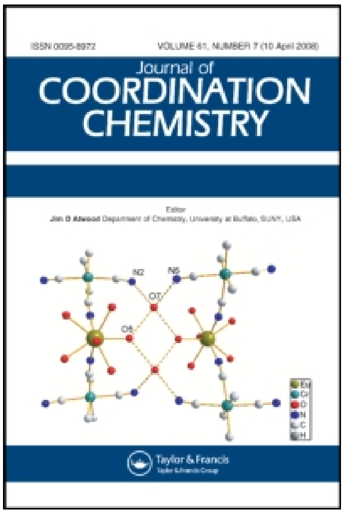

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Theoretical analysis of transition states in the exchange reaction of hydrogen and methane involving σ-bond metathesis

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Theoretical analysis of transition states in the exchange reaction of hydrogen and methane involving σ-bond metathesis

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Silica supported zirconium hydride species are used to model heterogeneous catalysts for industrially-relevant reactions such as hydrogenation of paraffins. This work explores the exchange reaction between methane and hydrogen in the presence of a silica-supported zirconium or titanium hydride catalyst in order to determine the preferred transition state. Calculations at the B3LYP/LanL2DZ level of theory are used to model two distinct pathways for the reaction. Orbital interactions are analyzed to elucidate the relative stability of the two transition states.

Keywords: Zirconium hydride; Exchange reaction; Bond metathesis; Density functional theory; Transition state

1. Introduction

The development of heterogeneous analogs to organometallic catalysts has been the focus of research efforts aimed at creating species that preserve the activity and selectivity of homogeneous catalysts while adding the benefits of improved stability and ease of process control of heterogeneous catalysts [1]. Zirconium hydride complexes anchored to a silica surface are an example of such analogs that have been employed to catalyze olefin polymerization [2]. Specifically, reactions of paraffins with silica supported zirconium hydride species are assumed to proceed by a σ-bond metathesis mechanism [3]. In order to better understand the nature of this type of catalysts, Casty *et al.* have investigated the mechanism of H/D exchange reactions, concluding that they indeed proceed via σ-bond metathesis. However, they could not determine which of two transition states is favored [1]. The goal of this work is to compare the two proposed transition states and determine which one is favored.

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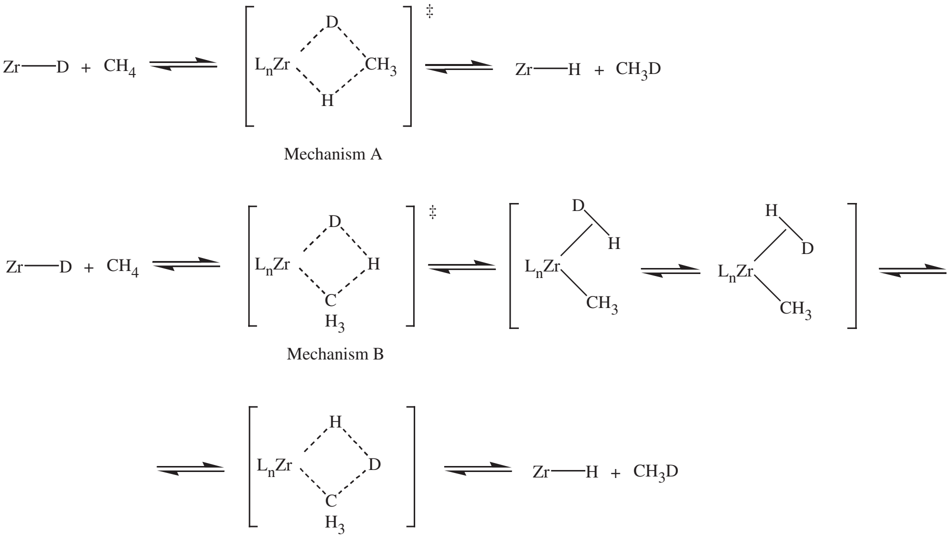

Scheme 1. The two proposed mechanisms for the exchange reaction.

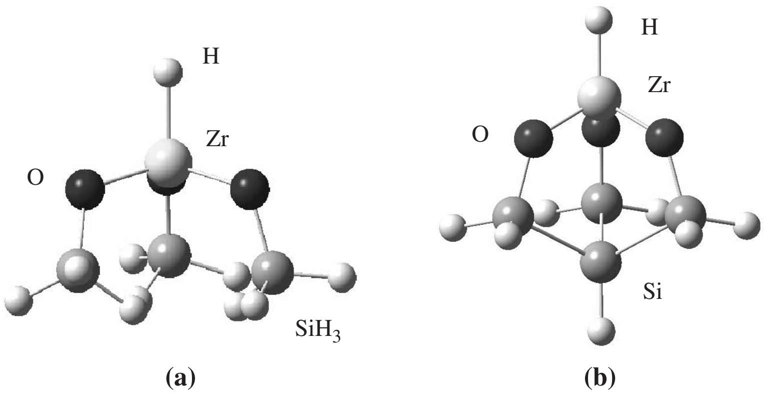

Figure 1. Models of the zirconium hydride catalyst. (a) Frozen model; (b) Tied model.

2. Details of calculations

All calculations were carried out using Density Functional Theory [4]. Specifically, the hybrid method B3LYP was used, which includes Becke's three parameter exchange-correlation hybrid functionals [5] and the correlation functional of Lee *et al.* [6]. The LanL2DZ basis set was used on all atoms [7].

The initial geometry for each molecule was created with *GaussView 03W* [8] and subsequent molecular orbital calculations were carried out using *Gaussian 03W* [9]. Each structure was optimized using the Berny algorithm [10] to either a minimum (for reactants and products) or a saddle point (for transition state structures). In the optimization of the frozen model of the catalyst, the three H–Zr–O–Si dihedral angles and the three Zr–O–Si angles were fixed. For all compounds, force constants and resulting vibrational frequencies were computed analytically. Once the saddle

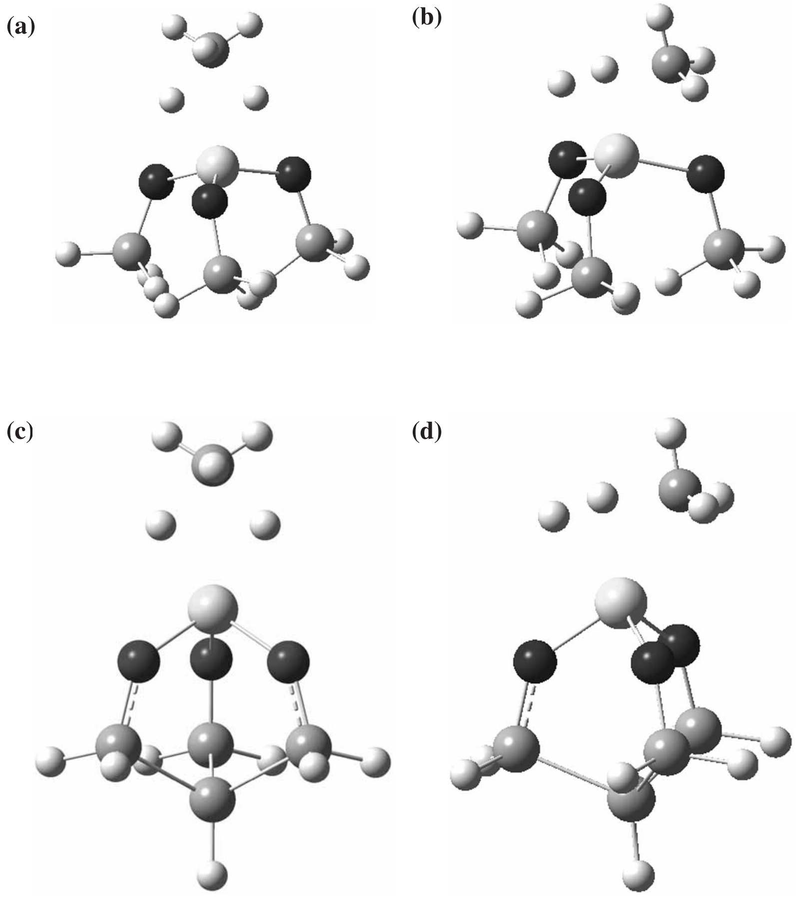

Figure 2. Optimized structures for (a) Transition state A, frozen model; (b) Transition state B, frozen model; (c) Transition state A, tied model; (d) Transition state B, tied model.

points for each proposed mechanism were identified, an IRC calculation [11] was performed to verify the reaction pathway.

To determine whether the LanL2DZ basis set produced valid results, one set of calculations was carried out using the 6-311+G basis set [12]. Specifically, the activation energy for both pathways using the frozen model of the catalyst and Ti as the metal was calculated with both basis sets. Similar results were obtained: in particular, the B transition state was more favorable in both cases and the difference in activation energies was also comparable (42.7 kcal mol^{-1} using the LanL2DZ basis set and 43.4 kcal mol^{-1} using the 6-311+G basis set). Consequently, all remaining calculations were carried out using the LanL2DZ basis set.

3. Results and discussion

The two proposed mechanisms for the exchange reaction are shown in scheme 1 [1]. The first transition state (TS A) is much more symmetrical than the second one (TS B). Also, the second pathway leads to an intermediate where the HD molecule

Table 1. Activation energies and their differences.

		Activation energy (kcal mol^{-1})	Difference in activation energy (kcal mol^{-1})
M = Zr			
Frozen model	Pathway A	79.5	42.9
	Pathway B	36.6	
Tied model	Pathway A	80.7	48.9
	Pathway B	31.8	
M = Ti			
Frozen model	Pathway A	76.5	42.7
	Pathway B	33.8	
Tied model	Pathway A	78.4	43.6
	Pathway B	34.8	

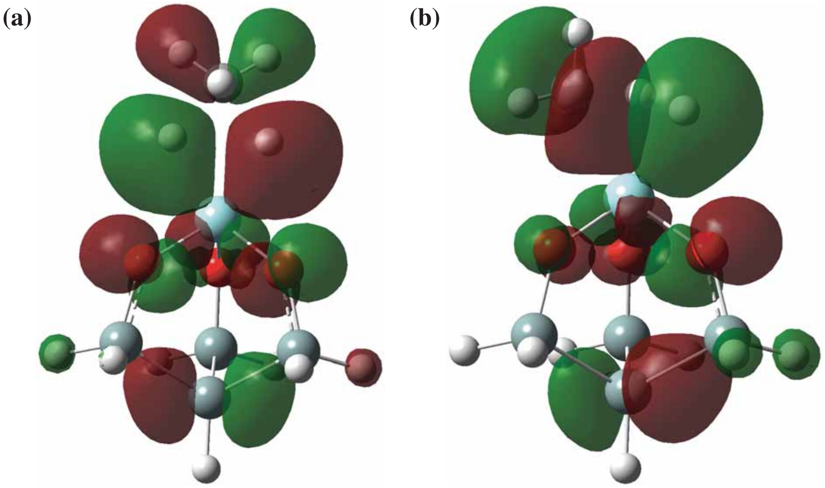

Figure 3. HOMO surfaces for transition states A and B (tied model, M = Zr). Light blue sphere is zirconium, red spheres are O, grey spheres are Si, and white spheres are H.

binds to the metal in an η^2 fashion. While TS A minimizes steric interactions, TS B exhibits a favorable kite-shaped structure. Such kite-shaped transition state configurations have been found to be energetically favorable in σ-bond metathesis reactions involving Sc complexes [13a,b], H/F exchange reactions catalyzed by lanthanide complexes [13c,d], and C–H activation reactions at d^0 metal centers [13e].

To investigate the reaction in scheme 1, it is necessary to develop a model for the silica-supported zirconium hydride catalyst: the model structures used in this work include three $OSiH_3$ groups bonded to the Zr–H moiety [1]. In order to mimic a silica surface, the Si atoms must be kept in a plane perpendicular to the Zr–H bond. This is accomplished in two ways: freezing the bottom portion of the molecule (Frozen model, shown in figure 1a) and adding a fourth Si atom to tie the other three in place (Tied model, shown in figure 1b).

From these two models, corresponding structures for transition states A and B are developed, as shown in figure 2. Activation energies for both pathways are listed in table 1. Whether the frozen or tied model of the catalyst was used and whether

Table 2. Energy of HOMO and LUMO orbitals for transition states A and B (tied model, M = Zr).

Pathway	HOMO (a.u.)	LUMO (a.u.)	HOMO – LUMO Gap (eV)
A	−0.21961	−0.06681	4.161
B	−0.23791	−0.04095	5.364

the metal was Zr or Ti, transition state B was lower in energy, thus making pathway B the preferred pathway for this reaction.

The reasons for the results in table 1 are further investigated by analyzing the orbital interactions that differentiate pathway A from pathway B. This part of the analysis is carried out using the tied model for the catalyst and Zr as the metal. As the reagent molecules start to interact, the LUMO of the Zr complex interacts with the HOMO of methane. The resulting highest-occupied molecular orbitals are shown in figure 3. The surfaces suggest that transition state B is favored because the HOMO of CH_4 interacts with the LUMO of the zirconium complex in a σ fashion, while in transition state A the interaction is π, resulting in a smaller degree of overlap. Similar results have been observed for titanium and scandium metal hydrides [13b]. In addition, transition state B is a more stable structure, as indicated by the HOMO/LUMO gaps for both transition states shown in table 2.

4. Conclusions

The results obtained from molecular orbital calculations performed on two possible transition state complexes for the exchange reaction between methane and hydrogen indicate that transition state B is at lower energy than transition state A, despite the fact that pathway B has lower symmetry. This conclusion holds for both tied and frozen models of the silica-supported metal hydride catalyst and when the metal is silicon or titanium. Pathway B is lower in energy because of the favorable interaction between the valence orbitals of the reactants in the transition state configuration. Specifically, the HOMO of CH_4 has the correct symmetry to overlap with the LUMO of the zirconium complex in a σ fashion, while in transition state A the interaction has π symmetry and therefore a smaller overlap.

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