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Investigation of Reduction Mechanism in the Borohydride-Mediated Synthesis of Silver
Nanoparticles



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Submitted to the Department of Chemistry of Chulalongkorn University in partial fulfillment
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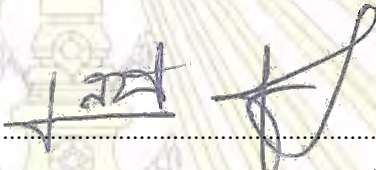
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Abstract

The silver nanoparticles have been used in various industrial applications. The conventional synthesis method is the reduction of silver(I) ion with borohydride solution, but the mechanism for this reaction has unknown. Here, the investigation of reduction mechanism of silver(I) ion by borohydride, synthesis of silver nanoparticles, was studied by *ab initio* and Density Functional Theory (DFT) calculation. The HF/6-31++G** and B3LYP/6-31++G** levels were used in this study. LANL2DZ an Effective Core Potential (ECP) basis set was used in the calculation of the silver(I) ion. In parts of the transition state and activation energy (E_a), the QST2 was selected as the method for calculations. Mechanism modeling was proposed in three mechanisms that was mechanism I ($\text{BH}_4\text{-Ag}$), mechanism II ($2\text{BH}_4\text{-Ag}^-$) and mechanism III ($\text{BH}_3\text{OH-Ag}^-\text{-BH}_4^-$) borohydride-mediated in transition state, respectively. The results showed that the mechanism II and mechanism III modeling could display the transition state. The mechanism III exhibit less activation energy, and produces more exergonic energy than mechanism II. Therefore, the mechanism III was a reasonable pathway for the synthesis of silver nanoparticles.

Keywords: *Ab initio*, Borohydride, DFT, Silver nanoparticles, Transition state

ชื่อโครงการ การตรวจสอบกลไกการเกิดปฏิกิริยารีดักชันในสารตัวกลางโบโรไฮไดรด์ของการสังเคราะห์อนุภาคนาโนเงิน

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บทคัดย่อ

อนุภาคนาโนเงินนำมาใช้ในงานอุตสาหกรรมต่าง ๆ มากมาย วิธีการสังเคราะห์โดยทั่วไปคือการรีดักชันของสารละลายโบโรไฮไดรด์กับไอออนเงิน(I) แต่ยังไม่ทราบกลไกสำหรับปฏิกิริยานี้ การตรวจสอบกลไกการเกิดปฏิกิริยารีดักชันของไอออนเงิน(I) ด้วยไอออนโบโรไฮไดรด์ในการสังเคราะห์อนุภาคนาโนเงิน ใช้เทคนิคการคำนวณทางเคมีควอนตัม *ab initio* และ Density Functional Theory (DFT) โดยคำนวณในระดับ HF/6-31++G** และ B3LYP/6-31++G** ใช้ LANL2DZ เป็น Effective Core Potential (ECP) basis sets สำหรับการคำนวณไอออนเงิน(I) ในการศึกษาสภาวะทรานซิชั่นและค่าพลังงานก่อกัมมันต์ของกลไกการเกิดปฏิกิริยาใช้วิธี QST2 ในการคำนวณ แบบจำลองกลไกการเกิดปฏิกิริยาเสนอเป็นสามกลไก ได้แก่ กลไกการเกิดปฏิกิริยาที่หนึ่ง กลไกการเกิดปฏิกิริยาที่สอง และกลไกการเกิดปฏิกิริยาที่สาม ซึ่งมีสารตัวกลางโบโรไฮไดรด์ในสภาวะทรานซิชั่นเป็น $(\text{BH}_4\text{-Ag})$ $(2\text{BH}_4\text{-Ag}^-)$ และ $(\text{BH}_3\text{OH-Ag}^-\text{-BH}_4)$ ตามลำดับ ผลการศึกษาที่ได้พบว่าสามารถตรวจสอบสภาวะทรานซิชั่นจากแบบจำลองกลไกการเกิดปฏิกิริยาที่สองและแบบจำลองกลไกการเกิดปฏิกิริยาที่สาม โดยกลไกการเกิดปฏิกิริยาที่สามมีค่าพลังงานก่อกัมมันต์น้อยกว่ากลไกการเกิดปฏิกิริยาที่สองและคายพลังงานออกมามากกว่ากลไกการเกิดปฏิกิริยาที่สอง ดังนั้นกลไกการเกิดปฏิกิริยาที่สามจึงเป็นวิถีทางที่เหมาะสมในการสังเคราะห์อนุภาคนาโนเงินได้

คำสำคัญ: *ab initio* โบโรไฮไดรด์ ดีเอฟที สภาวะทรานซิชั่น

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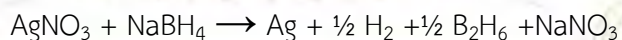
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Chapter I

Introduction

Nanotechnology is an important field of modern research dealing with design, synthesis, and manipulation of particles structure ranging from approximately 1-100 nm. There are many materials that were developed into nano size to study the properties of them such as, gold nanoparticles, platinum nanoparticles, copper nanoparticles and especially silver nanoparticles¹⁻⁴.

Silver nanoparticles are widely studied because of the unique properties which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products, and electronic components⁵⁻⁶. Several physical and chemical methods have been used for synthesizing and stabilizing silver nanoparticles. One of the most popular methods to synthesize silver nanoparticles is the use of sodium borohydride to reduce silver nitrate⁷⁻⁸. A large excess of sodium borohydride is needed both to reduce the ionic silver and to stabilize the formed nanoparticles. The silver nitrate reduction reaction can be written as



The above reaction produces a lot of heat, exergonic energy, and very fast reaction. However, there is no research study on the mechanism of the reaction. Moreover, there has been no research study of bond length between boron and silver atom which is an important data for studying the mechanism in the borohydride-mediated silver nanoparticle formation. Since there is no report of bond length between boron and silver atom, the bond length between boron and other metals will be required in this study. From the literature review, Lippard S. J. and Melmed K. M. studied the structure of transition complex of borohydride and copper(I) and reported that the bond length was approximately 2.184 Å⁹, shown in **Figure 1**. Hence, we selected copper as a model for this study because copper being in the same periodic element group with silver, has similar properties.

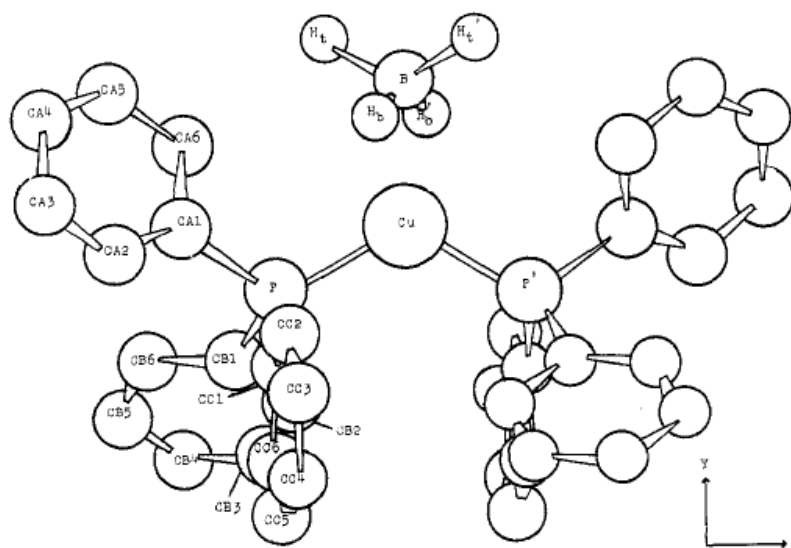


Figure 1: Structure of transition complex of borohydride and copper(I)

Because the experiments cannot provide the energy and the transition state of the reaction, computational modeling has thus become an important device to investigate the reduction mechanism¹⁰⁻¹². The methods in computational chemistry are *ab initio*, density functional theory, molecular mechanics, and molecular dynamics. Generally, the questions of computational investigation involve the molecular geometry, energies of molecules and transition state, chemical reactivity, the physical properties of substances and the interaction of a substrate with enzyme, IR, UV, and NMR spectra¹³

This study demonstrated the transition state of the reduction mechanism in the borohydride-mediated synthesis of silver nanoparticles with the computational chemistry and calculated by Gaussian 09 program¹⁴ to optimization. We selected the split valence (6-31++G**) and effective core potential (ECP) basis sets. There are three steps for this study. Firstly, we optimize borohydride and copper(I) to verify the ECP basis sets. Secondly, we propose some mechanisms of borohydride and silver(I) ion. Finally, we elucidate the mechanism with B3LYP, HF and MP2 in gas and solution phases, and utilize TS and QST2 methods to derive the transition state.

Chapter II

Theory

2.1 Introduction to quantum chemistry

Classical mechanics describe the motions and the interactions of mass, but it cannot describe the phenomena of black-body radiation, the photoelectric effect and the hypothetical wave-particle dualism of electron or photon. Because atoms and molecules have tiny mass and volume, the study of atoms or molecule cannot be explained by the classical mechanics. The quantum mechanics is an alternative approach to account atoms and molecules. The wave function, which is the coordinate of particles at time-independent to predict the properties of atoms and molecules, can be obtained from the solution of Schrödinger equation¹⁵.

Calculation of quantum mechanics can be classified into two groups of methods. First, *ab initio* is supported by an atomic and molecular orbitals theory. Density Functional Theory (DFT) is another approach, which is based on the electron density.

2.2 *Ab initio*

The *ab initio* is a computational method, which used for quantum chemistry to solve the Schrödinger equation connected to electron distribution. The wave function of atom or molecule can be written in a form of Slater determinant with coordination x , y and z of the orbital. Moreover, it composed of spin orbitals, spin up (α) or spin down (β). This method is used for calculating of molecular geometries, energy, vibrational frequencies, spectra, ionization potentials and electron affinities.

2.2.1 The Hartree-Fock method

The Hartree-Fock (HF) method is one of the *ab initio* calculations, and HF is pseudo-eigenvalue equation¹⁶⁻¹⁷ because of the Fock operator depending on Ψ ,

$$\hat{F}(1) = \hat{H}^{core}(1) + \sum_{j=1}^n (2\hat{J}_j(1) - \hat{K}_j(1))$$

when \hat{J} and \hat{K} are 2-electrons integral operators, \hat{J} refers Coulombic integral operator and \hat{K} is Exchange integral operator depending on Ψ . In the Fock operator (\hat{F}), the term \hat{H}^{core} is core Hamiltonian.

The aim of HF calculation is the energy of system which can be written as

$$E^{HF} = 2 \sum_{i=1}^n \epsilon_{ii} - \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij}) + \sum_{I>J}^{nuclei} \sum_{J=1}^{nuclei} \frac{Z_I Z_J}{R_{IJ}}$$

In the HF equation, there are 3 terms of calculation. The first term is a summation of single electron. The second term is the corrected term of the first term and the last term is an inter-nuclei repulsion of the system.

After calculating, the previous wave function is improved to a new one and a calculation uses this wave function. The procedure calls self-consistent field (SCF) method, used for calculation of a minimum energy that the different between a new wave function and a previous is sufficiently small.

2.2.2 The Møller-Plesset Perturbation Theory

The Møller-Plesset (MP) Perturbation Theory is a computational theory of *ab initio* method¹⁸. It improves the Hartree-Fock method by adding correlation effects of electron. Calculation has many levels such as zeroth-order (MP0), first-order (MP1) and second-order (MP2) which referred by MPn where n is the order of the perturbation theory in shortened.

The MP2 energy can be calculated as a sum of the Hartree-Fock (HF) energy and correction term, which h is a perturbation adjustment.

$$E_{MP2} = E_{HF}^{total} + E^{(2)}$$

$E^{(2)}$ is a sum of terms that models the promotions of pairs of electrons to the virtual from the occupied orbitals. Electron has more room to move, easier to avoid one another and decreases inter electronic repulsion resulting in a lower electronic energy.

2.3 Density Functional Theory

Density functional theory (DFT)¹⁹ uses for investigating the electronic structure of many electrons or molecules system. The DFT is based on two theory of Hohenberg-Kohn²⁰. First, the demonstration of the ground state of many-electron system determines via electron density with the spatial coordination. Second, the determination of energy functional for the system proves the correct electron density of the ground state, which minimizes the energy functional. The difference between MO and DFT theory are that MO theory optimizes a wave function while DFT optimizes an electron density.

2.3.1 B3LYP

B3LYP²¹ is a hybrid exchange-correlation functional, expressed by a combination of Becke 1988 (B88)²² exchange and Lee-Yang-Parr (LYP)²³ correlation GGA functional, Slater (S) exchange²⁴ and Vosko-Wilk-Nusair (VWN) correlation²⁵ LDA functional, and the HF integral with three parameters.

$$E_{xc}^{B3LYP} = (1 - a) E_x^{LSDA} + a E_x^{exact} + b \Delta E_x^{B88} + (1 - c) E_c^{LSDA} + c E_c^{LYP}$$

Where, E_x^{LSDA} , E_x^{exact} and E_x^{B88} are exchange functional terms, E_c^{LSDA} and E_c^{LYP} are the correlation functional terms, and an a , b , and c are 0.2, 0.72, and 0.8 respectively. These parameters are determined by the prediction and the experimental data fitting. B3LYP is a popular DFT functional because it gives very accurate results for a wide variety of chemical properties.

2.4 Transition State Theory

Transition-state theory (activated-complex theory or theory of absolute reaction rates potential energy curve) is a theory about the energy transition states treatment of a chemical reactions and the other processes, which is regarded by a continuous change in the relative positions and potential energies of the atoms and molecules. For the arrangement of the atoms or molecules, there is an intermediate configuration having a maximum of the potential energy. This intermediate configuration is known as the activated complex and its state is the transition state. In transition state theory, the activated complex is considered to form in equilibration state with the atoms or molecules in the initial state. Hence, its statistical and thermodynamic properties can be specified. The rate at the final state is obtained by the number of activated formed complexes and the frequency, which go over to the final state. These quantifications can be calculated by using statistical-mechanical principles. The rate constant of the process can be expressed in terms of atomic and molecular dimensions, atomic masses, and interatomic or intermolecular forces. Then, the transition state theory can be formulated in the terms of thermodynamics.

2.4.1 QST2

Quadratic synchronous travel (QST) is a method, used to search the maximum along a bended way (parabola) that connecting to reactants and product and to find the minimum whole directions perpendicular to the bended way. By parabolic interpolation, this method provides for lower level bound of the energy boundary. The most extreme along those QST ways is better estimate of the transition structure. Frequently, one can discover a structure very near the quadratic area of the TS from where the semi Newton techniques may control. For example, QST2 obliges two atom specifications, for the reactant and product, as it enter the reactant, the product, and a starting structure to the transition state, respectively. The order of the atoms must be identical within all molecule specifications.

At a transition structure for a practically equivalent to response may be not accessible a QST2 methodology may be used to produce a starting guess of the transition

structure for the optimization. In this approach, a structure on the reactant side and one on the product side are used to provide a crude evaluation of the TS geometry to estimate the direction of the reaction path.

2.5 Polarizable Continuum Model (PCM)

A standard method to deal with the understanding about the solvation is the Polarizable Continuum Model (PCM). This model is based on the idea of generating of overlapping sphere of each atom within the molecule inside of a dielectric continuum. It is different from Onsager methodology techniques, which utilizes a single sphere to encompass those entire atom and for more correctness over figuring out the solute-solvent interaction energy. This strategy treats the continuum as a polarizable dielectric and may be referred to the dielectric PCM (DPCM). The PCM model calculates the free energy for solvation by endeavoring to sum over three different terms.

2.6 Basis sets

Basis sets are sets of mathematical functions, or called basis functions, which relate to the distribution of electrons around an atom. When the atomic basis functions, which give the distribution of electrons in the molecule, are combined, it is called the linear combination of basis functions or linear combination of atomic orbitals.

2.6.1 Split Valence Basis Sets

Split valence basis functions, such as 6-31G and 6-311G. They are in need of one contracted Gaussian-type function for core orbitals and multiple contracted functions for valence orbitals. Mostly, valence orbitals contribute to chemical bonds in molecules while core orbitals are less interactive. Therefore, the usage of basis functions for valence orbitals is reasonable for calculating states of electrons accurately while all basis functions are saved.

Pople-type basis functions, and also the 6-31G basis, are included in this type of basis function. “6-31” means the scope of the contraction and split, in which “6” is contracted basis functions of 6 fundamental functions used for core orbitals and “31” is doubly-split basis functions which consist of contracted basis functions of 3 primitive functions and one uncontracted basis function used for valence orbitals. “6-311G” is in need of triply-split basis functions for valence orbitals.

2.6.2 Polarization Basis Sets

Polarization function-supplemented basis functions, such as 6-31G* and 6-31G(d), need polarization functions in order to unite the anisotropic nature of molecular orbitals having origin from chemical bonds. Comparing to the atomic orbitals, polarization functions usually have higher angular momenta than the highest level of the other which create the molecular orbitals. In the Pople-type basis functions, when polarization functions are included, it is represented by an asterisk “*” such as “6-31G*.” For a single asterisk, it means that all atoms except hydrogen atoms are added by one polarization function, while a double asterisk means that each hydrogen atom is also added by one p orbital function. Recently, the form of polarization function is often written explicitly, such as “6-31G(d),” because this basis function is added by a d orbital function.

2.6.3 Diffusion Basis Sets

Diffuse-function-augmented basis functions, such as 6-311+G(d) and 6-311++G(2df,2pd), use the diffuse functions to consider bound electrons weakly. Particularly, these diffuse functions are necessary in the calculations of the anions and excited states of small molecules. If diffuse functions are added, it is shown by a plus “+” in Pople-type basis functions. “6-311+G(d)” means increasing sp diffuse functions which merge s and p orbitals for all atoms except hydrogen atoms, and “6-311++G(2df, 2pd)” means adding two d and one f diffuse functions for all atoms except hydrogen as well as two p and one d orbital functions for hydrogen.

2.6.4 Effective Core Potential (ECP) Basis Sets

Effective core potential (ECP) basis functions, such as LANL2DZ and Stuttgart-ECP, are nearly same as core orbitals, which have small effect on reactions and properties in most systems, while effective potentials start to reduce the number of basis functions rapidly. Particularly, ECP basis functions are used for the fourth-period atoms or later in most cases, excluding the reactions and properties in which core electrons participate, and have high accuracy in the calculated results. The most widely used ECP is the relativistic ECP (RECP) which unites the relativistic effects of the core electrons. The best known ECP basis functions are LanL2DZ of Los Alamos National Laboratory (USA), the Stuttgart relativistic small core (STRSC) and large core (STRLC) ECP basis functions (Germany). Moreover, the *ab initio* model potential (AIMP) basis functions are developed to reproduce the *ab initio* potentials of core orbitals with nodes in order to study the indirect effects of core electrons.



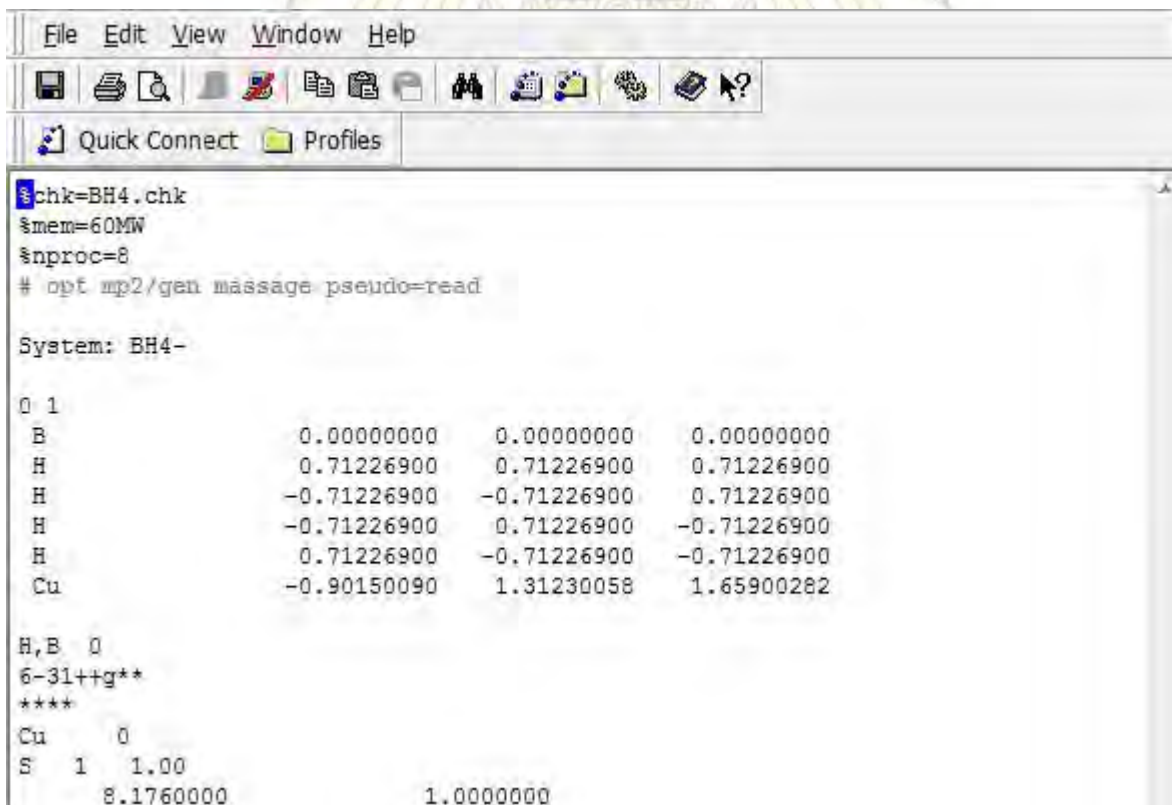
Chapter III

Computational Details

In this study, we utilized the Gaussian 09 program for optimizing atom, molecule, and mechanism. The B3LYP, HF and MP2 methods were employed to study the interaction between borohydride (BH_4^-) and silver(I) ion (Ag^+). Then, TS and QST2 were employed to study the transition state. Moreover, we selected 6-31++G** and LANL2DZ basis sets for accuracy results of these systems.

3.1 Verification of basis set

The structures of copper(I) and borohydride were drawn by the GaussView program and optimized by MP2 method, coupling with the 6-31++G** basis sets, shown in **Figure 2**.



```
chk=BH4.chk
$mem=60MW
$nproc=8
# opt mp2/gen message pseudo=read

System: BH4-

0 1
B          0.00000000    0.00000000    0.00000000
H          0.71226900    0.71226900    0.71226900
H         -0.71226900   -0.71226900    0.71226900
H         -0.71226900    0.71226900   -0.71226900
H          0.71226900   -0.71226900   -0.71226900
Cu        -0.90150090    1.31230058    1.65900282

H,B  0
6-31++g**
****
Cu    0
S  1  1.00
    8.1760000    1.0000000
```

Figure 2: Input for optimization between copper(I) and borohydride

The calculations for studying bond length between copper(I) and borohydride have several ECP basis sets of copper(I), such as CRENBL ECP, CRENBS ECP, LANL08, LANL08(f), LANL2DZ ECP, LANL2TZ(f), SBKJC VDZ ECP, and Stuttgart RSC 1997 ECP.

3.2 Propose the reduction mechanism

3.2.1 Mechanism I

This mechanism is proposed from the basic reaction between borohydride and silver(I) to synthesize silver nanoparticles⁸. The borohydride and silver(I) are mixed together in a gas solution, forming the borohydride-mediated (BH₄-Ag) in transition state. The resulting products are the silver nanoparticles, hydrogen gas and diborane, shown in **Figure 3**.

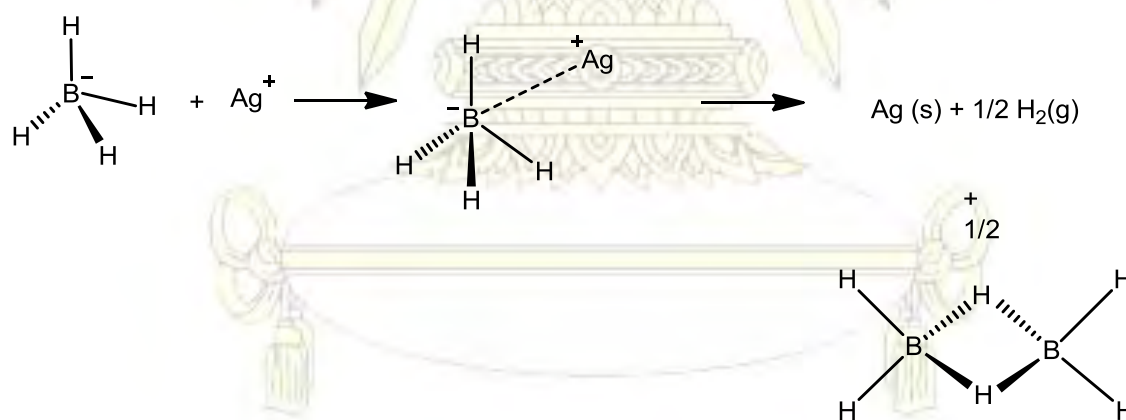


Figure 3: Mechanism I

3.2.2 Mechanism II

This mechanism is proposed from the reaction between borohydride and silver (I) to synthesize silver nanoparticles similar to the mechanism I, but we add one molecule of borohydride to produce borohydride-mediated in 1:2 ratio between silver(I) and borohydride. Firstly, silver(I) ion and two molecule of borohydride react, forming the borohydride-mediated ($2\text{BH}_4\text{-Ag}^-$) in transition state and producing hydrogen gas. Secondly, the borohydride-mediated reduces silver(I) ion. Finally, the resulting products are the silver nanoparticles and BH_3 , shown in **Figure 4**.

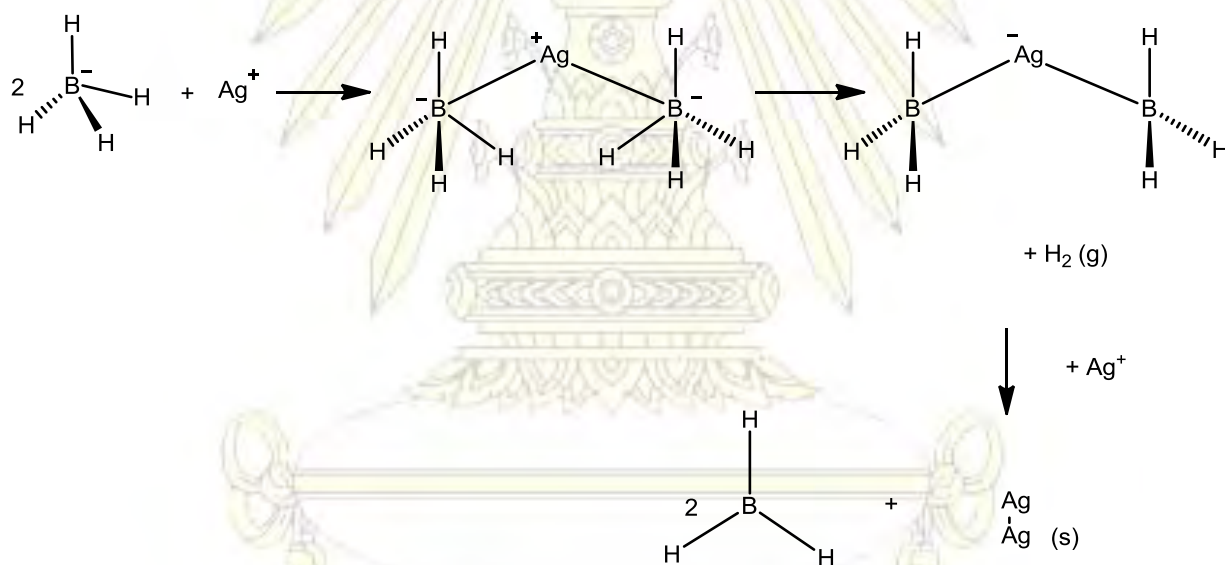


Figure 4: Mechanism II

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3.2.3 Mechanism III

This mechanism is proposed from reaction between borohydride and water to produce hydrogen gas²⁶. Firstly, the borohydride and water react, forming borohydride-mediated (BH_3OH) in transition state and producing hydrogen gas. Secondly, the BH_3OH and silver(I) ion to give $\text{BH}_3\text{OH-Ag}$ and the borohydride which then forming the borohydride-mediated ($\text{BH}_3\text{OH-Ag}^-\text{BH}_4^-$) in the transition state and producing water. Finally, the resulting products are the silver nanoparticles and BH_3 , shown in **Figure 5**.

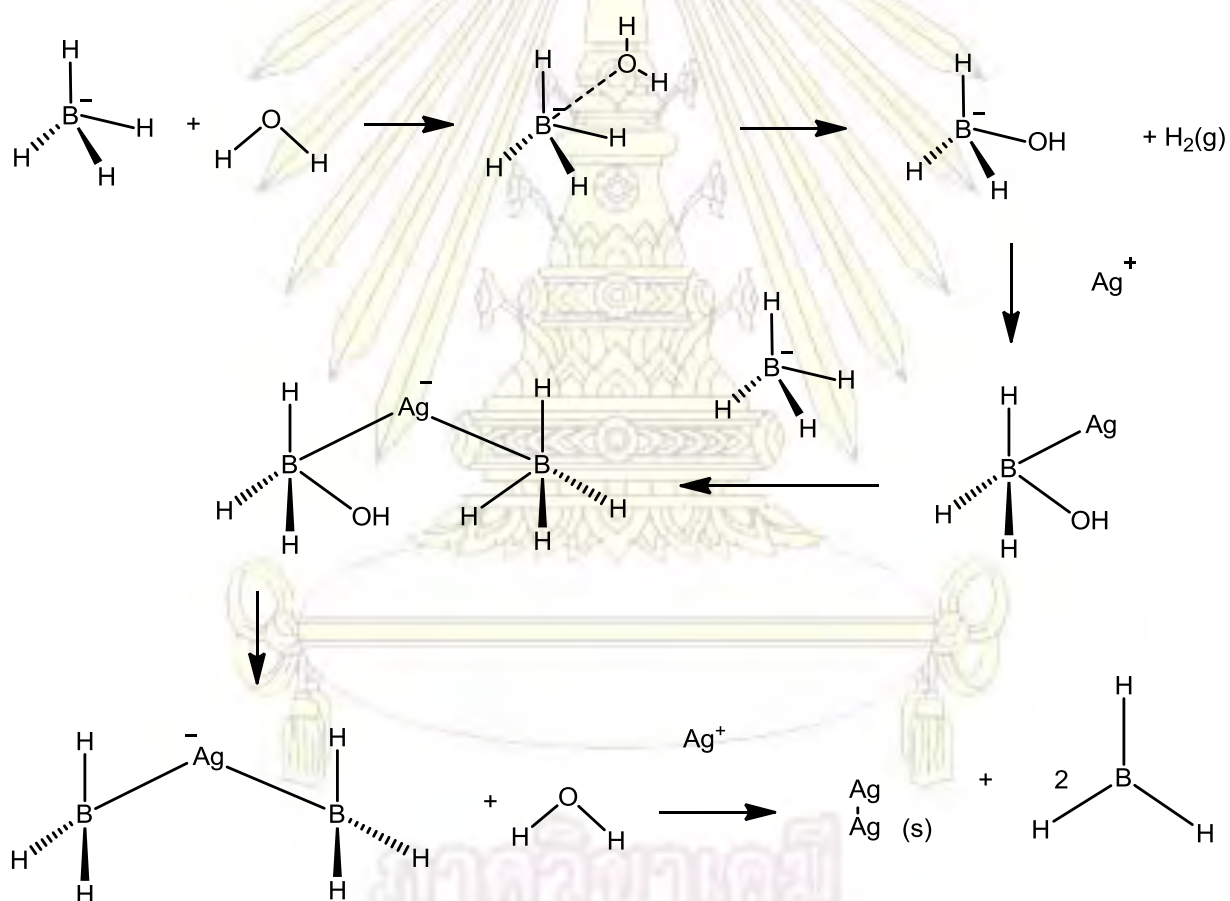


Figure 5: Mechanism III

There were several sections in this work, the first section was the optimizations of the systems by HF, MP2, and B3LYP. The second section was the optimizations of the system with PCM in calculations to study an effect of solvent. The last section was the optimizations of the transition state of borohydride-mediated by TS and QST2.

The interaction energies between reactants and products of all mechanisms are calculated through the following equation:

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$



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Chapter IV

Results and Discussions

In the calculations with the computational methods for investigation of reduction mechanism in the borohydride-mediated of silver nanoparticles, we separated the result into two sections. At first, we optimize bond length between copper(I) and borohydride by MP2 for the verification of a suitable basis set in further calculations the verification of a suitable basis set in further calculations. Then, we optimize mechanism I, mechanism II and mechanism III by B3LYP, MP2, PCM, and HF for optimizing structure, and TS and QST2 for optimizing the transition state.

4.1 Verification of basis set

According to the available experimental data of copper(I) and borohydride⁹, we optimized copper(I) and borohydride by MP2 method, coupling with 6-31++G** basis sets and numerous ECP basis sets of copper(I). Then we worked on the similar ECP basis sets ,which applied in silver(I) and borohydride is shown in **Table 1**.

Table 1. Bond length between copper(I) and borohydride compare with bond length between silver(I) and borohydride obtained by MP2 optimizations.

| Basis sets | B-Cu bond length (Å) | B-Ag bond length (Å) |
|------------------------|----------------------|----------------------|
| CRENBL ECP | 2.001 | 2.337 |
| CRENBS ECP | 2.106 | 2.366 |
| LANL08 | 2.062 | 2.346 |
| LANL08(f) | 2.05 | 2.303 |
| LANL2DZ ECP | 2.109 | 2.393 |
| LANL2TZ(f) | 2.049 | 2.304 |
| SBKJC VDZ ECP | 2.016 | 2.333 |
| Stuttgart RSC 1997 ECP | 2.012 | 2.318 |
| Explt | 2.184 | - |

The bond length between Cu atom and B atom from the experiment is 2.184 Å. From **Table 1**, bond length between Cu atom and B atom that resembles experimental value is value obtained from LANL2DZ ECP (2.109 Å). The bond length between Ag and B atom optimized by LANL2DZ is longest bond among all basis sets studied similar to B and Cu atom. Therefore, we have selected the LANL2DZ ECP basis sets for silver atom to calculate all mechanism in this work.

4.2 Optimization the transition state of reduction mechanisms

4.2.1 Mechanism I

This mechanism propose from the basic reaction between borohydride and silver(I) to synthesize silver nanoparticles⁸. Then, we optimize the mechanism by Gaussian 09 program, shown in **Figure 6**. Firstly, the borohydride and silver(I) are mixed together in a gas solution.

Then, they form the borohydride-mediated in transition state. Finally, the resulting products are the silver nanoparticles, hydrogen gas and diborane.

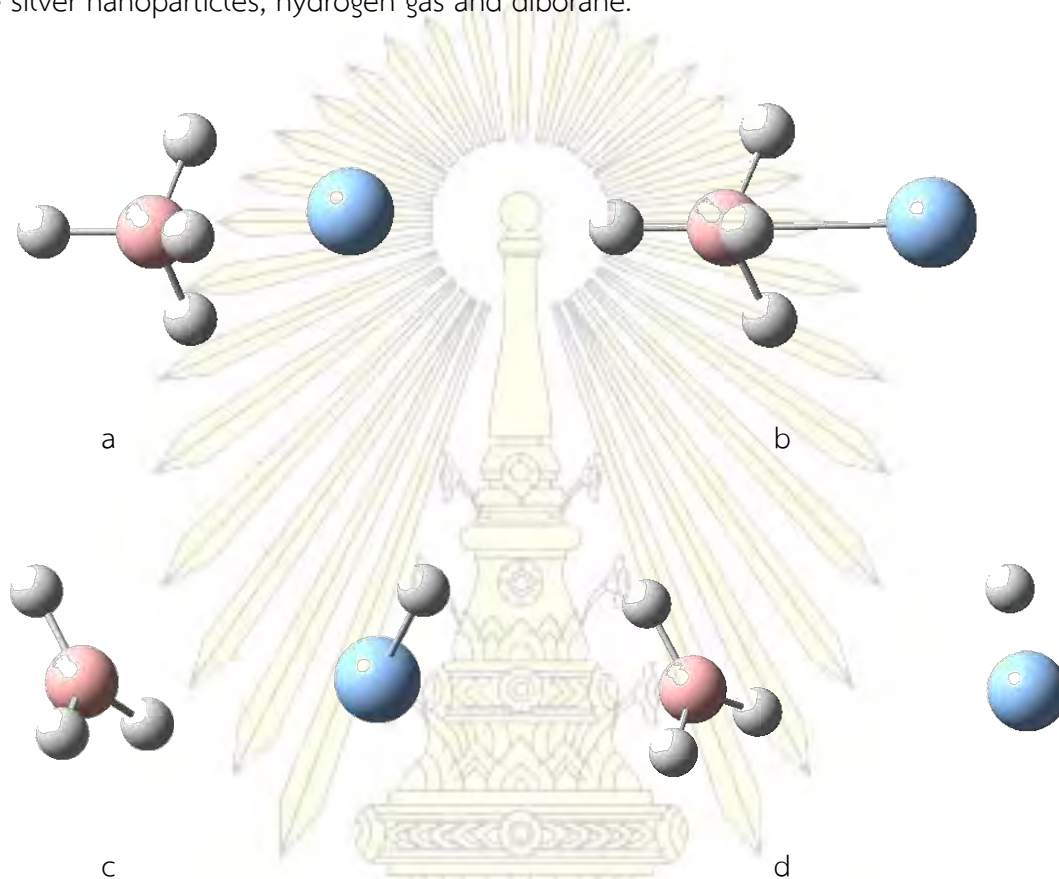


Figure 6: (a) borohydride and silver(I) ion before optimization, (b) borohydride and silver ion after optimization, (c) borohydride and silver(I) ion optimization in transition state and (d) borohydride and silver(I) ion optimization in transition state with PCM method.

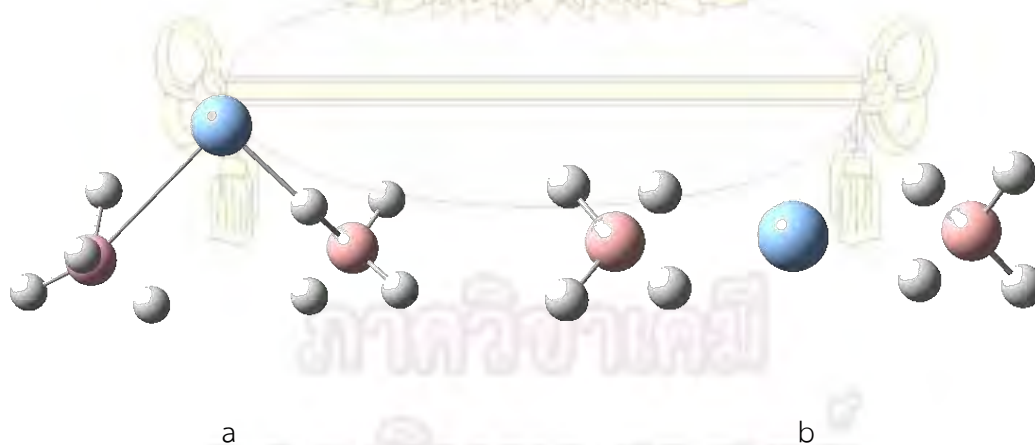
Table 2 Result of optimization mechanism I

| Methods | Results of optimization |
|---------|-------------------------|
| MP2 | Done |
| TS | Error |
| TS-PCM | Error |

From the optimizations of the transitions state of mechanism I, we can optimize the structure of mechanism I with MP2 method. However, the transition state with TS and TS-PCM method are unable to calculate due to the two negative eigenvalues in the structure of transition state, but the optimization requires only one negative eigenvalue. Hence, this optimization stopped. If the transition state optimization's achieved, it will form (c) or (d) in **Figure 6**.

4.2.2 Mechanism II

This mechanism is proposed from the reaction between borohydride and silver (I) to synthesize silver nanoparticles like the mechanism I, but one molecule of borohydride is added because the mechanism may produce borohydride-mediated in 1:2 ratio between silver(I) and borohydride. Then, we optimize the mechanism by Gaussian 09 program, shown in **Figure 7**. Firstly, silver(I) ion and two molecule of borohydride react. Secondly, they form the borohydride-mediated in transition state and produce hydrogen gas. Thirdly, the borohydride-mediated reduces silver(I) ion. Finally, the resulting products are the silver nanoparticles and BH_3 .



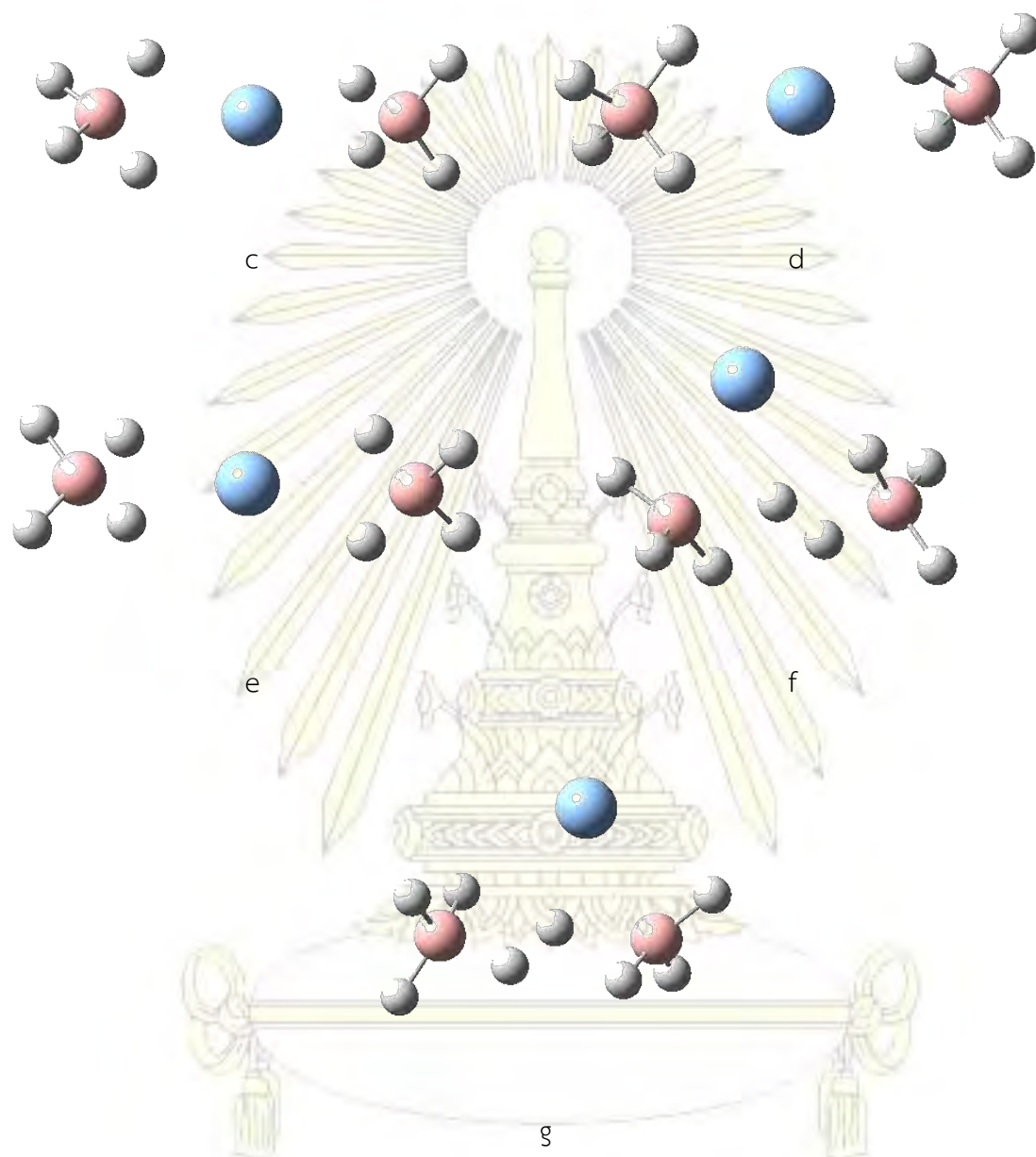


Figure 7: (a) borohydride 2 molecule and silver(I) ion before optimization, (b) borohydride 2 molecule and silver(I) ion after optimization, (c) borohydride-mediated optimization in transition state and (d) borohydride-mediated optimization in transition state with PCM method, (e) borohydride-mediated optimization by B3LYP, (f) borohydride-mediated optimization in transition state with QST2 method, (g) borohydride-mediated optimization in transition state by HF with QST2 method.

Table 3 Result of optimization mechanism II

| Methods | Results of optimization |
|----------|-------------------------|
| MP2 | Done |
| TS | Error |
| TS-PCM | Error |
| B3LYP | Error |
| MP2-QST2 | Error |
| HF-QST2 | Done |

From optimization of the transition state in mechanism II, we can optimize structure of mechanism II with MP2 method but we cannot optimize the transition state with TS, TS-PCM, and MP2-QST2 methods. The structures of mechanism II have five negative eigenvalues, but the optimization requires only one negative eigenvalue. Again, the optimization of this mechanism has stopped.

MP2 method may have great accuracy but it's a complicated optimization. Therefore, we selected HF method, which was less complicated than MP2, to optimize this mechanism. Then mechanism II can achieve the optimization, shown in **Figure 7 (g)**. Mechanism II has activation energy (E_a) of $84.31 \text{ kcal.mol}^{-1}$ and ΔE of $-91.80 \text{ kcal.mol}^{-1}$. Thus, mechanism II is an exergonic reaction, shown in **Figure 8**.

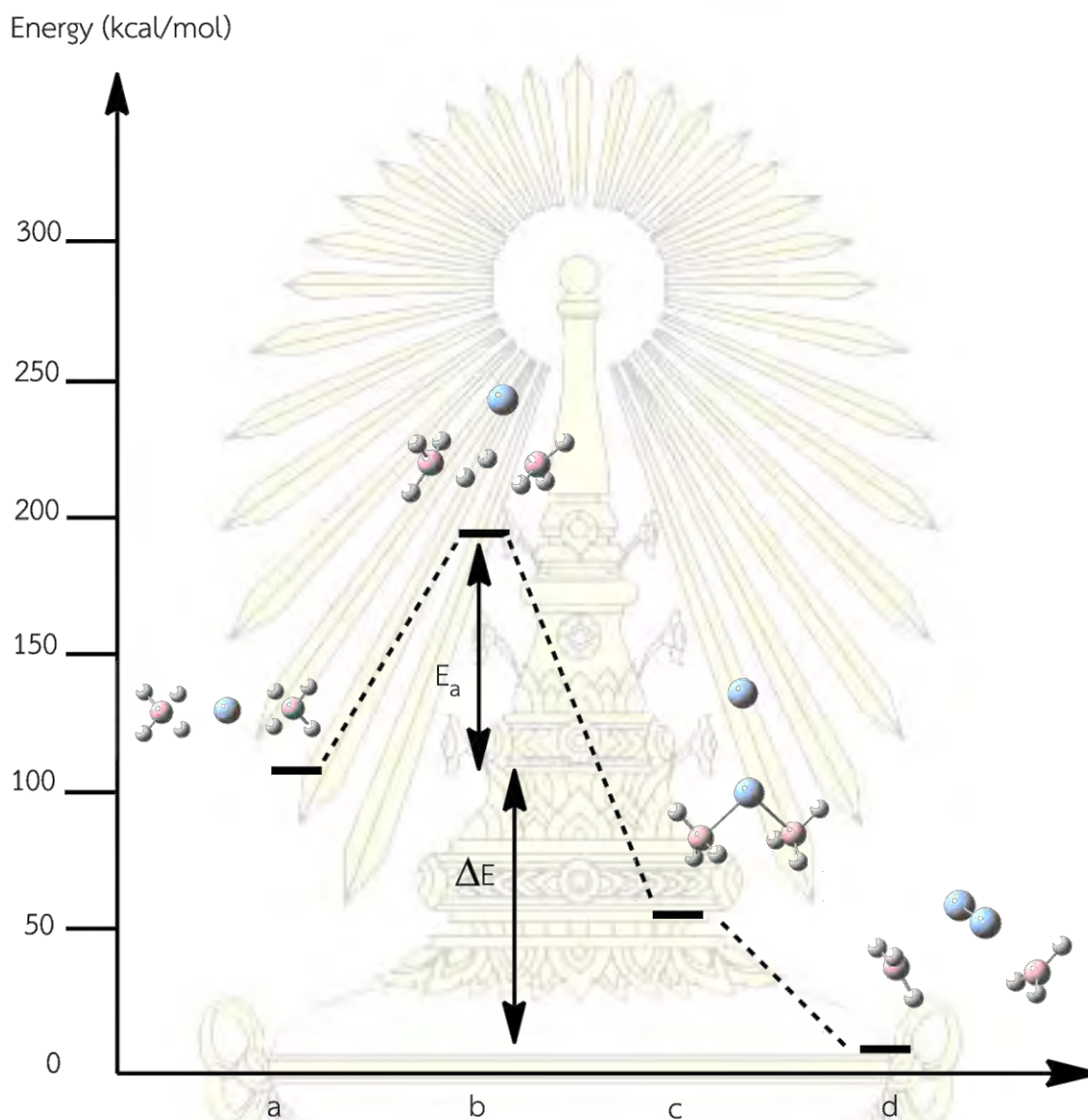
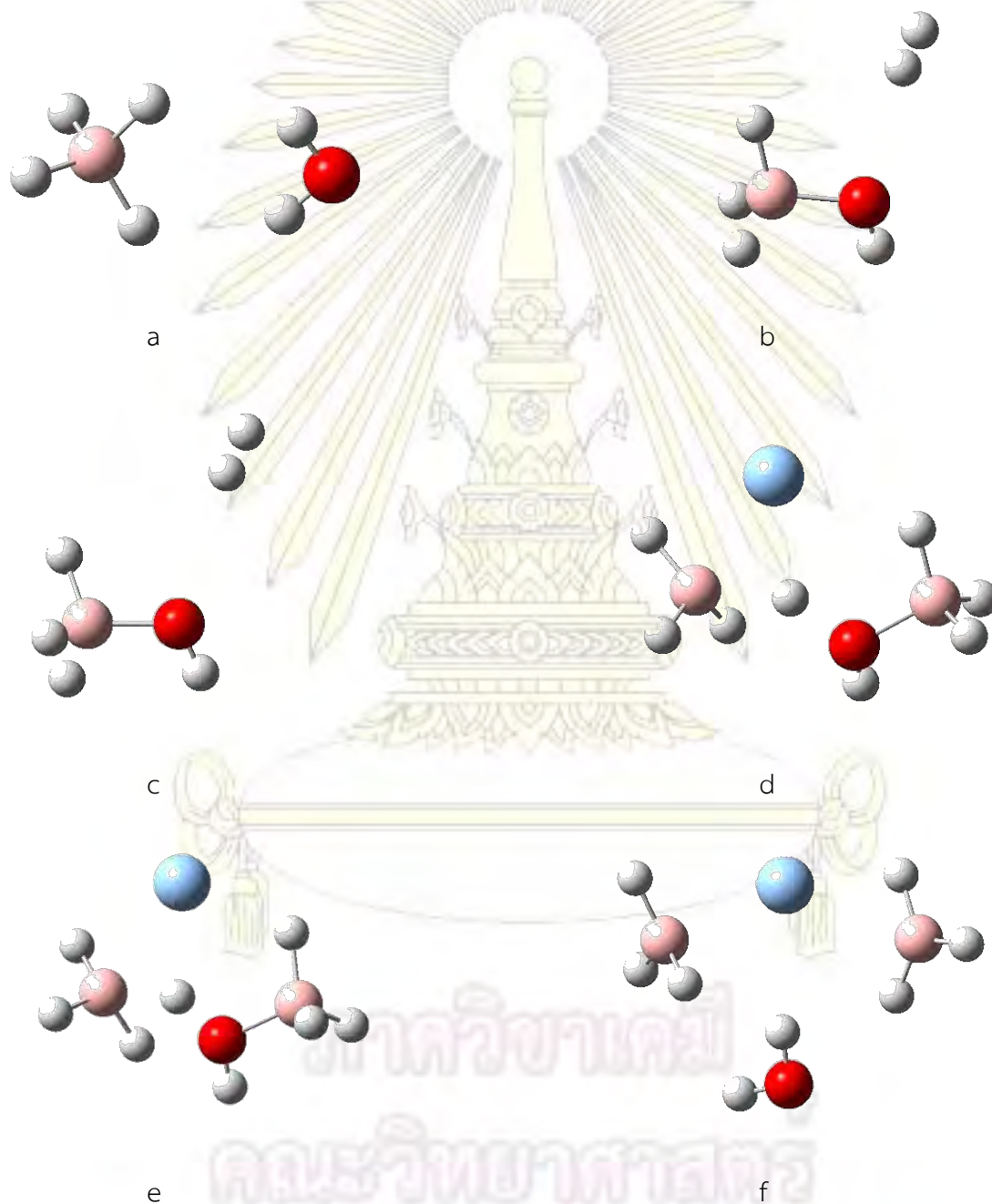


Figure 8: Transition state of mechanism II

4.2.3 Mechanism III

This mechanism is proposed from reaction between borohydride and water to produce hydrogen gas²⁶. Then, we optimize the mechanism by Gaussian 09 program, shown in **Figure 9**. The borohydride reacts with water. Then, they form borohydride-mediated (BH₃OH) in transition state and produce hydrogen gas. Next, the BH₃OH reacts with silver(I) to

the $\text{BH}_3\text{OH-Ag}$. After that the $\text{BH}_3\text{OH-Ag}$ reacts with borohydride form the borohydride-mediated ($\text{BH}_3\text{OH-Ag}^-\text{BH}_4^-$) in the transition state and produce water. Finally, the resulting products are the silver nanoparticles and BH_3 .



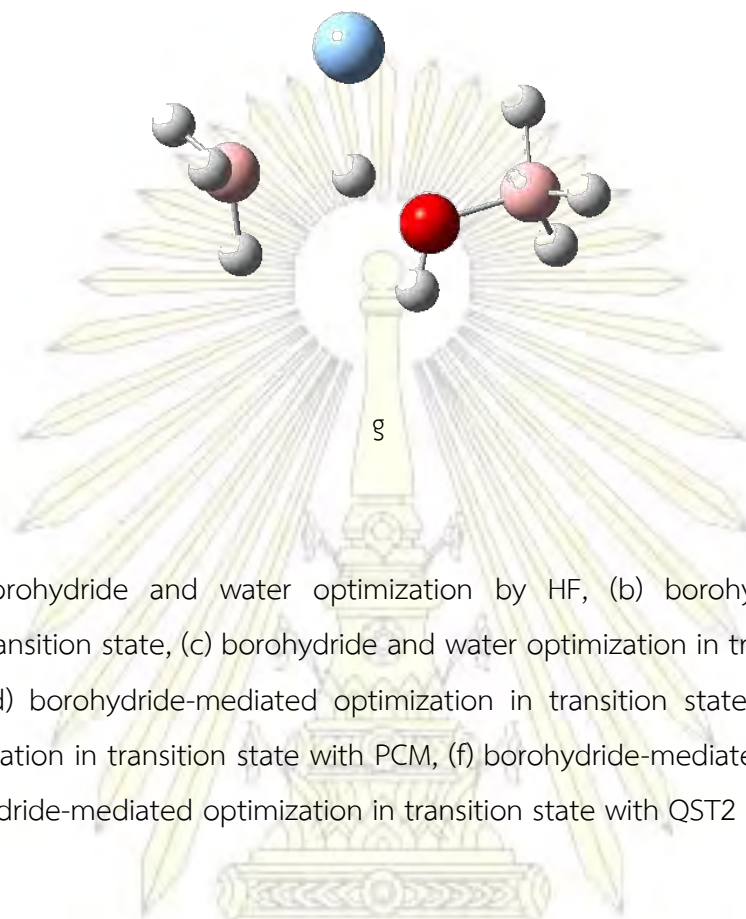


Figure 9: (a) borohydride and water optimization by HF, (b) borohydride and water optimization in transition state, (c) borohydride and water optimization in transition state with QST2 method, (d) borohydride-mediated optimization in transition state, (e) borohydride-mediated optimization in transition state with PCM, (f) borohydride-mediated optimization by B3LYP, (g) borohydride-mediated optimization in transition state with QST2 method.

Table 4 Result of optimization mechanism III

| Reaction | Methods | Results of mechanism III |
|--|---------|--------------------------|
| Borohydride and water | HF | Done |
| | TS | Error |
| | QST2 | Error |
| Borohydride-mediated ($\text{BH}_3\text{OH-Ag}^- \text{-BH}_4^-$) | TS | Error |
| | TS-PCM | Error |
| | B3LYP | Error |
| | QST2 | Done |

From the optimizations of the transition state in mechanism III, we can optimize structure of mechanism III (Borohydride and water) with HF method. Unfortunately, we cannot optimize the transition state with TS, TS-PCM, and QST2 method since the structures of mechanism III (Borohydride and water) have three negative eigenvalues while the optimization require only one negative eigenvalue. Hence, this mechanism's optimization stopped. In the part of borohydride-mediated ($\text{BH}_3\text{OH-Ag}^-\text{-BH}_4^-$), we cannot optimize structure using B3LYP method. Moreover, we cannot optimize the transition state with TS and TS-PCM methods. These structures have four negative eigenvalues, but the optimization requires only one negative eigenvalue. Therefore, this mechanism's optimization stopped. Finally, we can optimize the transition state with QST2 method, shown in **Figure 9 (g)**.

Although, we cannot optimize the transition state of borohydride and water, but we can optimize the energy of each molecule for calculating the possibility of a reaction. This mechanism is exergonic reaction that has ΔE of $-3.98 \text{ kcal.mol}^{-1}$. Moreover, borohydride-mediated transition state is an exergonic reaction, which has ΔE of $-276.39 \text{ kcal.mol}^{-1}$. The mechanism is unable to calculate the activation energy (E_a), because this mechanism display the increasingly reaction and produce the high thermal (exergonic reaction). Hence, effect from the character mechanism have impact on the calculation of the activation energy is shown in **Figure 10**.



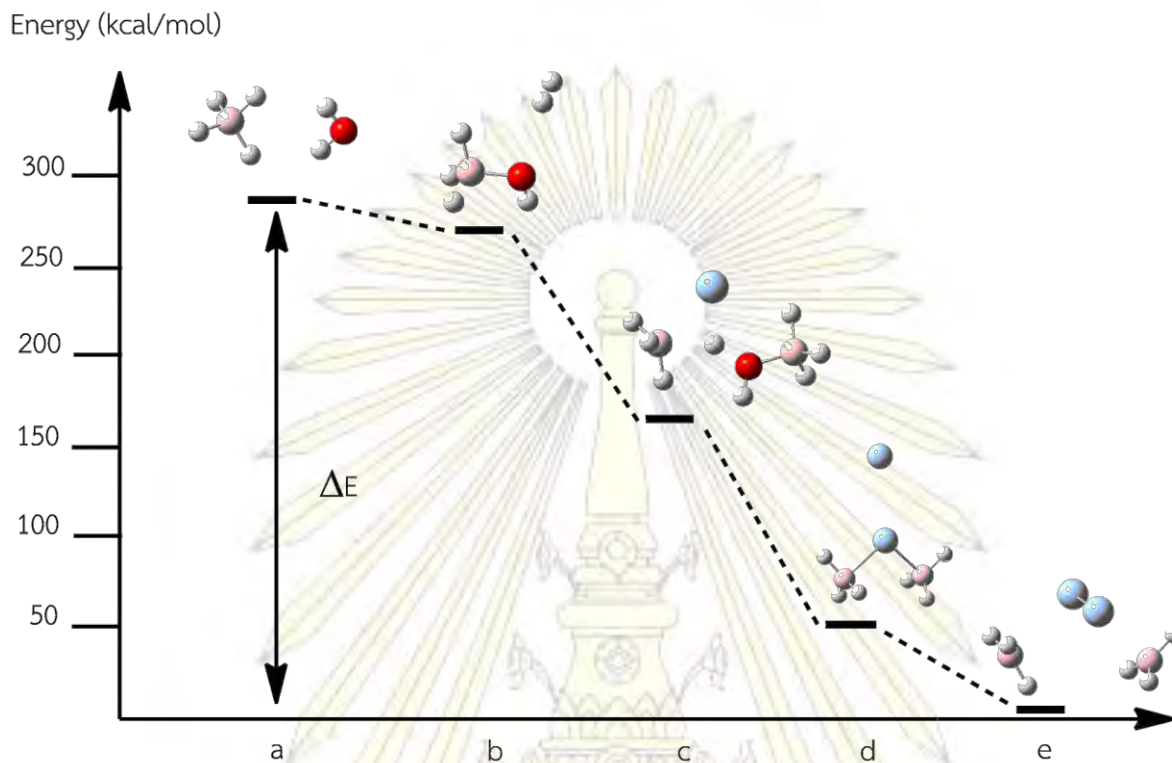


Figure 10: Transition state of mechanism III

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Chapter V

Conclusions

In this study, we select 6-31++G** and LANL2DZ ECP basis sets to optimize all mechanisms. We optimized the systems by HF, MP2 and B3LYP methods and the transition state of borohydride-mediated by TS and QST2 methods in gas and PCM phases. The optimization by QST2 and HF are the most suitable method to calculate the transition state because the optimization can be achieved. The proposed mechanisms, which could optimize the transition state, was mechanism II ($2\text{BH}_4\text{-Ag}^-$) and mechanism III ($\text{BH}_3\text{OH-Ag}^- \text{-BH}_4^-$) borohydride-mediated in transition state, respectively. The mechanism II has the activation energy (E_a) of $84.31 \text{ kcal.mol}^{-1}$ and releases the energy (ΔE) of $-91.80 \text{ kcal.mol}^{-1}$. Moreover, mechanism III releases energy of $-276.39 \text{ kcal.mol}^{-1}$. The mechanism III releases more energy than mechanism II by of $-184.59 \text{ kcal.mol}^{-1}$. In summary, we can understand and describe the reduction mechanism of borohydride-mediated to synthesize silver nanoparticles. Moreover, silver nanoparticles are synthesized from mechanism III satisfying a reasonable pathway.

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Vitae

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