Theoretical Study of C-H σ-Bond Activation and Related Reactions

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Various theoretical studies of σ-bond activation of organic molecules by transition metal complexes are reviewed. In the homolytic σ-bond activation, the d orbital energy level of the central metal is an important factor, as well known. At the same time, the electron-withdrawing substituent which stabilizes the sp^3 orbital accelerates the homolytic σ-bond activation. In the heterolytic C-H σ-bond activation of RH by MXL_n, the X-H bond formation is an important driving force, where MRL_n and HX are formed as products. The heterolytic σ-bond activation is also understood in terms of the electrophilic attack of the metal center to the substrate.

Key Words : C-H bond activation, Theoretical study, Transition metal complex, Heterolytic bond fission

Introduction

C-H σ-bond activation of alkane and aromatic compounds is of considerable interest in the recent transition metal catalytic chemistry, because one can introduce several functional groups into alkane and aromatic compounds through the σ-bond activation. In my understanding, the C-H σ-bond activation is classified into two categories; one is homolytic σ-bond activation (eq. 1) and the other is heterolytic σ-bond activation (eq. 2).

$$ML_n + R\text{-}H \rightarrow M(H)(R)L_n \quad (1)$$
$$MXL_n + R\text{-}H \rightarrow M(R)L_n + HX \quad (2)$$

In the product of the homolytic σ-bond activation, both the H atom and the R group are bound with the metal center, where R represents either alkyl or aromatic group. Since the H atom and the R group coordinated with the metal center are considered to be anion in a formal sense, the oxidation state of the central metal increases by two in this reaction. Thus, the homolytic σ-bond activation is understood in terms of the oxidative addition. In the products of the heterolytic σ-bond activation, the R group is bound with the metal center but the H atom is bound with one of the ligands of the metal complex. As a result, the metal oxidation state does not change in a formal sense.

Because of the importance of the C-H σ-bond activation, a lot of theoretical works have been performed so far. However, there remain many issues to be investigated theoretically; for instance, only few attempts have been made to clarify the ligand effects and the substituent effects in the homolytic σ-bond activation. Moreover, the heterolytic σ-bond activation has not been sufficiently investigated except for several theoretical works. In this mini review, I wish to discuss the theoretical studies of homolytic C-H σ-bond activation and the heterolytic C-H σ-bond activation by transition metal complexes.

Homolytic C-H σ-Bond Activation

Many theoretical studies of this reaction have been reported by Hoffmann,[1] Morokuma,[2] Goddard,[3] Siegbahn,[4] Hall,[5] and Sakaki[6] groups. The transition state of the H-H σ-bond activation was first optimized by Morokuma group.[2] After their works, various quantitative works have been carried out. The important results from those works are summarized, as follows: The first important result to be noted is that the σ-bond activation of H_2 easily occurs but the C-H σ-bond activation of CH_4 occurs with a difficulty, as shown in eqs 3 and 4.

$$Pt(PH_3)_2 + H_2 \rightarrow \textit{cis}\text{-}Pt(H)_2(PH_3)_2 \quad (3)$$

Ea = 2.2 kcal/mol and ΔE = -15.9 kcal/mol from the GVB calculation,[3]

$$Pt(PH_3)_2 + CH_4 \rightarrow \textit{cis}\text{-}Pt(H)(CH_3)(PH_3)_2 \quad (4)$$

Ea = 24.5 kcal/mol and ΔE = 7.2 kcal/mol from the GVB calculation.[3]

This difference is discussed in terms that the H atom has a spherical 1s valence orbital but the methyl group has an sp^3 orbital as its valence orbital; in other words, the methyl group must change its direction towards the metal center because the sp^3 orbital is directional. This direction change induces the energy destabilization of the σ-bond in the homolytic σ-bond activation, which leads to the large activation barrier of the C-H σ-bond activation of CH_4.[1,3a]

The next important result is that the Pt(0) complex can activate the H-H and C-H σ-bonds with a lower activation barrier and larger exothermicity than those of the Pd(0) complex.

$$Pd(PH_3)_2 + H_2 \rightarrow \textit{cis}\text{-}Pd(H)_2(PH_3)_2 \quad (5)$$

Ea = 5.2 kcal/mol and ΔE = 3.6 kcal/mol from the GVB calculation,[3]

$$Pd(PH_3)_2 + CH_4 \rightarrow \textit{cis}\text{-}Pd(H)(CH_3)(PH_3)_2 \quad (6)$$

Ea = 42.2 kcal/mol and ΔE = 43.6 kcal/mol from the GVB calculation.[3]

This is because Pt d-orbital is at a higher energy than Pd d-orbital. This difference between Pt and Pd atoms relates to the electron configuration of these atoms; Pt and Pd atoms

take d^9s^1 and d^{10} electron configurations, respectively, in their ground states, because the d electrons of Pd are at a lower energy than those of Pt. In general, the 5d orbital of the third transition series element is at a higher energy than the 4d orbital of the second transition series element, because the inner s orbital shrinks due to relativistic effects to shield well the nuclear charge and to raise the outer d orbital in energy.[6]

Though the Pd(0) complex is not useful for the homolytic σ-bond activation as discussed above, the Pd(0) complex becomes active for this reaction by coordination of the chelate diphosphine.[7a] This is because the chelate diphosphine destabilizes the d orbital in energy; actually, the activation barrier and the endothermicity decrease in the order, $Pd(PH_3)_2$ > Pd(dipe) > Pd(dipm), where dipe and dipm represent models of diphosphinoethane and diphosphinomethane, respectively.

The substituent effects on the C-H σ-bond activation is also interesting. Introduction of electron-withdrawing group to the sp^3 C atom facilitates the homolytic C-H σ-bond activation by stabilizing the transition state and the metal-alkyl bond.[7b]

$$Pd(PH_3)_2 + CH_3CN \rightarrow \textit{cis}\text{-}Pd(H)(CH_2CN)(PH_3)_2 \quad (7)$$

Ea = 31.9 kcal/mol and ΔE = 23.2 kcal/mol from the MP4(SDQ) calculation,[7b]

$$Pd(PH_3)_2 + CH_2(CN)_2 \rightarrow \textit{cis}\text{-}Pd(H)[CH(CN)_2](PH_3)_2 \quad (8)$$

Ea = 25.1 kcal/mol and ΔE = 10.8 kcal/mol from the MP4(SDQ) calculation.[7b]

When the chelate diphosphine coordinates with the Pd center and the two CN groups are introduced to the sp^3 C atom, the C-H activation by the Pd center easily takes place.

$$Pd(dppe) + CH_2(CN)_2 \rightarrow \textit{cis}\text{-}Pd(H)[CH(CN)_2](dppe) \quad (9)$$

Ea = 19.3 kcal/mol and ΔE = -6.0 kcal/mol from the MP4(SDQ) calculation,

where dppe represents diphosphinoethane.

The homolytic Si-H σ-bond activation of silane by the Pt(0) complex is involved in the Pt-catalyzed hydrosilylation of alkene. Since silane is the Si analogue of methane, the comparison of reactivity between Si-H and C-H bonds is of considerable interest. As shown below, the Si-H σ-bond activation easily takes place with a much smaller activation barrier and larger exothermicity than those of the C-H σ-bond activation.[8]

$$Pt(PH_3)_2 + CH_4 \rightarrow \textit{cis}\text{-}Pt(H)(CH_3)(PH_3)_2 \quad (10)$$

Ea = 30.4 kcal/mol and ΔE = 6.5 kcal/mol from the MP4(SDQ) calculation,[8]

$$Pt(PH_3)_2 + SiH_4 \rightarrow \textit{cis}\text{-}Pt(H)(SiH_3)(PH_3)_2 \quad (11)$$

Ea = 0.7 kcal/mol and ΔE = -25.6 kcal/mol from the MP4(SDQ) calculation.[8]

These significant differences are clearly interpreted in terms of the stronger Pt-SiH_3 bond than the Pt-CH_3 bond and the weaker Si-H bond than the C-H bond. The σ* orbital of the Si-H bond also contributes to the large reactivity of silane, as follows: Since the σ* orbital of the Si-H bond is at a much lower energy than that of the C-H bond, the charge-transfer from the occupied d orbital to the σ* orbital is formed more favorably in the Si-H σ-bond activation than that in the C-H σ-bond activation.

The σ-bond activation of the Si-B bond easily occurs, as shown in eq. 12, while the C-B bond activation does not occur because of the significantly large endothermicity.[9]

$$Pd(PH_3)_2 + (HO)_2B\text{-}SiH_3 \rightarrow \textit{cis}\text{-}Pd(SiH_3)[B(OH)_2](PH_3)_2 \quad (12)$$

Ea = 1.2 kcal/mol and ΔE = -13.7 kcal/mol from the MP4(SDQ) calculation.

The reason is discussed in terms of the Pd-SiH_3 bond energy and the charge-transfer interaction between the occupied d orbital of the metal center and the empty p orbital of the boryl group. Since the Pd-SiH_3 bond is much stronger than the Pd-CH_3 bond, the product, cis-$Pd(SiH_3)[B(OH)_2](PH_3)_2$, is more stable than the CH_3 analogue, which increases the exothermicity of the reaction. Also, the boryl group possesses the empty p orbital perpendicular to the boryl plane and this empty p orbital participates in the charge-transfer interaction between the central metal and the substrate.

In general, the transition state is considered to be planar so as to form the strong charge-transfer interaction between the occupied d orbital of the central metal and the σ* orbital.[10] The planar transition state is certainly observed in the C-H and Si-H σ-bond activations. However, the transition state is not planar in the C-C and C-Si σ-bond activations by $Pt(PH_3)_2$.[11] There are two reasons; one is the steric repulsion between the subsituents on the C (or Si) atom and phosphine ligands, and the other is that the σ-bond is not broken in the transition state.

Though we expect that the non-dynamical correlation is important in the σ-bond activation, the activation barrier and the reaction energy converge upon going to the MP4(SDQ) method from the MP2 method. Thus, it would be concluded that the single reference wave function is useful to represent the transition state, probably because the σ-bond breaking does not occur significantly in the transition state.

Heterolytic C-H σ-Bond Activation

Compared to the homolytic C-H σ-bond activation, the heterolytic C-H σ-bond activation has not been sufficiently investigated except for several pioneering works. Here, I wish to report the detailed study of the C-H σ-bond activation of benzene and methane by Pd(II) and Pt(II) complexes. Though the C-H σ-bond activation of benzene by the Pd(II) acetate complex was very previously reported in the experimental field,[12] the theoretical study has not been carried out until our theoretical work. One of the interesting results is that the Pd(0) complex is not useful for the C-H σ-bond activation but the Pd(II) acetate complex can activate

the C-H bond of benzene.[12] Our computational study clearly shows that the Pd(II) formate complex, a model of the Pd(II) acetate complex, can activates the C-H σ-bond of benzene with a moderate activation barrier.[13] The difference between the Pd(0) and Pd(II) complexes comes from the fact that the strong O-H bond is formed in the product of the heterolytic σ-bond activation to stabilize the product.

$$Pd(\eta^2\text{-}O_2CH)_2 + H\text{-}Ph \rightarrow Pd(Ph)(\eta^2\text{-}O_2CH)(HCOOH) \quad (13)$$

Ea = 14.1 kcal/mol and ΔE = -17.5 kcal/mol from the MP4(SDQ) calculation,[13]

E(C-H) = 119.0 kcal/mol; E(Pd-O) = 23.2 kcal/mol; E(Pd-Ph) = 51.4 kcal/mol; E(O-H) = 107.0 kcal/mol from CCSD(T) calculations,[13]

$$Pd(PH_3)_2 + H\text{-}Ph \rightarrow \textit{cis}\text{-}Pd(H)(Ph)(PH_3)_2 \quad (14)$$

Ea = 24.1 kcal/mol and ΔE = 17.2 kcal/mol from the MP4(SDQ) calculation,[13]

E(C-H) = 119.0 kcal/mol; E(Pd-H) = 49.5 kcal/mol; E(Pd-Ph) = 51.4 kcal/mol from CCSD(T) calculations,[13]

where E(C-H) etc represents the C-H bond energy calculated with the CCSD(T) method. In the heterolytic C-H σ-bond activation, both the C-H bond of benzene and the Pd-O coordinate bond should be broken and the Pd-Ph and O-H bonds are formed. In the homolytic C-H σ-bond activation of benzene by $Pd(PH_3)_2$, on the other hand, only a C-H bond of benzene should be broken, but the Pd-H bond that is formed in the reaction is much weaker than the O-H bond. In other words, the formation of the strong O-H bond is an important driving force of the heterolytic σ-bond activation. From the population change, the heterolytic σ-bond activation is also understood in terms of the electrophilic attack of the metal center to the substrate.

The similar Pt(II) formate complex is less useful for the heterolytic σ-bond activation of benzene, unexpectedly, because the intermediate Pt(II)-benzene complex is too stable.

$$Pt(\eta^2\text{-}O_2CH)_2 + H\text{-}Ph \rightarrow Pt(Ph)(\eta^2\text{-}O_2CH)(HCOOH) \quad (15)$$

Ea = 20.9 kcal/mol and ΔE = -24.1 kcal/mol from the MP4(SDQ) calculation.

In these heterolytic σ-bond activations, the DFT method provides a much smaller activation barrier than the MP2-MP4(SDQ) and CCSD(T) methods. This would be because the DFT method is not useful very much for the ionic interaction.

The similar heterolytic σ-bond activation of H_2 is observed in the product-releasing step of the Ru-catalyzed hydrogenation of CO_2 into formic acid.[14]

$$Ru(H)(\eta^1\text{-}OCOH)(PH_3)_3 + H_2 \rightarrow Ru(H)_2(HCOOH)(PH_3)_3 \quad (16)$$

The transition state resembles well that of the C-H σ-bond activation of benzene by the Pd(II) formate complex.

Summaris and Perspectives

The homolytic C-H σ-bond activation has been well investigated theoretically. We have now detailed knowledge of the transition state and the important factors to this reaction. However, there remain several issues to be investigated theoretically. One of them is the activation of various σ-bonds such as the C-C, C-O, O-H, and N-H bonds. Though several pioneering works have been reported, the real system that can perform these σ-bond activations has not been predicted. If one can theoretically propose a good system that activates the C-C σ-bond, the conversion of alkane to organic compounds would be achieved.

The heterolytic C-H σ-bond activation is of considerable interest, because the formation of the H-X bond is one of important driving forces of this reaction. Utilizing this driving force, one can expect to perform the σ-bond activation with various metal complexes. It is necessary to clarify what combination of the metal center and the ligand is the best for this heterolytic σ-bond activation. Theoretical method should be powerful to provide reliable prediction of such system.

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