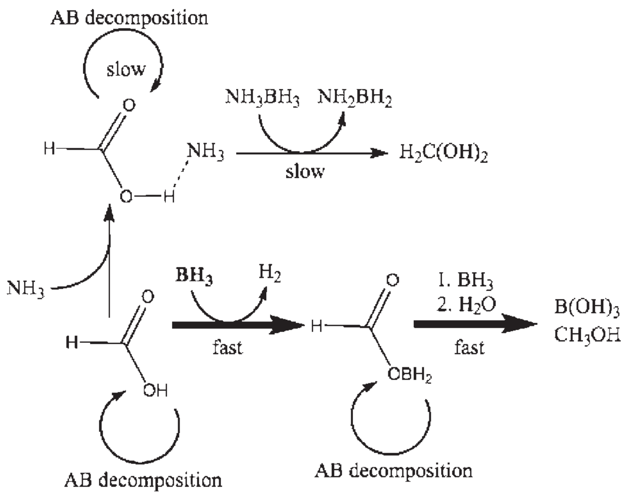


Figure 3. LUMO (top) and HOMO (bottom) along the reaction coordinate of the two-hydrogen-transfer step. As the reaction proceeds, the LUMO localizes on AB and the HOMO on CO_2. This represents a transfer of two electrons concomitant with the transfer of the two hydrogens, with the largest amount of charge transferring through the hydride to the carbon.

Scheme 2. Pathways for the Reaction of NH_3 and BH_3 with HCOOH and AB[a,14]



[a] While the reaction of BH_3 with HCOOH is facile, $HCOOBH_2$ also catalytically decomposes AB. The route through excess BH_3 to reduce HCOOH to CH_3OH is highlighted in bold.

dissociation energy of AB is 25.3 kcal/mol. In THF, however, the polarization of the N−B bond increases the free energy of AB dissociation to 33.6 kcal/mol, making dissociation uncompetitive. Consequently, the resulting small concentrations of NH_3 and BH_3 relative to AB and the significantly larger AB dissociation barrier relative to the two-hydrogen-transfer barriers of less than 27 kcal/mol cause reactions with

AB to predominate over those involving NH_3 or BH_3. Nevertheless, despite the small amount of NH_3 and BH_3 present, we considered reactions involving NH_3 or BH_3 to determine how the reactivity will change in excess NH_3 or BH_3.

Scheme 2 shows the most competitive pathways for NH_3 and BH_3 reaction with HCOOH. To initially create NH_3 and BH_3, both S_N1 (with a barrier equal to N−B's bond strength of 33.6 kcal/mol) and S_N2 reactions are possible. S_N2 attack on AB's BH_3 by HCOOH has a significant barrier (32.0 kcal/mol above the HCOOH−AB adduct) and therefore S_N1 and S_N2 mechanisms closely compete in breaking of the N−B bond. On the other hand, the formation of a HCOOH−BH_3 complex is exothermic by 18.9 kcal/mol. This complex then reacts via a 6.9 kcal/mol barrier to yield $HCOOBH_2$ and H_2. However, $HCOOBH_2$ catalytically decomposes AB into NH_2BH_2 and H_2 with an overall barrier of 19.8 kcal/mol by simultaneously accepting a proton and hydride to yield $HCOHOBH_3$ and subsequently eliminating H_2. Because of this low AB decomposition barrier, reduction by two-hydrogen transfer is not favorable in the presence of small amounts of BH_3. However, with excess BH_3, HCOOH is reduced and then hydrolyzed into CH_3OH.[14] Conversely, when BH_3 is not in excess, $HCOOBH_2$ favorably binds to NH_3 by lone-pair donation into the p orbital of boron, and this complex decomposes into NH_2BH_2 and HCOOH via a 35.4 kcal/mol barrier. The formation of this species ($HCOOBH_2NH_3$) reduces the extent of AB decomposition by HCOOH but does not favor further reduction of CO_2.

NH_3 and HCOOH form a complex 11.2 kcal/mol below the separated species in THF. This acid−base complex slows the acid-catalyzed decomposition of AB but does not facilitate the reduction of HCOOH by two-hydrogen transfer. Ultimately, because AB dissociation involves barriers higher than 32 kcal/mol, reactions involving NH_3 or BH_3 do not compete with the feasible reactions that proceed over barriers of less than 25 kcal/mol unless excess NH_3 or BH_3 is present. Excess BH_3, however, might be added to direct the overall reaction toward CH_3OH following HCOOH formation.

Conclusions

With the growing demand for liquid fuels and concern over rising atmospheric CO_2 levels caused by fossil fuels, effective CO_2 reduction to liquid fuels presents a considerable opportunity. Unfortunately, the currently well-known pathways each possess significant drawbacks: (1) single-electron reduction of CO_2 involves prohibitively high energetics;[15] (2) proton-coupled electron transfer, which may occur in CO dehydrogenases,[1] requires physically separated electron and proton pathways elaborately coupled in a manner that is difficult to mimic synthetically; (3) reductions on metal surfaces are generally not selective toward particular products. The chemistry we propose here based on highly accurate ab initio simulations elucidates an alternative mechanistic approach to CO_2 reduction: simultaneous two-hydrogen transfer through $H^{\delta+}$ and $H^{\delta-}$ present on the same reagent. This mechanism circumvents high-energy single-electron-reduced intermediates that greatly limit the rate of reaction. Repeated two-hydrogen transfers will result in the formation of $CH_2(OH)_2$ and ultimately in the selective formation of CH_3OH. Two-hydrogen transfer has been shown to be the operating mechanism for the reduction of imines by AB[1a] and could be active elsewhere.

Although AB exemplifies this simple yet elegant chemistry, effective approaches would need to be developed to overcome AB's susceptibility to acid decomposition. Although adding a base like ammonia will slow this decomposition, the reduction will still stop at HCOOH. Furthermore, although AB regeneration schemes are being developed to support its use as a hydrogen storage material,[16] employing catalysts that efficiently utilize this two-hydrogen-transfer mechanism for CO_2 reduction is likely a better strategy. These catalysts would not utilize AB as a stoichiometric reagent but would preferably use H_2 or H_2O as a hydrogen source to reduce CO_2 beyond HCOOH and a renewable source to supply the required energy. While AB will likely not serve as a practical two-hydrogen-transfer reagent for CO_2 reduction, the two-hydrogen-transfer mechanism discussed herein reveals a significant opportunity and extensive chemical space that can be explored for the difficult, but central problem of CO_2 reduction. Approaches like two-hydrogen transfer or frustrated acid−base activation[17,18] will be needed to design reactions that exploit CO_2's amphoteric nature. Furthermore, two-hydrogen transfer may be the working mechanism of catalysts such as the GaP photocatalyst proposed by Bocarsly et al.,[20] which produced CH_3OH in high yield. Materials such as B−N nanotubes or surfaces or other species possessing neighboring $H^{\delta+}$ and $H^{\delta-}$[12,19] that can simultaneously transfer acidic and hydridic hydrogens might prove effective for the reduction of CO_2.

Computational Details. All geometries were optimized using Møller−Plesset second-order perturbation theory (MP2)[21] with the cc-pVTZ triple-ζ quality basis.[22] Transition states were confirmed by normal mode and intrinsic reaction coordinate analysis. Zero-point vibrational energies are obtained at the same geometry and level of theory. Single-point energies at all MP2 geometries are computed with the highly accurate coupled-cluster singles, doubles, and perturbative triples method [CCSD(T)][23] using the aug-cc-pVTZ augmented triple-ζ basis.[22] Solvent free-energy corrections are obtained with the implicit solvent conductor-like polarizable continuum model[24] utilizing THF as a representative solvent at the MP2/aug-cc-pVTZ level of theory.

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All simulations are performed using *Gaussian03*[25] and NWCHEM.[26] Additional computational details are available in the Supporting Information.

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Supporting Information Available: Comprehensive scheme detailing the pathways studied in this work and geometries of all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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