Basics of Catalysis and Kinetics

Nobel laureates in catalysis:

Haber (1918) Ziegler and Natta (1963) Wilkinson, Fischer (1973) Knowles, Noyori, Sharpless (2001) Grubbs, Schrock, Chauvin (2006) Ertl (2007) Heck, Negishi, Suzuki (2010) The concept of catalyst was first introduced by Berzelius in the 19th century.

Subsequently, Ostwald came up with the definition that we still use today:

"A catalyst is a substance that increases the rate of a chemical reaction, without being consumed or produced"...

Berzelius, J. J. Ann. Chim. Phys. **1836**, *61*, 146-151 Ostwald, W. Z. Phys. Chem. **1894**, *15*, 705-706

The Catalyst and the Rate of a Reaction



The catalyst changes only the rate of the reaction, and does not change the thermodynamics.

However, the temperature can affect equilibrium concentrations: $\Delta G = \Delta H - T \Delta S$

Historical basis for the Analysis of Catalytic Kinetics

The Michaelis-Menten Kinetics



Thermal, Catalyzed, Inhibited, and Promoted Reactions



Thermal, Catalyzed, Inhibited, and Promoted Reactions



Thermal versus TM-catalyzed Paths



Reaction Progress

Often the catalytic reaction occurs by a mechanism that is completely different from that of the corresponding uncatalyzed process. In the catalyzed process the reaction typically occurs by more steps, but the activation energy of each step is lower than that of the uncatalyzed process. The resulting global energetic barrier is thus lower that of the uncatalyzed reaction.

Alkene hydroboration with $(RO)_2BH$ is an example.



- Alkene-borane π -complex
- Concerted 4-membered step

Efficiency of the Catalytic Cycle (TON and TOF)

A catalyst is not eternal and after certain number of turns it decomposes, thereby losing its catalytic activity. It is thus useful to define the *turnover number* (*TON*) of a catalyst as *the number of moles of substrate that a mole of catalyst can convert before becoming inactivated*. Of course, the TON is a function of the chemical yield.

The **turnover frequency (TOF)** is the number of moles of product per mole of catalyst per unit time, that is to say, the turnover number per unit time. As the rate may change with the time, reported TOF's are usually average.



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The Hammond's Postulate

The Hammond's postulate is a hypothesis derived from transition state theory, and states that the structure of a transition state resembles that of the species nearest to it in free energy. That is to say, that the transition state of an endothermic reaction resembles the products (late transition state), while that of an exothermic reaction resembles the reactants (early transition state).



Hammond, G. S. (1955). J. Am. Chem. Soc. 1955, 77, 334-338

The Curtin-Hammett Principle

The Curtin-Hammett principle states that, for a reaction that has a pair of reactive intermediates or reactants that interconvert rapidly (for example conformers), each going irreversibly to a different product, the **product ratio** will depend both on the **free energy of the transition state going to each product (usually essentially)** and the difference in energy between the two conformers (usually to a little extent). Hence, the product distribution will not necessarily reflect the equilibrium distribution of the two intermediates



Seeman J. I. (1983 Chemical Reviews 1983, 83, 83–134

Example of a Generic Tolman Catalytic Cycle



The Tolman cycle is a clockwise catalytic cycle composed only by organometallic species. The concentration of the active catalyst is represented by the sum of the concentrations of all catalytic species within the cycle. Maximum efficiency is achieved when all of the catalyst is active and lies within the catalytic cycle. If the rate of a step is sufficiently high, it may overwhelm an unfavorable preceding equilibrium present in the cycle (*kinetic coupling*).

In a catalytic cycle the net rates of step are identical

Although the rate constants of the different steps in a catalytic cycle may be different, once the system has reached the *steady state, the net rates*¹ of each *step are identical*. Indeed, the rate of each step is proportional to the rate constant and to the concentration of the reagents and species involved in the catalytic cycle. As a consequence, the concentrations of the species that lie in the cycle vary to make the rate of each step of the catalytic cycle identical!

The rate with the smallest pseudo-first order² rate constant ($k_n[reagent_n]$) is called **turnover-limiting step (TLS)**. This step controls the efficiency of the catalytic process as the rate of a catalytic reaction cannot exceed k_{TLS} ·[cat_n][reagent_n].

Most of the catalyst consists of the species preceding the TLS,³ which is normally the *resting state*, the species present in the highest amount.

- 1) For a step $cat_n + reagent_n \rightarrow cat_{n+1}$ the net rate is $k_n [cat_n][reagent_n]$ menus the reverse rate
- 2) Within the cycle the concentration of the catalyst remains constant.
- 3) It is erroneous to call the TLS the "slow step", as all the steps proceed with the same net rate.



The *energetic span* (δE) is related to the *turnover frequency TOF* of the catalytic cycle. The smallest it is, the fastest the catalysis.

Thus, a good catalytic cycle must consist of low-lying transition states with high-lying intermediates!

Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254. Kozuch, S.; Amatore, C.; Jutand, A. Shaik, S. Organometallics, **2005**, *24*, 2319. Kozuch, S.; Shaik, S. *Acc. Chem. Res.* **2011**, *44*, 101-110. Kozuch, S.; Martin, J. M. L. *ChemPhysChem* **2011**, *12*, 1413.



 $Nu^{-} + RCH_2 - X \implies Nu - CH_2R + X^{-}$ $Nu^{-} = F^{-}, I^{-}$



Trying to improve the rate of the slowest step of a catalytic cycle by increasing the energy of its reactant, so as to decreases its E_a , has (in contrast to a stoichiometric reaction) no chance of success, if the catalytic sequence is preserved otherwise.

Indeed, the result is opposite, as the gain in lowering Ea is more than lost due to the increase of ΔE ! As a result, the net effect is that the energetic span δE increases and the global rate decreases.

About the Definitions of Rate Determing Step

- 1. The step with the smallest rate constant
- 2. The step with the highest energy TS
- 3. The step with the rate constant that exerts the strongest effect (IUPAC)



Result: The RDS is a bad model. The **States** [TOF determining Intermediate (**TDI**) and TOF determining TS (**TDTS**)] exert the strongest effect on the overall rate.





PhBr + PhB(OH)₃⁻ → PhPh (L = SPhos)



Kozuch, S.; Martin, J. M. L. Chem. Commun., 2011, 47, 4935

PhBr + PhB(OH)₃⁻ → PhPh (L = InPhos)



