5.09 Photolysis of ethanal (5 points)

Safety

Wear safety glasses whenever you are using the vacuum rig. Do not look at the light from the mercury-vapour lamp - silica windows are used to allow uv light from the lamp into the reaction cell; staring at the light could damage your eyes.

Introduction

In this experiment you will study the kinetics of the gas phase photolysis of ethanal (acetaldehyde) at 300^0C by pressure measurement and by product analysis using gas chromatography. One mole of ethanal gives two moles of products, so if ethanal is photolysed completely at 300^0C, the final pressure is almost exactly double the initial pressure and the pressure change Δp at any time is a measure of the progress of the reaction. It is convenient to monitor the reaction by following this pressure change.

The primary process in the decomposition of ethanal is absorption of radiation:

$$CH_3CHO + h\nu \rightarrow CH_3^{\cdot} + CHO^{\cdot} \qquad (1)$$

GC analysis shows the products consist almost entirely of methane and carbon monoxide, with about 1% ethane. This suggests chain propagation steps:

$$CH_3^{\cdot} + CH_3CHO \rightarrow CH_4 + CH_3CO^{\cdot}$$
$$CH_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CO$$

At 300^0C there is no sign of products such as diacetyl or glyoxal, which are formed on low temperature photolysis. The chain propagation steps can therefore be combined to give

$$CH_3^{\cdot} + CH_3CHO \rightarrow CH_4 + CO + CH_3^{\cdot} \qquad (2)$$

which assumes that the acetyl decomposes on formation. The ethane must arise from the termination step:

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6 \qquad (3)$$

We can now write down equations for the rates of consumption of aldehyde and formation of products. For example,

$$-\frac{d[CH_3CHO]}{dt} = I_{abs} + k_2[CH_3^{\cdot}][CH_3CHO] \qquad (4)$$

where I_{abs} is the rate at which photons are absorbed (the rate of the primary photochemical step), and k_2 is the rate constant for reaction 2. As the chain length is long (the ratio of methane to ethane in the products tells us this), the amount of aldehyde decomposed in step 1 is small compared to that which reacts in step 2. To a first approximation, therefore, we can neglect the term I_{abs} .

By setting up a similar equation for the formation of methyl radicals and applying the steady-state approximation, $d[CH_3^{\cdot}]/dt = 0$, we obtain an expression for $[CH_3^{\cdot}]$ which we can substitute in (4) to give an expression for the rate of reaction of aldehyde; this will contain a term in I_{abs}. Although the amount of light absorbed should be an exponential function of the aldehyde pressure, both the extinction coefficient and the amount of light absorbed are small. Under these conditions, the early part of the exponential absorption curve is nearly a straight line and $I_{abs} \approx k[CH_3CHO]$

You should now be able to obtain an expression for the overall rate of reaction in terms of the aldehyde pressure and velocity constants only. Apply a similar treatment to obtain an expression for the rate of formation of ethane. We can compare this expression with experimental data gathered from GC analysis of the reaction mixture.

Photolysis takes place inside a silica reaction vessel within a furnace. UV radiation at 310nm (near the maximum of the ethanal absorption) from a high pressure mercury lamp is passed into the vessel through silica windows. Radiation in the visible is not energetic enough to cause photolysis, and the mercury resonance line at 254nm is not emitted by lamps of this type, being re-absorbed by the high pressure of mercury in the lamp envelope. Light from the lamp is roughly collimated and focused by a spherical quartz flask filled with water, which acts as an inexpensive large diameter lens. The reaction vessel is connected to a capillary manometer and is isolated through a two-way tap. The system is evacuated by an oil diffusion pump, backed by a mechanical pump.

Products of the photolysis are analysed on a gas chromatograph equipped with a flame ionisation detector. As different materials emerge from the chromatography column, they pass through a tiny hydrogen flame. This ionises the species in the vapour phase, changing the conductivity across the flame. This minute change in conductivity is measured, amplified, and passed to a chart recorder for output.

Procedure

Check that the lamp shutter (the metal slider at the left-hand side of the oven) is closed (pushed fully in). Turn on the mercury vapour lamp.

Start the rotary pump. Turn the red/black tap, which is on the connection to the rotary pump, through 180 degrees to evacuate the diffusion pump. After five minutes, turn on the diffusion pump heater and cooling fan (the two toggle switches on the black section of the diffusion pump). Turn on the Pirani gauge; (the Pirani detector is normally plugged into Head 2). This will initially show the vacuum given by the rotary pump (about 1mm Hg); as the oil in the diffusion pump boils the pressure should drop to about 0.07 torr. When the diffusion pump is operating, cautiously open the black and red taps to evacuate the sample cell in the oven, but leave the green tap closed. (The section of the rig which can be evacuated by opening the green tap will be used in the second part of the experiment to trap a small sample of gas for analysis.)

With the blue tap at the centre bottom of the apparatus closed, remove, clean and dry the ethanal reservoir (the small sealed tube with a B10 male fitting).

Ask the lab technician for some liquid nitrogen. Half fill the small Dewar (Thermos flask) with liquid nitrogen. (CARE! Liquid nitrogen can burn you and there is a danger of implosion. Wear safety glasses.) Fetch the ethanal from the fume cupboard and fill the reservoir about one-third full. Grease the joint with a small quantity of AP 101 grease (a fluorocarbon grease which is not dissolved by ethanal.) Fit the reservoir onto the vacuum line, but do not open the tap yet, and freeze the liquid by immersing it in liquid nitrogen.

When the ethanal is completely frozen (about two minutes) evacuate the reservoir by opening the blue tap and pumping for one minute. Shut the tap, remove the liquid nitrogen and allow the ethanal to thaw completely; you will see bubbles of dissolved gases appearing as the solid melts. (The purpose of this freeze-thaw cycle is to remove dissolved oxygen, which is an efficient radical-scavenger; its presence in the reaction vessel would badly disrupt the experiment.)

Re-freeze the sample, open the tap, evacuate for a further minute, close the tap and allow to thaw. Repeat a third time. Finally shut the tap and allow the sample to warm to room temperature.

Determination of the overall order of reaction

Tap the manometer gently to ensure the mercury level is stable and take the manometer reading for the completely evacuated reaction vessel. Close the black tap, open the red tap to the lower position so that ethanal will be able to expand into the sample vessel.

Open the blue tap to admit about 100mm Hg pressure ethanal to the reaction vessel. Shut the red tap, then take the manometer reading to find the initial pressure of ethanal vapour. Note the time and open the lamp shutter. Record the manometer reading every 30 seconds, tapping the manometer gently before taking readings.

When the reaction is about 25% complete, close the shutter and evacuate the vessel for 2 minutes. Repeat at a series of initial pressures between about 50 and 500 mm Hg.

The order with respect to ethane formation

Your graphs of Δp vs t should be nearly linear up to at least 10% reaction. You can, therefore, obtain the initial rates of formation of products at any pressure by sampling at 10% reaction, determining the partial pressures of products from the analysis and calculating the rates of formation by dividing by the time required to reach 10% reaction at that initial pressure.

In the second part of the experiment samples of the products are analysed by GC. The signal due to ethane is much smaller than that of methane, so you may need to change the sensitivity of the instrument part way through a chromatogram. This procedure is described shortly.

Following the instructions below, turn on the chromatograph and allow it to warm up. Introduce a pressure of about 150mm Hg of ethanal into the reaction vessel and photolyse to approximately 10% completion. Record the time required for this. Follow the instructions below to analyse your sample by GC.

If you have done the analysis correctly, you will still have reaction mixture in the vacuum line, so you may repeat the determination if the first chromatogram has not turned out properly. (There are two common reasons for this: [a] You may have selected a RANGE factor which lead to peaks being too small to measure, or off-scale; [b] for runs at high ethanal pressure, the first sample fed into the GC may be predominantly unreacted ethanal, which was contained in the volume between the reaction vessel and tap A.)

If your chromatogram is successful, evacuate the vacuum line and start the next photolysis; you can do this as soon as it is obvious that the methane and ethane peaks are acceptable - the next photolysis may be begun while the acetaldehyde is still emerging from the column.

Carry out a series of experiments over a full range of initial pressures, sampling for analysis at 10% reaction.

Gas Chromatography

Instructions for the gas chromatograph are given below. Read them carefully before attempting to use the apparatus. The gas syringe used for taking and injecting samples is a delicate and costly item; please handle it carefully. Injecting samples through the injection port of the instrument without bending the needle requires care - advice about doing this is also given below.

Gas chromatography is a simple and elegant technique for the quantitative analysis of mixtures of volatile components. A metal or glass column is filled with a granular packing on which an oil is adsorbed; a stream of inert carrier gas (generally helium) is passed through the column and carries gaseous components over the packing. Column packings usually consist of a support phase, which is a porous, inert granular powder, such as powdered pumice, coated with an involatile liquid such as silicone oil, a high boiling ester, polyethylene glycol etc. This type of packing gives rise to the term gas-liquid chromatography or GLC. We need a packing which gives good separation of each mixture to be analysed. There are guidelines for this - polar columns hold back polar constituents and will separate them from otherwise similar non-polar materials. One can also separate molecules on the basis of their size.

At the entrance to the column there is a port, closed by a rubber septum, through which a sample (typically 1-5 μl liquid or 1 cm^3 vapour) can be injected by syringe. At the end of the column a detector gives an electrical signal when something other than pure helium emerges. There are many types of detector. The present instrument contains a pair of flame ionisation detectors (one for each of the two columns in the instrument), whose output can be fed to chart recorders. The injection block, columns and detectors can be heated individually to a temperature at which all the mixture constituents are in the vapour state.

When a sample is injected it is immediately vaporised, if not already in the vapour phase, and carried into the column by the flow of carrier gas. Here adsorption onto the oil which coats the column packing, and subsequent desorption into the carrier gas, take place repeatedly in each successive volume element of packing along the column. Substances more strongly adsorbed, more soluble in the liquid phase or less volatile will move less rapidly along the column than components with the opposite properties, so the original mixture separates into its constituents. This behaviour is similar to that occurring in a fractional distillation column. In fact, gas chromatograph column performance is often expressed in terms of 'theoretical plates', but chromatography columns are far more efficient than distillation columns and 10^3 to 10^4 theoretical plates per metre of column are quite usual.

As each component emerges from the column and enters the detector, its presence is indicated as a peak on the recorder. The time between injection and detection of a particular constituent is called its retention time and serves to identify it; the magnitude of the recorder response gives the amount.

For the present application we use a simple adsorptive packing without a liquid phase, a granular porous styrene - divinyl benzene copolymer (Chromosorb 102) which is non-polar. It desorbs water, alcohols and low molecular weight hydrocarbons in order of their molecular weights.

Use of the gas chromatograph

a) Check that the needle valve of the helium cylinder regulator is closed and that the pressure-regulating valve (the large two-winged handle on the front of the regulator) is turned fully anticlockwise, which is the closed position (do not force this handle; turn it gently until a *slight resistance* is felt). Open the main connection from cylinder to regulator and check that the gauge shows a positive reading. Turn the winged handle clockwise to give a reading of 1.5 bar (which equals 1.5 atmospheres) on the regulator dial. Open the needle valve one turn.

b) The GC contains two columns with different characteristics; you will use the right-hand column for this experiment. The column inlet (zone 1) the detector (zone 2) and the chart recorder for this column are all marked with a large yellow blob.

c) Open the vertical flap on the left hand front face of the instrument and turn the right topmost knob, which controls the flow of helium through the column, until the pressure reads 150 kPa. If that pressure cannot be obtained, cautiously turn the winged handle on the regulator to allow a higher pressure into the gas supply line.

d) Close and latch the oven door if it is open. Turn on the power (the on/off switch is located at the bottom front right of the instrument; you will have to bend down to see it.) Turn on the upper amplifier (top right) if it is not already on; the switch is at the rear of the unit. The instrument will start to warm up to its operating temperature (it should be already set at 210°C for this experiment). You should not need to touch any of the set of buttons on the keypad at the bottom right of the instrument, which are mainly concerned with temperature programming.

e) Turn on the air cylinder, observing the same precautions as you used with the helium cylinder. Set the pressure at the regulator to 1.2 bar. Turn the knurled knob at the bottom right below the dial labelled "air" on the GC to give a pressure of 100 kPa.

f) Turn on the hydrogen cylinder, observing the same precautions as before. Set the hydrogen regulator pressure to 0.8 bar. In the flame ionisation detector the effluent of the column is fed through a minute hydrogen/air flame situated at the end of the column in zone 2. The tiny changes in conductivity across the flame caused by changes in composition of the gas exiting the column are picked up by the EL980 detector and amplified before being sent to the chart recorder. Use the knurled knob to set the hydrogen pressure to 65 kPa.

g) Wait for two minutes to allow hydrogen to reach the detector unit, then press the green "Ignite" button at the left of the EL980 unit. There wil be a very faint pop as

the flame is lit. DO NOT PRESS THE IGNITE BUTTON FOR THAN THREE SECONDS OR YOU MAY DAMAGE THE INSTRUMENT.

h) Check that the flame is lit by holding for a moment the chunky mirror (kept on the shelf behind the instrument) at an angle just to the side of one of the holes at the top of the detector mounting. If the flame is lit, a small patch of condensation will appear on the mirror, showing that water vapour is being formed. If the flame will not light, seek help.

i) The **range** and **attenuation** buttons on the detector unit control the detector sensitivity. Set the **range** initially at 1 and **attenuation** at 8. You can vary these by pressing the keys below the display. Raising the attenuation cuts down ("attenuates") the sensitivity; each change of one unit in attenuation changes the output signal by a factor of two.

j) Samples are injected into the column using a delicate syringe. This is easily damaged, so must be handled with great care. To take a sample, evacuate the section on the experimental rig containing the septum (take care not to suck away your photolysis products!) by opening the green tap while keeping the red and black taps closed. Close the green tap, then turn the red three-way tap through 180 degrees to allow the sample to expand into the sampling volume. Close the red tap once the gas has been allowed into this volume.
Open the tap on the syringe and blow out the gas within. Gently slide the needle through the septum - only gently pressure should be required. Withdraw the plunger most of the way to introduce sample into the barrel. Close the tap on the syringe and depress the plunger most of the way in order to pressurize the gas within. Do not force the plunger all the way down, or you may cause the syringe to burst - a dangerous and expensive mistake!

k) Hold the syringe vertically over the column inlet. The needle must be pushed centrally through the septum. Lower the end of the needle onto the septum then, holding the syringe vertically, carefully slide the needle through the septum. Little force should be required - do not try to force the needle through, or you will bend it and ruin the syringe. If the needle seems not to want to penetrate the septum, move to a slightly different place on the septum and try again.

l) When the syringe has been inserted as far as it will go push the plunger down gently (remember it is fragile) but fairly quickly. Mark the injection time on the chart recorder by momentarily moving the pen across the chart paper using one of the arrow knobs on the recorder. Ensure the pen is not hard against one of the edges or you may not see any spectrum. Carefully withdraw the syringe, and return it to a safe place; do not leave it lying on the bench from where it may roll onto the floor and break.

m) Under the conditions of the experiment a peak corresponding to elution of one component should appear after about 30 seconds, while a second should appear after about 120 seconds.

n) The chromatograph column packing has a finite life at the operating temperature; do not leave the chromatograph turned on for long periods if you are not performing analyses. At the end of the experiment turn off power to all the components, and close all valves and regulators.

Calculations

To find the overall rate of reaction, plot a graph of the change in pressure as a function of time for each set of measurements. Draw a tangent to each plot at the origin to obtain a value for the initial rate of reaction at this pressure. Use these data to obtain the overall rate of reaction with respect to acetaldehyde.

Measure the areas of the methane and ethane GC peaks by cut-and-weigh or by using the light box to estimate area using a piece of overlaid graph paper, and adjust for different range factors. If the CH_4 and CO peaks cannot be separated, determine the total area and divide by 1.8 to find the area for CH_4. Calibrations with pure gases have shown that the detector is 1.88 times as sensitive for ethane as for methane. The peak areas can, therefore, be converted using this factor into relative partial pressures. We want to know the absolute partial pressures in the reaction vessel at the time of sampling; for this we can use methane as a reference. Each mm partial pressure of acetaldehyde decomposed gives very nearly 1mm pressure of CH_4. The pressure change up to the moment of sampling, Δp, can thus be taken as the CH_4 partial pressure.

Determine the order with respect to ethane formation from your results and compare with the value derived from the proposed mechanism. Calculate the overall chain length of the photolysis. Comment on the source and size of errors in your results.