



Mechanism of formation of ketones by palladium-catalysed desulfitative reaction: A density functional theory study



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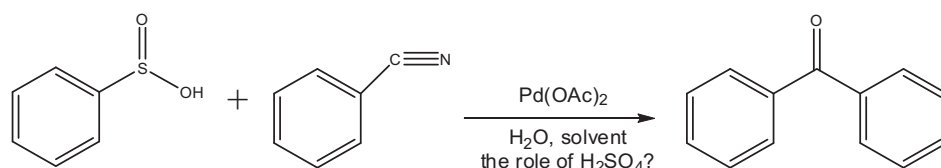
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ABSTRACT

A fast and efficient synthesis of the production benzophenone by palladium(II)-catalysed desulfitative reaction from benzenesulfonic acid and benzonitrile has been developed experimentally by the following equation. In this work, the reaction mechanism has been studied with the help of density functional theory calculations and the whole process of the reaction was elucidated in detail. The results show that the acetate present in the catalyst was found to directly participate in the reaction and the additive H₂SO₄ plays an important role in promoting the catalytic reaction.



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1. Introduction

Aryl ketones are fundamental building blocks in pharmaceuticals natural products and functional molecules [1–4]. Since the first synthesis of aryl ketones was targeted, the reaction has been intensively developed as an important branch of organometallic chemistry [5]. Over the past several years, many methods have been studied in order to generate aryl ketones by chemists, such as Friedel–Crafts acylation of aromatic compounds using the corrosive AlCl₃ [6], but it is difficult to separate the desired products from the isomeric mixtures using the method [7,8]. Transition-metal-catalysed cross-coupling reactions have become a powerful tool in generating aryl ketones. Among transition metals, palladium(II) complex has been the most commonly used in cross-coupling reactions, due to its ability to catalyze diverse reactions

and its high-functional group tolerance [2–4]. In recent years, increasing attention has been paid to palladium(II)-catalysed synthesis of aryl ketones and a great success has been achieved in experiments [9–15], e.g., Pd(OAc)₂ (Palladium acetate) has a well-catalysed performance. Nevertheless, the reaction mechanism is still not clear [16]. Solution of above-mentioned problems will be helpful to finding out the reaction details for palladium-catalysed desulfitative reaction. This task requires us not only to continue the experimental screening of new ligands and reaction conditions but also to employ a theoretical study to gain a rational understanding of the reaction mechanism [17,18]. In this work, the mechanism of palladium-catalysed desulfitative reaction of aryl-sulfonic acids with aryl nitriles to afford ketones will be elucidated in detail using the density functional theory (DFT) method [19–21]. In addition, the additive H₂SO₄ can effectively promote the palladium-catalysed desulfitative reaction in experiments, implying that H₂SO₄ plays an important role in the reaction. Here, the interaction details of H₂SO₄ in the reaction will be explored and

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research results are very significant for understanding the reaction mechanism and directing the formation of ketones by palladium-catalysed desulfurative reaction.

2. Computational methods

All theoretical calculations were carried out using the Gaussian 09 package [22], and all of the reported compounds were fully optimized at the Becke3LYP level [23,24] of density functional theory. The LanL2DZ with the effective core potential (ECP) basis set [25] was used for the S and Pd atoms, and the 6-31G(d) basis set [26,27] was used for the other atoms. Frequency calculations at the same level were performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Meanwhile, the intrinsic reaction coordinate (IRC) method [28,29] was further performed to confirm the transition states found connected relevant reactants and products. To consider the solvent effect, all the solvation energies were estimated by employing a conductor-like polarized continuum solvation model (CPCM) [30] with UFF sets of radii.

3. Results and discussion

Firstly, we investigate the mechanism of reaction in the absence of additive H_2SO_4 . The role of the acetate in the palladium catalyst will also be discussed. Then we investigate the mechanism of the reaction in the presence of additive H_2SO_4 , to shed light on how

the added H_2SO_4 promotes the reaction effectively. The relative free energies given in the potential energy profiles will be used to discuss related problems, unless otherwise stated.

3.1. Reaction mechanisms in the absence of additive H_2SO_4

Based on our work, the favorable reaction mechanism in the absence of additive H_2SO_4 has been shown in Figs. 1–3, where the benzenesulfonic acid and $\text{Pd}(\text{OAc})_2$ was taken as the energy reference point (see -). The reaction is found to undergo five major processes: (1) $\text{Pd}(\text{OAc})_2$ catalyst reacts with the benzenesulfonic acid to form a palladium salt (R \rightarrow A) in Fig. 1; (2) the elimination of SO_2 leads to the formation of intermediate B (A \rightarrow B) in Fig. 1; (3) intermediate B inserts into the C–N triple bond of benzonitrile to form a C–N double bond (B \rightarrow C) in Fig. 2; (4) reaction of hydrogen addition to generate a benzhydrylimine (C \rightarrow D) in Fig. 2; (5) in the acidic condition, hydrolysis of benzhydrylimine D to produce the product (D \rightarrow P) in Fig. 3. Calculated geometries together with key structural parameters (\AA) for selected species are illustrated in Fig. 4.

3.1.1. $\text{Pd}(\text{OAc})_2$ catalyst reacts with benzenesulfonic acid (R \rightarrow A)

As shown in Fig. 1, due to the strong coordination of Pd atom, the deprotonation reaction occurs between $\text{Pd}(\text{OAc})_2$ catalyst and benzenesulfonic acid. It can be clearly seen from Fig. 1, the formation of intermediate TS1-F does not require any barrier. The catalytic $\text{Pd}(\text{OAc})_2$ attacks benzenesulfonic acid via transition state TS1

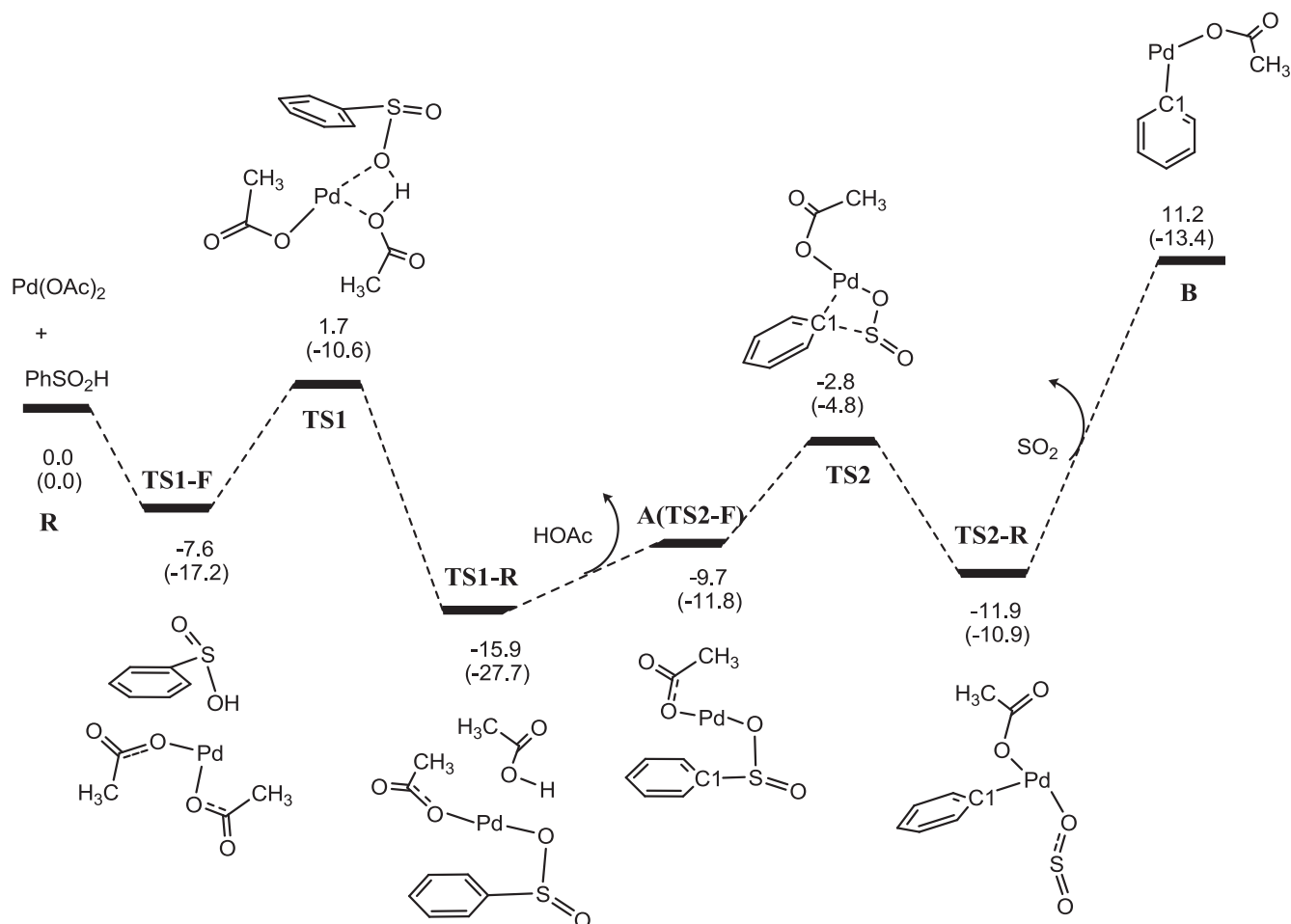


Fig. 1. Potential energy profile for palladium-catalysed desulfurative reaction in the absence of H_2SO_4 . Part 1: From R to B. The relative free energies and relative enthalpic energies (in parentheses) are given in kcal/mol.

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