

Gas Phase Kinetics Using a Stirred Flow Reactor

Introduction

There are many ways to measure gas phase rate constants. The most direct method involves monitoring one or more of the reactants or products on a continuous basis, for example spectrophotometrically. Then plots of concentration vs. time can give the order and rate constant for the reaction. Alternatively, some physical property of the system is measured, such as pressure or thermal conductivity, and then the rate constant is derived from a plot of something vs. time.

A different method involves using a steady state condition. One example of this is the **stirred flow reactor**. Reactants enter continuously at the inlet of the reactor and a mixture of product and reactants is continuously withdrawn at the outlet. Rapid, vigorous stirring of the mixture ensures that the concentrations of products and reactants are uniform throughout the reactor volume. After a certain time, a steady state is reached and the composition of the mixture in the reactor then remains unchanged, as long as the conditions (flow, temperature, etc.) remain unaltered. The rate constant is determined by measuring concentrations in the inlet and exit streams and the average residence time of molecules in the reactor.

Consider the unimolecular reaction:



in which n moles of B are produced for each mole of A which decomposes. Let the inflowing gas contain $[A]_0$ mol l⁻¹ of A at a flow rate of u ml s⁻¹ into a stirred reactor of volume V . At a steady state, the average concentrations of A and B in the reactor become $[A]$ and $[B]$, and these will be the concentrations observed in the exit stream. The equation for the conservation of molecules of A is,

$$V \{d[A] / dt\} = u [A]_0 - k [A]^\alpha V - u [A] \quad (2)$$

Where k is the rate constant for the decomposition of A and α is the order of the kinetic process. The first term on the right of Equation 2 represents the inflow of A , the second term accounts for the disappearance of A by reaction, and the third represents the outflow of A from the reactor. Steady state conditions have been reached when $\{d[A] / dt\} = 0$. Inserting this condition into Equation 2 and solving for a first order reaction ($\alpha = 1$) gives,

$$k = (u / V) \{ [A]_0 - [A] \} / [A] \quad (3)$$

Note that the term (u / V) has units of s⁻¹. Its inverse, $\tau = (V / u)$, is called the contact time or residence time; this is the average time it would take an unreactive molecule to pass through the reactor. **Caution:** the flow rate to be used in these expressions is the flow rate of the gas *at the temperature of the reactor!*

Experimental Procedure

This experiment uses a stirred flow reactor that is enclosed in a small oven. A gas chromatograph is used for measuring inlet and outlet concentrations. The reactor vessel has a volume of $101.6 \pm 0.7 \text{ cm}^3$. Some di-tert-butyl peroxide (TBP) vapor is added to a steady flow of an inert carrier gas (nitrogen). Gas flow rates are measured with a bubble flow meter and a timer. The flow meter is a burette with a soapy liquid and the bubble is timed to calculate the flow rate in ml s^{-1} . The temperature of the reaction vessel is monitored with a type K thermocouple and a voltmeter. The voltmeter should be set to read temperature directly.

Gas Chromatograph: Currently we are using a Varian Chrompack CP 3380 Gas Chromatograph. The settings for this particular GC experiment should be close to the following:

Injector temp=125°C Column temp= 50°C Detector temp=300°C

The heaters are left on all quarter. At the beginning of the lab period, start the GC using the following procedure.

1. Open the main valve on the helium, air, and hydrogen cylinders. The outlet pressures should be approximately 80, 55, and 45 psig (pounds per square inch gauge) respectively.
2. Turn the instrument detector electronics On: push the “detector” button on the GC control panel, select “Electronics” with the cursor and switch it On with the “Incr” or “Decr” buttons. Push Enter, and go back to the main screen with “Status/Enter”
3. Make sure the Helium flow is at 4-5 psi (front panel gauge) and adjust the needle valve (V5) as necessary (Careful, this valve is extremely sensitive)

Right after ignition the FID output (GC monitor) will go to some tens of millivolts and then stabilize to less than 1 mV after 15-20 minutes of warm up time. If the FID output suddenly goes to zero, check the pressure of the gas cylinders and make sure the needle valves are opened.

Data Collection:

1. Place a few cm^3 of liquid TBP into the glass bottom flask, and cool it to 0°C with an ice-water bath before starting the carrier gas flow. (If the liquid TBP is used at room temperature, the carrier gas tends to become supersaturated and liquid TBP is deposited downstream, which is undesirable) At the end of each lab period cap the flask and store it in the fridge. After finishing all tests, dispose of the TBP properly.
2. Start the carrier gas (Nitrogen) flow (the starting rate should be $\sim 1 \text{ ml s}^{-1}$). The flow can be controlled with the needle valve at the cylinder regulator and with the needle valve right before the sample container. Turn on the stirrer and slowly increase the stirring rate to about 3 to 4. Then turn on the Variac to bring the oven to temperature (Variat around 40). After a little while, when the oven temperature has stabilized, you are ready to begin sampling.
3. The TBP vapor in nitrogen is sampled using a gas tight syringe both on the inlet stream and on the exit stream of the stirred flow reactor. The sample is injected into the GC through the top port (stick needle $\sim 90\%$ of the way in, straight down). The volume of the sample, 2.00 cm^3 , is critical

and you should practice until you can get reproducible peak heights. It is recommended to change the septa on the input and output, and the GC inlet port before starting the lab (ask the TA).

4. To control the GC, refer to the appendix for descriptions on the computer programs available. In order to start a GC run you have to:
 - a. Click the Start green button on the GC instrument and wait for the ready light (you only need to do this at the beginning of each lab period)
 - b. Click the Start button on the software
 - c. Inject the sample into the machine

The TBP peaks will come out at 1-3 min depending on the Helium flow, ignore earlier peaks.

5. While analyzing the gases, record the temperature and measure the gas flow several times and then calculate the average and standard deviation of this parameter.
6. The gas flow and/or the reactor temperature may then be changed in preparation for the next set of measurements.
7. At the end of each lab period, turn off the detector electronics, close all gas cylinders, and turn off the stirrer and the variac. Finally, remember to cap the sample flask and store it in the fridge

It is strongly recommended that you work up your data after each lab, or even during the lab, and place the calculated rate constants on an Arrhenius plot. This will serve to guide your experiments during the next lab period.

Kinetic Runs and Data Analysis:

1. At 190°C the half-life of TBP is around one minute. You should explore temperatures in the 170-260°C range. You can control both the carrier gas flow rate (and thus τ) and the oven temperature. Do not conduct a series of runs by always increasing or always decreasing the temperature; some extraneous drift with time, for example a growing leak in the flow system, might be interpreted as a temperature effect. Always try to vary your experimental conditions in a random but intelligent manner. Try to measure the inlet and exit streams as close in time as possible to minimize any drift effect. Repeat the experiment, for a single temperature, three or four times to estimate the uncertainty. Analyze your data to determine the activation energy and the entropy of activation for this reaction. (Remember to correct the flow rates you measure to the higher temp. flow rates in the reactor.)
2. Verify that the reaction follows first order kinetics ($\alpha = 1$) by measuring k at different flow rates while keeping the reactor temperature constant and fitting your data to solve for α in Equation 2.
3. For a given temperature, what is the optimum percent decomposition of TBP, so that the relative error in k will be a minimum? Assume that the relative error in u is constant, and that the absolute errors in A and A_0 are the same. (Your report has to include an answer to this question)
4. Compare your activation energy to typical bond strengths. What bond in TBP is being broken in the rate determining step?
5. What does the entropy of activation tell you about the transition state?

References

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3. A. B. Littlewood, "Gas Chromatography", 2nd ed., Academic Press, 1970.
4. J. W. Moore and R. G. Pearson, "Kinetics and Mechanism", 3rd ed., Wiley & Sons, New York, 1981.
5. J. F. Griffiths, Ann. Rev. Phys. Chem. 36, 77 (1985). This review article discusses some of the complex effect that can be observed in TBP decompositions due to self-heating. For the dilute mixtures used in Chem 114, self-heating is of minor importance

APPENDIX- Software for the gas chromatographer


On the upper part of the desktop, there should be a tool bar for Star Chromatography



Click on the quick start icon:

The Quick Start window will open with the preloaded 114 method. At the bottom of this window you will find the green Start button to start each run. You will specify Operator name (optional), Sample name, and Folder for Data File Storage. The program will save the files with the following format: 1adcb.16m-dd-yyyyname00x.run, where *name* is the sample name you specified before, and x is the run number. Be patient, after you hit start it will take the software about a minute to actually start the run. Inject the sample only after you see the software running.



To select and analyze the different files, click on the  icon: An analysis window will open. From the file menu you can open the different runs. Move the red arrows at the bottom of the screen to select the integration limits and click on "reintegrate now" (middle integration icon)

Then position the mouse on top of the peak of interest and a small white window on the lower right corner will show the integrated area in mVolts*sec