



## Full Length Article

# Proton sponge as a new efficient catalyst for carbon dioxide transformation to methanol: Theoretical approach



Hossein Sabet-Sarvestani, Mohammad Izadyar\*, Hossein Eshghi, Nazanin Noroozi-Shad, Mehdi Bakavoli

Computational Chemistry Research Lab., Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this research, thermodynamic and kinetic aspects of methanol production by carbon dioxide in the presence of the proton sponge as the reaction catalyst and borane molecule as the reductive reagent were investigated theoretically. Proton sponge as the super base plays a key role in the carbon dioxide activation reaction. A comprehensive study was performed on the reaction mechanism and the most probable routes of the reaction. The function of six proton sponges on the catalytic cycle of methanol production was evaluated in the gas phase and in solvent. It was shown that the catalyst performance is proportional to the dihedral angles ( $\theta$ ) between their aromatic rings. Finally, one of the proton sponges was anticipated as the best catalyst for the reaction. In the mechanism evaluation, three routes were considered for the reaction, one route has been proposed as the most possible route of the reaction through the thermodynamic and kinetic analyses.

## 1. Introduction

One of the noteworthy carbon sources is carbon dioxide. It is very plentiful, non-toxic, nonflammable and easily available in comparison to other C1 sources which employed by the chemical industries. On the other hand, carbon dioxide is a greenhouse gas and has the most important contribution to the global warming. Since the Industrial

Revolution in the early 18th century, CO<sub>2</sub> concentration in the atmosphere has risen by more than 35% and has increased more rapidly with 2.25 ppm (12 billion tons) per year until 2010 [1]. Therefore, numerous political initiatives have been applied to reduce the carbon dioxide emission. One of the most interesting issues in many fields of chemistry is the application of CO<sub>2</sub> as the reactant in the production of valuable materials [2–6]. Since carbon dioxide is thermodynamically and

\* Corresponding author.

E-mail address: [izadyar@um.ac.ir](mailto:izadyar@um.ac.ir) (M. Izadyar).

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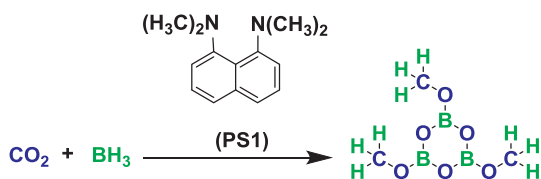


Fig. 1. Catalytic reduction of CO<sub>2</sub> to methanol by borane and proton sponge 1 (PS1) as the Lewis base catalyst.

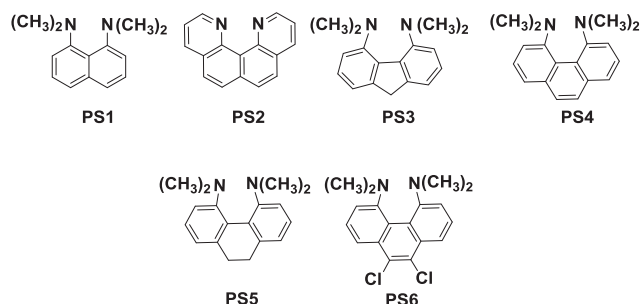


Fig. 2. All proton sponges considered in cycle 1.

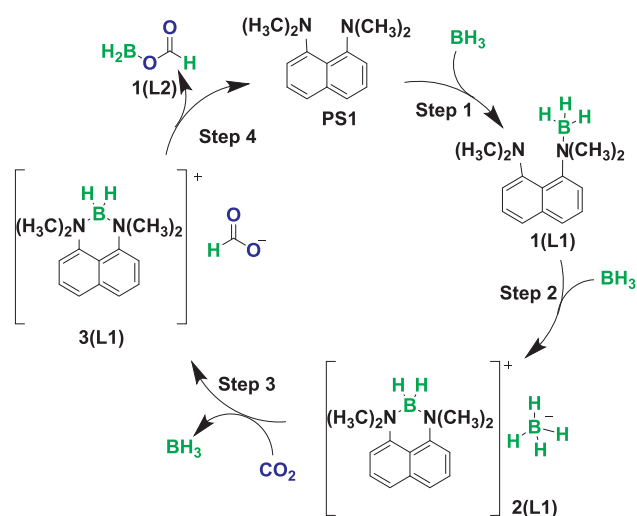


Fig. 3. The proposed mechanism in cycle 1.

kinetically stable, CO<sub>2</sub> activation process is generally required for the chemical reaction. Because of the electron deficiency of the carbonyl carbons, CO<sub>2</sub> has strong reactivity toward the nucleophiles and electron donor reagents. Therefore, in order to defeat the thermodynamic and kinetic barrier, an efficient catalyst is necessary for converting CO<sub>2</sub> to useful compounds. Most of the known investigations used highly reactive substrates or intense reaction conditions to activate CO<sub>2</sub>. Compounds such as organometallic reagents, three-membered heterocyclic compounds, hydrogen and other reductive reagents and materials which contain oxygen or nitrogen react with CO<sub>2</sub> and produce valuable materials such as urea derivatives, cyclic carbonates, polycarbonates, acetylsalicylic acid and salicylic acid [1]. For example, the catalytic coupling of CO<sub>2</sub> with high energy substrates, such as epoxides and aziridines, to generate polycarbonates, polycarbamates, cyclic carbonates, and carbamates has considerable attention over the past decades [7]. In this viewpoint, hydrogenation of CO<sub>2</sub> to energy sources products, such as formic acid, methanol, methane, and hydrocarbons is highly favorable.

The reduction of carbon dioxide to methanol is an important conversion that has attracted much attention. This transformation is the center of the methanol economy that was illustrated by Nobel laureate George A. Olah [8]. Numerous heterogeneous catalysts in carbon

dioxide reduction to methanol, have been introduced which some of them have been commercialized [8]. From this viewpoint, some transition metal-based systems have been used for the reduction of carbon dioxide to methanol [9–13]. However, the study of the modern homogeneous catalysts, which improve the activity, and selectivity of the processes is still in progress. Recently, several attempts for development and designing of the metal-free catalytic systems for the reduction of carbon dioxide have been made. For example, some highly reactive catalysts such as aluminum [14,15] and silylium cations [16] have been used to reduce carbon dioxide with low selectivity to methane, methanol, and other alkylation side-products. Among the reductive reagents, hydroboranes are one of the most efficient reagents in this catalytic reduction of carbon dioxide to methanol. The formation of the strong B–O bond is the driving force of the reaction. Nevertheless, hydride transfer as the first step of the reduction reaction needs a catalyst which can be a metal hydride complex, an amphiphilic compound, a strong Lewis base or a hydroborate compound [17]. For example, phosphine–borane systems, derived from 9-BBN, catalyze the hydroboration of CO<sub>2</sub> [18]. Sodium or lithium borohydride reduces CO<sub>2</sub> to a mixture of formate and methoxy products without using a catalyst [19]. The application of the hydroboranes in the presence of the transition metal catalysts has been reported for CO<sub>2</sub> reduction. Transition metal catalysts activate the B–H bonds, which facilitates the reaction [9,20,21]. Recently, a complete review of the role of Boron-mediated in the activation of the carbon dioxide has been reported by Bontemps [17].

Fontaine and coworkers reported the transformation of carbon dioxide to methoxyborane in the presence of borane molecules and different base catalysts [22]. Among the various base catalysts, proton sponge 1 (PS1) has been claimed as an efficient catalyst for this conversion in dichloromethane solvent. It has been reported that PS1 and borane molecule constitutes a boronium–borohydride ion pair, which acts as a reducing agent of carbon dioxide. Methoxyborane (MeOBO)<sub>3</sub> is also reported as the reaction product, which is converted to methanol and boric acid in the presence of water. Fig. 1 shows the overall reaction.

A worthwhile investigation was reported for the reaction of sodium borohydride and carbon dioxide in aqueous solution [23], in which the hydride transfer to CO<sub>2</sub> was very favorable and competitive with the hydrogen formation mechanism. Another theoretical study was presented on the mechanism aspects of the NaBH<sub>4</sub> hydrolysis in the aqueous solvent, which shows the solvent plays a significant role in the hydrolysis reaction [24]. These investigations show that borohydrides are unique reducing reagents toward reduction reaction theoretically. Keith and coworkers reported another important study about the solvent effects on the CO<sub>2</sub> reduction by reducing agents such as NaBH<sub>4</sub>. They showed that solvent molecules and counter ions of the reducing agents have significant effects on the reaction energies [25]. Based on the previous experiences on the theoretical carbon dioxide activation and transformation to methanol by borohydride salts [26–30], in this work, two catalytic cycles have been considered for the reaction, which is denominated by “cycle 1” and “cycle 2”. Cycle 1 shows the reduction of CO<sub>2</sub> by boronium–borohydride ion pair, leads to COHOBH<sub>2</sub> compound (1(C2)) (C is abbreviated of the “Cycle” word). Cycle 2 shows the reaction between 1(C2) compound as the product of the cycle 1 and borane molecules, which produces methoxyborane (MeOBO)<sub>3</sub>. In this research, a comprehensive study was carried out on the probable mechanisms of these cycles in gas and dichloromethane as the reaction solvent. In addition to the proton sponge, which was used by Fontaine and coworkers (PS1), the performance of five proton sponges was considered and compared in the catalytic reduction cycle.

## 2. Computational details

The structures of the reactants, transition states (TSs) and products of the reaction have been optimized, using Gaussian 09 computational

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