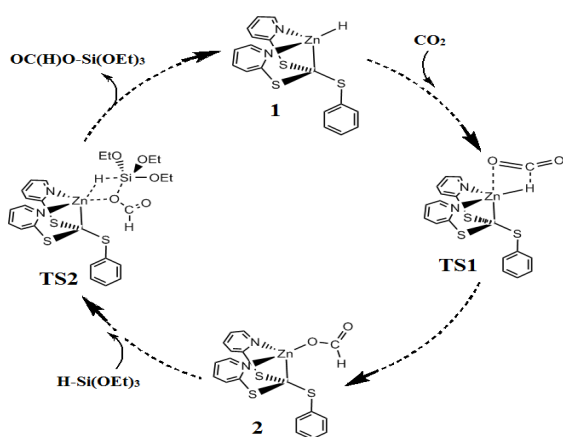# 1P-096

Reaction between CO_2 and Zinc Hydride: Interesting Theoretical Insights

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[Introduction] Transition metal complexes are shown by number of studies that they can act as effective catalyst for variety of conversion of chemical entities into desired products. The CO_2 fixation with reactive substrates such as epoxides, alcohols, amines, and alkynes has been achieved by several transition metal complexes. The reaction of CO_2 with a hydrosilane (R_3SiH) in presence of transition metal catalyst has been shown to be thermodynamically favorable process to give a silyl formate and believed as a promising route for the CO_2 reduction. Rh,[1(a)] Ru,[1(b)] and Ir[1(c)] complexes were reported for the synthesis of silyl formates by hydrosilylation of CO_2. However, the catalytic activity of these complexes was reported to be low. Also, these metals are costly.
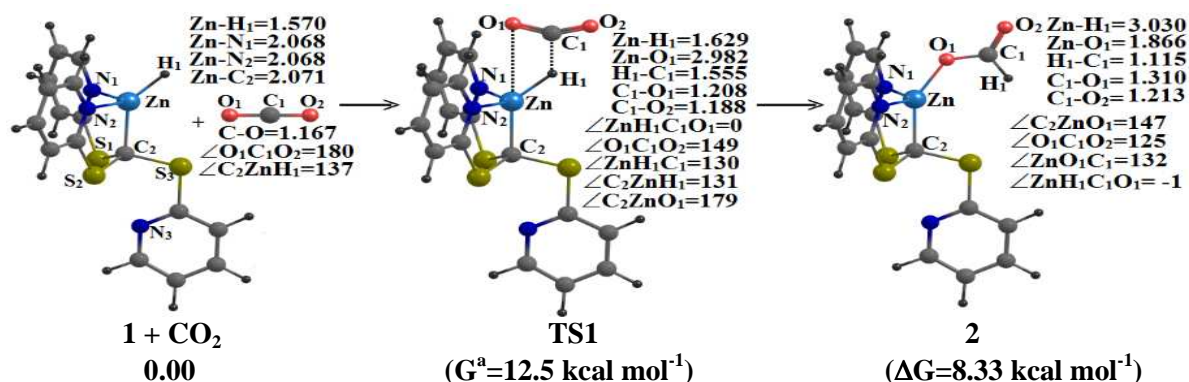

Recently, Sattler and Perking[2] reported that a zinc hydride catalyst **1** (see Scheme 1) acts as a multifunctional catalyst and can be effectively used for the hydrosilylation of aldehydes, ketones and most notably that of CO_2. Further, the hydrosilylation of CO_2 by **1** was reported to be very rapid process. The regeneration of catalyst **1** starting from **2** with silane was also shown to be rapid process. However, the details of the mechanism of these processes have not been discussed and also important factors for these rapid reactions are not clear in their work.

Scheme1: Catalytic cycle for the reaction of CO_2 with **1**.

In this work, we theoretically investigated the reaction mechanism of the CO_2 reaction with **1** and proposed a complete catalytic cycle (Scheme 1). Our purposes are to understand why CO_2 functionalization is rapidly achieved by catalyst **1** and to elucidate the electronic processes involved in the above reactions.
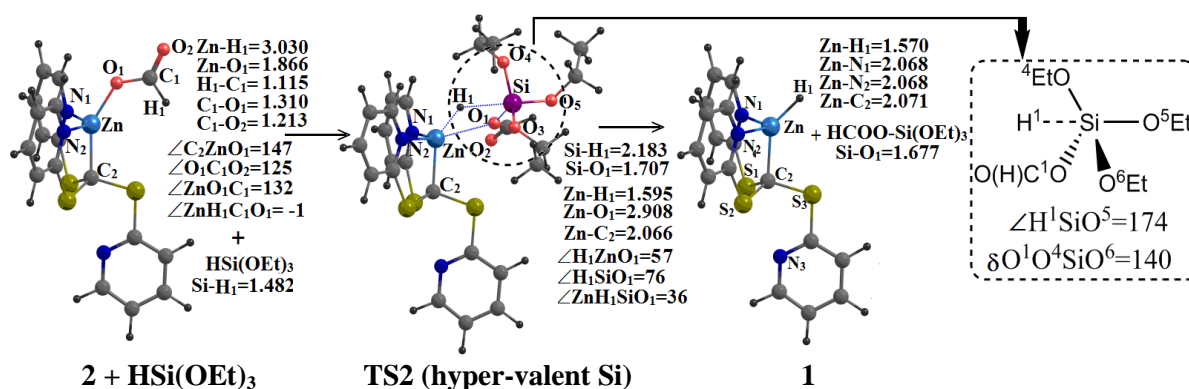
[Computational Details] Geometries of all the complexes were optimized by DFT with B3PW91 functional. Two kinds of basis set systems, BS-I and BS-II, were used. In BS-I, 6-31G* basis sets were employed for all atoms. The BS-I was employed for the geometry optimization. The better basis set system, BS-II was employed for calculations of energy and various properties of these complexes. In BS-II, a (311111/22111/411) basis set was employed for Zn, where its core electrons were replaced by Stuttgart-Dresden-Born (SDD) ECP. 6-311G(d) basis sets were used for C and N atoms, 6-311+G(d) basis sets for H, O, Si, and S atoms. Also one set of polarization functions were added to hydride (H) of ZnH catalyst and H atom of silane, and one set of diffuse functions were added to O and C atoms of CO_2 groups. The MP2, SCS-MP2, MP4, and CCSD(T) levels of theory were used to evaluate energy changes. For these calculations, BS-II was employed.

[Results and Discussion] When going from reactant to transition state **TS1**, the CO_2 molecule approaches to the Zn-H bond of **1** from the top side in a such a way that the C of CO_2 interacts with the H of **1** and one of the O atoms of CO_2 interacts with the Zn-center (Figure 1). The sidewise approach of CO_2 to the Zn-H bond of **1** is energetically unfavorable and leads to a higher **TS** in energy by 7 kcal mol^{-1}. Hence this sidewise approach of CO_2 was not investigated further. This CO_2 insertion occurs with the moderate activation barrier (G^a=12.5 kcal mol^{-1}) and is exothermic process (ΔG=-8.33 kcal mol^{-1}). In **TS1**, considerable large Zn-H^1 and short H^1-C^1 distances suggests that the bonding interactions are well established. The analysis of electronic structures suggests a strong charge transfer (CT) from the valence s- and p-orbital of Zn to the CO_2 moiety. This CT from Zn to CO_2 was attributed to small activation for barrier of this reaction.

Figure 1: Detailed mechanism for the reaction of CO_2 with catalyst 1.

Figure 2: The reaction mechanism for the regeneration of catalyst **1** from **2** and $HSi(OEt)_3$

The regeneration of catalyst **1** starting from **2** with silane occurs through **TS2** (Figure 2). A close look at **TS2** suggests that Si in **TS2** takes hypervalent structure, where one of the -OEt groups and H^1 take axial position. This geometry is favorable for the formation of hypervalent silicon center. A very small activation barrier and a small endothermicity suggest that the regeneration of catalyst **1** using **2** and $HSi(OEt)_3$ occurs rapidly. However, the activation barrier increases and reaction becomes endothermic, when $PhSiH_3$ was employed.
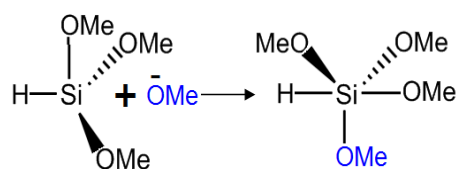
Scheme 2: Model reaction for stability of hyper-valent silicon

Table 1: ΔG and G^a for regeneration of **1** using **2** and Silane

Silane	G^a for **TS2** (kcal mol^{-1})	ΔG^a (kcal mol^{-1})	$\Delta E_{Stabilization}$[a, b] (kcal mol^{-1})
$HSi(OEt)_3$	4.23	0.71	-62.84
$PhSiH_3$	16.59	20.97	-54.48

[a] MP2 level was employed.
[b] Stabilization energy of hyper-valent silicon as in Scheme 2

These differences in the reactivity of $HSi(OEt)_3$ and $PhSiH_3$ is explained in terms of the stability of hypervalent silicon structure in the transition state **TS2**. As seen in Table 1, the smaller activation barrier for regeneration of **1** with $HSi(OEt)_3$ than that with $PhSiH_3$ is correlated well with the higher stability of hypervalent silicon in the former case than in the later one.

[References]

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