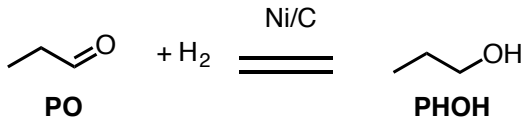
ChE-403 Problem Set 2.4

Week 8

Problem 1

Let's consider the hydrogenation of propanal to propanol over a supported nickel catalyst:



Assume that the rate-limiting step is the reversible chemisorption of PO on the surface and that dihydrogen adsorbs dissociatively on the Ni surface.

Can you propose a complete (and reasonable) sequence of steps and a kinetics expression that satisfies the following experimentally measured rate?

$$r = \frac{cst1\ P_{PO} - cst2\ P_{PHOH}/P_{H_2}}{1 + cst3\ P_{H_2}^{0.5}}$$

Hint: the expression should suggest a simplification to you.

Problem 2

Consider the following reaction that happens over an activated carbon catalyst:

$$CO + Cl_2 \Longrightarrow COCl_2$$

From computational studies it is likely that the rate-limiting step is a surface reaction. From previous studies we know that Cl_2 and $COCl_2$ tend to bind to the catalyst. No information is available for CO. Cl_2 does not dissociate when binding.

Can you propose at least two potential (and reasonable) mechanisms and derive the associated kinetics? Can you suggest a potential experiment that would allow you to differentiate between these two mechanisms?

Problem 3

In class we were studying the following reaction:

$$A \Rightarrow B$$

With the following steps:

$$\begin{aligned} &(1) \quad A + * \rightleftharpoons A* \\ &(2) \quad A* \rightleftharpoons B* \\ &(3) \quad B* \rightleftharpoons B + * \end{aligned}$$

In case 1 and 3 we assumed that the overall reactions could be reduced to a RDS and a single equilibrium reaction. In doing so, we also assumed a MARI. What if we assumed that we kept two equilibrium steps and did not assume a MARI? This would lead to the following mechanisms:

Case 1:

$$\begin{aligned} &(1) \quad A + * \rightarrow A* \\ &(2) \quad A* \rightleftharpoons B* \\ &(3) \quad B* \rightleftharpoons B + * \end{aligned}$$

Case 2:

$$\begin{aligned} &(1) \quad A + * \rightleftharpoons A* \\ &(2) \quad A* \rightleftharpoons B* \\ &(3) \quad B* \rightarrow B + * \end{aligned}$$

Would the result be different?