Composite Reaction Mechanism

A detailed sequence of steps for a reaction
Reasonable mechanism:

1. Elementary steps sum to the overall reaction

2. Elementary steps are physically reasonable

3. Mechanism is consistent with rate law and other experimental observations (generally found from rate limiting (slow) step(s)

A mechanism can be supported but never proven

We can now see how our knowledge of elementary reactions can help us propose mechanisms for composite reactions.
\[
\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2
\]

**Observed rate = \( k \ [\text{NO}_2]^2 \)**

Deduce a possible and reasonable mechanism:

\[
\begin{align*}
\text{NO}_2 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{NO} \quad \text{slow} \\
\text{NO}_3 + \text{CO} & \rightarrow \text{NO}_2 + \text{CO}_2 \quad \text{fast}
\end{align*}
\]

Overall, \( \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \)

Is the rate law for this sequence consistent with observation?
Yes (every \( \text{NO}_3 \) formed in step 1 very rapidly reacts with \( \text{CO} \))

Does this prove that this must be what is actually happening?
No! **Note the \( \text{NO}_3 \) intermediate product!**

Now we look in more detail at the reaction.
NO\textsubscript{2} + CO reaction

We proposed a two-step mechanism

That means there should be two elementary steps that could each be represented by an Arrhenius rate constant

\[ k = Ae^{-E_a/RT} \]

and the corresponding potential energy profile.

What is a reaction coordinate?

Let's look at the NO\textsubscript{2} + CO reaction pathway in one dimension.
\[
\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2
\]

**High barrier**

**TS for step 1**

**Reactants:**

\[
\text{NO}_2 + \text{NO}_2 + \text{CO}
\]

**Bottleneck**

**Step 1**

**Lower barrier**

**TS for step 2**

**Products:**

\[
\text{NO} + \text{CO}_2
\]

**Step 2**

**Potential Energy**

**Reaction Coordinate**
In this two-step reaction, there are two barriers, one for each elementary step.

The well between the two transition states holds a reactive intermediate.

A reactive intermediate is a compound formed transiently, but absent in the overall reaction.

Related to (but different from) transients that we see in the steady-state approximation.

This rxn coordinate is a complicated beast!

We need to do better than just using a 1-D energy slice, namely a multidimensional potential energy surface!
Potential Energy Surfaces

- \(n\) electrons and \(M\) nuclei: Quantum Mechanics
- \(3n + 3M\) degrees of freedom \(\rightarrow\) \((3n + 3M)\) coupled 2\textsuperscript{nd} order partial differential equations (for \(O_3\) alone, there are 78 degrees of freedom)
- Computational difficulty scales as \(~(3n + 3M)^6\)
- Impossibly difficult to calculate fully the dynamics of large systems!
- Simplification essential!
- Can separate the center of mass (c.m.) motion and rotation from other motions (eliminates 6 nuclear degrees of freedom).
- This helps, but much more is needed before we can do anything useful.
- We need to separate the electron and nuclear motions, to the extent that this is possible. Fortunately it is possible, using the Born-Oppenhemier approximation.
The Born Oppenheimer approximation: motion of electrons is sufficiently fast compared to nuclei that the electrons adiabatically adjust to the changing nuclear positions, giving an “effective electron force” that governs the nuclear positions.

- Allows us to consider nuclear motions separately from electron motions (most of the time), rather than requiring us to describe everything simultaneously.

- Allows description of molecules by nuclear positions and the corresponding repulsions, coupled with an “effective” electron force that depends on nuclear position, but NOT the spatial location of each individual electron.

- We have only waved our hands, with NO QM, but this is THE key approximation that allows chemistry to be the positions of the nuclei, and not worry about all the electrons all the time.
The Born Oppenheimer approximation:

Generally a very accurate approximation, and one of the most important concepts in all of physical science.

Without it, there would be no chemistry as we know it.

B-O approximation allows the construction of potential energy surfaces for molecules and reactions.

Still too many nuclear degrees of freedom!

Select only important ones – example: H +H₂→H₂+H : restrict to collinear geometry, big limitation, but
Collinear $H + H_2$ Reaction

$$H_\alpha + H_\beta H_\varepsilon \rightarrow [H_\alpha -- H_\beta -- H_\varepsilon]^\dagger \rightarrow H_\alpha H_\beta + H_\varepsilon$$

This simplification leaves only two nuclear co-ordinates, $r_{\alpha\beta}$ and $r_{\beta\varepsilon}$. I can plot that!
Collinear $H + H_2$ Reaction

$H_\alpha + H_\beta H_\epsilon \rightarrow [H_\alpha--H_\beta--H_\epsilon]^\dagger \rightarrow H_\alpha H_\beta + H_\epsilon$

Reactants

$H_\alpha + H_\beta H_\epsilon$

minimum energy path

Reaction co-ordinate?

$R(H_\alpha - H_\beta)$

$R(H_\beta - H_\epsilon)$

Activated state (col)

Products

$H_\alpha H_\beta + H_\epsilon$
How experiment is done: Molecular Beam Scattering

\[ M + RX \rightarrow MX + R \]
Consider a single collision between $A$ & $BC$ in the vacuum of the beam machine. The center of mass remains in unchanging motion, as no external forces are acting. The collision is much simpler when viewed in the c.m. frame.
Reaction Surface Showing Contour Lines

$A + B - C \rightarrow [A - - - B - - - C]^\dagger \rightarrow A - B + C$
Trajectories on Potential Energy Surface

\[
H + HBr \rightarrow H_2 + Br
\]
(exothermic process)

Small energy barrier of 9.4 kJ/mol for forward reaction

Large energy barrier of 87.5 kJ/mol for reverse reaction

Part of \( H_2 + Br_2 \) chain reaction (Next week)

"Some Reactions" on Textbook CD
Consider \( H + HBr \rightarrow H_2 + Br \) (exothermic process)

Small energy barrier of 9.4 kJ/mol for forward reaction

Large energy barrier of 87.5 kJ/mol for reverse reaction

A “moderately” early TS (clear in picture)

"Some Reactions" in Ch 9 on Textbook CD