

The Secrets of Gold Catalysis

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We have studied so far more than 200 homogeneous catalysis reactions (including Ti, Fe, Ni, Cu, Zr, Rh, Pd, Hf, Re, Pt, and Au) utilizing the Unified Reaction Valley Approach (URVA). [1] URVA describes reaction path and reaction valley, which are traced by the reaction complex from the van der Waals region to the transition state and, then, out into the exit channel where the products are located. Changes in the electronic structure of the reaction complex are registered by an accurate scanning of the potential energy surface. Especially, the curving of the reaction path is connected to the chemical processes such as bond breaking/forming, charge polarization and transfer, rehybridization, etc.

The usefulness of URVA is demonstrated for Au-catalyzed reactions such as the rearrangement of allylic acetate, the alkyne carboxylation and the gold catalyzed Rautenstrauch rearrangement. [2] These reactions have in common that the non-catalyzed reaction has a high barrier. For example, the curvature diagram for the allylic acetate rearrangement reveals the existence of a “hidden intermediate” in the vicinity of the transition state. The hidden intermediate is a transient point along the reaction path at which the reaction complex “rests” after one and before the next major electronic structure change. A hidden intermediate can be converted into a real intermediate with the help of a suitable catalyst thus making out of a one-step high-barrier reaction a two-step reaction with low energy barriers. We will demonstrate how URVA provides valuable information for *de novo* catalyst design.

[1] T. Sexton, E. Kraka, and D. Cremer, *J. Phys. Chem. A.*, 120, 1097-1111 (2016).

[2] M. C. Reis, C. Silva López, E. Kraka, D. Cremer, and O. Nieto Faza, *Inorg. Chem.*, 55, 8636-8645 (2016).