Catalysis

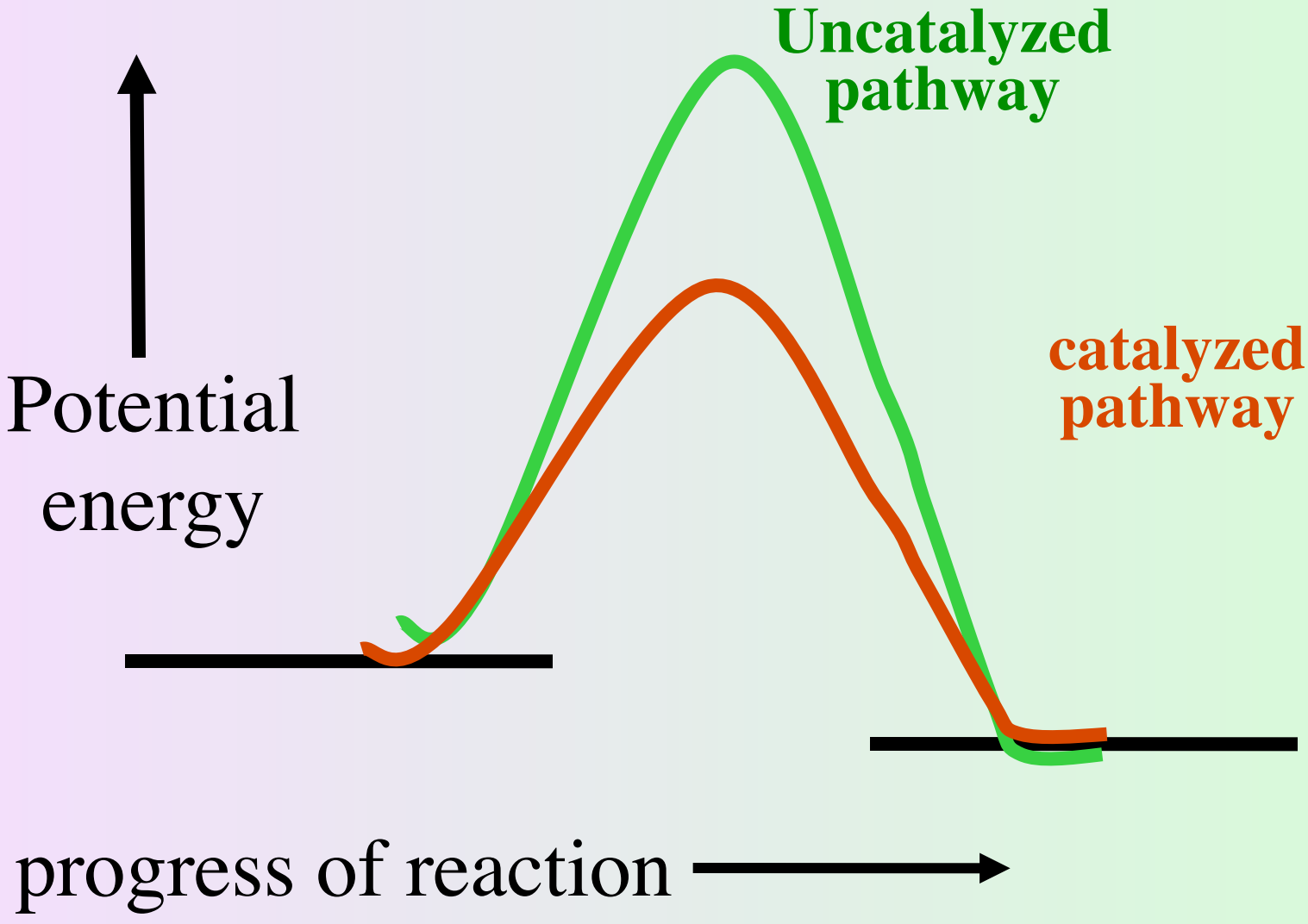
Catalyst

Increases reaction rate, but is not consumed in the reaction

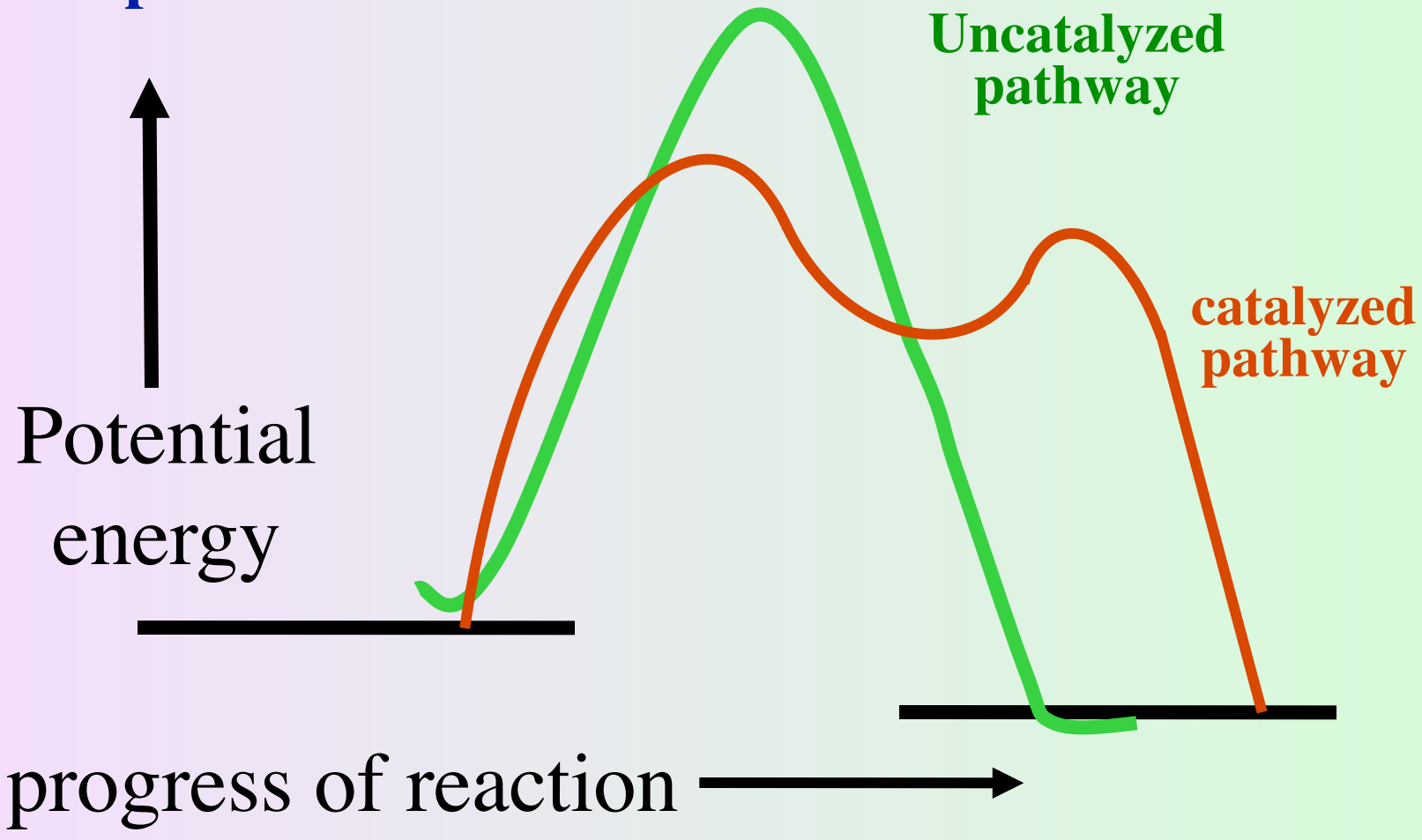
Increases the rate, by lowering activation energy

Causes a shift in mechanism

The diagram is instructive, but not strictly correct



Replace one-step process with high activation energy by a Two-step process with low activation energy for each step



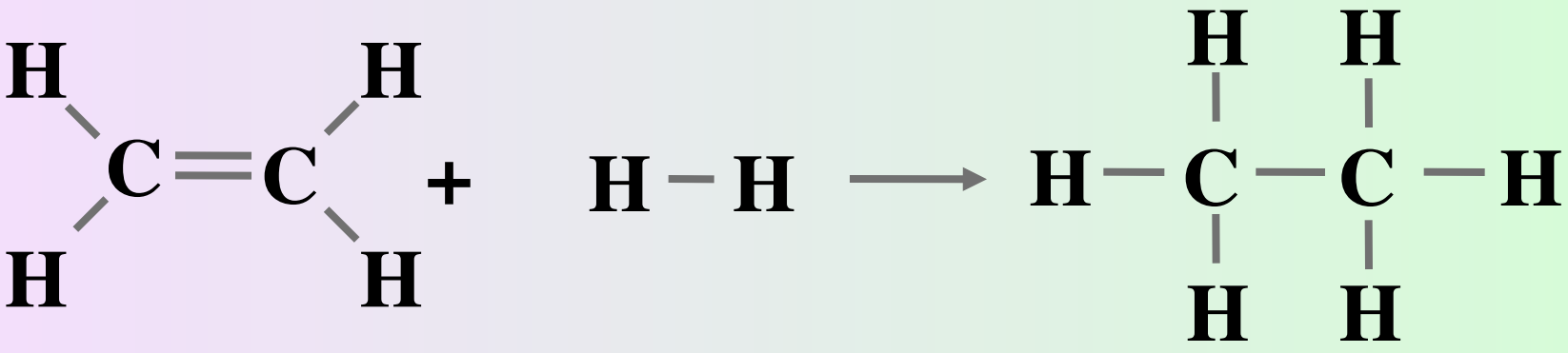
Heterogeneous Catalysis

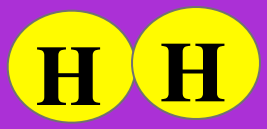
catalyst is present in a different phase than reactants

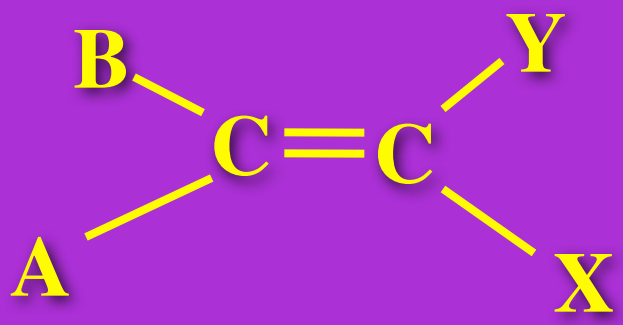
Hydrogenation of ethylene

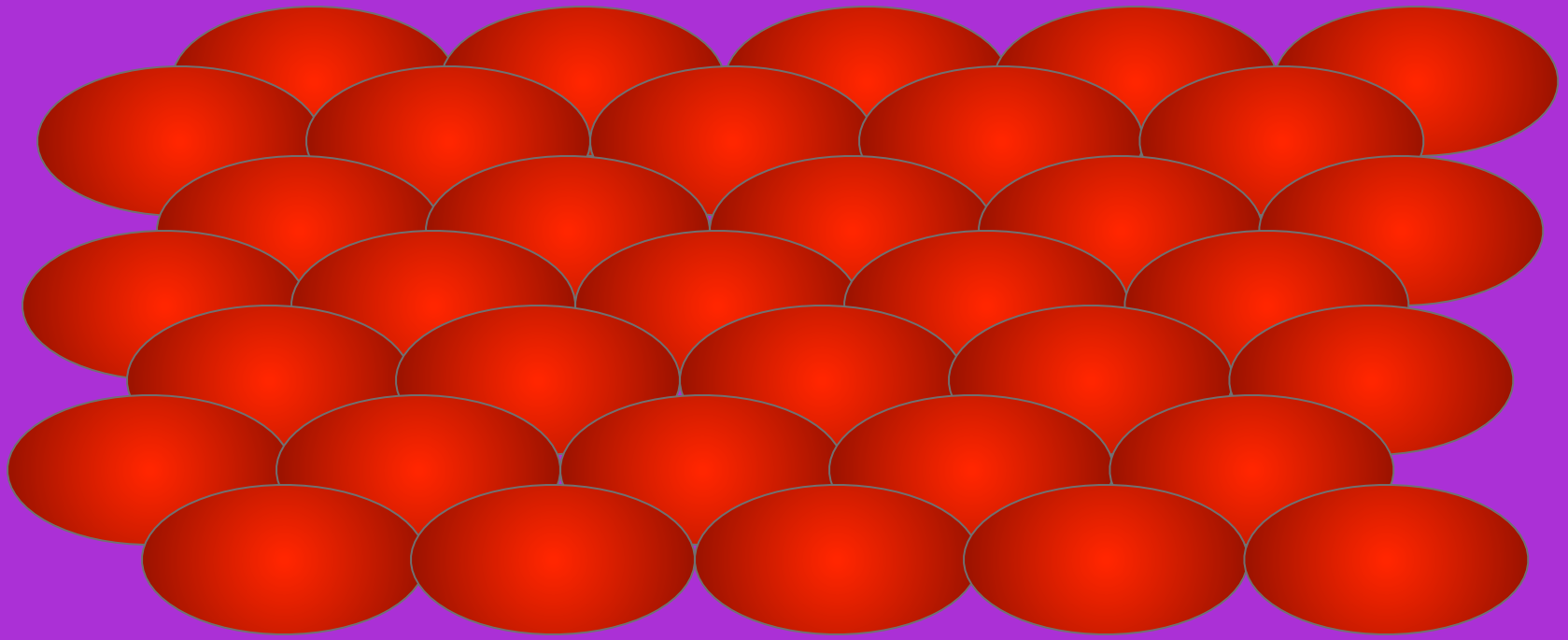
Exothermic ΔE^{o} = -136 kJ/mol

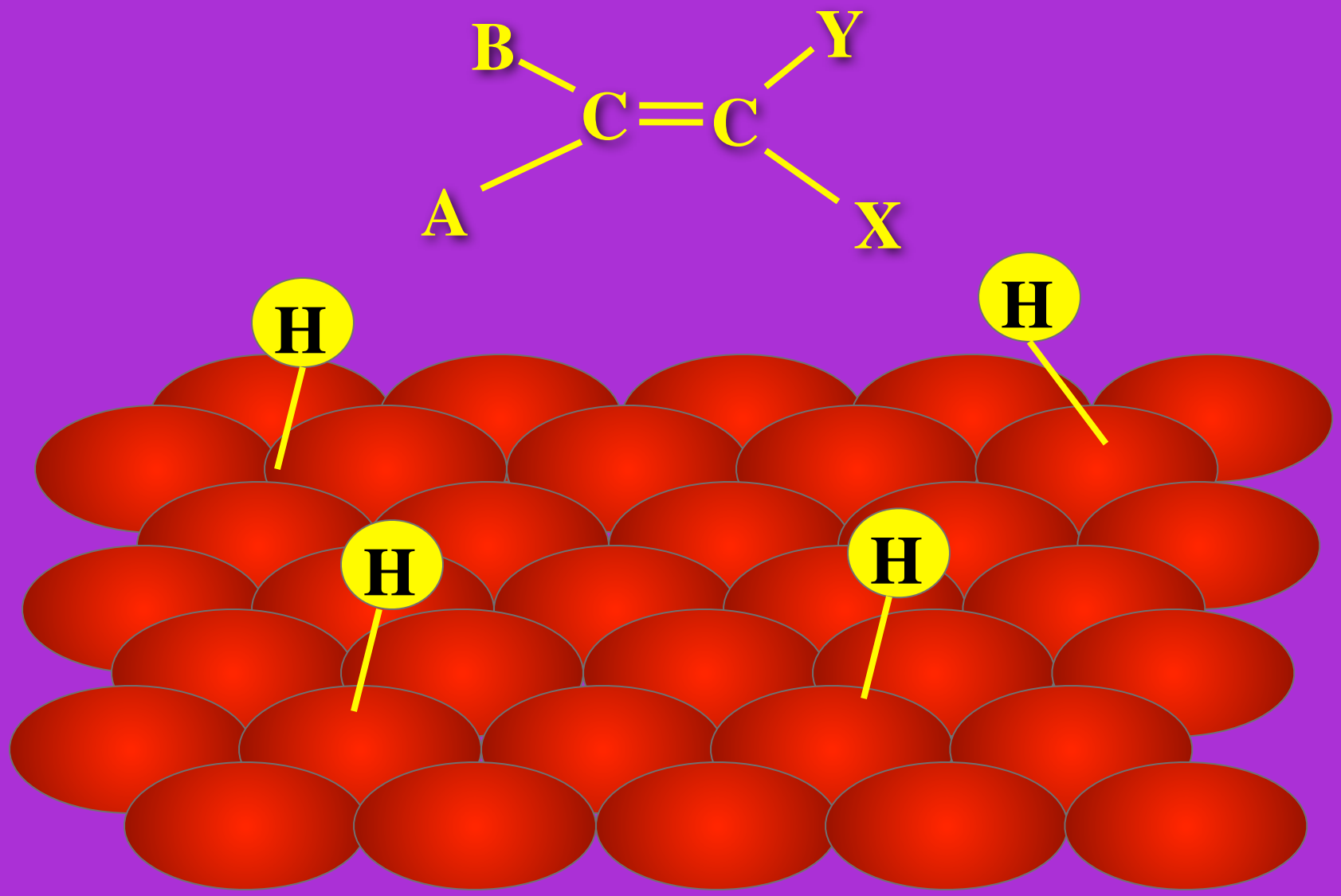
catalyzed by finely divided Pt,Pd, Rh, Ni

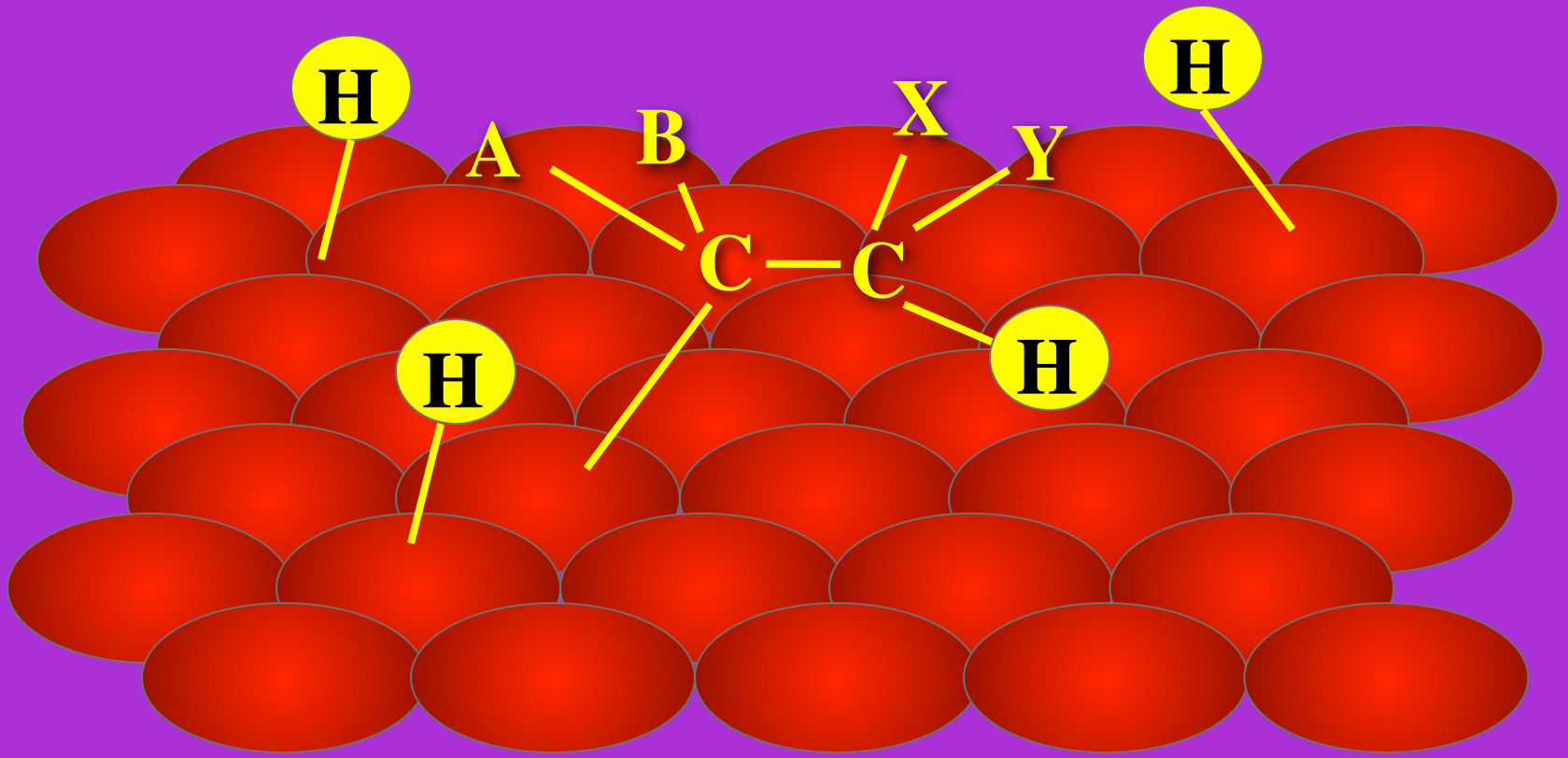


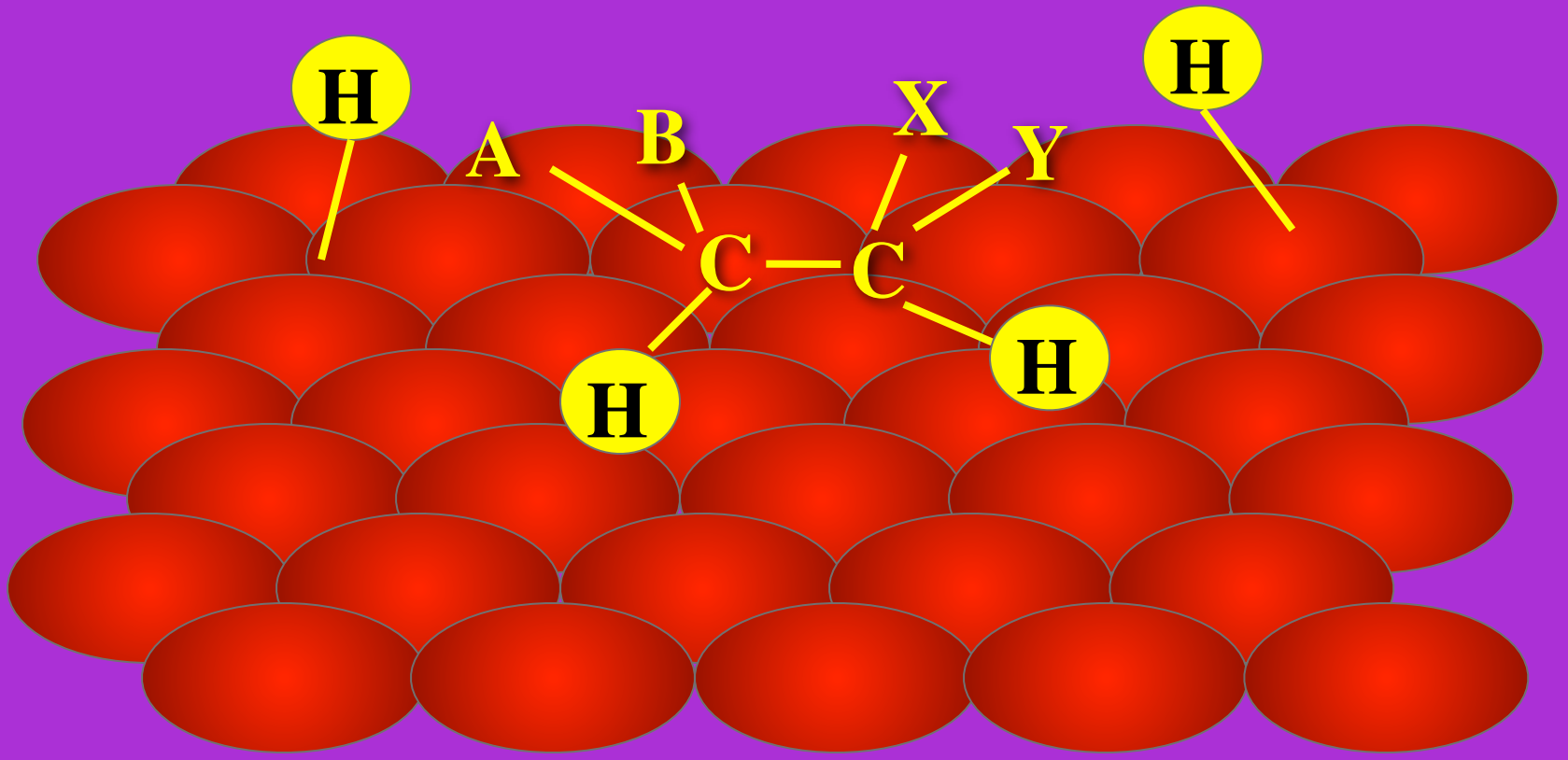

H
H

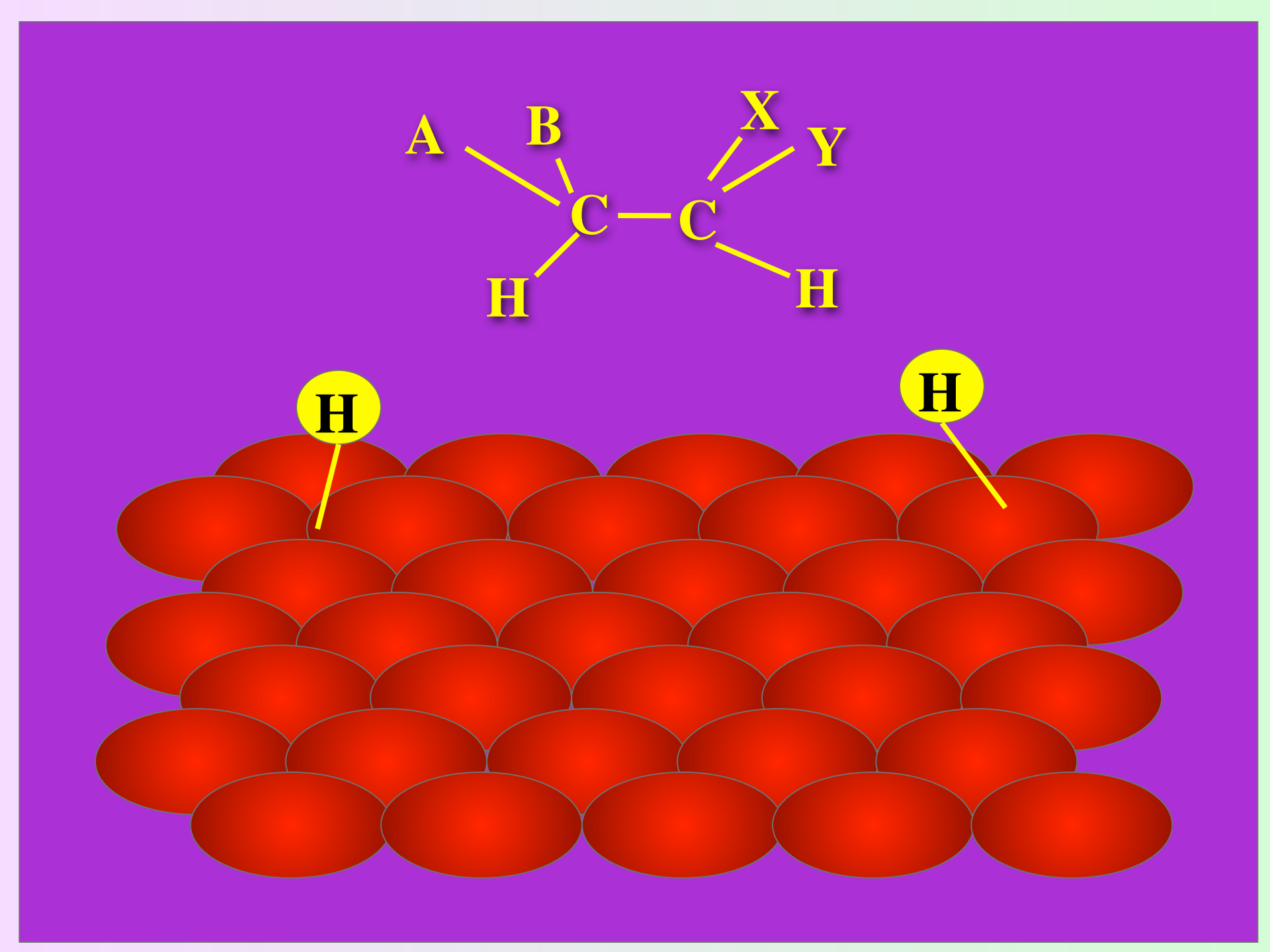

B
Y
C
C
A
X




B
Y
C
C
A
X
H
H
H
H


H
A
B
X
Y
H
C
C
H
H


H
A
B
X
Y
H
C
C
H
H


A
B
X
Y
C
C
H
H
H
H

Homogeneous Catalysis

catalyst is present in the same phase as the reactants

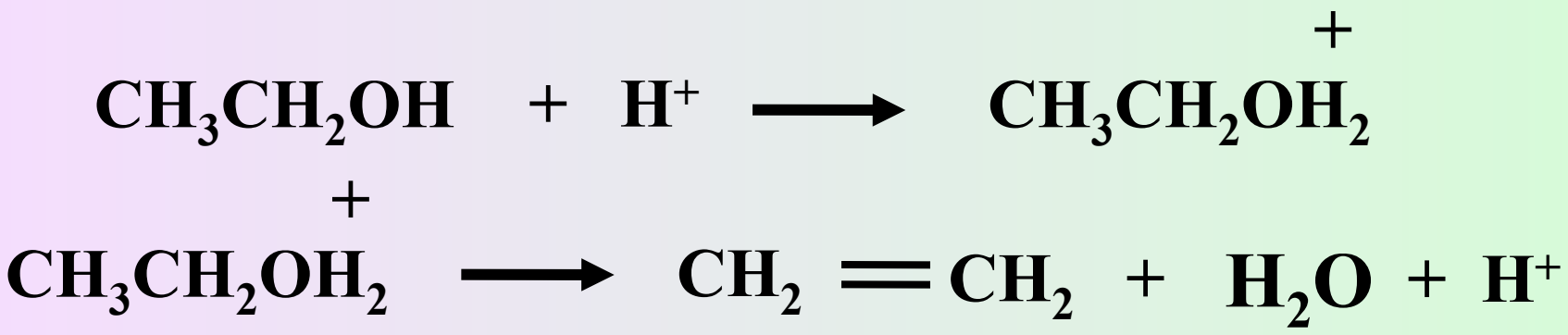
Example

Rapid reaction in the presence of an acid catalyst;

Example

Rapid reaction in the presence of an acid catalyst; very slow in the absence of a catalyst

Role of the acid catalyst



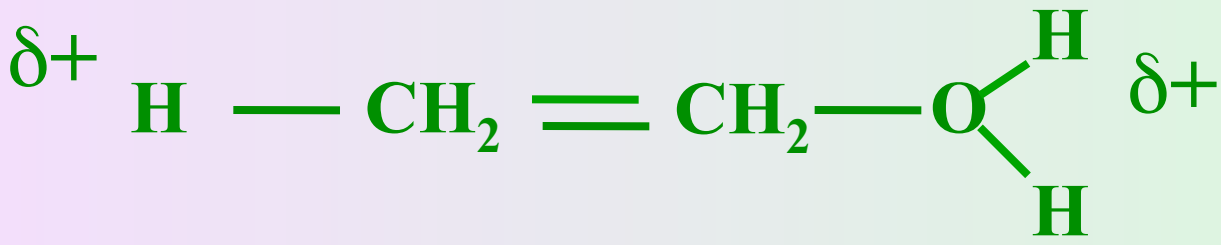
Role of the acid catalyst

$$CH_3CH_2OH + H^+ \longrightarrow CH_3CH_2OH_2^+$$

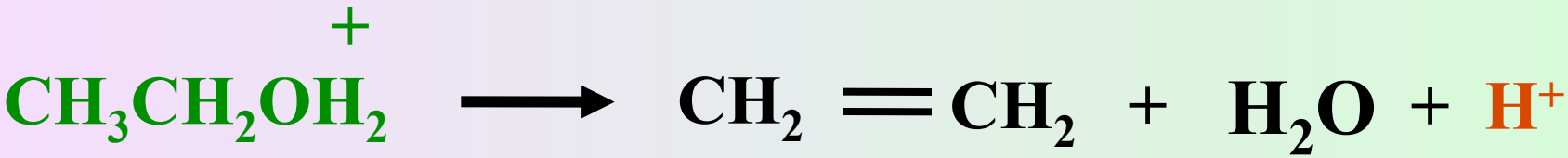
$$CH_3CH_2OH_2^+ \longrightarrow CH_2{=}CH_2 + H_2O + H^+$$

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$$

intermediate



Role of the acid catalyst



The acid catalyst enters the reaction and is retrieved at the end

Example

In recent years ozone has been depleted at an alarmingly fast rate by chloroflorocarbons (CFCs).

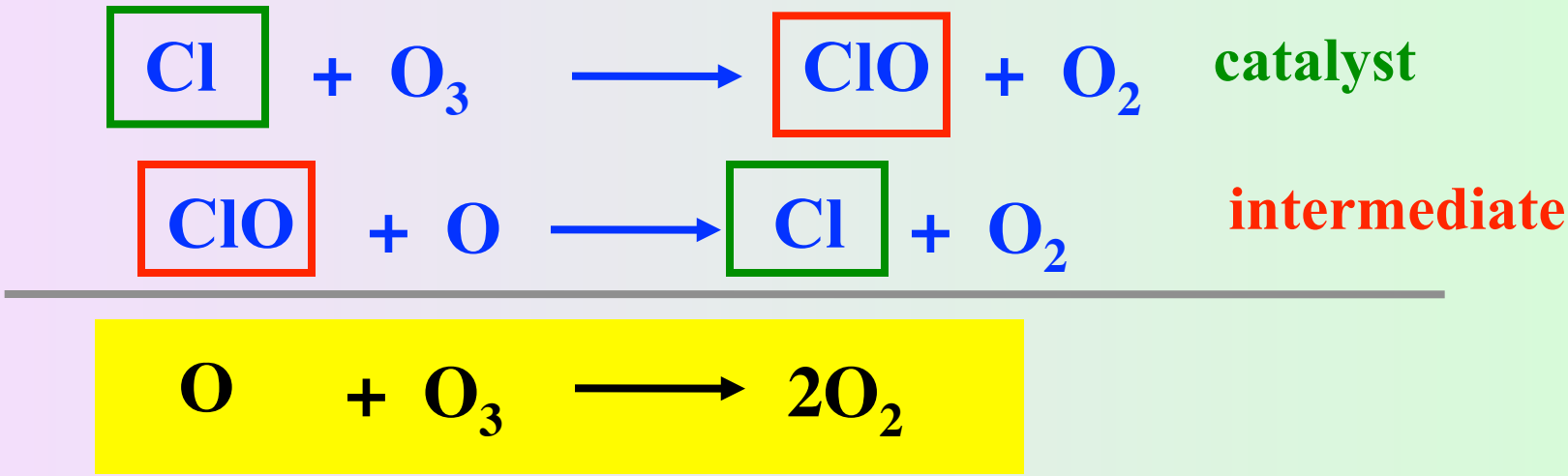
A CFC molecule such as $CFCl_3$ is first decomposed by UV radiation:

$$CFCl_3 \longrightarrow CFCl_2 + Cl$$

The chlorine radical then reacts with ozone as follows

$$Cl + O_3 \longrightarrow ClO + O_2$$

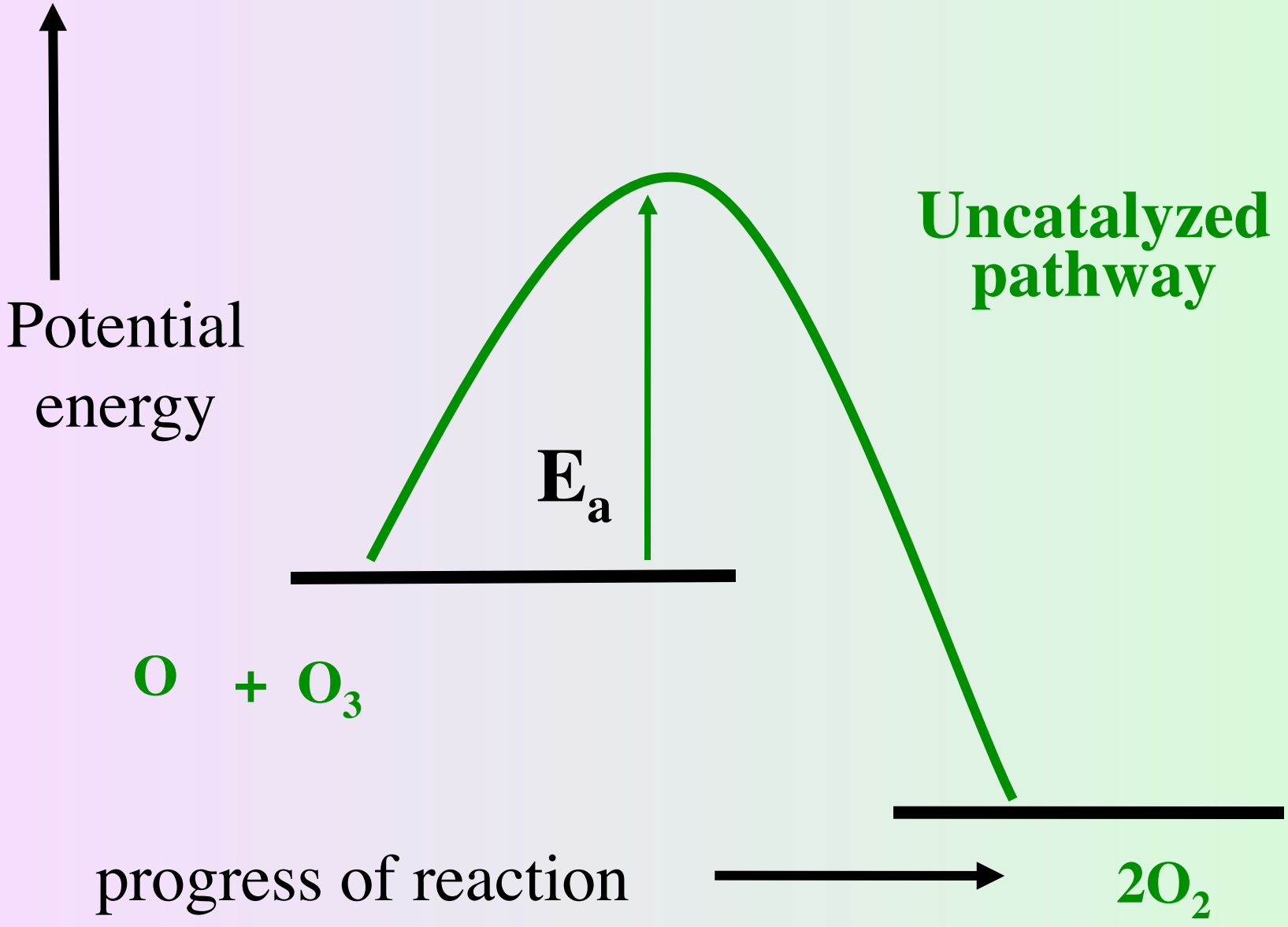
$$ClO + O \longrightarrow Cl + O_2$$

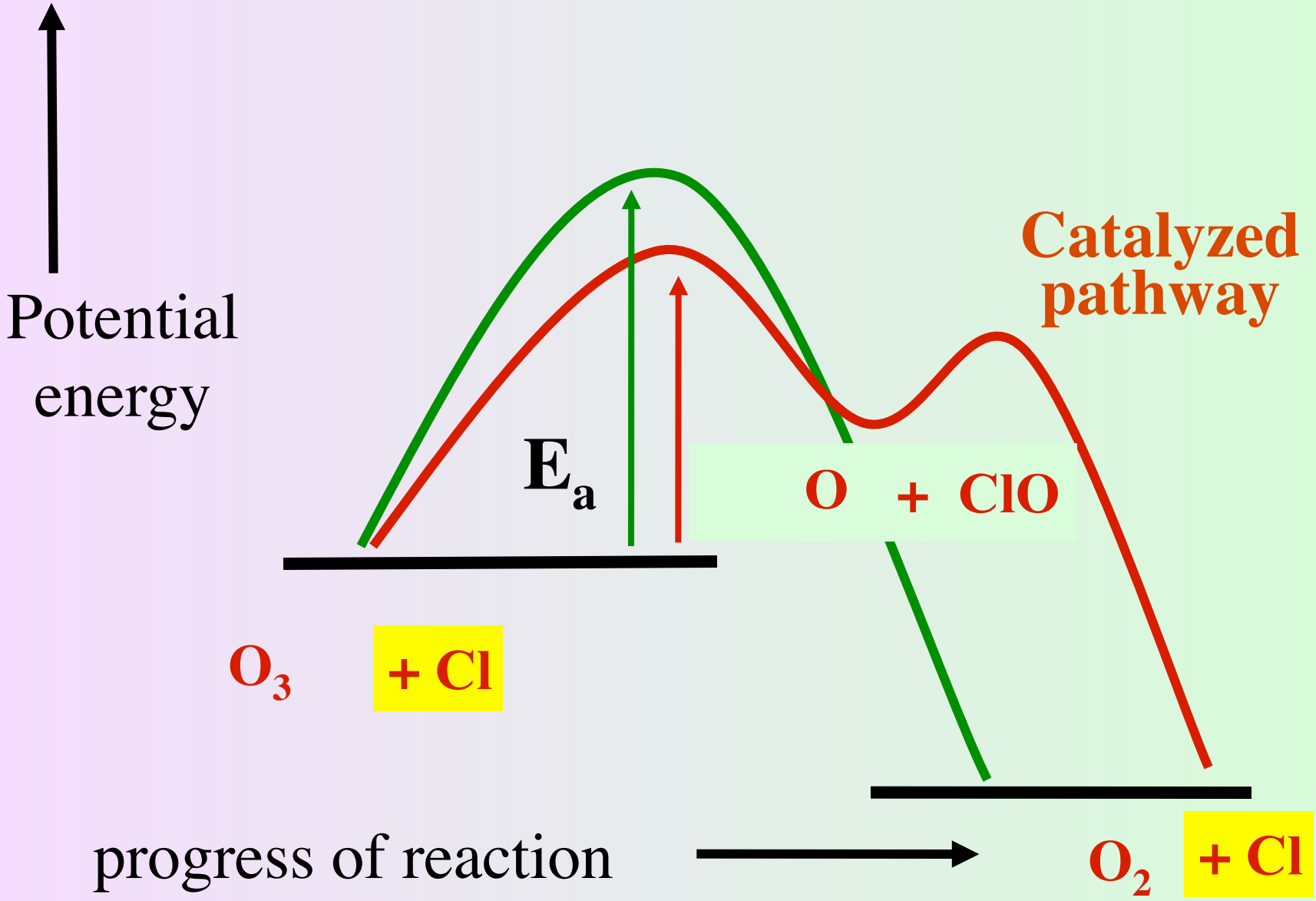


Write the overall reaction for the last two steps.

What are the roles of ClO and Cl ?

Draw the potential energy versus reaction progress diagrams for the uncatalyzed and catalyzed destruction of ozone.


Potential energy
Uncatalyzed pathway
E_a
$O + O_3$
progress of reaction
$2O_2$


Potential energy
Catalyzed pathway
E_a
O + ClO
O_3 + Cl
progress of reaction
O_2 + Cl

$$O + O_3 \longrightarrow 2O_2$$

A reasonable mechanism for the formation of oxygen from ozone is given by two elementary steps.

$$Cl + O_3 \xrightarrow{\text{slow}} ClO^- + O_2$$

$$ClO + O \xrightarrow{\text{fast}} Cl + O_2$$

Which of the following statements concerning this proposed mechanism is true.

A. ClO- is a catalyst

B. ClO- is an intermediate

C. The mechanism can't be correct because it involves a species (OCl-) that does not appear in the balanced equation

D. The rate -determining step is unimolecular

$$O + O_3 \longrightarrow 2O_2$$

A reasonable mechanism for the formation of oxygen from ozone is given by two elementary steps

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$$ClO + O \xrightarrow{\text{fast}} Cl + O_2$$

What must the observed rate law be in order for the mechanism shown in problem to be correct.

A. Rate = k [O_3] [O]

B. Rate = k [O_3] [ClO]

C. Rate = k [O_3] [O]

D. Rate = k [O_3] [O]