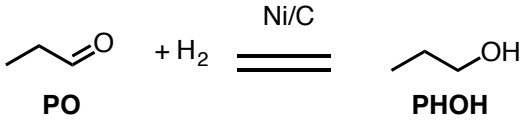
ChE-403 Problem Set 2.4

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.

Solution:

The following mechanism can be proposed.

$$PO + * \rightleftarrows PO*$$

$$H_2 + ** \rightleftarrows 2H*$$

$$PO* + H* \rightleftarrows PHO* + *$$

$$PHO* + H* \rightleftarrows PHOH* + *$$

$$PHOH* \rightleftarrows PHOH + *$$

The first two steps are given and the following steps can be assumed to be at equilibrium because at this point we don't know any better.

The rate expression obtained experimentally strongly suggests that H* is the MARI. Indeed, what is under the fraction bar usually represents what is on the surface and only the expression representing H* is there.

Therefore, let's start with the RDS:

$$r = k_1[PO][*] - k_{-1}[PO\ *]$$

Let's apply all the equilibria:

$$[PO\ *] = \frac{[PHO\ *][*]}{K_3[H\ *]}$$

$$[PHO\ *] = \frac{[PHOH\ *][*]}{K_4[H\ *]}$$

$$[PHOH\ *] = \frac{[PHOH][*]}{K_5}$$

We take them all together to get:

$$[PO\ *] = \frac{[PHOH\ *][*]^2}{K_3K_4[H\ *]^2} = \frac{[PHOH][*]^3}{K_3K_4K_5[H\ *]^2}$$

With:

$$K_2 = \frac{[H\ *]^2}{[H_2][*]^2}$$

We have:

$$[PO\ *] = \frac{[PHOH][*]}{K_2K_3K_4K_5[H_2]}$$

With the site balance with H* as the MARI:

$$[*] = [*]_0 - [H\ *] = [*]_0 - [*](K_2[H_2])^{1/2}$$

$$[*] = \frac{[*]_0}{1 + (K_2[H_2])^{1/2}}$$

With all that, we have:

$$r = k_1[PO][*] - k_{-1}[PO\ *] = \frac{k_1[PO][*]_0 - \frac{k_{-1}[PHOH][*]_0}{K_2K_3K_4K_5[H_2]}}{1 + (K_2[H_2])^{1/2}}$$

Which is the expression we were looking for…

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?

Solution:

1) An first mechanism could be:

$$Cl_2 + * \overset{K_1}{\rightleftharpoons} Cl_2*$$

$$CO + * \overset{K_2}{\rightleftharpoons} CO*$$

$$CO* + Cl_2* \xrightarrow{k_3} COCl_2* + *$$

$$COCl_2* \overset{K_4}{\rightleftharpoons} COCl_2 + *$$

Let's write the RDS, which is a Langmuir-Hinshelwood step (see section 2.4.2).

Therefore the kinetics are:

$$r = k_3[CO ** Cl_2] = k_3 \frac{[CO *][Cl_2 *]}{[*]_0}$$

$$[Cl_2 *] = K_1[Cl_2][*]$$

$$[CO *] = K_2[CO][*]$$

$$[*] = [*]_0 - [Cl_2 *] - [CO *] - [COCl_2 *]$$
$$= [*]_0 - K_1[Cl_2][*] - K_2[CO][*] - K_4[COCl_2][*]$$

$$[*] = \frac{[*]_0}{1 + K_1[Cl_2] + K_2[CO] + K_4[COCl_2]}$$

$$r = \frac{k_3 K_2 K_1 [*]_0 [Cl_2][CO]}{(1 + K_1[Cl_2] + K_2[CO] + K_4[COCl_2])^2}$$

2) A second possible mechanism could be an Eley Rideal mechanism with CO (because we don't know if it is actually present on the surface):

$$Cl_2 + * \overset{K_1}{\rightleftharpoons} Cl_2*$$

$$CO + Cl_2* \xrightarrow{k_2} COCl_2*$$

$$COCl_2* \overset{K_3}{\rightleftharpoons} COCl_2 + *$$

In this case the RDS is simpler:

$r = k_3[CO][Cl_2 *]$

$[Cl_2 *]$ is given by the same expressions as above (except that there is no CO on the surface so it does not appear in the site balance):

$$[Cl_2 *] = K_1[Cl_2][*] = \frac{K_1[*]_0[Cl_2]}{1 + K_1[Cl_2] + K_3[COCl_2]}$$

$$r = \frac{k_3K_1[*]_0[Cl_2][CO]}{1 + K_1[Cl_2] + K_3[COCl_2]}$$

You could differentiate using any experiment in which you varied $[Cl_2]$, $[CO]$ and $[COCl_2]$ and fit the rate data to see which expression fit. A particularly easy experiment would be to work at high CO pressure compared to the other components and see if $r \propto 1/[CO]$ (case 1) or $r \propto [CO]$ (case 2).

Problem 3

In class we were studying the following reaction:

$$A \Rightarrow B$$

With the following steps:

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

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:

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

Case 2:

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

Would the result be different?

Solution:

Case 1:
We start by writing the RDS:

$$r = k_1[A][*]$$

With the site balance (A* is no longer the MARI):

$$[*] = [*]_0 - [A*] - [B*]$$

$[A*] = K_{2'}[B*]$
I am using $K_{2'}$ to differentiate from K_2 that we saw in class.

and

$$[B*] = K_3[B][*]$$

$\rightarrow [*] = [*]_0 - (K_2, + 1)K_3[B][*]$

$$[*] = \frac{[*]_0}{1 + (K_2, + 1)K_3[B]}$$

This is just like what we found in class except that we have $(K_2, + 1)K_3$ instead of just K_2 as the constant. But since they are constants, this is effectively the same expression.

Case 2:
We start by writing the RDS:

$$r = k_3[B*]$$

$[B*] = K_2,[A*]$

Here I am using the convention where I write the equilibrium in the direction of the (former) MARI. However, we can also write it the other way and get $1/K_{2'}$.

$$[A*] = K_1[A][*]$$

$\rightarrow [B*] = K_2,K_1[A][*]$

The site balance: $[*] = [*]_0 - [A*] - [B*]$

$\rightarrow [*] = [*]_0 - (1 + K_2,)K_1[A][*]$

$$[*] = \frac{[*]_0}{1 + (1 + K_2,)K_1[A]}$$

$\rightarrow [B*] = K_2,K_1 \frac{[A][*]_0}{1+(1+K_2,)K_1[A]}$

$$r = k_3K_2,K_1 \frac{[A][*]_0}{1 + (1 + K_2,)K_1[A]}$$

This is not exactly what we found in class. It is only equivalent to the class expression if $K_2, \gg 1$. If this is the case we have K_2,K_1, which would be equivalent to the K_1, expression from class. Note that if $K_2, \gg 1$ then $[B*] \gg [A*]$, confirming our assumption from class that B* is the MARI. However, even if we did not have $K_2, \gg 1$, it would have the same functional form as what we found in class but would lead to a different value for k_3. Therefore, assuming a MARI here will not change how well the model fits the data and futher experiments would be needed to know wheather there was a MARI or not…