I. General Overview

Kinetics for Synthetic Chemists

Bibliography:

J. H. Espenson, "Chemical Kinetics and Reaction Mechanism", 1st or 2nd Ed.

A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd Ed. (not 3rd), 1961.

G. G. Hammes, "Principles of Chemical Kinetics"

K. J. Laidler, "Chemical Kinetics"

Journal of Chemical Education, http://jchemed.chem.wisc.edu/

•*J. Chem. Educ.* is a great kinetics journal

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Course Goals:

1. Survey standard rate equations

2. Explore methods used to extract clues from raw rate data for the formulation of a rate equation.

3. Develop an intuitive feel for kinetics.

4. Provide a reference document.

5. We will not cover...

   a. Statistics (except the "eye test")
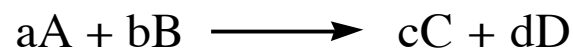
   b. Numerical Simulations

   c. Higher Mathematics

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I. General:

A. Reaction Rates:

1. Given:

aA + bB $\longrightarrow$ cC + dD

- a, b, c, and d are stoichiometric coefficients.

2. Rate:

$$\frac{-d[A]}{dt} \ or \ \frac{-d[B]}{dt} \ or \ \frac{d[C]}{dt} \ or \ \frac{d[D]}{dt}$$
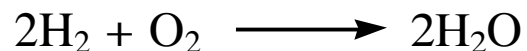
- Negative signs, by convention, give positive rates.

3. Stoichiometries:

$$\frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

• Assumes no observable intermediates.

Example

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$\frac{-1}{2}\frac{d[H_2]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

• Often stoichiometries are omitted if equalities are not emphasized.

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B. <u>Monitoring Rates</u>:

IR	$[\alpha]_D$
NMR	pressure change
UV	pH
GC	conductivity (i.e. ions)
HPLC	

• Refining the analysis is the toughest part! Continuous monitoring and automated data collection are both key.

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C. <u>Rate Equation</u>: simplest form

$$-d[\text{Starting Material}]/dt = d[\text{Product}]/dt = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

not always true

1. <u>Individual Reaction Orders</u>: α, β, γ

    a. negative or positive

    b. integers or fractions

    c. zero

    d. irrational looking (non-integer)

2. <u>Overall Reaction Order</u>: Sum of individual orders; often irrelevant.

3. <u>Molecularity</u>: number of particles in a single elementary step or transition structure.

  • The "overall reaction order" and "molecularity" are not related in a simple way.

4. <u>Rate Constant, k</u>:

  • The units are chosen so that the rate is expressed as concentration per unit time:

$$-d[A]/dt \Rightarrow \frac{\text{moles}}{\text{liter} \cdot \text{sec}} = M \cdot \text{sec}^{-1}$$

  a. <u>1st-Order Rate Constants</u>:

    $-d[A]/dt = k[A]$

    such that $k = \text{sec}^{-1}$

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b. <u>2nd-Order Rate Constants</u>:

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

such that $k = M^{-1}sec^{-1}$

c. <u>Pseudo-1st-Order Rate Constants</u>:

If [B] is kept constant by using a large excess, then...

$-d[A]/dt = k_{obsd}[A]$

such that...

$k_{obsd} = k_1[B]$

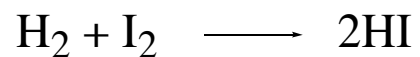$\bullet k_{obsd} = sec^{-1} \qquad k_1 = M^{-1}sec^{-1}$

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5. <u>Stoichiometry vs. Rate Equation</u>:

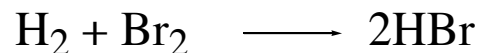The following examples show that there is <u>no</u> simple relationship....

a. <u>Case 1</u>:

$$H_2 + I_2 \longrightarrow 2HI$$

$$1/2 \, d[HI]/dt = k[I_2][H_2]$$

- So far so good, but...

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b. <u>Case 2</u>:

$$H_2 + Br_2 \longrightarrow 2HBr$$

$$1/2 \; d[HBr]/dt = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

"Although the reactions of H_2 with I_2 and Br_2 follow similar stoichiometric equations, *the rate equations* are of quite different forms."

-Frost & Pearson.

c. <u>Take-home Lessons</u>:

i. Stoichiometries do not equate with reaction orders.

ii. Analogies with "related cases" are dangerous.

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D. <u>Origins of a Rate Equation</u>:

    1. Studies of rates vs. reagent concentrations

    2. Knowledge of possibilities (bias!)

    3. Frost and Pearson quote rephrased....

"Although the reactions of H_2 with I_2 and Br_2 follow similar stoichiometric equations, the rate data are consistent with rate equations of quite different mathematical forms."

• The reference to "the rate equation" suggests "uniqueness" that is misleading (to me, at least). Rate equations are never unique.