

2P082

Theoretical Study on Rhodium-Catalyzed Hydrosilylation of C=C and C=O Double Bonds

Liming Zhao¹, Naoki Nakatani², Yusuke Sunada³, Hideo Nagashima³, Jun-ya Hasegawa²

¹ Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan

² Institute for Catalysis, Hokkaido University, Japan

³ Institute for Materials Chemistry and Engineering, Kyushu University, Japan

[Abstract]

Rhodium containing catalysts for hydrosilylation reactions have attracted much research interests in academia and industry. In this work, Rh-catalyzed hydrosilylation of acetone and ethylene were theoretically investigated with DFT method. Besides existing mechanisms, we also proposed two new mechanisms, alternative Chalk-Harrod (aCH) mechanism and double hydride (DH) mechanism. In the ethylene case, DH mechanism is competitive with modified Chalk-Harrod (mCH) mechanism which is the most possible mechanism ($\Delta G^\ddagger = 11.2$ kcal/mol). In the acetone case, newly found DH mechanism is the most favorable mechanism ($\Delta G^\ddagger = 13.6$ kcal/mol). ACH mechanism was found to have similar activation energy to CH mechanism.

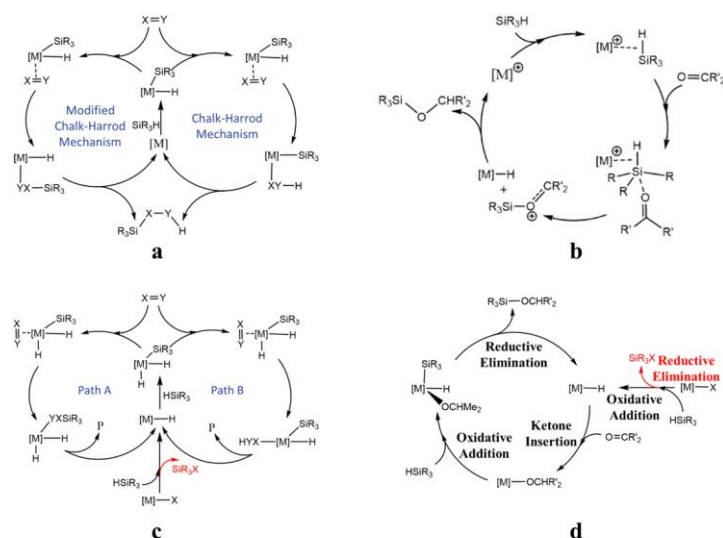
[Introduction]

Various catalytic system can promote the hydrosilylation of carbonyl compounds, especially metal complexes such as Iron-, Ruthenium-, Nickel-, Platinum- complexes. Among these different kinds of catalysis, Rh-catalyzed hydrosilylations of carbonyl compounds occupy a prominent place in hydrosilylation reactions because very mild reaction conditions are available.

In the literature, there are two proposed mechanisms for catalytic hydrosilylation of alkenes: one is Chalk-Harrod (CH) mechanism (C=C insertion into M-H bond), and the other is modified Chalk-Harrod (mCH) mechanism (C=C insertion into M-Si bond) (Scheme 1a).^[1] Due to strong affinity of O atom to Si atom, it has long been believed that the modified Chalk-Harrod is only a possible reaction pathway in the Rh-catalyzed hydrosilylation of carbonyl groups, however, there is no direct evidence neither from experimental nor from computational studies. An alternative pathway, the outer-sphere mechanism (scheme 1b), was recently proposed from the catalytic hydrosilylation of carbonyl compounds by the cationic Ir-complex.^[2] In simple terms, there is no clear conclusion in the catalytic mechanism for the hydrosilylations of carbonyl compounds, and therefore, it is worthy of revisiting the catalytic hydrosilylation by a common Rh-catalyst. In this study, already proposed mechanisms as well as newly possible reaction pathways, named double-hydride mechanism and alternative Chalk-Harrod (aCH) mechanism (Scheme 1c and 1d) will be explored to reveal this reaction theoretically.

[Methods]

Both geometry optimization and energy calculation were carried out with the DFT method using the ω B97XD functional implemented in Gaussian 09 program. In this work, a smaller basis set system BS-I where ECPs and valence electrons of Rh were represented with SDD, the 6-31+G* for P, O and Cl atoms and 6-31G* for other atoms and a larger basis set system BS-II in which the SDD with a f polarization function for Rh, the 6-311+G** for P, Cl and O atoms and the 6-311G** for other atoms were adopted. BS-I was used for geometry optimizations, vibrational frequency calculations and IRC analyses while BS-II was employed for the evaluation of energy changes which are sensitive to the basis set. In the energy evaluation, the Gibbs free energy correction in solution phase was also made by Whiteside's scheme.^[3]



Scheme 1. Mechanisms that have been considered. (a) Chalk-Harrod mechanism and modified Chalk-Harrod mechanism. (b) Outer-sphere mechanism. (c) Double-hydride mechanism. (d) Alternative Chalk-Harrod mechanism.

[Results and Discussion]

Basing on the optimized geometries, the free energy surfaces were calculated. Important conclusions were summarized as followings.

For the Rh-catalyzed hydrosilylation of acetone, the rate-determining steps for CH and mCH mechanism are both acetone insertion reaction with the energy barrier of 20.2 kcal/mol and 43.4 kcal/mol, respectively. Different from what have long been believed, mCH mechanism should be ruled out for its large energy barrier. Outer-sphere mechanism was also ruled out because no stable intermediate can be found. As for aCH and DH mechanism, the rate-determining steps are also both acetone insertion reaction where the activation energies are 20.9 kcal/mol and 13.6 kcal/mol, respectively. Thus DH mechanism is the most favorable reaction pathway for the lowest energy barrier. Partially broken C=O double bond in the insertion reaction explains why DH mechanism has the lowest energy.

For the Rh-catalyzed hydrosilylation of ethylene, CH and mCH mechanism has been well studied in Sakaki's work.^[1] We got similar result as the literature in this part. In the consideration of newly proposed mechanisms, we found the aCH mechanism preforms equally to CH mechanism where the rate-determining steps are both Si-C reductive elimination reaction with activation energies of 24.1 kcal/mol and 21.9 kcal/mol, respectively. Consequently, aCH and CH mechanism are competitive in both C=C and C=O double bond hydrosilylation. On the other hand, DH mechanism has similar energy barrier ($\Delta G^\ddagger=12.7$ kcal/mol) as mCH mechanism ($\Delta G^\ddagger=11.2$ kcal/mol) and they are two most favorable reaction pathways in this reaction. The agostic interaction was found to play an important role in stabilization the transition state of the rate-determining step in DH mechanism.

[References]

- [1] S. Sakaki, M. Sumimoto, M. Fukuhara, M. Sugimoto, H. Fujimoto and S. Matsuzaki, *Organometallics* **2002**, *21*, 3788-3802.
- [2] T. T. Metsänen, P. Hrobárik, H. F. T. Klare, M. Kaupp and M. Oestreich, *J. Am. Chem. Soc.* **2014**, *136*, 6912-6915.
- [3] M. Mammen, E. I. Shakhnovich, J. M. Deutch and G. M. Whitesides, *J. Org. Chem.* **1998**, *63*, 3821-3830.