



XII. Interpretation of the Rate Equation:

Taking a brief break from rate equations, we will examine what can be learned from a rate equation without knowing the explicit mechanistic assumptions.

Edwards, J. O.; Greene, E. F.; Ross, J. J. *Chem. Educ.* **1968**, 45, 381.

A. Given:



(B is assumed to be in excess.)

B. Rate Equation and Transition Structure Stoichiometry:

We have been discussing a very important principle of kinetics.
To reiterate...

The rate equation tells you the stoichiometry of the rate limiting transition structure relative to the reactants. If you've assigned the structures of your reactants correctly, the rate equation provides the absolute stoichiometry of the rate limiting transition structure.



XII. Interpretation of the Rate Equation:

1. Simple Rate Expressions:

$$-d[A]/dt = k[A][B]^2$$

You may conclude...



- Although the steps leading to the rate limiting transition structure are unclear, the stoichiometry of the transition structure is well-defined. This assumes that the structure of your starting material is correctly assigned.

XII. Interpretation of the Rate Equation:

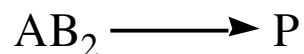
2. Importance of Reactant Structure:



If AB₂ does not form appreciably, then...

$$d[P]/dt = k'[A][B]^2$$

If AB₂ becomes observable, then...



Since B is in large excess, [AB₂] is dependent upon [A], but is *independent* of [B]. However, if you don't realize AB₂ forms, you will incorrectly conclude that B is not in the rate limiting transition structure. In other words...



Similarly, if the dinuclear complex AB forms, then the reaction will appear to be 1st order (rather than 2nd order) in B.



XII. Interpretation of the Rate Equation:


3. Complex Rate Equations:

- By considering all limiting behaviors, we can ascertain the stoichiometries of the different transition structures. Of course, we must also consider the consequences of observable intermediates.

a. Given:

$$d[\text{P}]/dt = \frac{k'[\text{A}][\text{B}]^2}{1 + k''[\text{B}]^2}$$

such that k' and k'' are constants, possibly composite rate constants.



XII. Interpretation of the Rate Equation:

b. Limiting Case 1: $k''[B]^2 \gg 1$

$$d[P]/dt = k'''[A]$$

Therefore, at high [B] there is predicted to be a rate limiting transition structure of $[A_T]^\ddagger$ stoichiometry.

c. Limiting Case 2: $1 \gg k''[B]^2$

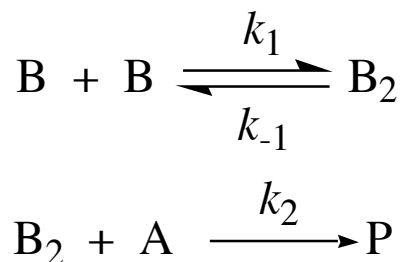
$$d[P]/dt = k'[A][B]^2$$

Therefore, at low [B] there is predicted to be a rate limiting transition structure of $[A_T(B_T)_2]^\ddagger$ stoichiometry.

XII. Interpretation of the Rate Equation:


d. Consider Four Mechanisms:

i. Mechanism 1:



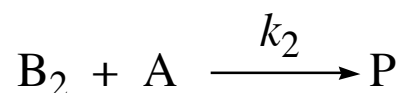
$$d[\text{P}]/dt = \frac{k'[\text{A}][\text{B}]^2}{1 + k''[\text{B}]^2}$$

- If $[\text{B}_2]$ stays low, the rates of both steps increase in proportion to $[\text{B}]^2$. Changing $[\text{B}]$ will not change the rate limiting step and will not afford two limiting behaviors.



XII. Interpretation of the Rate Equation:

- If $[B_2]$ is not observable at low $[B]$ and becomes observable at high $[B]$, we would predict two limiting behaviors. At low $[B]$, the second step would be rate limiting with a rate limiting transition structure of $[AB_2]^\ddagger$ stoichiometry. This is consistent with the rate law. However, at high $[B]$ affording observable B_2 (i.e., $[B_2] \propto [B_T]$), mechanism 1 reduces to...



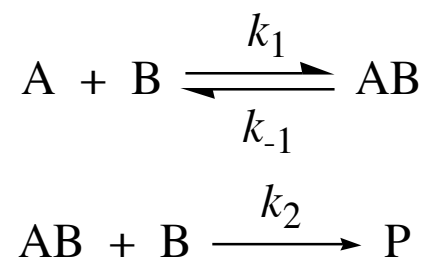
and the rate equation reduces to

$$d[P]/dt = k'[A][B_T]$$

This is inconsistent with the given rate law.


XII. Interpretation of the Rate Equation:

ii. Mechanism 2:



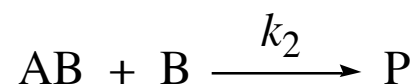
$$d[\text{P}]/dt = \frac{k'[\text{A}][\text{B}]^2}{1 + k''[\text{B}]^2}$$

- If $[\text{AB}]$ stays low, then either the first step is rate limiting ($[\text{AB}]^{\neq}$) or the second step is rate limiting ($[\text{AB}_2]^{\neq}$). This is inconsistent with the limiting behaviors described above.



XII. Interpretation of the Rate Equation:

- If [AB] is not observable at low [B] and becomes observable at high [B], we would predict two limiting behaviors. At low [B], the second step would be rate limiting with a rate limiting transition structure of $[AB_2]^\ddagger$ stoichiometry. This is consistent with the rate law. However, at high [B] affording observable AB (i.e., $[AB] = [A_T]$), mechanism 2 reduces to...



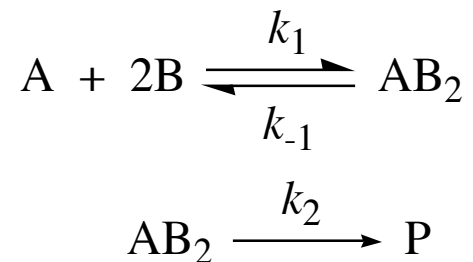
The rate law simplifies to...

$$d[P]/dt = k'[A_T][B]$$

This is inconsistent with the original rate law.

XII. Interpretation of the Rate Equation:

iii. Mechanism 3:



$$d[\text{P}]/dt = \frac{k'[\text{A}][\text{B}]^2}{1 + k''[\text{B}]^2}$$

- At low [B], A would be observable. Rate limiting conversion of AB₂ would afford...

$$d[\text{P}]/dt = k_{\text{obsd}}[\text{A}_\text{T}][\text{B}]^2$$

consistent with transition structure $[\text{AB}_2]^\ddagger$.

- At high [B], AB₂ would become observable. Rate limiting conversion of observable AB₂ would afford...

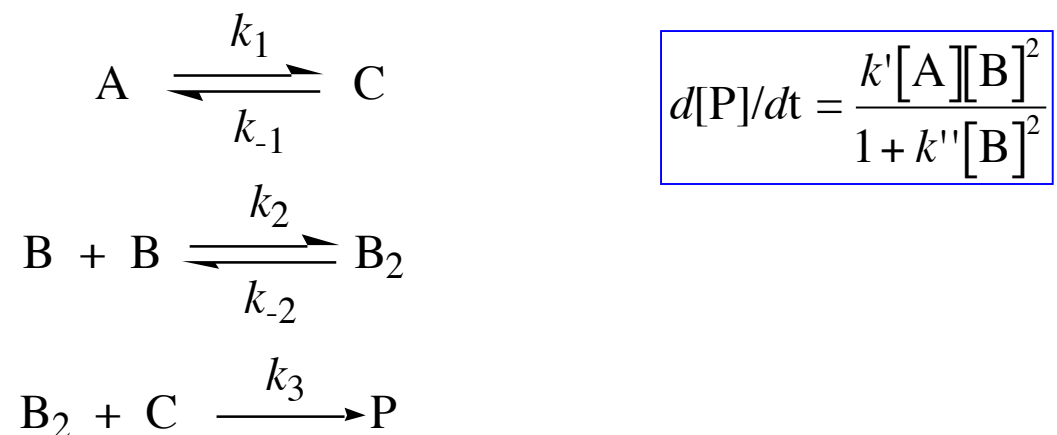
$$d[\text{P}]/dt = k_{\text{obsd}}[\text{A}_\text{T}]$$

consistent with transition structure $[\text{A}_\text{T}]^\ddagger$ assuming that AB₂ formed, but went undetected.

XII. Interpretation of the Rate Equation:

iv. Mechanism 4:

Illustrating the ambiguity of saturation kinetics...



- If $[\text{B}_2]$ stays low, then $[\text{B}_2] \propto [\text{B}]^2$, and the last step could be rate limiting with a transition structure of $[\text{AB}_2]^\ddagger$ stoichiometry. At high $[\text{B}]$, the concentration of $[\text{B}_2]$ could be sufficiently high (although not yet observable) to efficiently scavenge $[\text{A}^*]$ as it forms. The first step becomes rate limiting with a transition structure of $[\text{A}]^\ddagger$ stoichiometry. Both limiting behaviors are consistent with the original rate equation.