Density Functional Study of σ Bond Cleavage in P–P Multiple Bond of Phosphinophosphinidene

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Recently, the synthesis of phosphinophosphinidene, which is a phosphorus analog of carbene, has been reported. Subsequent experimental reports have shown that phosphinophosphinidene acts as an electron acceptor. Because the terminal phosphorus atom inherently acts as an electron donor, chemical reactions may lead to the σ bond cleavage at the phosphorus atom through charge-transfer interaction. In this study, we explore the possibility of the σ bond cleavage in H–H, C–H, O–H, N–H, and B–H bonds by means of the density functional method using the model molecules, H₂, CH₄, H₂O, NH₃, and BH₃. For H₂ and CH₄, the H–H and the C–H bonds were found to be broken at the single site of the terminal phosphorus atom by the charge-transfer interactions. The potential energy barrier of about 22–24 kcal/mol is similar to that for carbene, suggesting the possibility of σ bond cleavage in phosphinophosphinidene. In contrast, for H₂O and NH₃, the O–H and N–H bonds are broken at the two sites of both phosphorus atoms by the abstraction of hydrogen as a proton. In the case of BH₃, cleavage of the B–H bond occurs easily at both the single and dual sites of the phosphorus atoms.

Keywords: Density functional method, Phosphinophosphinidene, σ Bond cleavage, Reaction mechanism

1 INTRODUCTION

The cleavage and formation of chemical bonds are essential elementary steps in various reactions for synthesizing chemical compounds. Transition metal complexes are often used in reactions to achieve the cleavage and formation of chemical bonds, because the electron donor and acceptor characteristics of the metal atom in transition metal complexes promote charge-transfer interactions with the substrate, consequently facilitating cleavage and formation of the chemical bonds. However, in addition to metal complexes, nonmetal and metalloid compounds, which also possess both electron donor and acceptor character, have been recently reported. The observation that atoms other than metals can break the chemical bonds is of interest to chemists.

For example, in 2007, Bertrand et al. reported that carbene, which is originally known to have both electron donor and acceptor character, has the ability to readily break the H–H and N–H bonds at a carbon atom [1]. It has also been reported based on experimental and theoretical studies that the phosphorus atom of a pincer complex, which has both electron donor and electron acceptor properties, is reactive for O–H and N–H bond cleavage [2, 3]. In 2013, Braunischweig et al. revealed that diboryne with N-heterocyclic carbene as ligands easily activates the CO molecule on the B≡B triple bond [4], which suggests charge-transfer interaction between the B≡B triple bond and the CO molecule. Afterwards, it was indicated experimentally and theoretically that this diboryne activates the H₂ molecule on the B≡B triple bond [5]. We have also suggested based on theoretical calculation [6] that the B≡B triple bond exhibits potential for τπσ bond cleavage in other molecules. Further, it is known that activation readily occurs on the σ and π bonds in the Ge = O double bond of germalone, synthesized by Tamao et al. in 2012 [7, 8].

Recently, phosphinophosphinidene A, which is a phosphorus analog of carbene, was successfully synthesized by Bertrand et al. using the substituent presented in Figure 1 [9], although phosphinophosphinidene has never been synthesized owing to its instability. The P–P bond of A is a multiple bond and A is more energetically stable in the singlet state than in the triplet state. Further experimental reports showed that A acts as an electron acceptor [10, 11]. The π bond or lone electron pair from various molecules undergoes addition reaction with the terminal phosphorus atom of A. Because the terminal phosphorus atom, which is negatively charged, inherently possesses electron donor property, breaking of the σ bond at the phosphorus atom is expected, as observed for...
In this study, we predict the reactivity of the P–P site of phosphinophosphinidene for σ bond cleavage by quantum chemical calculation. The calculations herein employ phosphinophosphinidene with the 2,6-diisopropylphenyl (Dip) group; has been trapped experimentally during some addition reactions. We examined the three patterns of σ bond activation as shown in Figure 2, that is, activation at the terminal phosphorus atom (pattern 1) and activation at the two phosphorus atoms (patterns 2 and 3). H₂, CH₄, H₂O, NH₃, and BH₃ are used as model substrates.

2 COMPUTATIONAL DETAILS

Calculations were performed for the singlet state, because the singlet state was confirmed to be energetically more stable by 19.7 kcal/mol than the triplet state, which is consistent with the previous results [9] mentioned in the Introduction where the singlet state is more stable by 17.2 kcal/mol than the triplet state. Geometry optimizations and energy calculations were carried out by the density functional theory (DFT) method at the M06-2X level [12]. The 6-31G (d) basis set was used for the 2,6-diisopropylphenyl (Dip) group and the 6–311++G (2d,2p) basis set was used for other atoms of the core part of the molecule. The M06-2X functional and the 6–311++G (2d,2p) basis set adopted herein are similar to those used in the precedent papers [9–11]. The equilibrium and transition state structures were identified by the number of imaginary frequencies calculated from the analytical Hessian matrix. The reaction coordinates were followed from the transition state to the reactant and the product by the intrinsic reaction coordinate (IRC) technique [13]. The atomic charge and the atomic orbital (AO) population were obtained by natural bond orbital (NBO) analysis [14]. The basis set superposition error (BSSE) included in the interaction (INT) energy for phosphinophosphinidene with the substrate was corrected by the counterpoise method [15, 16]. The thermochemical parameters were calculated with a scale factor of 0.971 [17] for the calculated vibrational frequencies at 298.15 K. All quantum mechanical (QM) calculations were performed using the Gaussian09 program package [18]. Herein, the suffixes added to the labels h, m, w, a, and b distinguish the substrates, H₂, CH₄, H₂O, NH₃, and BH₃, respectively. All optimized structures are displayed in the Supporting Information.

3 RESULTS AND DISCUSSION

We first focused on the bend of the P–P–x axis shown in Figure 3, because this bend has been confirmed in the CO and carbene adducts, as previously reported based on experiments and computations [10], and as also indicated in our present calculation. Here, X is the dummy atom that is placed at the middle point between the two nitrogen atoms of 1. It is expected that this bend would cause a shift in the energy level of the molecular orbitals of the P–P bond in the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) region in order to facilitate charge-transfer interaction with the substrate. Namely, the occupied and
vacant orbitals that are involved in the charge-transfer interaction would be energetically raised and lowered, respectively, by this bend. Accordingly, the changes in the energy level of the molecular orbitals of the P–P bond in the HOMO–LUMO region as a result of decreasing the angle $\angle$P–P–X were calculated. As shown in Figure 3, HOMO and HOMO-1 are the in-plane and out-of-plane $\pi$ orbitals and the LUMO is the out-of-plane $\pi^*$ orbital as previously reported [9]. The in-plane and out-of-plane $\pi$ orbitals of the P–P bond would act as the electron donor while the out-of-plane $\pi^*$ orbital would act as the electron acceptor in the charge-transfer interaction with the substrate, as mentioned below, which is similar to the case of diboryne [6]. In fact, the vacant orbital of the BH$_3$ molecule coordinates in the parallel and perpendicular orientations relative to the molecular plane, and the lone electron pair of the H$_2$O and the NH$_3$ molecules coordinates in a perpendicular orientation to the molecular plane (see structures, 2b, 4b, 2w, and 2a, Supporting Information). Upon decreasing the angle $\theta$, the electron in each orbital becomes highly localized on the terminal phosphorus atom, the energy levels of the $\pi$ orbitals become higher, and that of the $\pi^*$ orbital becomes lower as expected, leading to facile charge-transfer interaction.

The calculated energy profiles of the nonpolar molecules H$_2$ and CH$_4$ for the reaction patterns 1–3 shown in Figure 2 are presented in Figure 4. The P–P bond axis actually bends as the reaction proceeds, as previously reported for the CO and the carbene adducts [10]. In both the one-site and the two-site reactions, the stabilization of the $\pi^*$ orbital by this bond apparently makes the electron donation from the $\sigma$ orbital of the substrate easier, because the energy gap between the $\pi^*$ orbital and the $\sigma$ orbital becomes smaller. Although the upper and the lower sides of the P–P bond can both be considered as the reaction side for the one-site and the two-site reactions when the substrate approaches the bent P–P bond, the energetically favorable side is presented herein unless otherwise indicated. In the cases of H$_2$ and CH$_4$, $\sigma$ bond cleavage would proceed by charge-transfer interaction in both the one-site and the two-site reactions, as shown in case 1 in Figure 5. In the present study, a heterolytic feature reported for carbene [1] was not found in the geometry of the transition state. Figure 4 shows that the one-site reaction is much more energetically favorable than the two-site reaction for both H$_2$ and CH$_4$. This could be attributed to the fact that the energy levels of the $\pi$ and $\tau\pi$ $\pi$ orbitals involved in the electron back-donation are higher for the $\pi$ orbital involved in the one-site reaction than for the $\pi$ orbital involved in the two-site reaction, as shown in Figure 3. The smaller energy gap makes electron back-donation easier. The potential energy barrier of 22–24 kcal/mol for the one-site reaction is similar to that for H–H and N–H bond cleavage at the carbon of carbene [1], which suggests that $\sigma$ bond cleavage is also possible at the phosphorus atom of phosphinophosphinidene.

In contrast with the reaction of nonpolar H$_2$ and CH$_4$, the two-site reaction is energetically more favorable than the one-site reaction in the case of polar H$_2$O and NH$_3$. The energy profiles of...
the three patterns for σ bond cleavage are presented in Figure 6. Pattern 1 involving the one-site reaction and pattern 2 involving the two-site reaction proceed via the substrate-coordinated intermediate, because the lone electron pair of the H_2O and NH_3 molecules coordinates to the terminal phosphorus atom via electron donation to the π* orbital, as shown in case 2 in Figure 5. The interaction energy (INT) for phosphinophosphinidene with the substrate in the intermediate was calculated to be 14.2 kcal/mol for H_2O and 38.2 kcal/mol for NH_3. However, there is an energy barrier for the coordination of both H_2O and NH_3, because some amount of energy is required to bend the P–P axis. Coordination of the lone electron pair of the substrate to the terminal phosphorus atom promotes the abstraction of hydrogen as a proton from the polar molecules of H_2O and NH_3 in the case of the two-site reaction, as we reported for diboryne [6] and germanone [8]. As shown in Figure 5, the negative charge of the other phosphorus atom would increase while the positive charge of the O–H or N–H hydrogen atom of the substrate would increase upon coordination of the lone electron pair of the oxygen or the nitrogen atom. As a result, hydrogen, as a proton, would be abstracted by the other phosphorus atom. In fact, as shown in Figure 7, it was confirmed that the population of the p⊥ atomic orbital of the other phosphorus atom and the positive charge of the reactive hydrogen atom of the substrate increase significantly when the lone electron pair of H_2O or NH_3 approaches the terminal phosphorus atom. Calculations were also performed for σ bond cleavage mediated by an additional substrate to confirm that the reaction proceeds by proton abstraction. If the hydrogen atom is abstracted as a proton, the reaction mediated by the additional substrate will proceed. As shown in Figure 8, hydrogen transfer mediated by the additional substrate actually proceeded in the case of both H_2O and NH_3. However, the energy barrier was not reduced compared to that without mediation. It is thought that the transition state geometry is not relaxed but is stressed owing to the steric congestion. In fact, the steric congestion is explicitly reflected in the angle of the mediating substrate. The angles, ϕ–H–O–H and ϕ–H–N–H, for the mediating substrates in the cases of H_2O and NH_3 decrease by 14.0° and 11.2°, respectively, compared to those of the free substrates. Although the two-site reaction via pattern 3 proceeds without pre-coordination of the substrate, this reaction follows a hydrogen abstraction mechanism similar to that mentioned before.

The energy profile for cleavage of the B–H bond in BH_3 molecule is presented in Figure 9. The BH_3 molecule can coordinate to one site of the terminal phosphorus atom or the two sites of both phosphorus atoms by the electron donation from the ππ orbital and the ππ* orbital of the P–P bond to the vacant p orbital of the boron atom perpendicular to the molecular plane. This indicates that the PP site of phosphinophosphinidene exhibits electron donor character in addition to the electron acceptor character documented by Bertrand et al. [9, 10]. Both BH_3-coordinated intermediates are energetically very stable, and these coordination steps are energetically downhill without an energy barrier. These BH_3-coordinated intermediates enable B–H bond breaking at both the single site and the two sites of the phosphorus atoms with a small energy barrier of 5–10 kcal/mol, although the two-site reaction is more favorable.
than the one-site reaction. In the case of the two-site reaction, the $\text{B–H}$ hydrogen would be abstracted as $\text{H}^+$, similar to the case of $\text{B–H}$ bond breaking on the $\text{G = O}$ double bond of germanone [8]. The natural atomic charge was calculated by natural population analysis to observe migration of the electron. The overall charge of $\text{BH}_3$, which is originally zero, becomes $\sim-0.442$ e when $\text{BH}_3$ coordinates to the phosphorus atom. Thus, the electron migrates to the hydrogen atom, and finally, the strongly negatively charged hydrogen would be abstracted by the other phosphorus atom, as shown in case 2 in Figure 5.

4 CONCLUDING REMARKS

Phosphinophosphinidene, which is a phosphorus analog of carbene, has been experimentally shown to have electron acceptor character. Because the terminal phosphorus atom would have inherent electron donor ability, chemical reaction involving $\sigma$ bond cleavage on the phosphorus atom through charge-transfer interaction is expected. In this study, we explored the possibility of $\sigma$ bond cleavage by phosphinophosphinidene by means of the density functional method using $\text{H}_2$, $\text{CH}_4$, $\text{H}_2\text{O}$, $\text{NH}_3$, and $\text{BH}_3$ as model substrate. It was predicted that the PP site of phosphinophosphinidene is reactive for $\sigma$ bond cleavage in both polar and nonpolar molecules. When the reaction starts, the $\text{P–P}$ bond bends in any case. Therefore, the energy level of the $\pi$ and the $\pi^*$ molecular orbitals of the $\text{P–P}$ bond changes and the charge-transfer interaction with the substrate is facilitated. For nonpolar molecules (i.e., $\text{H}_2$ and $\text{CH}_4$), cleavage of the $\text{H–H}$ bond proceeds at an energy barrier of about 22–24 kcal/mol. In contrast, for polar molecules (i.e., $\text{H}_2\text{O}$ and $\text{NH}_3$), $\text{O–H}$ bond cleavage occurs at the two sites of the phosphorus atoms by the abstraction of hydrogen as a proton, with an energy barrier of less than 10 kcal/mol. For $\text{B–H}$ bond cleavage in $\text{BH}_3$, both the single and dual sites of the phosphorus atoms are available with an energy barrier of less than 10 kcal/mol.

SUPPORTING INFORMATION

Optimized equilibrium and transition state structures and their Cartesian coordinates (PDF).

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