

CHEM 3410: Physical Chemistry I — Fall 2008

November 24, 2008

Lecture 35: Chain reactions and polymerization

References

1. Levine, *Physical Chemistry*, Chapter 16

Key Concepts

- Some unimolecular reactions (ex: decomposition of acetaldehyde) do not fit with the above kinetics of unimolecular reactions.
- Chain reactions typically involve the formation and propagation of free radicals. This type of kinetic mechanism includes polymerization, explosions, and combustion.
- There are three main step types in a chain reaction mechanism:
 1. Initiation: start forming some radicals, Initiators can be photochemicals which react with light, unstable molecules like peroxides, or external radical species introduced to the system
 2. Simple propagation: a radical reacts with a molecules to produce another radical and another molecule
 3. Termination: two radicals react to form a molecule. Terminators are often scavengers of free radicals. Examples included tetraethyl lead and antioxidants such as vitamin C.
- It is also possible to have branching steps which involve reacting one radical to produce multiple radical species. Lots of radicals typically will increase the rate of the reaction and often lead to explosions.
- We examined the chain reaction mechanism for the decomposition of acetaldehyde. The key points in the analysis were:
 - Since we were interested in the rate of product formation we wrote a rate expression or law the involved steps where a product was formed or consumed.
 - The rate law we wrote for product formation contained the concentration of an intermediate radical species. We needed to eliminate this quantity by writing additional rate laws for the formation of the intermediate(s).
 - Since the radical species are consumed much faster than they are produced we used the steady-state approximation in order to solve for the steady-state intermediate radical concentration. By using this approximation we avoided having to solve a set of coupled differential equations.
 - The complicated-looking set of equations we generated actually simplified to a fairly compact rate law:

$$k_{obs}[CH_3CHO]^{\frac{3}{2}}$$

The fractional exponent could not be predicted from just looking at the overall reaction or the detailed mechanism.

- Polymerization involves a reaction that takes individual monomers (M) and connects them to form a long-chain molecule or polymer (M_n).
- The properties of a polymer are determined by the types of monomers and the associated side groups (-CH₃ vs. styrene) in addition to the length of the polymer chain.
- Polymerization often occurs by a radical chain reaction mechanism:
 1. initiation: $M \rightarrow M\bullet + e^-$
 2. propagation: $M\bullet + M \rightarrow M_2\bullet$
 3. termination: $M_m\bullet + M_n\bullet \rightarrow M_{m+n}$

- Multiple initiations will lead to short chain polymers but few or rare initiations will lead to long chain polymers.
- Copolymers involve multiple kinds of monomers. These can be random, arranged in a particular order, or block copolymers.
- Branching can result from diradical groups. The degree of branching can impact the properties of a polymer (ex: HDPE vs LDPE).