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The Influence of Excess Ammonia on the Mechanism of the Reaction of Boron Trichloride with Ammonia—An Ab Initio Molecular Dynamics Study**

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The reaction of boron trichloride with ammonia is well known. Already in 1921, BN was produced by ammonolysis of boron trichloride in liquid ammonia and subsequent heating of the primary products.[1] Today, the reaction of BCl_3 with NH_3 is used for the preparation of hexagonal and amorphous boron nitride by means of chemical vapor deposition (CVD).[2]

To shine light on the processes during the CVD of BN, Reinhardt et al. recently investigated the energetic course of the gas-phase reaction of BCl_3 with NH_3.[3] They were able to show that the substitution of the first chlorine atom of BCl_3 in the gas phase is a two-step reaction (Figure 1): the formation of an $NH_3 \cdot BCl_3$ adduct in the first step is followed by the elimination of hydrogen chloride to yield aminodichloroborane. The elimination requires the surmounting of a barrier of 25 $kJ\,mol^{-1}$ with respect to the reactants, or 151 $kJ\,mol^{-1}$ relative to the adduct. The second and third substitutions follow the same mechanism. The reaction barriers become lower with decreasing chlorine content, and the heats of reaction become smaller. As a result of its high-lying transition state, the first chlorine substitution is the rate-determining step, and the reaction that yields BN is expected to proceed only at elevated temperatures. However, the ammonolysis of BCl_3 is known to occur spontaneously in the condensed phase even at low temperatures and to be very exothermic.[1] It can therefore be concluded that additional NH_3 molecules strongly affect the energetic course and the mechanism of the reaction.

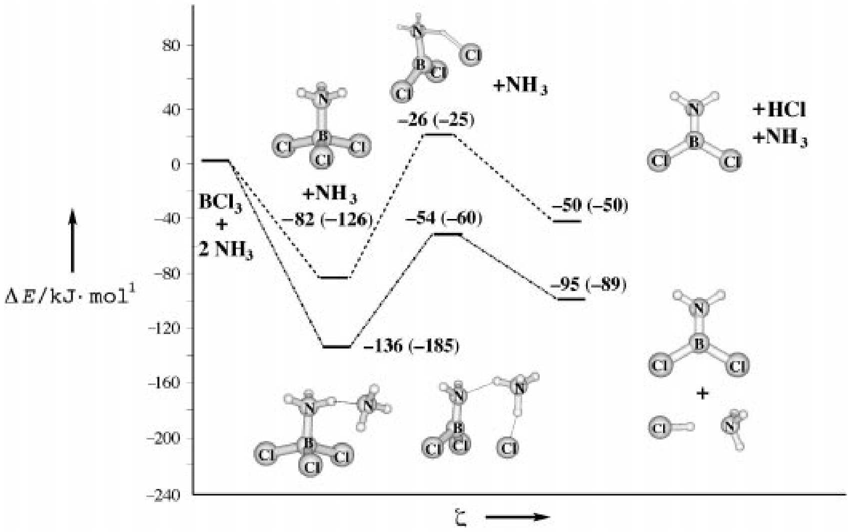

Figure 1. Energy course of the gas-phase reaction of boron trichloride with one ammonia molecule (top curve) and two ammonia molecules (bottom curve), determined at the BLYP level of theory (RI-MP2 values are given in parentheses). ζ = Reaction coordinate.

The aim of the work herein is to study the influence of additional ammonia molecules on the mechanism and on the energy profile of the first chlorine substitution by an amino group. According to the results of time-independent RI-MP2 calculations (see Calculation Methods), the barrier of the gas phase reaction is lowered in the presence of another NH_3 molecule owing to the formation of a six-centered transition state (Figure 1). However, with respect to the $H_3N \cdot BCl_3$ adduct the barrier is still rather high (125 $kJ\,mol^{-1}$). Furthermore, the product side of the reaction is only slightly stabilized by a single NH_3 molecule. Because solvent molecules participate actively in the reaction, the influence of excess NH_3 cannot be simulated by means of a continuum

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model. Instead, the breaking and formation of any of the covalent bonds in the system is modeled by means of a molecular dynamics method that allows a full quantum chemical treatment of solvent molecules. We have employed the Car–Parrinello molecular dynamics (CPMD) method, which uses periodic boundary conditions and represents a numerically very efficient first-principles molecular dynamics approach.[4–6]

Our simulations point to a reaction mechanism that differs markedly from the two-step gas-phase mechanism. In excess NH_3, the substitution of a chlorine anion in BCl_3 for an amino group proceeds in three steps (Figure 2): 1) formation of an $H_3N \cdot BCl_3$ adduct, 2) proton transfer to a solvent molecule to yield a salt-like intermediate, and 3) formation of the product (BCl_2NH_2) by elimination of a chloride ion. The emerging ammonium chloride is solvated by other NH_3 molecules. The ionic character of the saltlike intermediate was confirmed by analysis of the localized orbitals (Wannier orbitals) (Figure 3): The electron pair that originally connected the N and H atoms has become a lone pair on the nitrogen atom, and H^+ was transferred to an NH_3 molecule. Likewise, the B–Cl bond was cleaved heterolytically to yield a solvated Cl^- ion.

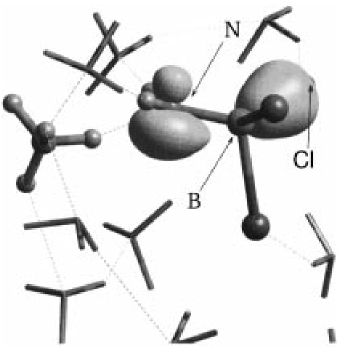

Figure 3. Wannier orbitals of the saltlike intermediate: The electron pair that formed the N–H bond remains at the N atom as a lone pair. The electron pair of the B–Cl bond is polarized towards the Cl atom and leaves the saltlike intermediate together with the Cl atom.

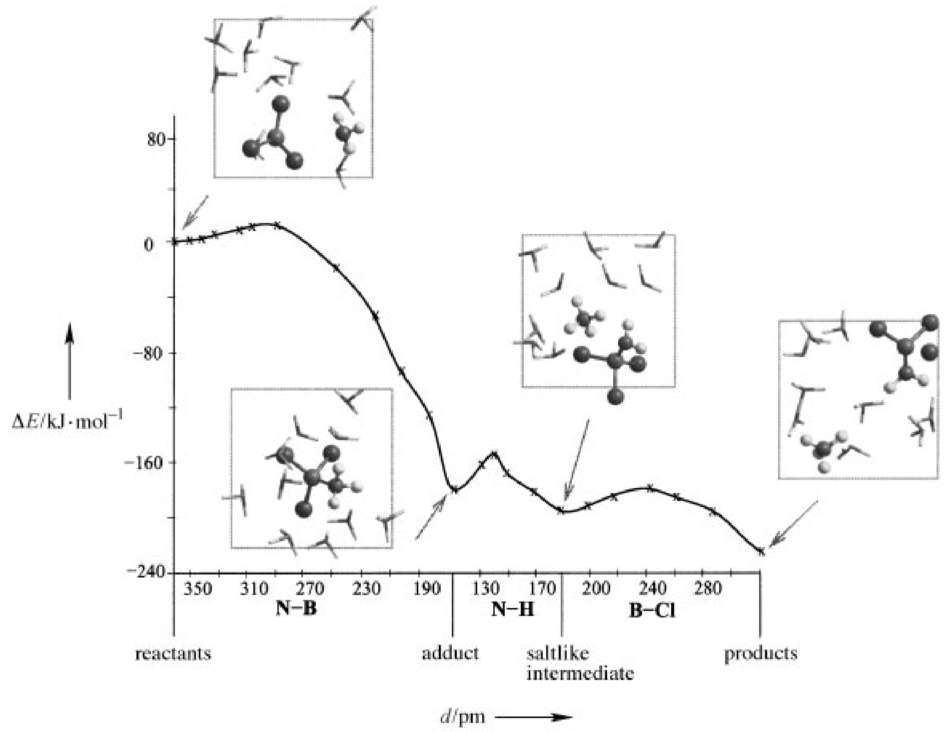

Figure 2. Mechanism and constrained minimum energy path of the reaction of one BCl_3 molecule with eleven NH_3 molecules. The reaction proceeds in three steps: 1) formation of an adduct complex ($H_3N \cdot BCl_3 + 10\,NH_3$); 2) elimination of a proton to yield a saltlike intermediate ($[NH_4^+][BCl_3NH_2^-] + 10\,NH_3$); 3) formation of the products ($BCl_2NH_2 + NH_4Cl + 10\,NH_3$) by abstraction of a chloride anion.

To analyze the energy profile of this reaction, two possibilities are at hand: a) analysis of the reaction times during the simulation or b) extraction of the minimum energy path along the trajectory (reaction coordinate). The first approach yields information about the free-energy barrier that has to be overcome in a real sample, whereas the minimum energy path can be compared to the results of the static calculations.

We performed CPMD calculations at seven temperatures between 200 and 700 K for three different starting geometries. The reaction mechanism remains the same in all cases. At 200 K the reaction is complete within 10.1 ps, and at 300 K within 8.1 ps. At temperatures of 400 K and above, the total reaction always proceeds in less than 4.4 ps. Although the statistics is not sufficient to produce a meaningful value for the free energy of the reaction, it is clear that the barrier for such an extremely fast reaction (picosecond range) has to be very small.

To compare with previously obtained results in static calculations we have determined a constrained minimum energy path (CMEP) in three steps: 1) stepwise approach of one NH_3 molecule towards the BCl_3 molecule to form the adduct, 2) successive increase of the N–H distance, and 3) stepwise elongation of the Cl–B bond. The reaction profile is shown in Figure 2. The overall reaction releases 219 kJ mol^{-1}, which is 169 kJ mol^{-1} more than the corresponding gas-phase reaction.[3] The energy released by the crystallization of NH_4Cl has not been taken into account. The obtained energy values should not be overinterpreted: first, the entropy contribution that is important in solution is neglected in such a calculation, and second, the specification of an internal coordinate as reaction coordinate does not necessarily lead to the optimal pathway. Every single step of the BCl_3 amination is exothermic in excess NH_3. Contrary to the gas-phase reaction, the adduct formation proceeds via a transition state. It can be assumed that this small barrier is a result of the release of the attacking NH_3 from the ammonia network. Furthermore, the proton transfer and the chlorine abstraction require the surmounting of small barriers. A comparison of the energy profiles shown in Figures 1 and 2 makes it clear that the three-step mechanism offers a much faster pathway.

To our knowledge, this alternative reaction mechanism has not been discussed before. However, the single steps can easily be interpreted: the Lewis adduct $H_3N\cdot BCl_3$, which contains a fourfold coordinated nitrogen atom, is a Brønsted acid in liquid NH_3. It loses a proton, which immediately forms an ammonium ion with one of the solvent molecules. The resulting anion is unstable and eliminates a chloride anion to form the neutral and stable BCl_2NH_2.

Calculation Methods

For all static calculations, a valence-triple-zeta basis set with a polarization function (TZVP) was used. The corresponding auxiliary basis sets were used for the resolution of identity (RI) approximation of the two-electron integrals.[7–9] The structures and energies were determined by RI-approximated second-order Møller–Plesset perturbation theory (RI-MP2)[10] by employing the TURBOMOLE 5.1[11, 12] and ef.x[13] programs. All simulations were performed by using the Car–Parrinello Molecular Dynamics code, Version 3.0 h.[14] For these calculations, we employed the Becke(88) exchange and Lee–Yang–Parr correlation functionals (BLYP).[15, 16] The reliability of various nonhybrid density functionals (SVWN, BLYP, HCTH, PBE) was tested by comparing the relative energies of stationary points on the potential energy hypersurface of the gas-phase reaction with results from previous RI-MP2 calculations.[3] BLYP showed the best performance of these functionals: the relative energies of the transition state and the products with respect to the reactants agree very well ($\pm 1\,\mathrm{kJ\,mol^{-1}}$). On the other hand, the adduct formation energy is underestimated by $44\,\mathrm{kJ\,mol^{-1}}$. An error of this size is typical for the description of dative bonds with DFT methods and cannot easily be remedied.[17] The valence electrons were described with a plane-wave basis set with an energy cutoff of 60 Ry ($\approx 131\times 10^{-18}$ J). An extension of the energy cutoff to 70 Ry ($\approx 153\times 10^{-18}$ J) has no significant effect on structure and energy. Troullier–Martins pseudopotentials were employed for the representation of the inner electrons.[18] The simulations at the microcanonical ($f(N,V,E)$) ensemble were performed with time steps of 4 a.u. (0.0968 fs) and a fictitious electron mass of 400 a.u (3.64×10^{-28} kg). One BCl_3 and eleven NH_3 molecules were placed in a cubic box ($(7.94\,\text{Å})^3$). This corresponds to a density of $\approx 1\,\mathrm{g\,cm^{-3}}$, comparable to the density of liquid BCl_3 at 286 K ($1.4\,\mathrm{g\,cm^{-3}}$) and the density of liquid ammonia at 240 K ($0.7\,\mathrm{g\,cm^{-3}}$). The energies of the arbitrarily chosen starting geometries were optimized ($T = 0$ K), that is, they constitute local minima on the potential hypersurface. The initial momenta of the ions were chosen according to a Maxwell–Boltzmann distribution. The delocalized molecular orbitals were transformed into localized Wannier functions to investigate the spatial localization of the electrons.[19, 20]

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DNA-Directed Functionalization of Colloidal Gold with Proteins**

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The utilization of nucleic acids and proteins as building blocks in the "bottom-up" self-assembly of nanoscale functional devices is of great current interest.[1] As an example, DNA has been applied to fabricate nanostructured molecular scaffolding and surface architectures,[2] and to selectively position proteins[3] and nanoclusters[4] on the nanometer scale. In earlier work, we reported the DNA-directed immobilization of proteins,[5, 6] which concerned the binding of single-stranded DNA-tagged immunoglobulins (IgG) or enzymes to surface-immobilized complementary capture oligonucleotides by means of the highly specific Watson–Crick base pairing. This method not only allows a surprisingly efficient and fully reversible adsorption of the proteins, but also it enables the simultaneous immobilization of many different DNA-tagged components in a single, site-selective process using a DNA microarray as a capture matrix. We here report on the DNA-directed immobilization of proteins at colloidal gold, as well as on applications of the resulting biofunctionalized nanoparticles in immunological detection methods.

To allow the modular functionalization of gold nanoparticles (Au-**1**) modified with oligonucleotide **1** (see Experimental Section), we chose the covalent DNA–streptavidin (STV) conjugate **4** as a molecular linker. **4** was obtained from the biotin-binding protein STV **3** and 5′-thiol-modified oligonucleotides **2**, using the heterobispecific amino/thiol-reactive

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