Kinetics Project
FCH 361
Spring 2003

Summary: The goal of this project is to have you simulate a complex kinetic system. You will be working in groups on this project, with the default assumption that everyone in a group will receive the same grade. This project is worth points towards your exam II grade. If a group turns in work that is worth less than half the available points, they will have to try again or do more work. I have selected a system to be modeled. If a group would prefer to model a different system of similar complexity, they should first discuss it with me.

The system: The system I have selected is based on an article that appeared in the journal *Physical Chemistry and Chemical Physics*, Volume 1 (1999) pages 3743-3752. You should get a copy of the article. You can access an electronic version of the article directly at the following URL (note that the links appear on the Homework web page for the course.

http://www.rsc.org/CFCart/displayarticlefree.cfm?article=8%2D9%223%24%5DVOB%218%27%5D%5CY%28%3F%3C%23R5%3DP7Q0%40%3D29%23%3C%0A

or indirectly through: http://www.rsc.org/is/journals/current/pccp/cpcon.htm

Key parts of the paper are Figure 3, which provides an overview of the chemistry, and Table 1, which shows the mechanism and rate constants used for simulation and fitting of experimental data.

The simulation program: Kintecus is an Excel-based program which is freely available on the Web at http://www.kintecus.com/. It has a fairly intuitive interface, and I have created files containing some of the mechanism and rate constants.

Preliminary tasks:

1) Download Kintecus and install it
Download the sample file(s) from the Homework web page for the course
Start Kintecus
Use Kintecus to open the sample file entitled KP1.03.xls (you may get a caution about danger from macros: you need to enable them!)

2) Examine the worksheet entitled "species"
Note that every entry in columns B and E will be zero, and that every entry in columns F and G will be No. Read the comments for the other columns! Note that "Display Output" is marked Y (for yes) only for a few species. You can change this, of course.

3) Examine the worksheet entitled "parm"
Note the units of concentration and activation energy, and note the temperature.

4) Examine the worksheet entitled "model"

This gives an abbreviated version of the model used in the paper. Study the first three columns which specify the temperature dependence of the rate constant as

$$k(T) = AT^m e^{-Ea/RT}$$

If *m* is set to zero then this is an Arrhenius expression, but this allows 3-paramter descriptions of the temperature dependence of the rate constant. Note that for most reactions, I have specified column A (the Arrhenius pre-exponential factor) as the rate constant in the paper, and set columns B and C to zero. Unless and until this is changed, this specification limits the use of the model to 293 K, which is fine for our purposes. Some of the reactions are pressure dependent, and I have specified the rate constant for the pressure used in the paper.

5) Examine the worksheet entitled "Control"

Click on the Run button.

When the screen comes up, hit "Return" 3 times to get through the simulation.

A pop-up screen will say there were errors an encourage you to look at the Kintecus output. This time, say yes. The warnings come because I am using numbers after chemical formulas to distinguish isomers (and naming one set of products "Products") and Kintecus can't verify that mass is conserved for these species.

In later steps, after you make modifications to the species and mechanism, you may get "Fatal Errors." These you will need to fix!

Back on the "Control" worksheet, click on "Plot results."
When the dialog box comes up, press "No."
Click on the "Concentrations" sheet

(All the concentration data is in the "CONC" worksheet, but the data plotted in the "Concentrations" sheet is limited to the species for which "Display Output" is marked Y on the "species" worksheet.)

First Set of Questions: Due Monday, March 21. Each group may turn in a single set of answers, although individual group members may attach their opinions, if different.

1) Do the concentrations of $C_4H_9O_2(1)$, or $C_4H_9O(1)$ reach constant values, so that they are obviously in steady state?
2) Is $d[C_4H_9O_2(1)]/dt$ or $d[C_4H_9O(1)]/dt$ small enough that the steady state approximation would work pretty well?
3) If $[NO]_o$ is doubled, what is the effect on the timing and value of the maximum of $[C_4H_9O(1)]$? Explain the direction of the shift in the value of the maximum of $[C_4H_9O(1)]$ and its timing.
4) If $[O_2]_o$ is doubled, what is the effect on the timing and value of the maximum of $[C_4H_9O(1)]$? Explain the reason why the effect of changes in $[NO]_o$ and $[O_2]_o$ are so different.

A Second Set of Questions:

To Be Announced later