

Ab initio molecular orbital studies of elementary reactions and homogeneous catalytic cycles with organometallic compounds

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Abstract : Results of ab initio molecular orbital studies are presented for one elementary reaction and two full catalytic cycles of organo-transition metal complexes: (i) the oxidative addition of H-H, C-H, N-H, O-H and Si-H bonds to CpRh(CO) in gas phase, (ii) the full catalytic cycle of hydroboration of olefin with Rh(PR₃)₂Cl, and (iii) the full catalytic cycle of hydroformylation of olefin with RhH(CO)₂(PR₃)₂.

I. Introduction

For the last decade, we have been studying the mechanism of "elementary" reactions of transition metal complexes with ab initio molecular orbital method, by determining the structures and energies of intermediates and transition states as well as of reactions and products (1,2). We have found that very often a seemingly simple reaction consists of several alternative paths, each of which is made up of several sequential steps or concerted stages. The full catalytic cycle, a consequence of several "elementary" reactions, thus is an array of many steps and stages of reactions. A careful molecular orbital study can unveil detailed structural and energetic changes associated with these individual steps, and provide insight into the mechanism of the reactions. In the present paper, we will report results of ab initio studies of two homogeneous catalytic cycles, hydroboration and hydroformylation, as well as a systematic comparison of bond activation reaction, all with Rh complexes.

II. Oxidative Addition of H-H, C-H, N-H, O-H and Si-H Bonds to CpRh(CO).

The first problem studied in this paper is the oxidative addition of the H-H, C-H, N-H, O-H and Si-H bonds of the H₂, CH₄, NH₃, H₂O and SiH₄ molecules, respectively, to the CpRh(CO) complex. The H₂, CH₄, NH₃, H₂O and SiH₄ molecules, some of whose making up a large percentage natural materials, are rather inert. Therefore their catalyzed chemical transformations have a great importance (3,4). The first step of these processes is the oxidative addition of these molecules to transition metal center, which has been in focus of chemists for long time (3,4). It has been found that the activation of the H-R bond of these molecules occurs on metal surfaces, on several biological systems that contain transition metal complexes at their active sites, and on some transition metal complexes. Intensive studies of the oxidative addition reaction of the H-R bond to transition metal center have shown some general trends as well as the marked differences among different metal centers and different H-R bonds.

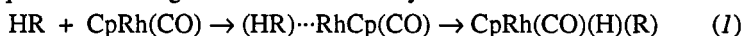
First, in spite of similarity of the H-H and C-H bond strengths, the H-H bond in the hydrogen molecule is found to be activated more easily by a large number of transition metal complexes than C-H bonds in saturated hydrocarbons. The reason of the difference between H-H and C-H activation has been explained in terms of the directionality of the metal-alkyl bond compared to the metal-hydrogen bond (5).

Second, in literature a prediction (5) has been made based on a significant attraction that should exist between lone pairs of the ligand R and empty d-orbitals of the

transition metal center M. According to this prediction, the reaction of water and ammonia, having lone-pairs, should be more exothermic for the transition metals to the left of the periodic table than that of methane. However, for transition metals to the right of the periodic table, which have more lone-pair d-electrons than empty d-orbitals, the trends in the M-R bonds (where $R = \text{CH}_3, \text{NH}_2$ and OH) should be completely different. This difference should be further accentuated if the Nyholm-Gillespie rules are applied, which state that the repulsion between d-electrons of metal and lone-pairs of ligands is stronger than between bond electrons. Thus, for atoms to the right of periodic table, the reaction should be less exothermic for water and ammonia than for methane. The linear relationship between the R-H activation barrier and R-H bond strengths has also been proposed; this means that the activation barrier should increase in the order: $(\text{C-H}) < (\text{N-H}) < (\text{O-H})$.

Third, a significant difference between H-SiH₃ and H-CH₃ bond activation on the transition metal complexes has been predicted, the origin of which for RhCl(PH₃)₂ complex is the stronger Rh-Si bond and the weaker Si-H bond, compared to Rh-C and C-H bonds, respectively (6).

Recently, Wasserman, Moore and Bergman (7) have shown that the activation of the strong H-H and C-H bonds in hydrogen and alkanes, respectively, readily occurs in gas phase by interaction with the coordinatively unsaturated 16-electron d⁸ complex CpRh(CO), produced from CpRh(CO)(H)(R) (where $R = \text{H}, \text{CH}_3$, etc.). They proposed the following reaction sequence involving formation of a weakly bound intermediate:



Since this reaction occurs in gas-phase, free of solvent and support interactions, it seems to be a best example to test the above mentioned trends and predictions for oxidative addition reactions of H-R bonds among H₂, CH₄, NH₃, H₂O and SiH₄ molecules. On the other hand, it is experimentally very difficult to detect the intermediate and the transition state, and therefore a quantum chemical calculation should be useful for study of the structure and stability as well as the nature of intermediate and transition state of the reaction (1).

The calculated potential energy profiles represented in the Fig. 1 clearly show that the barrier height of the H-R bond activation depends on the several factors.

1. The obvious factor is the strength of the H-R bonds. The oxidative addition reaction of H-H, H-SiH₃ and H-CH₃ bonds, weakest among the bonds considered, to CpRhCO takes place without barrier relative to the reactants. The activation barrier, relative to the reactants, of the strong N-H and O-H bonds increases with the increase in the H-R bond strengths, e.g. $\text{N-H} < \text{O-H}$. However, the barrier heights calculated relative to the prereaction molecular complex, CpRh(CO)·(HR), depend also on the complexation capability of the HR molecules, which strongly correlates with their Lewis basicity. The activation barrier relative to the CpRh(CO)·(HR) complex is larger for H-NH₂, 41.9 kcal/mol, than for H-OH, 25.9 kcal/mol, which in turn is larger than for H-CH₃, 5.5 kcal/mol.

This is essentially a consequence of the calculated complexation energies of 36.8, 20.5 and 7.7 kcal/mol for the NH₃, H₂O and CH₄ molecules, respectively. This suggests that in solution where the reaction should be considered to start from the prereaction complex,

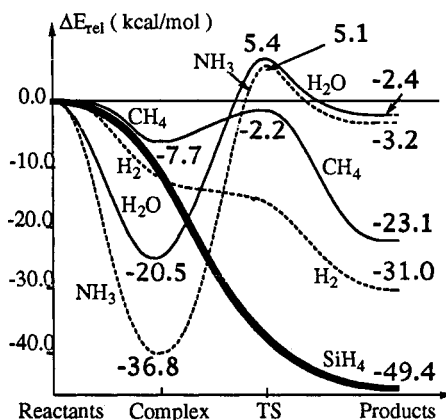


Fig. 1 The potential energy profile of the reaction of CpRh(CO) with molecules H₂, CH₄, H₂O, NH₃ and SiH₄.

$\text{CpRh}(\text{CO})\cdot(\text{HR})$, it will be very difficult to activate H-R bonds of molecules that have a strong Lewis base character.

2. Another factor is the directionality of the unpaired orbital of R formed by breaking the H-R bond. Comparison of the PESs of the reaction (1) for H_2 and CH_4 molecules clearly shows that, in spite of similarity of the H-H and C-H bond strengths, the H-H bond of the hydrogen molecule is activated without barrier, while the C-H bond of methane has a small (5.5 kcal/mol) activation barrier calculated relative to the molecular complex. This difference in the H-H and C-H activation can be explained in terms of the directionality of the CH_3 orbital compared to the H orbital, as suggested by Siegbahn et al. (5). Due to the spherical nature of the H orbital, the Rh-H bond can start to form at the same time as the H-H bond is weakened and therefore there is no barrier for the breaking of the H-H. In contrast, the directionality of the CH_3 unpaired orbital forces the C-H bond to be broken before the new Rh- CH_3 bond is formed, thus leading to a barrier for the reaction.

3. It is well known that there is a correlation between exothermicity of the oxidative addition reaction and the activation barrier from the reactants (6). The results represented in Fig. 1 for H- CH_3 and H-Si H_3 bond activations confirm this statement.

The exothermicity of the present reactions decreases in the order $\text{SiH}_4 > \text{H}_2 > \text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O}$. This is in a good agreement with the prediction (5) based on discussions of the nature of M-R bond, which states that for transition metal atoms to the right of periodic table the products should be bound less strongly for water and ammonia than for methane, due to a strong repulsion between lone-pair d-electrons of metal and lone-pairs of ligands.

II. Olefin Hydroboration Catalytic Cycle by $\text{Rh}(\text{PR}_3)_2\text{Cl}$.

We will now present the results of study of the mechanism of Rh(I)-catalyzed olefin hydroboration reaction. This study has been prompted by the recent surge of experiments in this field (8-11). It has been discovered that a number of transition metal complexes catalyze the olefin hydroboration with catecholborane, HBcat (where $\text{cat} = 1,2\text{-O}_2\text{C}_6\text{H}_4$) and TMDB (4,4,6-trimethyl-1,3,2-dioxaborinane). This process has demonstrated a variety of promising features, including regio-, diastereo-, and chemoselectivity, and has been attracting a substantial interest in connection to organic synthesis (8-11). In general, it has been found that: (i) the reductive elimination step is the slowest step in the overall transformation; (ii) Rh complexes are most suitable catalysts, among those the Wilkinson catalyst appears to be the most efficient; (iii) boron hydrides bearing oxygen ligands are the most successful reagents; and (iv) the rate of the catalyzed hydroboration reaction is very sensitive to the olefin substitution pattern, with terminal alkenes more reactive than highly substituted olefins.

However, the mechanism of this practically important catalytic reaction remains unclear. The mechanism proposed in early papers (8,9) for the Wilkinson catalyst involves oxidative addition of a B-H bond to the metal center, followed by olefin coordination to the metal center accompanied with dissociation of one of the two PPh_3 , further followed by migratory insertion of olefin into the M-H bond and subsequent reductive elimination of the B-C bond. However, still unresolved are several important questions; i) whether the reaction occurs with phosphine dissociation or not ? ii) which of the M-B and M-H bond insertions of olefin is energetically more favorable ? iii) How competitive is the " σ -bond metathesis" pathway involving coordination of the HBcat and olefin to the complex followed by simultaneous cleavage of the M-C and B-H bonds with formation of the M-H and B-C bonds ? Important proposed mechanisms of the rhodium(I)-catalyzed olefin hydroboration are shown in Scheme I.

Thus, detailed experimental and theoretical studies are highly desirable on the mechanism of the transition-metal catalyzed olefin hydroboration reactions, as well as on the role of the transition metal center, substrates, and electronic and steric factors in the mechanism. In the present paper, we present the first detailed ab initio MO study of possible reaction pathways illustrated in Scheme I. The pathways involving elimination of one of the phosphine ligands after olefin coordination presently under investigation, and is not a part of the present paper. We will study the hydroboration reaction of C_2H_4 with the boranes $\text{HB}(\text{OH})_2$ and $\text{HBO}_2(\text{CH}_2)_3$ catalyzed by the model Wilkinson catalyst $\text{RhCl}(\text{PH}_3)_2$.

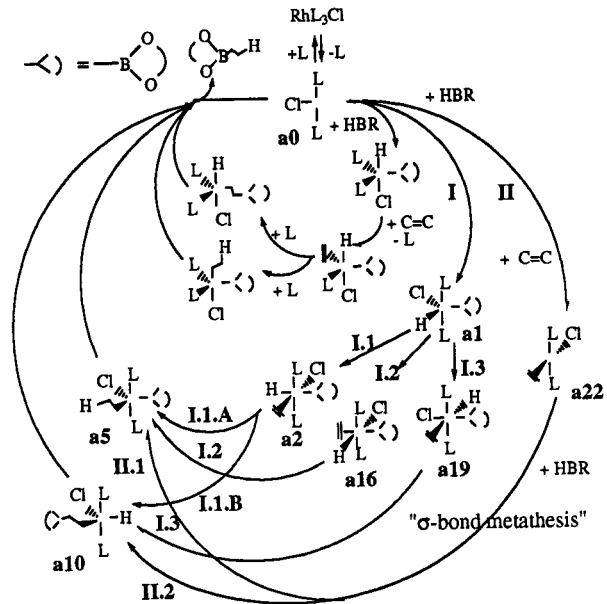
The calculated overall profile of the potential energy surface (PES) of the reaction with $\text{HB}(\text{OH})_2$ is given in Fig. 2. As seen in Fig. 2, the mechanism (I.1.B) has been

found to be the most favorable pathway of the catalytic hydroboration of C_2H_4 by $HB(OH)_2$ with the model Wilkinson catalyst, $RhCl(PH_3)_2$. Since the PES for the (I.1.B) mechanism for $HBO_2(CH_2)_3$ is nearly quantitatively the same with that for $HB(OH)_2$, the same conclusion should be applicable for reactions of real boranes experimentally studied. It involves oxidative addition the B-H bond of borane to the catalyst, **a1**, followed by coordination of olefin to the complex between B and H ligands, **a2**. The reaction further proceeds by insertion of $C=C$ into the Rh-B bond, followed by the coupling of H and C_2H_5BR , **a10**, or dehydrogenative reductive elimination of C_2H_5BR to give the product complex, **a14'**, and eventual dissociation of the C_2H_5BR . The activation energy for the last two steps of the mechanism, reductive elimination and dissociation, is calculated to be about 20 kcal/mol. Since in solution the endothermicity for the dissociation would be reduced by solvating of the regenerated catalyst, the coupling of H and C_2H_5BR is the rate-determining step. Our conclusion agrees with experimental observation that the reductive elimination step is the slowest in overall transformation (9).

The other competitive mechanism, (II.2), begins with addition of olefin to the catalyst, **a19**. The next step is " σ -bond metathesis", i.e. coordination of borane to the complex, **a22**, accompanied by simultaneous cleavage of Rh-C and B-H bonds with formation of B-C and Rh-H bonds. After an internal rotation, which does not require high activation energy, dehydrogenative reductive elimination of C_2H_5BR takes place. The final steps for the mechanism (II.2) coincide with those for the mechanism (I.1.B), and the rate-determining barrier for (II.2) corresponding to the metathesis process, 23.9 kcal/mol, is not much higher than the barrier for (I.1.B), 22.4 kcal/mol. However, along the (II.2) pathway, the system has to overcome both of these barriers.

The mechanisms (I.2) and (I.3), merging with (II) at (**a22**), have the same rate-controlling step as (II.2), because reductive elimination of borane from (**a16**) and (**a19**) requires lower energy lost, 17.6 and 13.7 kcal/mol, respectively, than the activation energy for the " σ -bond metathesis", 23.9 kcal/mol. Hence, the mechanisms (I.2) and (I.3) are also competitive with (II.2) and (I.1.B).

If the system has a choice for C-C bond insertion into the Rh-B or B-H with formation of a C-B bond, or to



Scheme I.

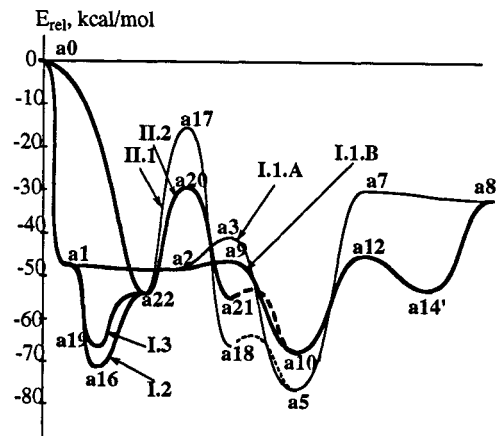


Fig. 2

insert into Rh-H or B-H with formation of a C-H bond, the former process is always significantly more advantageous kinetically. Therefore, the mechanisms (I.1.A) and (II.1) for the reaction of catalytic hydroboration seem to require high temperatures.

In the present paper, we have not considered some aspects of Rh(I)-catalyzed olefin hydroboration, worthwhile to be studied in future. For instance, another reaction mechanism, involving dissociation of one of the phosphine ligands of the catalyst after oxidative addition of borane and coordination of olefin, is possible, as shown at the top of Scheme I. Neither we have compared hydroboration reaction of terminal alkenes and highly substituted olefins, although the reaction rate is sensitive to the substitution pattern (9-11). Theoretical calculations on these questions are now under way.

III. Hydroformylation Catalytic Cycle by $\text{RhH}(\text{CO})_2(\text{PR}_3)_2$

Another catalytic cycle studied in this paper is the hydroformylation of olefin by the Rh(I)-complex. Hydroformylation of olefin by the rhodium complex (12-14) is one of the most well known homogeneous catalytic reactions. Despite extensive studies made for this industrially worthwhile reaction (15,16), the mechanism is still a point of issue. The active catalyst, which mediates the catalytic cycle, is considered to be $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ **1** as presented in Fig. 3. The most probable reaction cycle undergoes the phosphine dissociation to generate an active intermediate **2**. The intramolecular ethylene insertion, CO insertion, H_2 oxidative addition and aldehyde reductive elimination are followed as surrounded by the dotted line. We have optimized all the relevant transition states as well as the intermediates by the ab initio MO method to determine the full potential energy surface and revealed that the solvent molecule play a critical role in the determination of the potential energy surface. As a catalyst we chose $\text{RhH}(\text{CO})(\text{PH}_3)_3$, where PPh_3 was replaced by PH_3 . The olefin we adopted is ethylene, which was used also as a model of solvent.

We at first determined the structure of the intermediates and the transition states involved in the catalytic cycle at the Restricted Hartree-Fock(RHF) calculation level. Although the aldehyde-coordinate intermediate **9** is not included in the catalytic cycle proposed by Wilkinson et al., it exists between **7** and **8**. The potential energy surface of the catalytic reaction was determined by the second order Møller-Plessett(MP2) calculation at the RHF determined structures.

The potential energy surface for the entire catalytic cycle without solvent is presented in Fig. 4. As one can see, the entire potential energy surface is strange looking. In addition to ethylene and CO insertion steps, the first phosphine dissociation and the last aldehyde dissociation step have large barriers. Actually, the reaction takes place experimentally in solution, often with alkenes as solvent. Such solvent molecules can coordinate to coordinatively-unsaturated intermediates to stabilize them. For non-polar solvent like alkenes, the direct interaction of one (or a few) solvent molecule is much more important than the long-range interaction via a solvent reaction field. For instance, if a solvent ethylene molecule coordinates to the four-coordinate intermediate **2**, the solvated species will be nothing but the ethylene complex **3**. Therefore, we performed the optimization for the 16e four-coordinate intermediates **2**, **4**, **6** and **8** and the 17e five-coordinate transition states **TS(3-4)**, **TS(5-6)**, **TS(6-7)** and **TS(7-8)** with one ethylene as solvent. All 16e four-coordinate

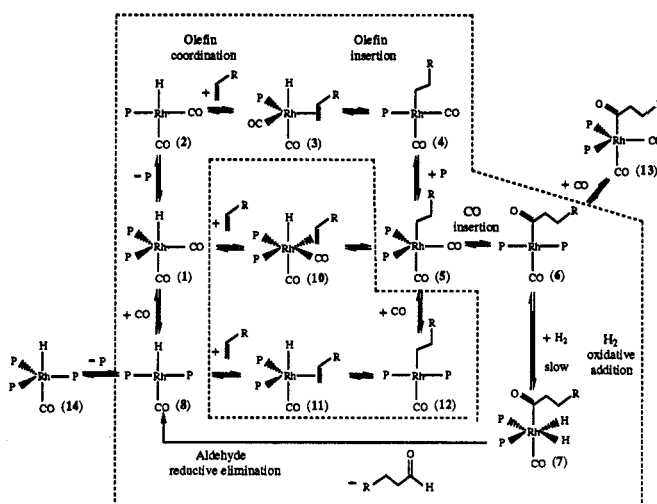


Fig. 3 Proposed mechanism of hydroformylation by $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ experimentally.

intermediates were more than 20 kcal/mol stabilized by the η^2 -coordination of a solvent ethylene, with their square-planar structure transformed to the trigonal-bipyramidal structure. On the other hand, the 17e five-coordinate transition states were only a few kcal/mol stabilized by the weak interaction of an ethylene with rhodium, with the Rh-ethylene bond distance of about 5Å, without large deformation of the structure.

The potential energy surface with solvent interaction taken into account is presented in Fig. 5. The feature of the entire potential surface is drastically changed. The large barriers in the reaction from 1 to 3 and from 9 to 1 have disappeared because of the stabilization of the four-coordinate

intermediates 2 and 8 by the solvation. The endothermic ethylene and CO insertion reactions became exothermic and the exothermic H_2 oxidative addition became endothermic, because the four-coordinate intermediate 4 and 6 were also stabilized by 25 kcal/mol. One can find the largest barrier in the H_2 oxidative addition step, in agreement with the experimental proposal that the H_2 oxidative addition is rate-determining. It is quite reasonable that the endothermic H_2 oxidative addition step has the largest barrier, because the ethylene insertion, carbonyl insertion and aldehyde reductive elimination steps are exothermic. The energy barrier in the ethylene insertion and carbonyl insertion step is, however, relatively large in spite of the exothermic reaction. Some improvement for this problem would be expected with the optimization of the structures with the electron correlation taken into account.

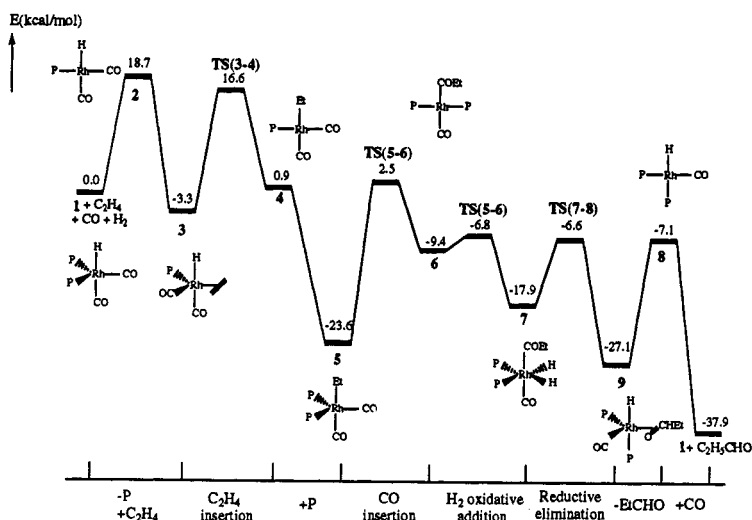


Fig. 4 MP2/II potential energy profile (in kcal/mol) for the entire catalytic cycle without solvent ethylene calculated at the HF/I optimized structure.

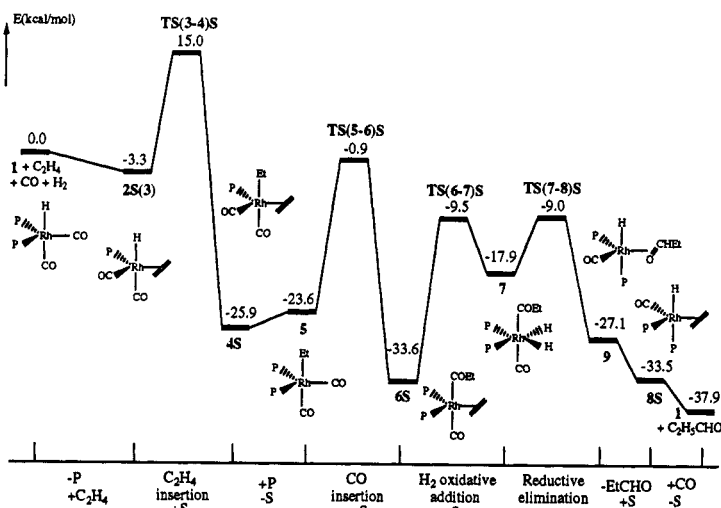


Fig. 5 MP2/II potential energy profile (in kcal/mol) for the entire catalytic cycle with solvent ethylene calculated at the HF/I optimized structure.

IV. Conclusion

Even though we have not included in the present paper, ab initio molecular orbital studies are not restricted to mononuclear complexes but can be extended to di- and trinuclear metal cluster complexes. For example, we have recently shown (17) that the hydride exchange reaction between the hydride bridging two metals and the hydride of μ_3 -CH in $M_3(CO)_9(\mu-H)_3(\mu_3-CH)$, $M=Os$ and Ru , follow a seven-step mechanism, consisting of (i) migration of the bridging hydride H^* to the nearby terminal position to form a seven-coordinate M , (ii) turnstile rotation around M , (iii) insertion of H^* into the $M-C$ bond, (iv) rotation of H^*CH through a symmetric transition state, and the reversal of steps (iii), (ii) and (i).

These ab initio studies of the potential energy profile of complicated catalytic cycles and other sequences of elementary reactions can provide information about the structure and energetics of intermediate and transition states, any of which is hard to obtain experimentally. This kind of theoretical information in turn gives a new insight for understanding the detailed electronic mechanism of complicated reactions.

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