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5.111 Principles of Chemical Science
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Reaction Mechanism

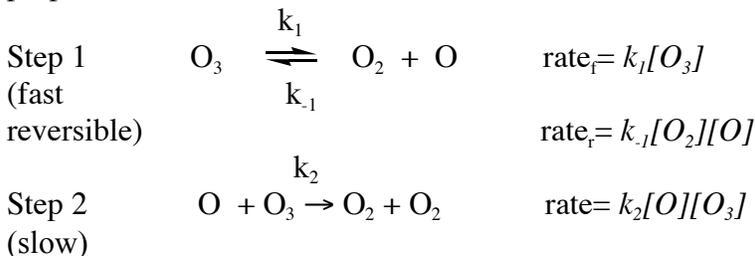
See lectures 32 and 33 for determining reaction mechanisms.

Example from pg. 4 of Lecture 33 notes: The reaction mechanism of natural ozone depletion:

Through a variety of catalytic cycles, Cl and Br ions catalyze the destruction of ozone in the stratosphere. However, at high concentrations, ozone decays into oxygen without metal catalysts required:



proposed mechanism:



The rate is determined by the slowest step

The rate of formation of O₂ is equal to 2 times the rate of the slow step ($k_2[\text{O}][\text{O}_3]$), since two molecules of O₂ are formed.

Thus, rate of formation of O₂ = $2k_2[\text{O}][\text{O}_3]$, but “O” is an intermediate, solve for “O” in terms of products and reactants and rate constants.

Since the first step is fast and reversible and the second step is slow, the first step is in equilibrium and we can write

$$\frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} = \frac{k_1}{k_{-1}} = K_1 \quad \text{or} \quad [\text{O}] = \frac{k_1 [\text{O}_3]}{k_{-1} [\text{O}_2]}$$

substituting:

$$\text{rate} = \frac{2k_2 k_1 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

$$\text{rate} = k_{\text{obs}} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

What is the order in O₃? 2
 What is the order in O₂? -1
 What is the overall order? 1

double O₃/rate will? multiply by 4
 double O₂/ multiply by 1/2
 double both O₃ and O₂/ double