

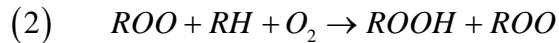
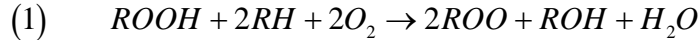
10.34 – Fall 2006

Homework #11

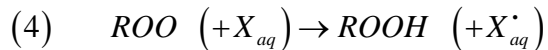
Due Date: Monday, December 11th, 2006 – 9 AM

Kinetic Monte Carlo

The oxidation of an organic droplet of diameter D in air-saturated water containing an antioxidant can be modeled with these reactions:



If the radical site on the ROO reaches at the surface of the droplet, it can react with the aqueous antioxidant:



Note that the second reaction is the radical-catalyzed oxidation of the organic, and the other reactions create or destroy the catalyst ROO. The back reactions are negligible under the reaction conditions of interest.

These equations are good models for the unhealthful oxidation of lipoprotein leading to arteriosclerosis, for reactions important in emulsion polymerization, and for the oxidative degradation of several commercial products. For initial conditions, take $[ROOH]=10^{-6}$ M. $[RH]=10$ M essentially constant, and due to rapid mixing, $[O_2]$ is constant at 10^{-4} M. T is fixed at 40 C. Stop the simulations if $[ROOH]$ reaches 10^{-2} M: by that time the patient is in big trouble, or the product will be unacceptable. We call the time it takes $[ROOH]$ to climb to 10^{-2} M the time-to-failure, and we call the reciprocal of the time-to-failure the “rate-of-failure”.

The average rate expressions (accurate for continuum kinetics) are (units are moles/L-s):

$$\text{Rate 1} = 10^{15} \exp\left(\frac{-15000}{T}\right)[ROOH]$$

$$\text{Rate 2} = 10^9 \exp\left(\frac{-6000}{T}\right)[ROO][RH]$$

$$\text{Rate 3} = 10^6 [ROO]^2$$

$$\text{Rate 4} = 0.01 \cdot \frac{k}{D}[ROO]$$

Where k (nm/sec) depends on the concentration and activity of the aqueous antioxidant.

Remember, the concentration and number of molecules in a droplet is related by:

$$[X] = N_x \left\{ 6.022 \times 10^{23} \left(\frac{\pi D^3}{6} \right) \right\}^{-1}$$

- 1) Solve the kinetic equation using the continuum approximation, for D values of 30 nm, 50 nm, 100 nm, 250 nm, 500 nm, 1.0 μm , and 2.5 μm , and for k = 1.0, 10, and 100. Plot the computed rate-of-failure as a function of D and k.
- 2) Now repeat the solutions for the D = 100, 500, 1000, and 2500 nm and k = 10 cases keeping track of the number of ROO and ROOH molecules, e.g. by using Gillespie's algorithm. Make histograms of the probability of observing a certain "rate-of-failure". How big does the droplet diameter D have to be before the average value of the rate-of-failure computed using Gillespie's algorithm matches the value computed by the continuum approximation to within 10%? When they disagree, which computation is more accurate? Comment on the width of the distribution, and how many trajectories need to be run to achieve good statistics on both the average and the width of the distribution.
- 3) For D = 250 nm, do simulations using Gillespie's algorithm for various values of k. Comment on the observed dependence on k. Physically, what is going on?