

Organometallic Chemistry and Homogeneous Catalysis

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Lecture N9

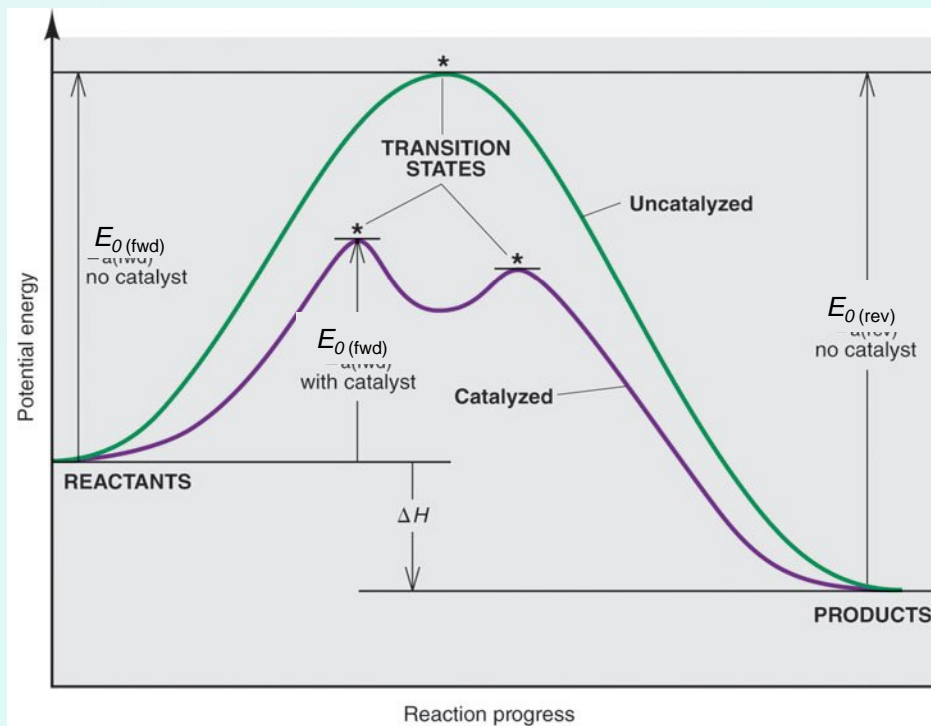
Kashiwa Campus, December 25, 2009



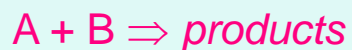
Reactions with a high barrier (E_0) have a high activation energy (E_a) and hence a slow rate because of the exponential factor:

$$k = Ae^{-E_a/RT}$$

A catalyst provides a lower energy pathway to products and hence a greatly enhanced reaction rate.

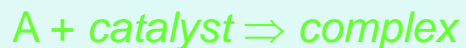


Uncatalyzed:



{slow}

Catalyzed:

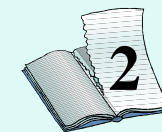


{fast}



{fast}

The catalyst is not consumed, but is regenerated along with the products.



Homogeneous Catalysis

- ▪ The catalyst is in the same phase as the reactants and

In homogeneous catalysis the reactants, products and catalyst are all in the same phase. Often the reactants, products and catalyst are all dissolved in the same solvent. Due to environmental considerations this solvent is often water. In these situations the catalyst may be a transition metal ion catalysing a redox reaction.

- ▪ Examples:

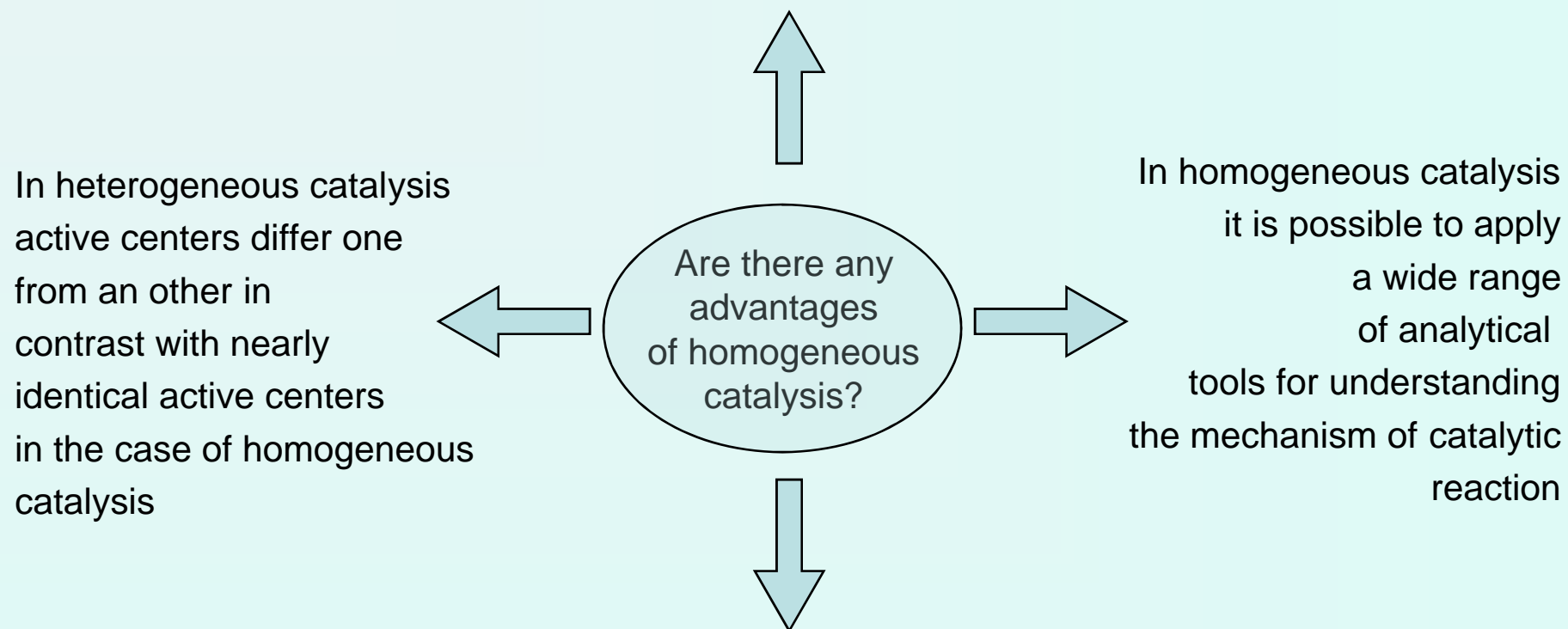
- 1) Hydrolysis of esters by acids (liquid-liquid)
- 2) Oxidation of SO_2 by NO_2 (vapour-vapour)
- 3) Decomposition of potassium chlorate by MnO_2 (solid-solid)

- ▪ Disadvantages:

- 1) Difficult to operate commercially.
- 2) Liquid phase operation places restrictions on temperature and pressure, so equipment is complicated
- 3) The catalyst must be separated from the products, imposing additional difficulties



In homogeneous catalysis any atom or molecule could act as an active center in contrast to the heterogeneous catalysis (where only about 5% of atoms act as active centers)



In homogeneous catalysis it is possible to tune the structure more target to increase activity



In homogeneous catalysis, a few general constraints can be defined:



- The catalytically active metal species must have a vacant coordination site, i.e. $NVE=16$ at most or even 14, in order to allow substrate molecules to coordinate. Sometimes, weak ligands or solvent ligands can be present and are easily displaced by substrate molecules. Bulky phosphines such as triphenylphosphine are easily dissociatively displaced and thus constitute a reservoir of vacant coordination sites that can be filled or emptied at will. In catalytic cycles, the various entities successively involved have most of the time NVEs alternating between 16 and 18.
- The role of the other ligands ("ancillary") is to avoid the precipitation of the metal and to insure a correct stereoelectronic balance (electronic density on the metal center, steric effect, trans effect) allowing all the individual reactions along the catalytic cycle to proceed at a good rate and with a good selectivity.
- The catalytic rings are represented in the following way:

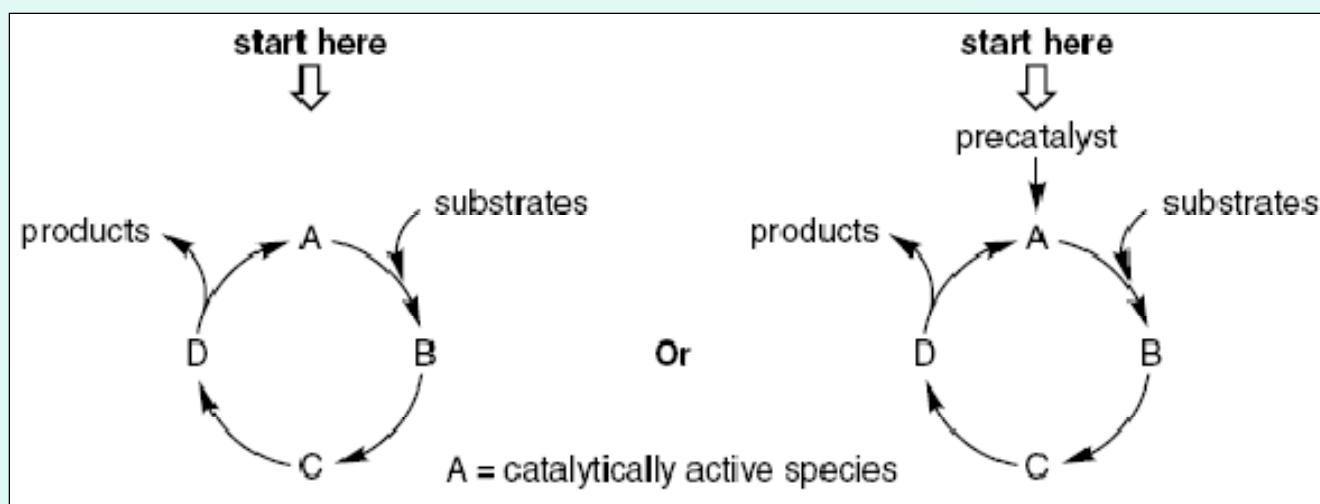
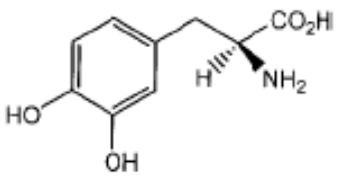
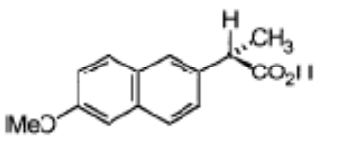
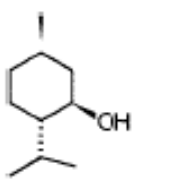
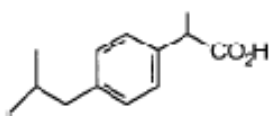
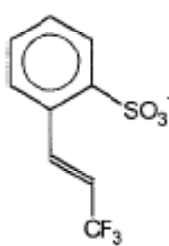
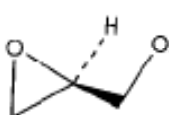
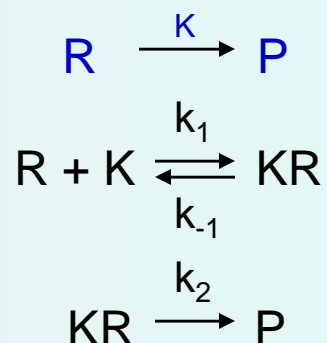


TABLE 1.1 Products of Homogeneous Catalytic Reactions

| Structure | Name and use | Process |
|---|---|---|
|  | L-Dopa Drug for Parkinson's disease | Asymmetric hydrogenation |
|  R - Liver toxin S - Anti-inflammatory | Naproxen® Anti inflammatory drug | Asymmetric hydroformylation or hydrocyanation or hydrogenation! |
|  | L-Menthol Flavoring agent | Asymmetric isomerization |
|  | Ibuprofen Analgesic | Catalytic carbonylation |
|  | An intermediate for Prosulfuron Herbicide | C-C Coupling (Heck reaction) |
|  | R-Glycidol One of the components of a heart drug | Asymmetric epoxidation (Sharpless epoxidation) |

About 15% of world chemical products are manufactured using homogeneous catalysts

Kinetics of homogeneous catalysis (general issues)



In a closed system at $V = \text{const}$ this reaction could be described with the following equations:

$$(1) \quad \frac{dC_R}{dt} = -k_1 C_R C_K + k_{-1} C_{KR}$$

$$(2) \quad \frac{dC_{KR}}{dt} = k_1 C_R C_K - k_{-1} C_{KR} - k_2 C_{KR}$$

$$(3) \quad \frac{dC_P}{dt} = k_2 C_{KR}$$

To these equations the material balance on the catalyst could be added:

$$C_K^0 = C_K + C_{KR}$$

C_K^0 – overall catalyst concentration

C_K – “free” catalyst in the reaction mixture

C_{KR} – catalyst, bonded to a complex with the reagent



According to the Bodenstein's method of quasi-stationary concentrations:



$$\frac{dC_{KR}}{dt} = 0$$

$$k_1 C_R C_K - k_{-1} C_{KR} - k_2 C_{KR} = 0$$

$$k_1 C_R (C_K^0 - C_{KR}) - k_{-1} C_{KR} - k_2 C_{KR} = 0$$

$$k_1 C_R C_K^0 - k_1 C_R C_{KR} - k_{-1} C_{KR} - k_2 C_{KR} = 0$$

$$C_{KR} = \frac{k_1 C_R C_K^0}{k_1 C_R + k_{-1} + k_2}$$

Now we can use this equation for C_{KR} in equation (3) to get the final equation for the rate of reaction:

$$\frac{dC_P}{dt} = k_2 C_{KR} = k_2 \frac{k_1 C_R C_K^0}{k_1 C_R + k_{-1} + k_2}$$

Analysis:

$$\frac{dC_P}{dt} = k_2 \frac{k_1 C_R C_K^0}{k_1 C_R + k_{-1} + k_2}$$

- (1) The rate of reaction has the first order on the concentration of catalyst
- (2) The rate of reaction has complicated dependence on the concentration of reagent

a) at low concentrations of R:

$$\frac{dC_P}{dt} = k_2 \frac{k_1 C_R C_K^0}{\underbrace{k_1 C_R + k_{-1} + k_2}_{\ll}} \cong k_2 \frac{k_1 C_R C_K^0}{k_{-1} + k_2}$$

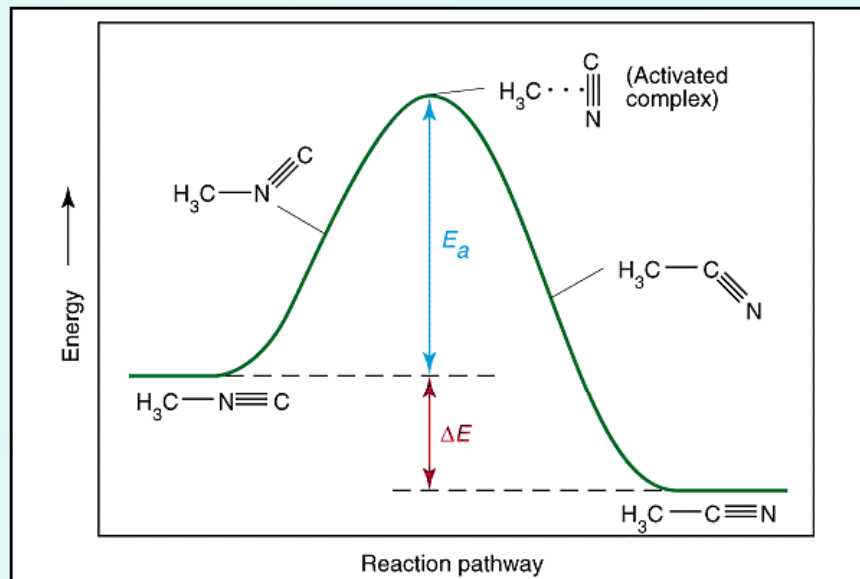
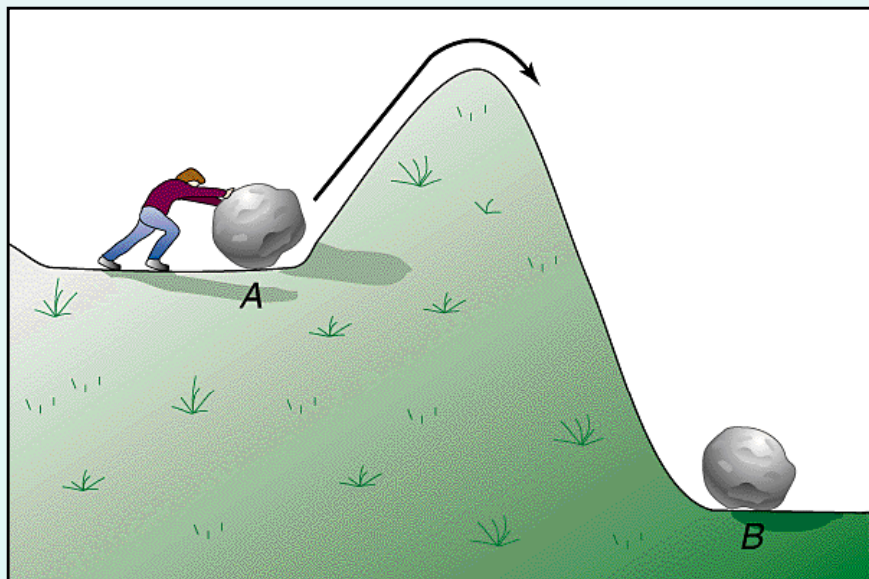
first order on the R concentration

a) at high concentrations of R:

$$\frac{dC_P}{dt} = k_2 \frac{k_1 C_R C_K^0}{\underbrace{k_1 C_R + k_{-1} + k_2}_{\gg}} \cong k_2 C_K^0$$

zero order on the R concentration

Energy of Activation of the Catalyzed Reaction



According to the Arrhenius equation:

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}$$

Catalyst may influence on both k_0 and E_a :

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}$$

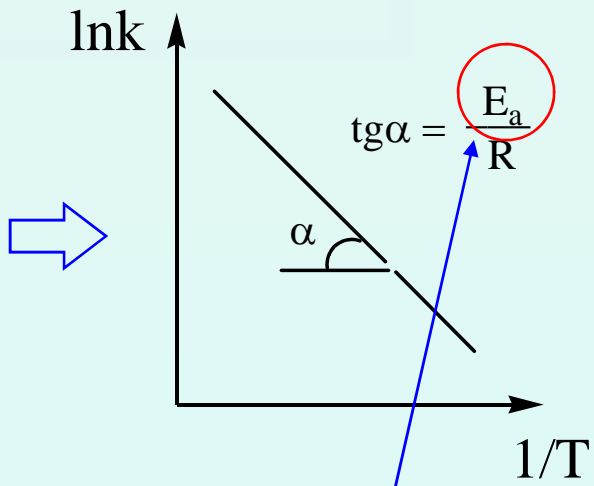


How to find the E_a from the experimental data?

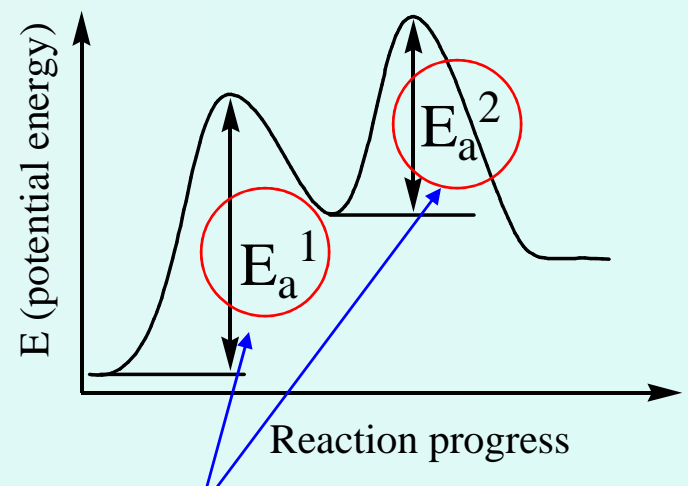
$$k = k_0 \cdot e^{-\frac{E_a}{RT}} \Rightarrow \ln k = \ln k_0 - \frac{E_a}{RT} \Rightarrow \ln k = f\left(\frac{1}{T}\right)$$

\parallel some constant \parallel some (other) constant

| T | k | 1/T | lnk |
|-----|-----|-----|-----|
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |

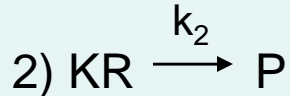
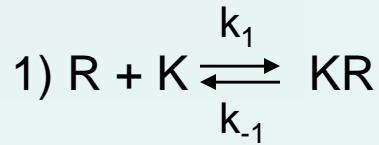
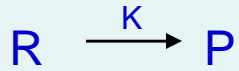


Effective Activation Energy



“True” Activation Energy

Effective & “True” Activation Energies are not always equal to each other!



$$\frac{dC_P}{dt} = k_2 \frac{k_1 C_R C_K^0}{k_{-1} + k_2}$$

$$\Rightarrow \frac{dC_P}{dt} = k_{ef} C_R$$

$$k_{ef} = \frac{k_1 k_2 C_K^0}{k_{-1} + k_2}$$

$$\Rightarrow \ln k_{ef} = \ln k_1 + \ln k_2 + \ln C_K^0 - \ln(k_{-1} + k_2) \Rightarrow$$

$$\Rightarrow \frac{d \ln k_{ef}}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_2}{dT} + \underbrace{\frac{d \ln C_K^0}{dT}}_{// 0, \text{ because } C_K^0 - \text{const}} - \frac{d \ln(k_{-1} + k_2)}{dT}$$



$$\frac{d \ln k_{ef}}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_2}{dT} - \frac{1}{k_{-1} + k_2} \frac{d(k_{-1} + k_2)}{dT}$$

Reminding:

$$d \ln x = \frac{1}{x}$$

but if x is a complex function:

$$\frac{d \ln x}{dy} = \frac{1}{x} \left(\frac{dx}{dy} \right)$$



$$\frac{d \ln k_{ef}}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_2}{dT} - \frac{1}{k_{-1} + k_2} \frac{d(k_{-1} + k_2)}{dT}$$

$$\frac{d(k_{-1} + k_2)}{dT} = \frac{dk_{-1}}{dT} + \frac{dk_2}{dT} = \frac{k_{-1}}{k_{-1}} \frac{dk_{-1}}{dT} + \frac{k_2}{k_2} \frac{dk_2}{dT} = k_{-1} \frac{d \ln k_{-1}}{dT} + k_2 \frac{d \ln k_2}{dT}$$



$$\frac{d \ln k_{ef}}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_2}{dT} - \frac{k_{-1} \frac{d \ln k_{-1}}{dT} + k_2 \frac{d \ln k_2}{dT}}{k_{-1} + k_2}$$

Reminding:

$$d\left(\frac{1}{x}\right) = -\frac{1}{x^2}$$

Let's come back to the Arrhenius equation:

$$\left. \begin{aligned} k &= k_0 \cdot e^{-\frac{E_a}{RT}} \\ \ln k &= \ln k_0 - \frac{E_a}{RT} \end{aligned} \right\} \Rightarrow \frac{d \ln k}{dT} = \frac{d \ln k_0}{dT} - \frac{d\left(\frac{E_a}{RT}\right)}{dT} \Rightarrow \frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

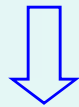
// 0, because k_0 - const

So, what we have:

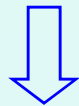


$$\frac{d \ln k_{\text{ef}}}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_2}{dT} - \frac{k_{-1} \frac{d \ln k_{-1}}{dT} + k_2 \frac{d \ln k_2}{dT}}{k_{-1} + k_2}$$

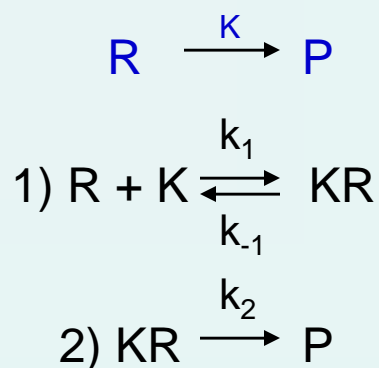
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$



$$\frac{E_{\text{ef}}}{RT^2} = \frac{E_1}{RT^2} + \frac{E_2}{RT^2} - \frac{k_{-1} \frac{E_{-1}}{RT^2} + k_2 \frac{E_2}{RT^2}}{k_{-1} + k_2}$$



$$E_{\text{ef}} = E_1 + E_2 - \frac{k_{-1} E_{-1} + k_2 E_2}{k_{-1} + k_2}$$

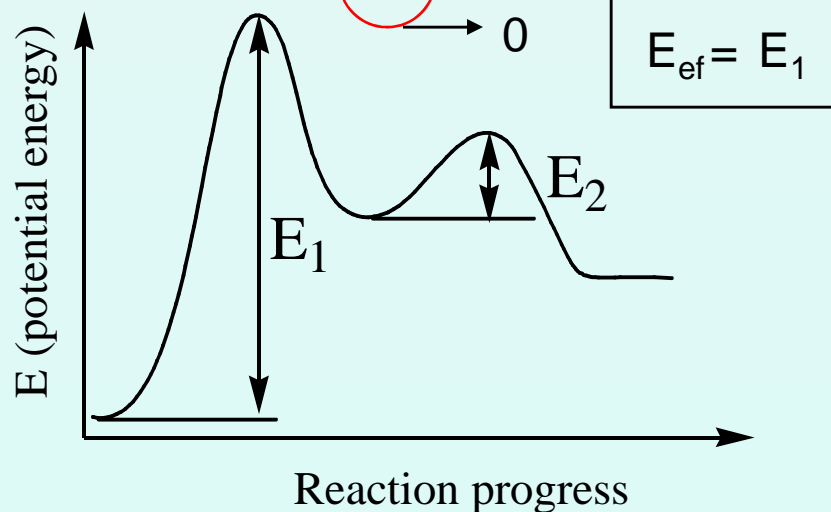


$$E_{ef} = E_1 + E_2 - \frac{k_{-1} E_{-1} + k_2 E_2}{k_{-1} + k_2}$$

First stage is a **rate determining step**

$$(k_2 \gg k_{-1})$$

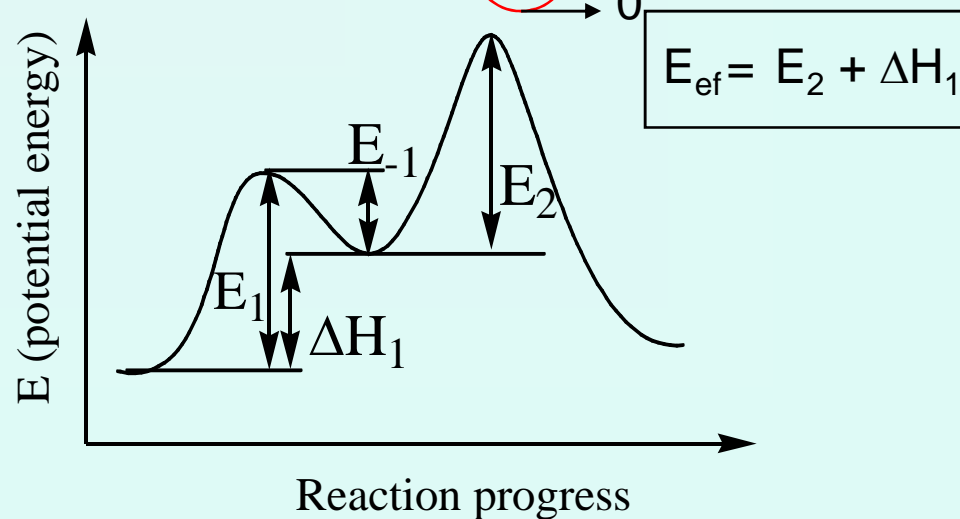
$$E_{ef} = E_1 + E_2 - \frac{k_{-1} E_{-1} + k_2 E_2}{k_{-1} + k_2} = E_1$$



Second stage is a **rate determining step**

$$(k_2 \ll k_{-1})$$

$$E_{ef} = E_1 + E_2 - \frac{k_{-1} E_{-1} + k_2 E_2}{k_{-1} + k_2} = E_1 + E_2 - E_{-1}$$



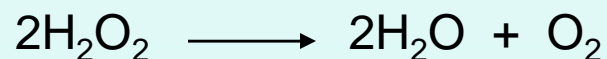
So, when the first step is a **rate determining step**, the effective activation energy is a “true” activation energy.



When there are fast steps prior to the **rate determining step**, the effective activation energy could have higher or lower value (in compare to the “true” activation energy of the rate determining step), depending on the sign (positive or negative) of the enthalpy of the fast step(s).

What values of the activation energy could be?

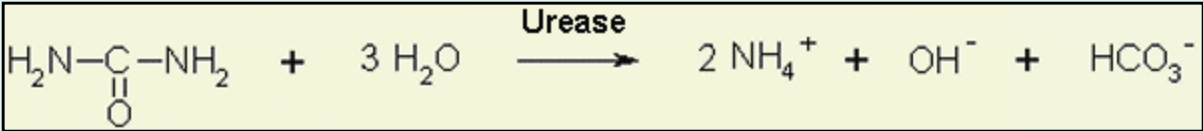
For the most chemical reactions E_a is in the range of 60-105 kJ/mole



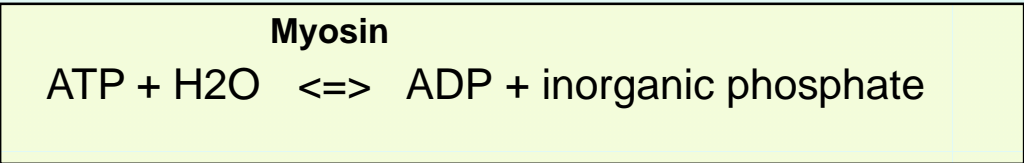
| Catalyst | E_a |
|----------------------------------|-------|
| without a catalyst | 75.6 |
| Fe^{3+} in a water sol. | 54.6 |
| Pt (powder) | 47.0 |
| catalase (enzyme) | 20.0 |

Catalyst may influence on both k_0 and E_a :

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}$$



| Substrate | Catalyst | k, s^{-1} | k_0, s^{-1} | $E_a, \text{kJ/mole}$ |
|-----------|------------------------|---------------------|----------------------|-----------------------|
| Urea | H_3O^+ | $7.4 \cdot 10^{-7}$ | $1.8 \cdot 10^{10}$ | 78.4 |
| Urea | Urease | $5.0 \cdot 10^6$ | $1.7 \cdot 10^{13}$ | 27.2 |



| Substrate | Catalyst | k, s^{-1} | k_0, s^{-1} | $E_a, \text{kJ/mole}$ |
|-----------|------------------------|---------------------|----------------------|-----------------------|
| ATP | H_3O^+ | $4.7 \cdot 10^8$ | $2.4 \cdot 10^9$ | 84.8 |
| ATP | Myosin | $8.2 \cdot 10^{26}$ | $1.6 \cdot 10^{22}$ | 84.0 |

According to the Transition State Theory (Theory of Activated Complex):



$$k_0 \sim e^{\frac{\Delta S^\ddagger}{R}}$$

So, k_0 is determined by the ΔS^\ddagger - entropy of activation.

ΔS^\ddagger includes very important information about the mechanism of catalytic reaction:

High negative values of ΔS^\ddagger (up to $-120 \text{ J}/(\text{mole}\cdot\text{K})$), means low k_0 , and such kind of reactions go through the activated complex where molecules of both reagents and active center of the catalyst are present together. In such an activated complex the cleavage of existing bonds and the formation of new bonds takes place simultaneously. For these reactions low k_0 is usually compensated by low E_a values.

Positive values of ΔS^\ddagger (up to $+20 \text{ J}/(\text{mole}\cdot\text{K})$), means high k_0 , and in such kind of reactions the cleavage of bonds in substrates takes place before the formation of activated complex. For these reactions E_a values are usually high, but anyway they are lower than for the non-catalytic reactions.

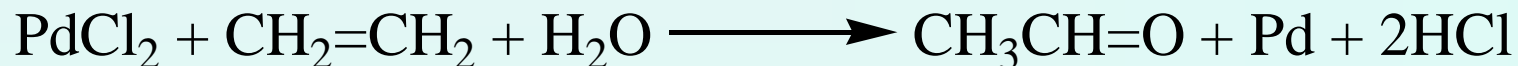


Organometallic Transition Metal-Complex in Catalysis



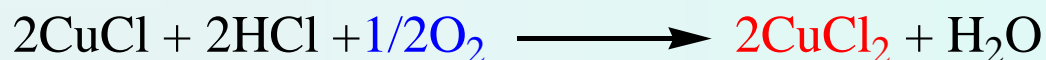
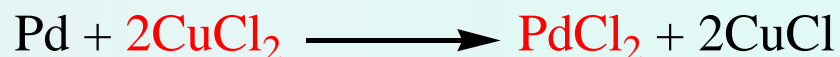
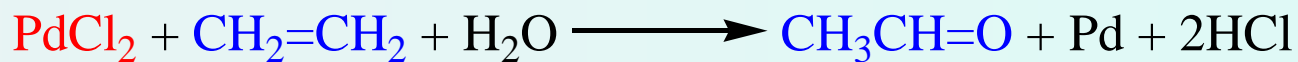
Wacker Process

The reaction of alkene oxidation with palladium chloride is known since 1884:



But only in the 1950th this process was applied as a catalytic process in industry by Waker Industries.

In this system there was absent a stage of catalyst regeneration, where $\text{Pd}^0 \rightarrow \text{Pd}^{+2}$. CuCl_2 appeared to be a suitable oxidizer:



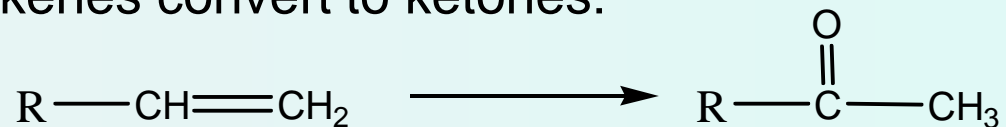
Features of this reaction:

- 1) $T = 20 - 60^\circ\text{C}$, $P \sim 3 \text{ atm}$, stepwise (one by one) air and ethylene addition
- 2) Catalyst: PdCl_2 or Na_2PdCl_4
- 3) Solvent: water or mixture of water and DMF (for alkenes with long chain)
- 4) Oxidizer: CuCl_2 – in industry, benzoquinone – in a lab (but also H_2O_2 , Fe^{3+} , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_3\text{PMo}_6\text{V}_6\text{O}_{40}$ could be used)
- 5) Not only ethylene but also other alkenes and other organic compounds with double $\text{C}=\text{C}$ bond could be used.

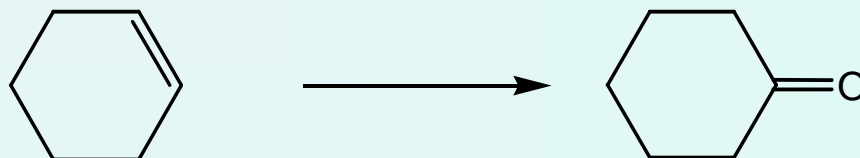
Other compounds with C=C double bond:



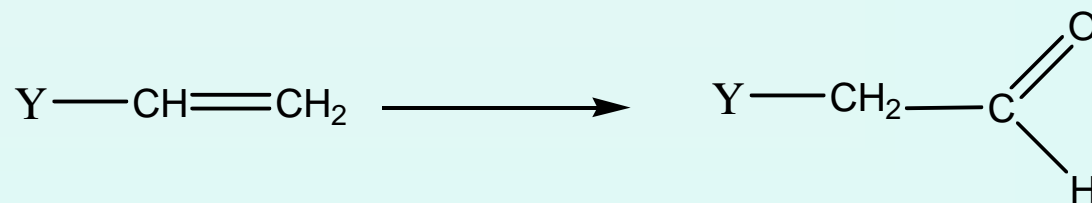
- Terminal alkenes convert to ketones:



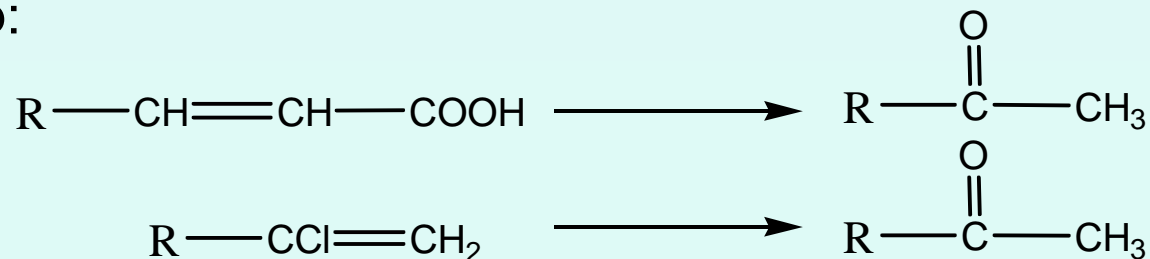
- Cycle alkenes convert to cycle ketones:



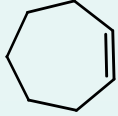
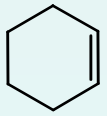
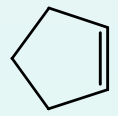
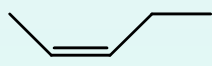
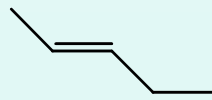




- Terminal alkenes with acceptor groups (-C≡N, -NO₂) convert to aldehydes:



- Alkenes with carboxylic group and vinyl halogenides are losing functional group:

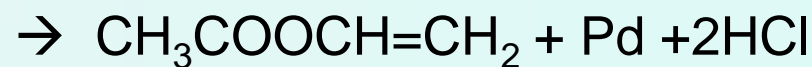
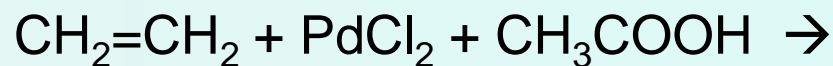


Structure – reactivity relationship

| Alkene | Relative rate of the reaction |
|---|-------------------------------|
|  | 1 |
|  | 8 |
|  | 70 |
|  | 80 |
|  | 90 |
|  | 220 |
|  | 380 |
|  | 480 |
|  | 850 |



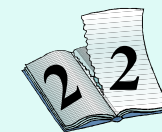
Most important modification of Wacker process is Moiseev reaction:



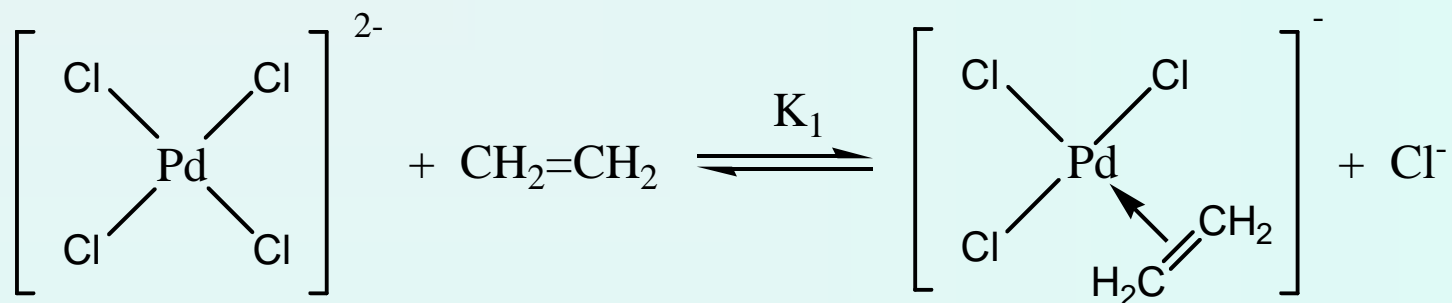
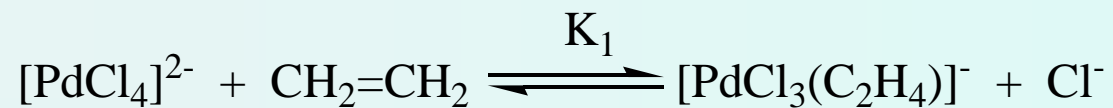
$$\omega = 90\%$$

This method completely replaced the method of vinyl acetate producing from acetylene and acetic acid in the presence of Hg^{2+} .

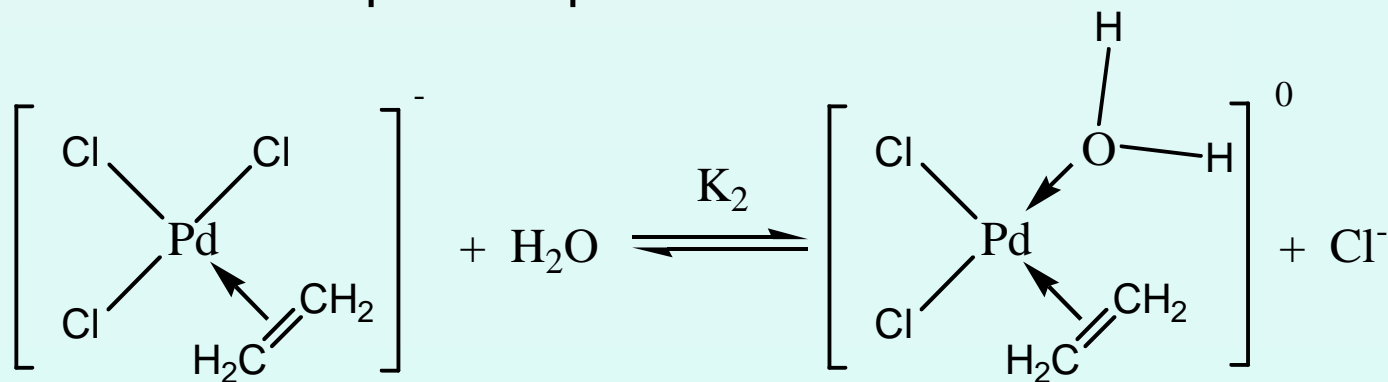
Mechanism of Wacker process



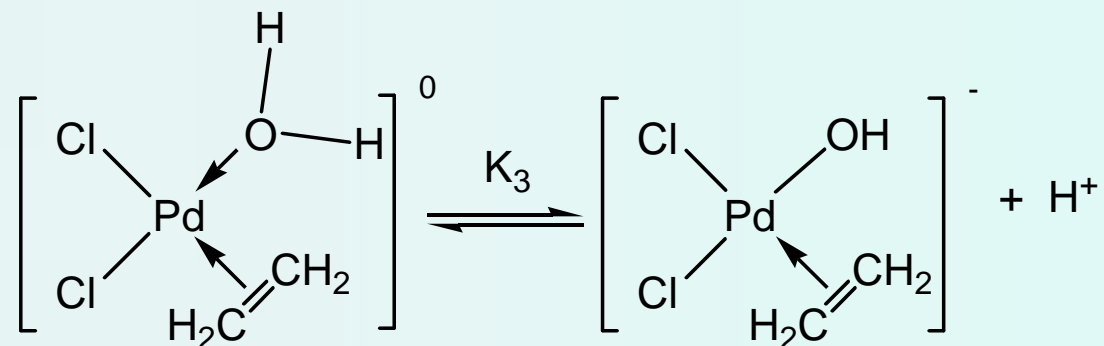
1. Formation of π -alkene complex



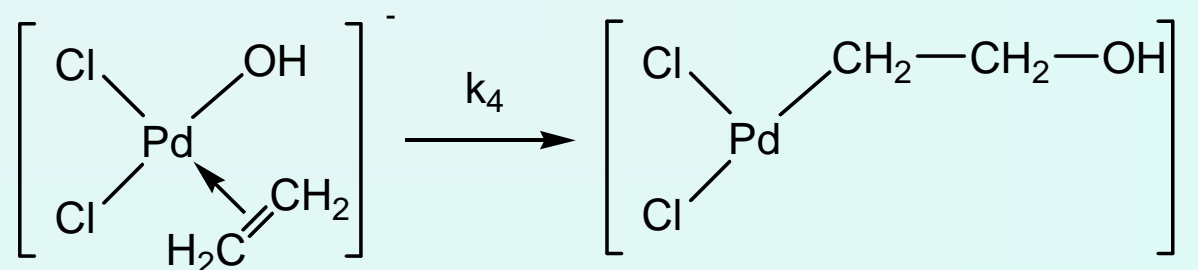
2. Formation of aqua-complex



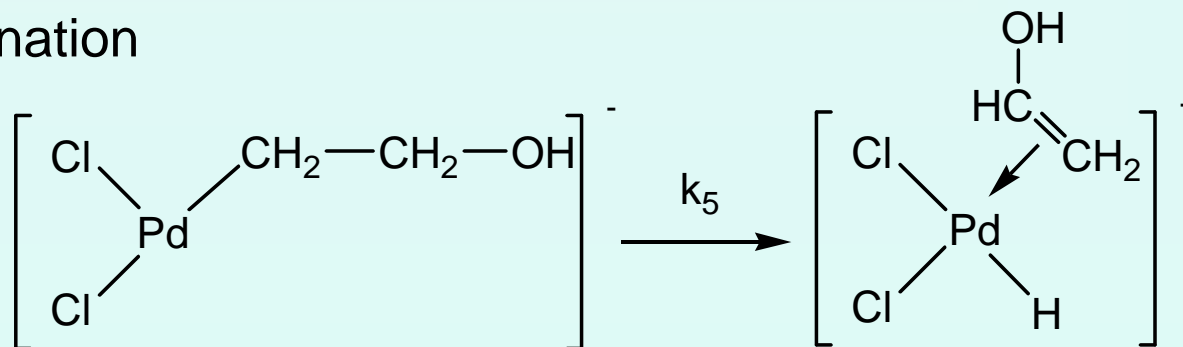
3. Formation of hydroxo-complex

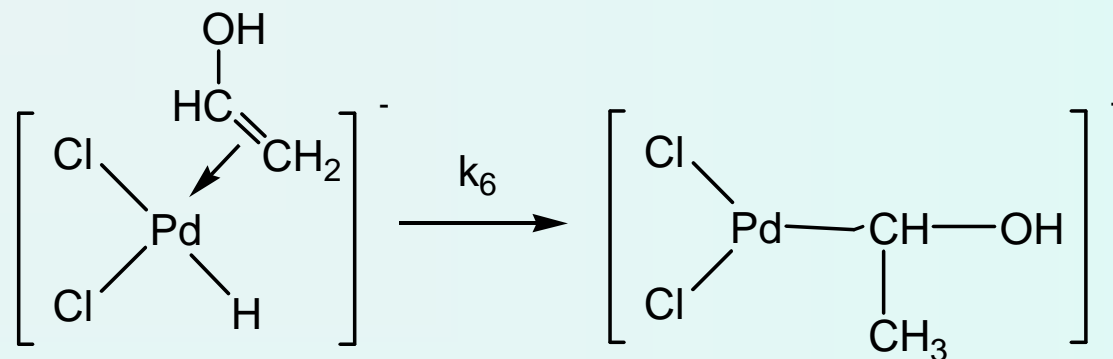
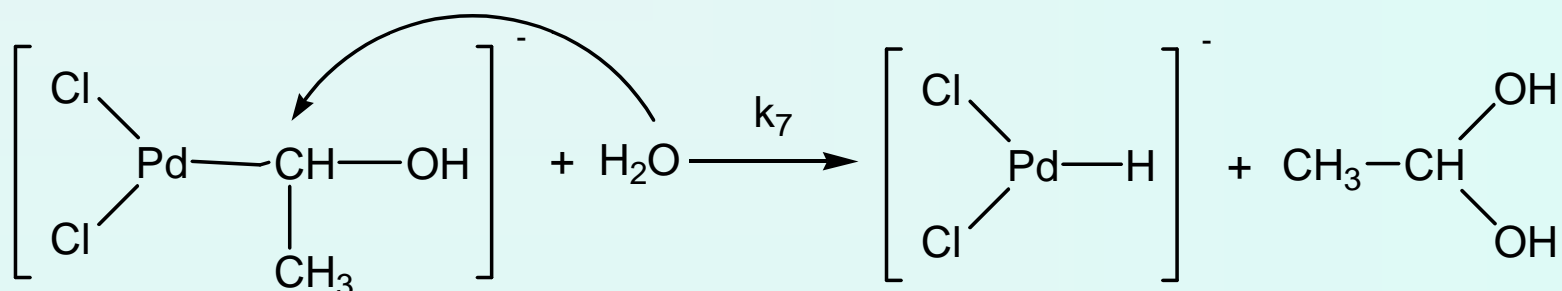
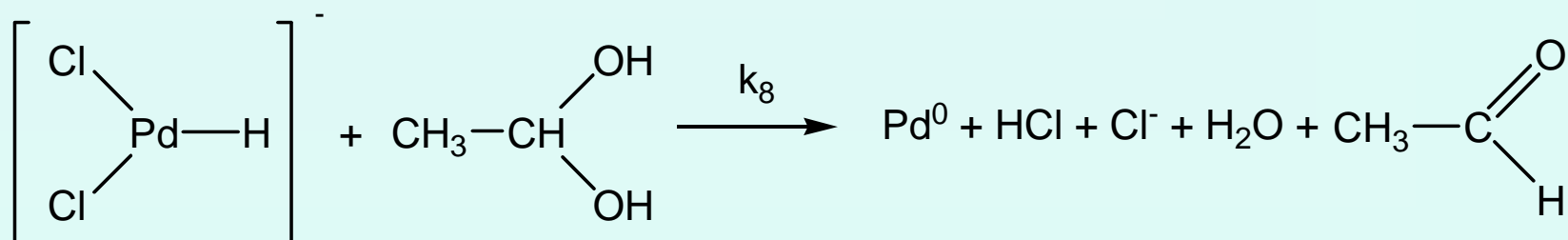


4. Olefin insertion into the Pd-OH bond



5. β -elimination

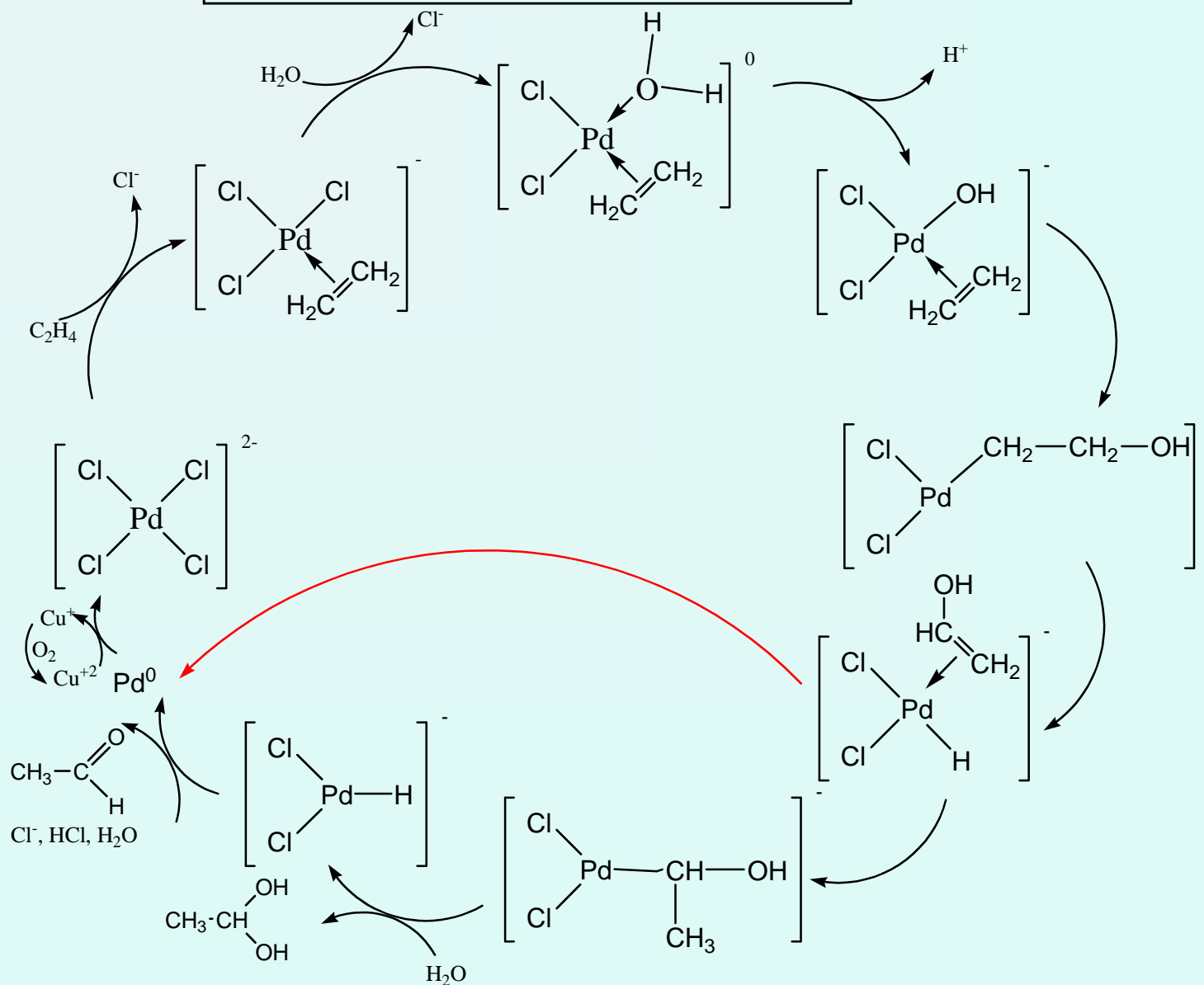


6. Olefin ($\text{CH}_2=\text{CH-OH}$) insertion into the Pd-H bond7. Nucleophilic attack of H_2O on the carbon atom8. Reductive elimination (formation of Pd^0)

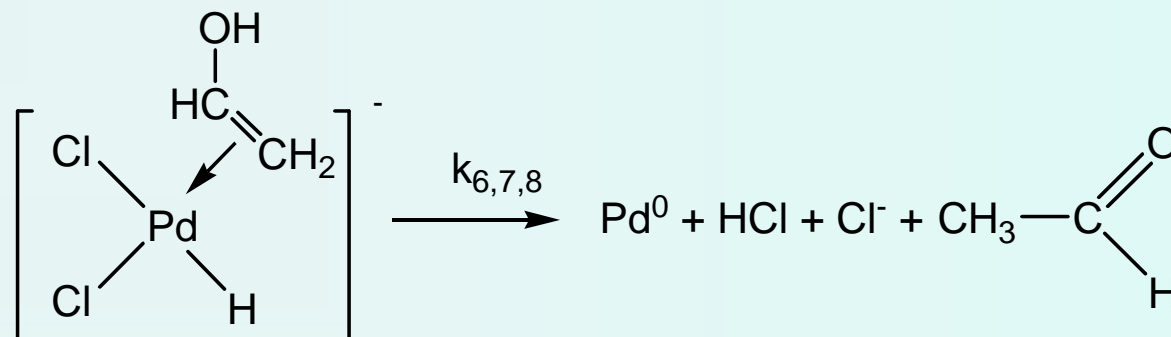
Rate-determined step is olefin insertion (step 4)



$$r = k_4 K_1 K_2 K_3 [H_2O] \frac{[PdCl_4^{2-}][CH_2=CH_2]}{[H^+][Cl^-]^2}$$

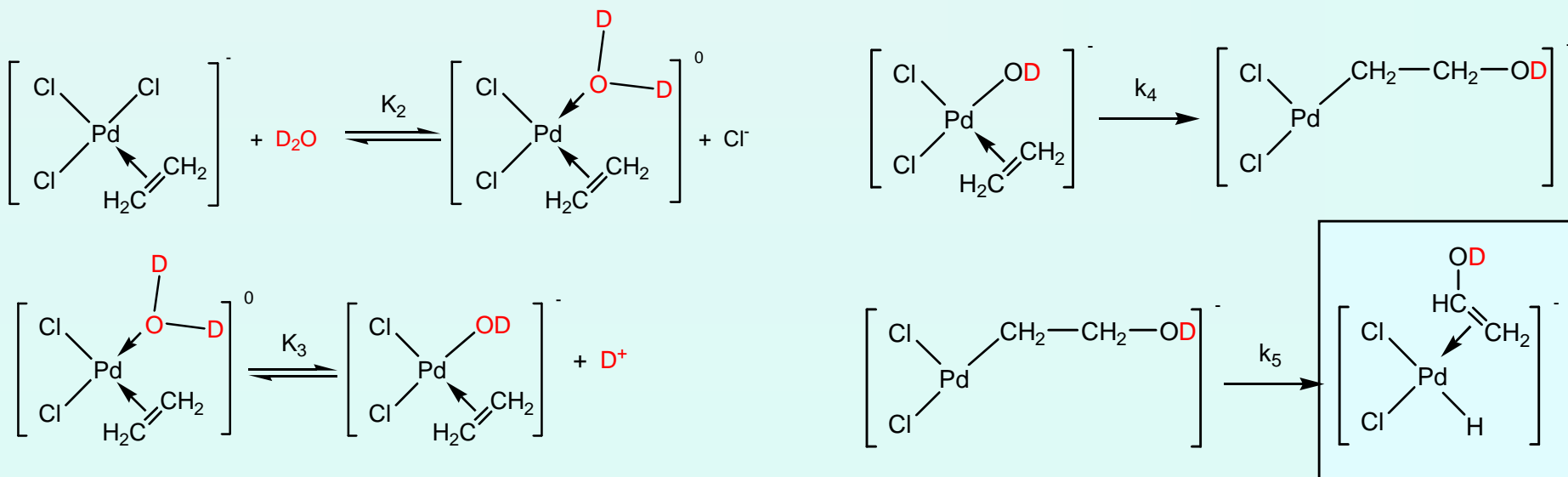


So, the question is: is it possible to simplify the mechanism, combining stages 6, 7 and 8 in one:

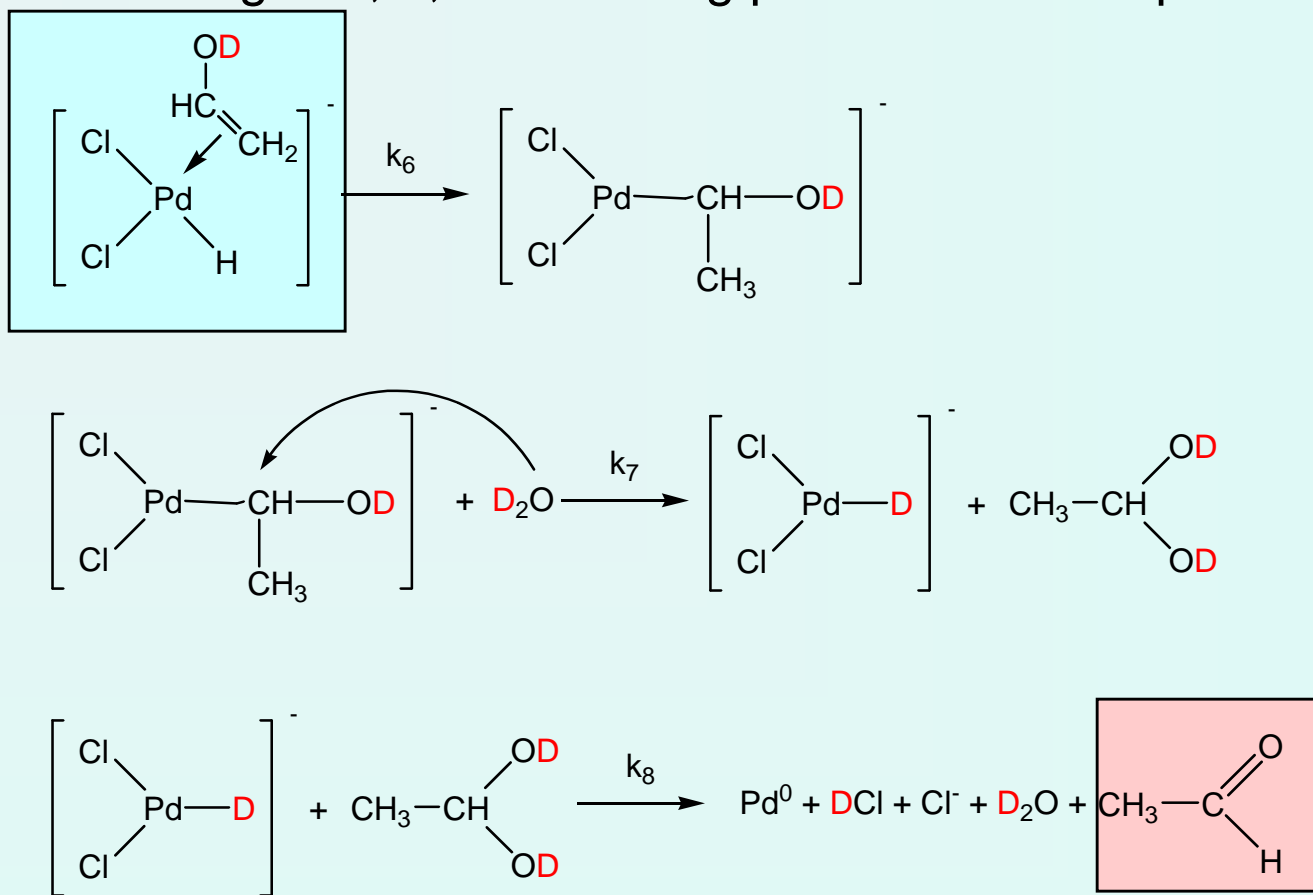


Let's make 2 experiments with labeled atoms:

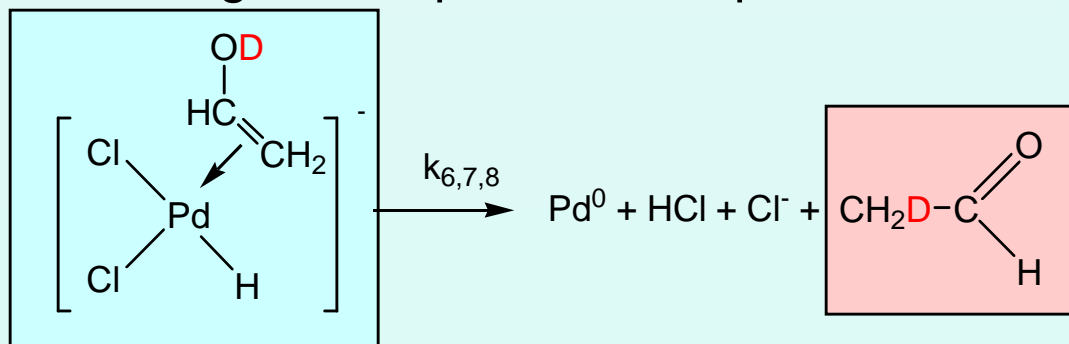
1) Wacker process in D₂O



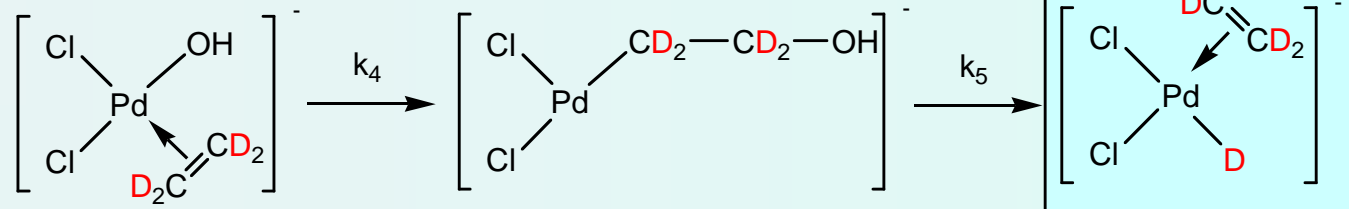
In the case of stages 6, 7, 8 are taking place non-labeled products forms



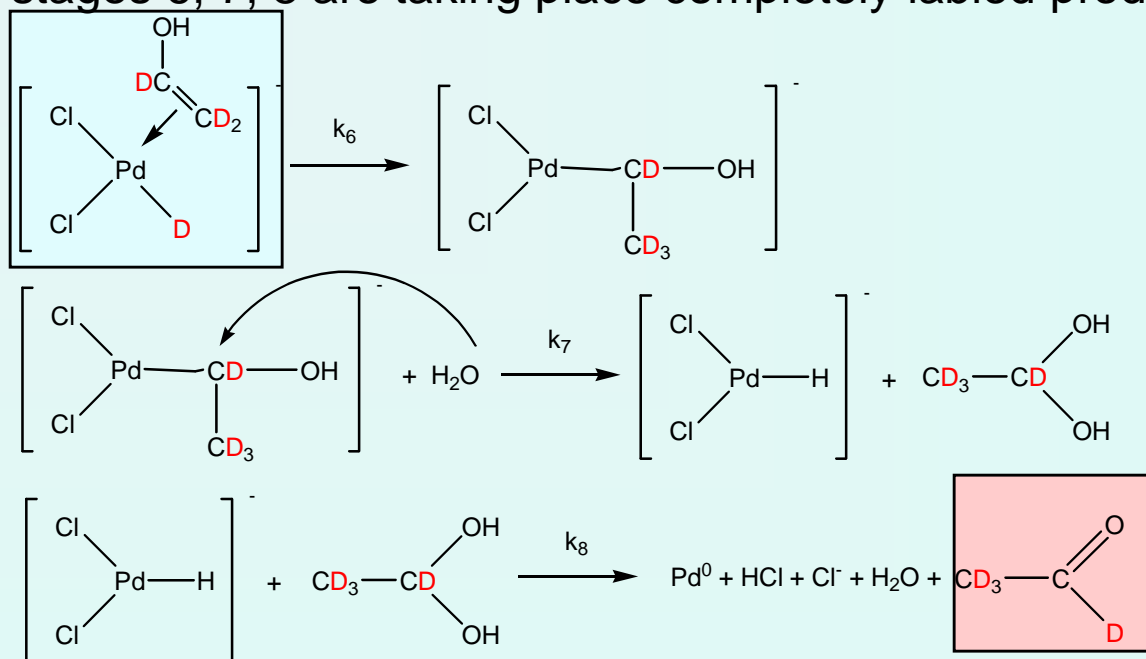
In the case of one stage takes place labeled products forms



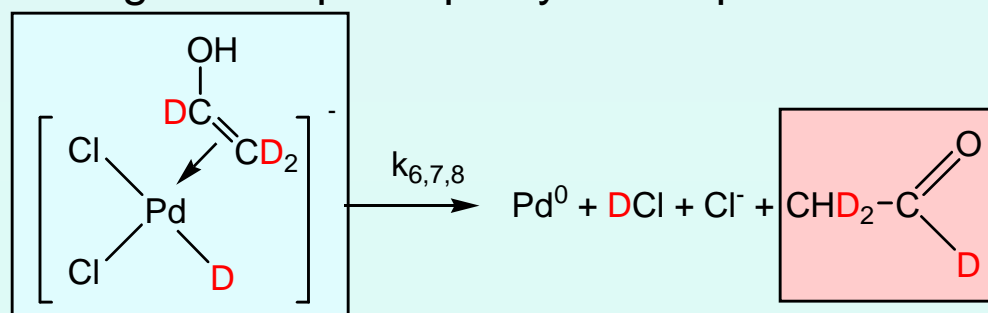
2) Wacker process with $\text{CD}_2=\text{CD}_2$



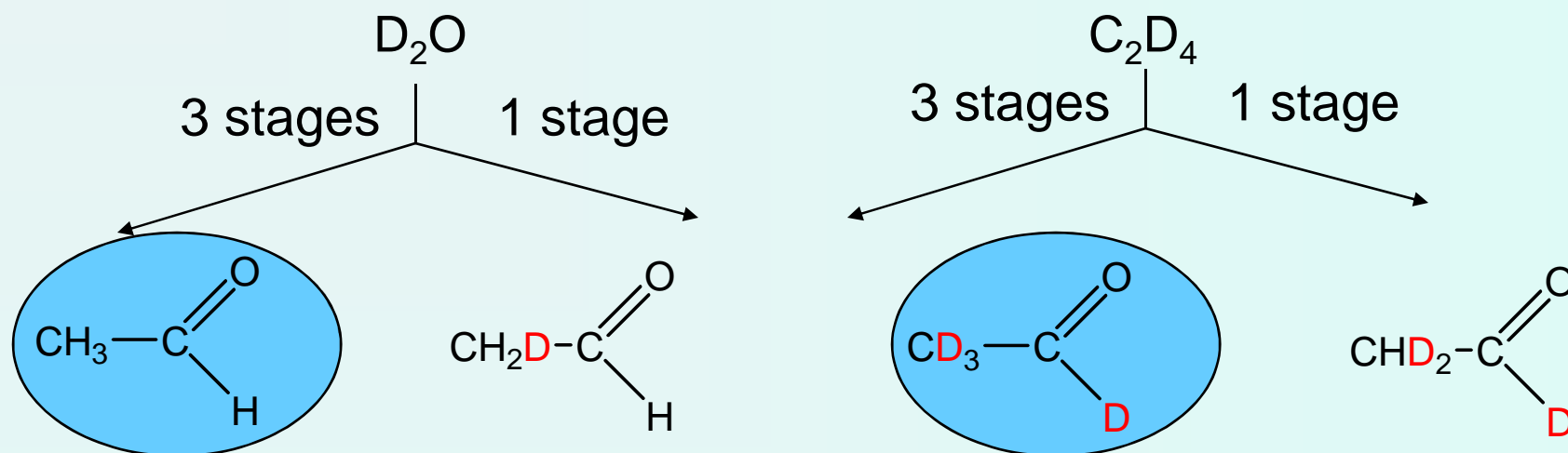
In the case of stages 6, 7, 8 are taking place completely-labeled products forms



In the case of one stage takes place partly labeled products forms



Experimental results:



So, stages 6, 7, 8 really take place

Disadvantages:

- High corrosive reaction media
- Producing of chloroethanal as a by-product
- Explosion of ethylene-air mixture could take place



Advantages:

- Mild reaction conditions: 100-110°C, 10 atm, selectivity >94%
- Simple catalytic system