

3P131

Theoretical Study of Rhodium-Catalyzed Hydrosilylation of Ketones: Chalk-Harrod vs. Modified Chalk-Harrod Mechanism

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[Introduction] Rhodium-catalyzed hydrosilylation of ketones yield siloxane which is an important industrial product and is widely used in human daily life. Thus it is of great use to take an insight into the mechanism of this typical reaction. It has long been believed that the Rh-catalyzed hydrosilylation of carbonyl group occurs via Modified Chalk-Harrod (MCH) mechanism from an analogy to the Rh-catalyzed hydrosilylation of alkenes.^[1] However, there is neither experimental nor theoretical evidence on the reaction mechanism. In this work, Both Chalk-Harrod (CH) mechanism, MCH mechanism and outer sphere mechanism were calculated as our purposes here are to investigate which mechanism is taken place in Rh-catalyzed hydrosilylation of ketones.

[Computational details] 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.

[Results and discussion] Fig. 1 simply explains the scheme of CH mechanism and MCH mechanism, as well as newly-proposed outer sphere mechanism. In the CH mechanism the acetone is inserted into Rh-H bond followed by isomerization because of strong trans-influence of silyl group, after which Si-C bond elimination reaction takes place to complete the catalytic cycle. In the MCH mechanism the acetone is inserted into Rh-Si bond, similarly followed by isomerization because of trans-influence of substituted alkyl group, then C-H bond elimination reaction is taken place to close the catalytic cycle. The rate determining steps (rds) in the two reaction paths are both acetone insertion reaction. Fig. 2 shows the potential energy profile of two mechanisms. From the Fig. 2 it can be easily found that the energy barrier in the MCH mechanism is higher than the CH mechanism by 12.9 kcal/mol from which we can clearly conclude that the Rh-catalyzed hydrosilylation of acetone is more likely to take place through the CH mechanism rather than the MCH mechanism. The reason for a larger activation energy in the MCH mechanism can be explained by the fact that sp^3 valence orbitals of SiMe_3 and sp^2 valence orbitals of oxygen must change their direction toward each other, while in the CH mechanism only CH_2 must change orbital direction to H. As for outer sphere mechanism,

a Si-O bond is formed through the carbonyl group attacking the Silyl group without hydrosilane addition to the metal complex. In this mechanism, a silylium ion-activated carbonyl group $R_3Si-O^+=CR_2$ and $M-H$ are two important intermediates. However, the total energy of these two important intermediates energy is much too higher than the former reactant which makes it unfavorable for Rh-catalyzed hydrosilylation of acetone.

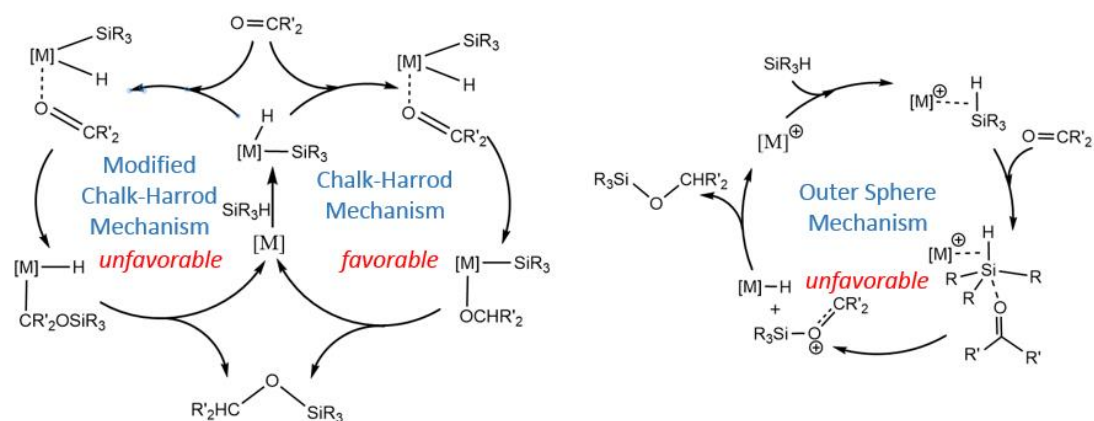


Fig. 1 scheme of the Chalk-Harrod, modified Chalk-Harrod mechanism (left) and ionic outer sphere mechanism (right)

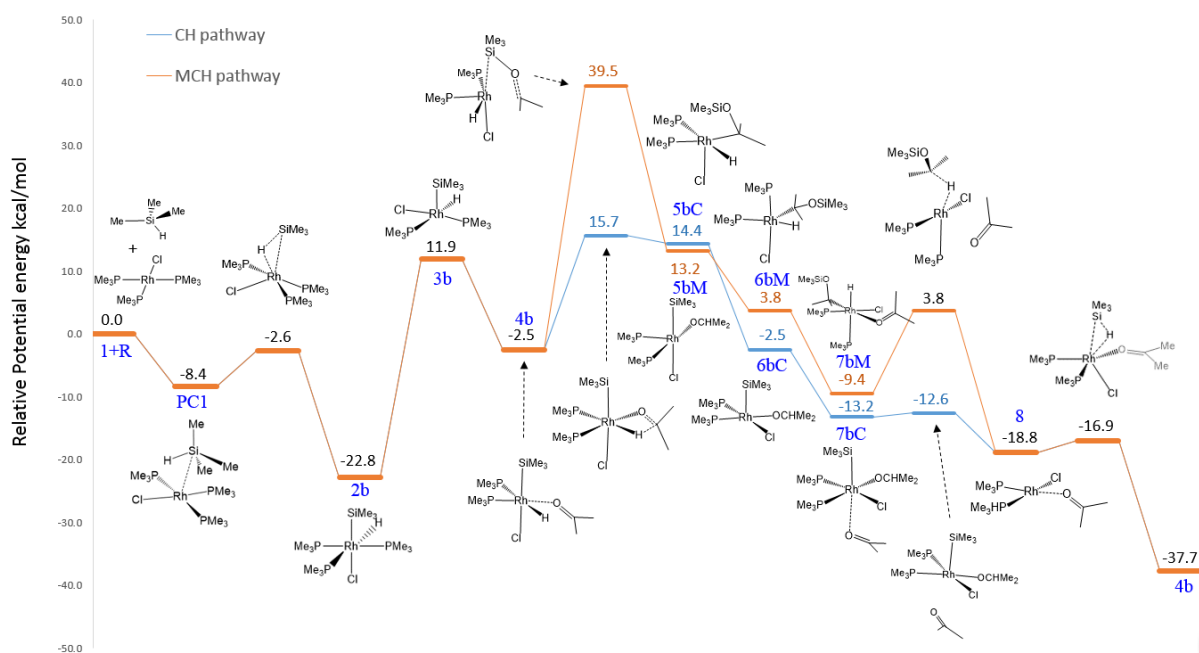


Fig. 2 Potential energy profile of the Chalk-Harrod mechanism and the modified Chalk-Harrod Mechanism

[Reference]

[1] K. Riener, M. P. Högerl, P. Gigler and F. E. Kühn, *ACS Catal.* **2012**, *2*, 613-621.