

Pseudo First Order Reaction

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Kinetic Experiments:

- Bromination of Reactive Aromatics
- Fading of Triphenylmethane Dyes
- Fading of Phenolphthalein in Alkaline Solution

The bromination of **acetanilide**, **4-nitrophenol** and **diphenylether** is based on a **second order reaction**:

$$-\frac{d[\text{Br}]}{dt} = k \cdot [\text{Ar}][\text{Br}] \quad (1)$$

If the initial concentration of the aromatic reactant (Ar) is much larger than the bromine concentration, the concentration of Ar will not change appreciably during the course of the reaction. The concentration of the aromatic reactant in excess remains (essentially) constant. Thus the rate's dependence on bromine can be isolated and the rate law can be written

$$v = -\frac{d[\text{Br}]}{dt} = k' \cdot [\text{Br}] \quad \text{where } k' = k \cdot [\text{Ar}] \quad (2)$$

Equation (2) represents the differential form of the rate law. Integration of this equation and determination of the integration constant **C** produces the corresponding integrated law.

Substituting $[\text{Br}] = c$ into equation (2) yields:

$$-\frac{dc}{c} = k' \cdot dt \quad (3)$$

Integrating equation (3) gives:

$$\ln c = -k' \cdot t + C \quad (4)$$

The constant of integration C can be evaluated using boundary conditions. At $t = 0$ the concentration of bromine is c_0 .

Therefore:
$$C = \ln c_0 \quad (5)$$

Accordingly is obtained:

$$\ln c = \ln c_0 - k' \cdot t \quad (6)$$

or
$$c = c_0 \cdot e^{-k' \cdot t} \quad (7)$$

The decrease in the bromine concentration can be followed by photometric measurement.

Combining equation (6) and Beer' Law:

$$A = \log \frac{P_0}{P} = -\log T = \varepsilon \cdot c \cdot d \quad (8)$$

A = absorbance , ε = molar absorptivity with units of $L \text{ mol}^{-1} \text{ cm}^{-1}$,
 c = concentration of the compound in solution, expressed in mol L^{-1} ,
 P_0 = radiant power for radiation entering; P = radiant power for radiation leaving

gives the relationship between k' and $\ln A$:

$$\ln A = -k' \cdot t + \ln c_0 + \ln(\varepsilon \cdot d) \quad \text{or} \quad \ln A = -k' \cdot t + C \quad (9)$$

One needs only monitor the relative concentration of Br as a function of time in a given experiment to obtain the „pseudo-first order rate constant“ k' . This k' value can then be divided by the known, constant concentration of the aromatic compound to obtain the true constant second order k :

$$k = \frac{k'}{[\text{Ar}]} \quad (10)$$

The „pseudo-first order rate constant“ can be also determined from the half-life $t_{1/2}$. The half-life of a reaction is the time required for the concentration of one of the reactants to decrease to half of its initial value.

If half of the reactant is used up, according to equation (7) is obtained:

$$k' \cdot t_{1/2} = \ln \frac{c_0}{c_0/2} \quad \text{or.} \quad k' = \frac{\ln 2}{t_{1/2}} \quad (11)$$