

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 occupies an important position in synthetic chemistry making it of great use to take an insight into the mechanism of this typical reaction. It has long been believed that this reaction 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 with density functional calculations.

[Results and discussion] Fig. 1 simply explains the scheme of three mechanisms. 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, while the energy barrier of the MCH mechanism is higher than the CH

mechanism by 12.9 kcal/mol leading to the conclusion that this reaction 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.

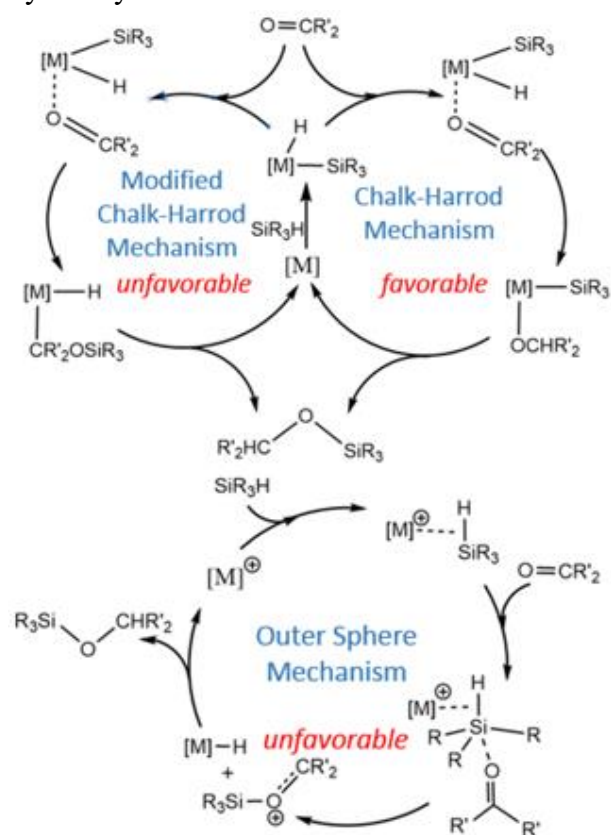


Fig. 1 scheme of the CH, MCH (up) and ionic outer sphere mechanism (down)

[Reference]

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