An electrophilic substitution ($S_N$) reaction of BN isosteres has been investigated for the dehydrogenation of ammonia borane (AB) by metal chlorides (MCl$_2$) using various ab initio calculations. In contrast to the typical $S_N$ reaction occurring at the carbon atom, the nitrogen atom in AB serves as the reaction center for the $S_E$ reaction with the boron moiety as the leaving group when the MCl$_2$ approaches the AB. The $S_2$ backside reaction is favored as a trigger step for the dehydrogenation of AB by the MCl$_2$. The $S_2$ reaction is found for 3d-transition-metal chlorides (e.g., FeCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$), while PdCl$_2$ leads to the dehydrogenation of AB by a direct B–H α-bond activation, similar to most organometallic catalysts. Interestingly, the polymerization of AB promoted by MCl$_2$ can be explained with the similar $S_2$ mechanism, and the dehydrogenation of the BN derivative 3-methyl-1,2-BN-cyclopentane (CBN) bearing a carbon backbone ring also follows the $S_2$ reaction. In particular, the experimental observation that the use of metal-chloride catalysis decreases the by-products obtained during the dehydrogenation of AB can be explained by our mechanism involving the $S_2$ reaction. This work is helpful for the development of novel metal-halide catalysts for practical hydrogen storage materials, including the BN moiety.

The $S_2$ reaction | hydrogen storage | ammonia borane | catalyst | ab initio

Substitution reactions, a class of chemical reactions in which one functional group in a chemical compound is replaced by another functional group, are ubiquitous in organic chemistry (https://en.wikipedia.org/wiki/Substitution_reaction). Substitution reactions are classified either as nucleophilic ($S_N$) or electrophilic ($S_E$), depending on the underlying mechanism. Although $S_N$ reactions are less common than $S_E$ reactions, the $S_E$ reaction mechanism is more complicated, indicating that the variation among these processes is wider, which in turn means that there is a higher probability of unknown reactions (1–5). Therefore, whereas the $S_N$ reaction has been usually observed in carbon systems, the $S_E$ reaction would be able to occur in noncarbon systems.

Recently, ammonia borane (AB) has received significant attention as a promising onboard hydrogen storage material for use in transportation due to its high hydrogen storage capacity (19.6 wt % H$_2$) (6–9). There has been considerable effort to lower the operating temperature for fuel cells to 80 °C; consequently, homogeneous catalysis has become a promising alternative means of lowering the activation energy barrier of the dehydrogenation reaction pathway (10–17). In particular, organometallic catalysts lower the dehydrogenation barrier of AB by the coordination of the hydrogen atoms bonded to boron or nitrogen to the metal centers of the catalyst (16), where the coordination activates the B–H or N–H bond, followed by hydrogen transfer to the metal center or ligands. Recently, the dehydrogenation mechanism of AB and amine borane by various complex metal hydrides has been thoroughly reviewed by Rossin and Peruzzini (18). As more cost-effective promoters than organometallic catalysts, metal halides have been considered as homogeneous catalysts for AB dehydrogenation (19–21). Homogeneous metal-halide catalysis has also been applied to improve the dehydrogenation of 3-methyl-1,2-BN-cyclopentane (CBN), which is a promising liquid-phase H$_2$ storage material (22). For catalytic reactions with metal halides, it has been suggested that similar to the case of organometallic catalysis, the metal cation in metal halides initiates AB dehydrocoupling and retains a B–N unit during AB dehydrogenation (19, 20); however, the details of this proposed mechanism have not been investigated further.

While extending our search for an optimal metal-halide catalyst for the efficient dehydrogenation of AB, we have thoroughly explored the reaction pathway and kinetics of the dehydrogenation process using ab initio calculations. These efforts have led to the finding that an $S_2$ reaction occurs between the metal center and AB at the initial step of dehydrogenation and determines the performance of metal-halide catalysts, showing the possibility of an $S_2$ reaction in a noncarbon system. In contrast to previous $S_N$ reactions, the possibility of such a reaction on the B–N unit in an AB molecule can provide an opportunity for BN isostere chemistry, particularly with regard to the replacement of two carbon atoms (C–C) by the B–N moiety to produce various structures with interesting electronic structure and chemistry (23–27). In this work, the catalytic effects of various metal halides in the $S_2$ reaction for AB dehydrogenation are explored by several ab initio calculations, and their catalytic activity is discussed on the basis of quantum-mechanical energetics and molecular orbital (MO) analysis. Our calculations are also supported by a comparison with previous experimental results. Furthermore, it is confirmed that a similar $S_2$ mechanism is also applicable to catalysis for the CBN system, which has been recently reported as a potential hydrogen storage medium (22).

Results and Discussion

Direct Hydrogen Activation. According to a previous study (28) of organometallic catalysts for AB dehydrogenation, the dehydrogenation reaction occurs through the activation of a B–H or N–H bond at a metal center. Thus, for the metal-halide catalysts considered in this work, the dehydrogenation mechanism of AB via MCl$_2$ catalysis using ab initio calculations. In contrast to a typical electrophilic substitution ($S_N$) reaction occurring at a carbon atom, the nitrogen atom in AB serves as the reaction center for the $S_E$ reaction with the boron moiety as the leaving group when MCl$_2$ approaches AB. In addition, the $S_2$ backside reaction is favored as the initial step for the dehydrogenation of AB by MCl$_2$. This work paves the way for the use of a new reaction in the field of BN chemistry.

Significance

Ammonia borane (AB) is a promising hydrogen storage material due to its high hydrogen storage capacity. AB dehydrogenation can be facilitated by metal-halide (MCl$_2$) catalysis. Here, we have elucidated the dehydrogenation mechanism of AB via MCl$_2$ catalysis using ab initio calculations. In contrast to a typical electrophilic substitution ($S_N$) reaction occurring at a carbon atom, the nitrogen atom in AB serves as the reaction center for the $S_E$ reaction with the boron moiety as the leaving group when MCl$_2$ approaches AB. In addition, the $S_2$ backside reaction is favored as the initial step for the dehydrogenation of AB by MCl$_2$. This work paves the way for the use of a new reaction in the field of BN chemistry.

Author contributions: S.S.H. designed research; S.J.P. performed research; S.J.P. and S.S.H. contributed new reagents/analytic tools; S.J.P. and S.S.H. analyzed data; and S.J.P. and S.S.H. wrote the paper.

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In this work, we first investigated the dehydrogenation mechanism occurring through B–H activation, similar to the behavior observed in the case of organometallic catalysts. SI Appendix, Fig. S1 shows the AB dehydrogenation reaction pathways via B–H activation of metal chlorides, where FeCl$_2$ and PdCl$_2$ are used as representatives of 3d- and 4d-metal halides, respectively. For FeCl$_2$ (SI Appendix, Fig. S1A), the iron atom binds with two $\sigma$-B–H bonds in the AB molecule with a binding energy of 29.6 kcal/mol. However, a careful investigation reveals that no further reactions occur. This indicates that the dehydrogenation via B–H activation is not favorable, in contrast to the experiments (21, 29) reporting that FeCl$_2$ can promote the dehydrogenation of AB.

We also investigated other 3d-metal halides, such as CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$, and found that similar to the FeCl$_2$ case, these metal halides cannot activate the B–H bond.

On the other hand, PdCl$_2$ can activate a B–H bond in AB (SI Appendix, Fig. S1B). PdCl$_2$ interacts with one $\sigma$-B–H bond, that B–H bond is shifted toward a neighboring H atom, and then a H$_2$ molecule is released in a step with an energy barrier of 12.9 kcal/mol. According to a previously reported experiment (21), the grinding of AB and PdCl$_2$ does indeed lead to H$_2$ generation. It is expected that the dehydrogenation reaction would occur via the mechanism shown in SI Appendix, Fig. S1B. This difference between FeCl$_2$ and PdCl$_2$ results from the fact that Fe$^{2+}$ is a hard acid, while both Pd$^{2+}$ and BH$_3$ are soft acids (30). Thus, PdCl$_2$ and BH$_3$ can interact more readily than FeCl$_2$ and BH$_3$.

**S$_2$2 Reaction at a B–N Unit.** Although our calculations indicate that direct B–H activation in AB by nonprecious metal halides is not favorable, several experiments reported their catalytic activity (19–21, 29), implying the possibility of an alternative route for the dehydrogenation of AB via MCl$_2$. The electrophilic nature of the metal centers in the metal halides and the electron-rich nature and attachment to a potential leaving group, BH$_3$, of the nitrogen atom in AB support the occurrence of an S$_2$2-type reaction in the AB and MCl$_2$ system for AB dehydrogenation, especially for the occurrence of an S$_2$2-type pathway over an S$_1$1-type pathway.

Although the S$_2$2 reaction occurs mostly through one route with rare exceptions (31), S$_3$2 reactions can proceed through various routes (2). Since there is no severe steric hindrance at the NH$_3$ or BH$_3$ group in AB, two plausible pathways for the MCl$_2$ + AB system can be considered: (i) the front-side open-retention pathway, S$_2$2(FS), and (ii) the backside inversion pathway, S$_2$2(BS). Fig. 1 shows the S$_2$2(FS) and S$_2$2(BS) pathways for FeCl$_2$ + AB system as calculated at the density-functional theory (DFT) with a dispersion correction for two-body energy (D2) level of theory. We have confirmed that the DFT-D2 reaction energies are similar to the coupled-cluster singles and doubles plus perturbative triples [CCSD(T)] energies, as shown in SI Appendix, Fig. S3. For the S$_2$2(FS) pathway, the Fe atom in FeCl$_2$ approaches the B–N bond, leading to an increase in the length of B–N bond from 1.63 to 2.80 Å, a reaction that is uphill by 15.9 kcal/mol and has an energy barrier of 16.6 kcal/mol. At the final state, full dissociation of the B–N bond did not occur because the H atom in BH$_3$ is bound to the Fe atom by electrostatic interactions. A further reaction does not occur, indicating that the S$_2$2 (FS) reaction does not lead to the dehydrogenation of AB.

On the other hand, for the S$_2$2(BS) reaction, the Fe metal center in FeCl$_2$ attacks the N atom in AB through the backside route, followed by the BH$_3$ group leaving. The transition state (TS) for the reaction involves an inversion of the tetrahedral geometry at the N center, as observed in typical substitution reactions. The calculated energy barrier is 5.7 kcal/mol, much lower than that for the S$_2$2(FS) route. Moreover, the reaction is slightly downhill. After the S$_2$2 reaction, an additional process involving the recombination of the B–N bond can occur due to the absence of steric or rotational hindrance between the two dissociated groups. The second activation energy for the dehydrogenation is 20.8 kcal/mol, much lower than that for AB in the absence of a catalyst (34.2 kcal/mol). A long distance (2.87 Å) between the Fe–N moiety and the BH$_3$ leaving group is the origin of the barrier-lowering effect, while in the noncatalyst case, a considerable contribution of the activation energy results from repulsion inducing the rotation and bending of the N and B atoms in AB (32, 33). Here, BH$_3$ can be an intermediate product during the dehydrogenation reaction of MCl$_2$ + AB. However, because BH$_3$ itself is a very active species, it combines with another BH$_3$ to dimerize into B$_2$H$_6$. According to a previous experiment (29), B$_2$H$_6$ was indeed observed as a by-product during the

![Fig. 1](image-url) Two plausible S$_2$2 reaction pathways for AB dehydrogenation with the help of FeCl$_2$. Upper and lower routes are S$_2$2(FS) and S$_2$2(BS), respectively. Numerical values in each structure are relative energies (in kilocalories per mole) to separate FeCl$_2$ and AB as a reference. In each structure, the B–N and M–N distances in angstroms are included.


dehydrogenation reaction of AB with various MCl₂ catalysts (e.g., FeCl₂, CoCl₂, NiCl₂, CuCl₂, and ZnCl₂). This result clearly supports our S₂2 mechanism.

**Comparison of Various Metal-Halide Catalysts for the Dehydrogenation of AB.** At this point, it is plausible that the catalytic reaction pathway through the S₂2(BS) route using FeCl₂ lowers the energy barrier to 20.8 kcal/mol (Fig. 1), enabling the reaction to proceed near 80 °C. However, according to an experimental report (29), not all metal halides are effective for the dehydrogenation of AB, and the catalyst efficiency is correlated with the intrinsic properties of the metal center, such as electronegativity. Although a higher electronegativity generally leads to more efficient catalysis, several exceptions to this rule are found for the first-row transition metals. For example, the electronegativities of Co and Ni are higher than that of Fe; however, their catalytic efficiencies are lower than that of Fe (29). Therefore, we need to further explore the dehydrogenation process involving the S₂2(BS) reaction pathway for various metal halides.

Using CCSD(T) calculations, we investigated reaction pathways involving the S₂2(BS) reaction for AB dehydrogenation by several first-row transition-metal chlorides (FeCl₂, CoCl₂, NiCl₂, CuCl₂, and ZnCl₂) and compared their reaction energies in Table 1. The information is also summarized in more detail in SI Appendix, Table S2. Here, it is necessary to mention that the dehydrogenation process is a two-step reaction involving the S₂2(BS) mechanism and the recombination of the B–N bond (RCBN). The energy barrier value is relative to the isolated AB and MCl₂. The energy difference (ΔE₂N–b*) between the x₂* MO level of single MCl₂ and the HOMO level at the TS for the S₂2 reaction is also compared. The energies are obtained at the calculation level of CCSD(T). All energies are in kilocalories per mole.

**Table 1. Comparison of the calculated energy barriers for AB dehydrogenation by various MCl₂**

| MCl₂  | S₂2(BS) | RCBN | ΔE₂N–b* | ΔE₂H₂* |
|-------|---------|------|---------|---------|
| FeCl₂ | 6.9     | 22.1 | 19.6    | 6.9     |
| CoCl₂ | 10.9    | 29.7 | 20.5    | 8.2     |
| NiCl₂ | 3.3     | 20.5 | 20.5    | 7.5     |
| CuCl₂ | 4.0     | 20.7 | 23.4    | 5.6     |
| ZnCl₂ | 13.0    | 19.8 | 15.9    | 8.2     |

Mechanism is similar to that shown in Fig. 1 and SI Appendix, Fig. S3. Dehydrogenation is a two-step reaction including the S₂2(BS) and the recombination of B–N bond (RCBN). The energy barrier value is relative to the isolated AB and MCl₂. The energy difference (ΔE₂N–b*) between the x₂* MO level of single MCl₂ and the HOMO level at the TS for the S₂2 reaction is also compared. The energies are obtained at the calculation level of CCSD(T). All energies are in kilocalories per mole.

To elucidate the effects of the MCl₂ catalysts on the S₂2 reaction barrier, we have also investigated the MCl₂ electronic structures. Because this S₂2 reaction accompanies a charge transfer similar to a general donor–acceptor interaction, the second-order perturbation stabilization energies from to u* [ΔE₂N–b*] were calculated using a natural bonding orbital (NBO) method, in which the interaction between occupied and vacant orbitals is represented to stabilize the superposition of each orbital. From the calculation, we find that the TS energy for the S₂2 reaction is mainly determined by an intrinsic energy-lowering effect of the donor–acceptor interaction between a lone-pair orbital of nitrogen in AB and an unfilled lone-pair orbital of boron, as shown in SI Appendix, Fig. S8. Calculated ΔE₂N–b* values are summarized in the third column of Table 1. A comparison of the ΔE₂N–b* values between MCl₂ catalysts shows that the energy is higher for a metal with a larger electronegativity (Cu > Ni > Co > Fe > Zn). Moreover, the energy inversely correlates with the energy barrier of the S₂2 reaction, with the exception of FeCl₂. In other words, the ΔE₂N–b* of FeCl₂ is expected to fall between those of CuCl₂ and NiCl₂ because the order of the S₂2 reaction barriers is CuCl₂ < FeCl₂ < NiCl₂ < CoCl₂ < ZnCl₂; however, it is in fact lower than those of CuCl₂ and NiCl₂. The exceptional case of FeCl₂ can be explained by another effect that is discussed below.

During the S₂2 reaction, a linear symmetry of the MCl₂ molecule is broken by interacting with the lone-pair orbital of the nitrogen atom (SI Appendix, Fig. S9), which reveals that the S₂2 energy barrier is also associated with an energy to retain this linear symmetry of the MCl₂ molecule. The π₂* – the highest-occupied MCl₂ MO (HOMO) level has a suitable symmetry for determining the dehydrogenation of AB involving the S₂2 reaction can still occur in solids of AB and a metal halide.

To confirm that the same mechanism for dehydrogenation of AB and metal halide also occurs in the solid state, periodic slab calculations were additionally performed, in which a nudged elastic band calculation (SI Appendix, Fig. S4) and a first-principles molecular dynamics simulation (SI Appendix, Fig. S5) were considered. The relevant computation details are described in SI Appendix. Indeed, both of the slab calculations clearly show that the dehydrogenation of AB involving the S₂2 reaction can still occur in solids of AB and a metal halide.
the $S_2$ reaction barrier with FeCl$_2$ lower than those with CoCl$_2$ and NiCl$_2$. Among the MCl$_2$ compounds considered in this work, CuCl$_2$ has the highest $\Delta E^{(2)}_{N \rightarrow B^*}$ and the lowest $\Delta E_{\Pi u^*}$, which leads to the lowest $S_2$ reaction barrier.

**Expansion of the $S_2$ Reaction to the Polymerization of AB and Other BN Derivatives.** Previous experiments reported that after the removal of a single H$_2$ molecule from AB, NH$_2$BH$_2$ oligomers, including dimers, trimers, pentamers, and other intermediates with the empirical formula (NH$_2$BH$_2$)$_x$, are generated (7, 35). Zimmerman et al. (36) reported that based on ab initio calculations, amine borane (NH$_2$BH$_2$) can serve as an autocatalyst for AB oligomerization by the addition of AB across the B=N double bond with an activation energy of 29.5 kcal/mol. However, in the presence of the MCl$_2$-type catalysts, the AB dimerization and even subsequent polymerization can be explained by the $S_2$ reaction framework in a similar manner to that for the monomer, as illustrated in Fig. 1 and SI Appendix, Fig. S3. Fig. 3 shows a

![Fig. 3](image-url). Calculated reaction pathway for AB dimerization with the help of FeCl$_2$ catalysis, where the DFT-D2 method was used.

![Fig. 4](image-url). Calculated reaction pathway for CBN dehydrogenation with the help of FeCl$_2$ catalysis, where the calculation is performed at the DFT-D2 level. Red numbers in parentheses indicate the energies considering the solvent effect.

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Fig. 3. Calculated reaction pathway for AB dimerization with the help of FeCl$_2$ catalysis, where the DFT-D2 method was used.

Fig. 4. Calculated reaction pathway for CBN dehydrogenation with the help of FeCl$_2$ catalysis, where the calculation is performed at the DFT-D2 level. Red numbers in parentheses indicate the energies considering the solvent effect.
calculated reaction pathway of AB dimerization with an FeCl₃ catalyst through the S₂ reaction. Following the removal of a single H₂ molecule from AB (m-Opt2 in SI Appendix, Fig. S3), the boron atom can become a radical center with a positive partial charge, allowing it to be reused as an electrophile. The boron site becomes a radical center with a positive partial charge, allowing it to be reused as an electrophile.

It is also known that the FeCl₃ catalyst improves the dehydrogenation mechanism of AB by the MC₁ catalysts using several ab initio calculation methods. A type of electrophilic substitution reaction in the B-N unit, in particular, an S₂ type reaction, was found during the catalyzed dehydrogenation reaction of AB catalyzed by MC₁. The S₂ reaction determines the catalytic activity of the metal chlorides for the dehydrogenation of AB, as supported by the reported experiments. Interestingly, a similar mechanism is also found in the AB polymerization reaction and even in the dehydrogenation reaction of a BN derivative with a carbon backbone ring (i.e., CBN). This work helps the development of metal-halide catalysts for practical hydrogen storage materials with the BN moiety. We also expect that this work could pave the way for the use of a new reaction in the field of BN chemistry.

**Models and Methods**

The catalytic effects of various metal chlorides (MC₁), type M = 3d- or 4d-transition metals) on the dehydrogenation reactions of AB were investigated with several ab initio calculation methods. To appropriately describe the long-range correlation effect on the substitution reactions occurring during the dehydrogenation, all MC₁ adducts were fully optimized in the Becke, three-parameter, Lee-Yang-Parr (B3LYP) (37, 38) DFT framework, with the 6-311++ G(d,p) basis set (39) plus Grimme’s empirical dispersion correction, called the DFT-D2 method (40). A TS for the dehydrogenation reaction was confirmed by the existence of one imaginary frequency, and the zero-point energy correction to the total energy was applied to the total energy.

When higher precision than that available from DFT was required, the CCSD (T) method (41) employing the correlation-consistent triple-ζ plus polarization basis set (42, 43) was applied to the structures fully optimized at the Moller-Plesset second-order perturbation theory (44, 45) level with the same basis set. To explore the relationship between their catalytic effect and electronic structure, we investigated the MO levels of the MC₁ compounds for the geometries that were fully optimized by CCSD(T). Here, the Stuttgar-Bonn set (SRSC) effective core potential (46) for transition-metal elements. In fact, we also attempted the calculations with the Los Alamos National Laboratory for double zeta quality (LANL2DZ) core potential (47) for transition-metal elements, which has been widely used in the field of organometallic catalysts; however, we found that this approach did not provide a correct energy change for FeCl₃, as a function of a multiplicity. The details are explained in SI Appendix.

In the case of CBN adducts, a solvation effect was taken into account using the polarized continuum model scheme (48, 49) with a dielectric constant of 2.38 corresponding to the toluene solvent used in a previous experiment (22). In this work, all atomic charges were calculated by the NBO 5.0 scheme (50, 51). All ab initio calculations were performed using the Q-Chem package (52).

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**Conclusion**

Thus far, we have elucidated the dehydrogenation mechanism of AB by the MC₁ catalysts using several ab initio calculation methods. A type of electrophilic substitution reaction in the B-N unit, in particular, an S₂ type reaction, was found during the catalyzed dehydrogenation reaction of AB catalyzed by MC₁. The S₂ reaction determines the catalytic activity of the metal chlorides for the dehydrogenation of AB, as supported by the reported experiments.
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