Radical reaction kinetics

Radical reactions are very fast- how do we measure rate data?

- Initiation techniques- laser flash photolysis, flow techniques
- Concentration over time measurement techniques- absorption spectroscopy, resonance fluorescence
- Temperature measurement techniques- thermocouple, thermometer

Rate of radical formation in the initiation step, rate of radical reaction in the propagation step, and the rate of radical destruction in the termination step. These are the three steps that have to be considered when looking at the kinetics of radical reactions.

One-step reactions can be unimolecular or bimolecular. The rate of a unimolecular reaction would be $v=k_{uni}[A]$ where the rate constant is limited by bond vibration. The rate of a bimolecular reaction would be $v=k_{bim}[A][B]$ where the rate constant is limited by the rate of diffusion.

The steady state approximation means that the concentration of the intermediate remains low and constant during the reaction (in radical reactions the intermediate is the radical). The SSA is a very useful tool for simplifying rate equation calculations, as we can simplify the rate of change of the intermediate over time to be zero e.g. $\frac{d[R.]}{dt} = 0$. Therefore, the overall rate law for a complex reaction now only need the concentrations of the [reactant] and the [product].

Question 1- Write the rate equations for the following reaction:

$A+B \leftrightarrow C \rightarrow D$ There are 3 rate constants (k_1, k_{-1}, and k_2).

The first rate equation is the rate of [A] and [B] going to C and back to [A] and [B] e.g.

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k1[A][B] + k - 1[C]$$

Then the second rate equation is the rate of change of [C] e.g.

$$\frac{d[C]}{dt} = k1[A][B] - k - 1[C] - k2[C]$$

Lastly, rate equation three is the formation of product (rate of change of D) e.g.

$$\frac{d[D]}{dt} = k2[C]$$

Arrhenius equation-

$$k = A_e(\frac{-Ea}{RT}) \quad \text{or} \quad Ink = InA - \frac{Ea}{RT}$$

k- rate constant

A-pre exponential factor

Ea- Activation energy

R-Gas Constant

T- Temperature

In an Arrhenius plot, we plot Ink vs 1/T.