MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Chemistry 5.68J Chemical Kinetics Chem. Eng. 10.652J Kinetics of Chemical Reactions

Problem Set #3

Note: This is a good practice problem for the Hour-and-a-half Exam on March 6

A scientist wants to measure the rate of:

 $C_6H_5 + C_2H_4$ $C_6H_5CH_2CH_2$ (reaction 1)

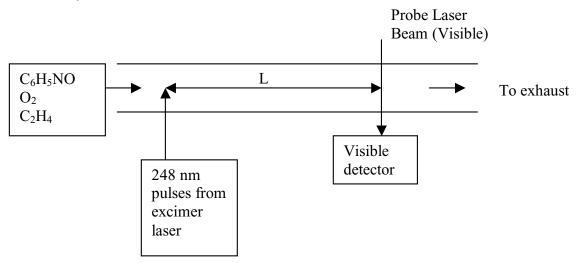
She prepares C_6H_5 by the 248 nm photolysis of C_6H_5NO :

 $C_6H_5NO + hv$ $C_6H_5 + NO$ (reaction 2) (estimated to be fast (~ 1 ns))

The reverse of reaction 2 has a high rate constant $\sim 10^{10}$ liter/mole s. C_6H_5 absorbs too weakly to be observed, but fortuitously she observes the visible absorption of C_6H_5OO formed by

$$C_6H_5 + O_2$$
 C_6H_5OO (reaction 3) estimated k ~ 10⁹ liter/mole s

where the O_2 originally came from an air leak in her apparatus. She sets up a new apparatus (no leak this time) that looks like this:



The experimental adjustables are flow distance L, the mass flow rates of each of the 3 input gases, the diameter of the tube d, the temperature T, and the pressure P. The measurable is the Intensity of visible laser light measured by the detector. The excimer is firing at a steady rate of 50 pulses per second and its average power of 5 W appears to be constant over the course of the experiment. The incident intensity of the visible (probe) laser beam is also constant in time.

Assuming that the system is perfectly 1 dimensional (perfectly mixed in the radial direction), and making any other clearly stated assumptions you think appropriate, write an equation for the variation in the concentration of C_6H_5OO at the position of the probe laser beam as a function of L, P, T, and the mass flow rates. Do we have enough information to determine k_1 ? If so, tell how you would

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determine it from the data you have. If not, tell what additional data you need. How would you carry out the experiments?