Laboratory session 5 : Kinetic Study of the Photochemical Oxidation of Triphenylphosphine.

Objectives. The objective of this practical is the kinetic study of the photochemical oxidation of triphenylphosphine in organic medium, which is followed by measuring the remaining fraction of triphenylphosphine through reverse phase HPLC chromatography. The obtained data allow us to calculate the order and the reaction rate constant, and to discuss the viability of the proposed reaction mechanism.

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1. Introduction

Triphenylphosphine, $P(C_6H_5)_3$, is an organophosphorus compound that is oxidized by oxygen according to the stoichiometric equation:

$$P(C_6H_5)_3 + \frac{1}{2}O_2 \xrightarrow{k} OP(C_6H_5)_3 \qquad (1)$$

At room temperature, oxidation proceeds slowly in the dark, making the preparation of air-stable $P(C_6H_5)_3$ solutions possible. However, oxidation proceeds relatively fast when solutions are illuminated with electromagnetic radiation with wavelength between 230-300 nm. The reaction progresses with greater speed the greater the intensity of illumination, I_0, to which the solution is exposed.

1.1. Reaction Rate Determination

The reaction rate can be expressed by equation (2). This indicates that the specific rate constant, k, is a function of both the intensity of the illuminating radiation and the amount of oxygen dissolved in the organic solvent, $[O_2]$. Since the reactor is stirred and open to the atmosphere, we will consider that the oxygen concentration remains constant in the solvent. Consequently, the kinetic equation takes the form given by the last part of equation (2). The experiment aims at determining the reaction order with respect to $P(C_6H_5)_3$, n, as well as the value of the specific rate constant k.

$$-\frac{d[P(C_6H_5)_3]}{dt} = k(f([O_2], I_0)\,[P(C_6H_5)_3]^n) = k[P(C_6H_5)_3]^n \qquad (2)$$

As equation (2) can be rewritten in terms of the remaining molar fraction of triphenylphosphine, $\alpha = \frac{[P(C_6H_5)_3]}{[P(C_6H_5)_3]_0}$, see equation (3), the reaction kinetics may be followed by determining the concentration of $P(C_6H_5)_3$ in aliquots of the reaction mixture extracted at regular intervals from the reaction flask.

$$-\frac{d\alpha}{dt} = (k\,[P(C_6H_5)_3]_0^{n-1})\,\alpha^n = k^*\alpha^n \qquad (3)$$

The determination of the α fraction will be carried out using *reverse phase chromatography*, a technique that allows the components of the reaction mixture to be analyzed. Each component appears as a "peak" in the chromatogram, its concentration being directly proportional to the peak area, *A*. For $P(C_6H_5)_3$, $A=\beta\,[P(C_6H_5)_3]$ where β is constant, so the fraction α will be given by equation (4):

$$\alpha = \frac{[P(C_6H_5)_3]}{[P(C_6H_5)_3]_0} = \frac{\beta[P(C_6H_5)_3]}{\beta[P(C_6H_5)_3]_0} = \frac{A}{A_0} \qquad (4)$$

2. Experimental Procedure

2.1. Reaction Kinetics Tracking

2.1.1. Solutions

Each pair of students will prepare 100 mL of a solution of $P(C_6H_5)_3$ 1.0×10^{-3}M using HPLC quality CH_3CN solvent. Because the solvent is in contact with the atmosphere it will become saturated with oxygen during the preparation process. Once the solution is prepared, keep it in the dark.

2.1.2. Eluent

The eluent should be available at the begining of the experiment. Otherwise, 1L of eluent will be prepared by mixing in a clean and dry bottle 0.9L of CH_3CN and 0.1L of distilled water of mQ quality. The mixture will then be filtered using a vacuum filtration assembly that includes a glass filter holder, an anodized aluminum clamp and a ground joint flask connected to the supplied vacuum source. After filtering, maintain the flask under vaccuum for a few more minutes. Filtration removes solid particles that could obstruct the capillary circuits in the chromatograph, and removes most of the air trapped during the mixing process. To finish degassing the solution, carefully transfer the contents of the vacuum flask to a 1L volumetric flask and place the flask inside the ultrasonic bath for 15 min.

2.1.3. Photochemical Reactor Assembly

A sketch of the complete assembled apparatus to be used is shown in figure 1. It consists of a cylindrical glass container surrounded by a thermostatic jacket, into which the additional cooling system (**A**) that encloses a quartz cylinder (**C**) containing the lamp (**B**), is introduced along the vertical axis (see figure 2).

The light source is a H_2 lamp connected to a high voltage source (**9**, see Figure 1). The source is operated with two switches: the power (on), and the lamp on (start). These lamps are dangerous because the emitted UV radiation can irreversibly destroy certain retina tissues and cause permanent blindness.

Therefore, they must NEVER be turned on if the reactor is not **perfectly covered. Whenever we approach the reactor we must protect our eyes with UV protection glasses.**

Figure 1: The complete assembled reactor: **1** Thermocouple sensor; **2** Central body of the reactor; **3** Reactants inlet; **4** Lamp cooling jacket; **5** Quartz vessel lamp; **6** Key for cleaning the reactor; **7a, b** Lamp cooling circuit; **8a, b** Reactor cooling circuit; **9** Lamp power supply; **10** Teflon tube for sampling; **11** Oxygen inlet.

To assemble the photochemical reactor follow the instructions given below. If the reactor is already assembled, follow the instructions from 9 to 18:

1. Make sure the high voltage source is disconnected.

2. Clean the flask with a few milliliters of CH_3CN and air-dry it.

3. Place the reactor on the magnetic stirrer and insert a stirrer bar inside.

4. Secure the reactor position with the clamps provided.

5. Insert the quartz cylinder **C** through the lamp cooling jacket **A**.

6. Insert the cooling jacket **A** (Figure 2) through the reactor body. Make sure the grids are in firm contact to avoid leaks of the water acting as a refrigerant.

7. Insert the lamp **B** into the quartz cylinder **C**.

8. Connect the rubber tubes of the reactor thermostat jacket and those of the lamp cooling jacket.

9. Insert the sampling tube through the septum and through the reactant inlet **3**.

10. Insert the thermocouple through hole **11**.

11. Check that the magnetic stirrer works before plugging the reactor in.

12. Cover the entire reactor, including its base, with aluminum foil so that radiation cannot escape from inside the reactor (the aluminum foil acts as a mirror and allows the reaction mixture to be illuminated in a homogeneous way; in addition, it prevents the UV radiation escaping into the laboratory).

13. Prepare the thermostatic bath at the working temperature (20ºC) and turn on the "cold finger".

14. Turn the high voltage source on by pressing the `on` key.

15. Turn the lamp on by pressing the `start` key once.

16. Wait for the thermocouple to mark a constant temperature.

17. Save approximately 2mL of the reaction mixture in a vial and keep it in the darkness. Insert the rest of the solution of $P(C_6H_5)_3$ through inlet **3** of the reactor using a funnel. Make sure that both the thermocouple (**1**) and the sampling tube **10** are submerged near the bottom of the flask. ***As soon as the photoreactor is filled, start the chronometer to measure the reaction time.***

18. Connect the magnetic stirrer and make sure that the reaction mixture is vigorously stirred .

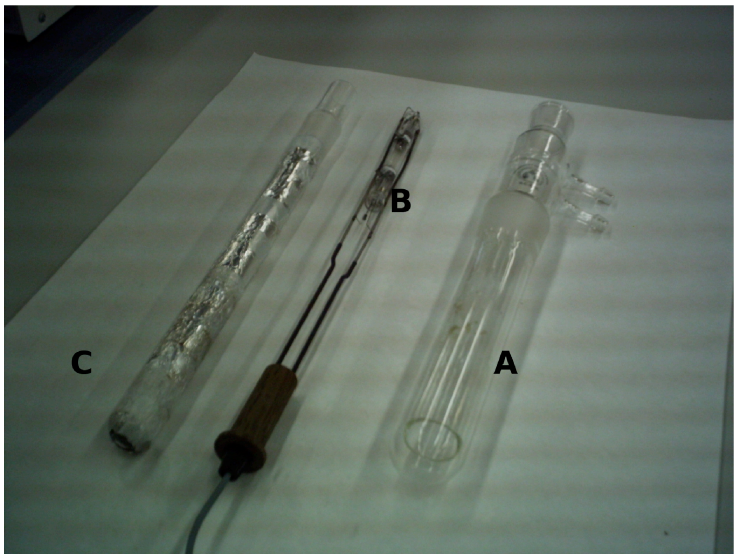

Figure 2: Hydrogen lamp assembly elements: **A** Lamp cooling jacket; **B** Hydrogen lamp; **C** Quartz support for the introduction of the lamp in the jacket cooling bath.

2.1.4. Sampling

Sampling will take place every 10-15 minutes. Samples will be extracted from the reactor following the procedure set out below:

1. Connect the 2.5 mL syringe to the sampling tube.

2. Take 0.5 mL from the reactor and use it to clean the syringe.

3. Take 1.0 mL from the reaction mixture and place it in a clean, dry vial. Write down the chronometer and digital thermometer readings exactly at that moment.

2.2. Sample Injection in the Chromatograph

Once the sample is taken, its chromatographic analysis should be carried out. To inject the sample follow the procedure detailed below:

1. Make sure the chromatograph is ready for chromatogram recording.

2. Turn the injection wheel until it reaches the `load` position.

3. Cleaning the syringe: Take ≈25µL of sample and discard the contents. Repeat this filling/emptying process four more times.

4. With the syringe full, insert the needle into the injection hole. Make sure the needle reaches the bottom and insert the solution into the injector. Repeat this process two more times.

5. Turn the injector wheel to the `inject` position.

6. When the first peak of the chromatogram appears, turn the injector wheel back to the `load` position and remove the syringe from the injector.

The following precautions must be taken into account when injecting the sample: Do not inject the air bubble remaining at the beginning of the plunger and always inject an amount greater than 20µL, the capacity of the injection circuit ("loop").

2.3. General Measurement Procedure

The following tasks will be carried out in the specified order to successfully carry out the experiment:

1. Start the UV100 detector (make sure the observation wavelength is set to 265 nm).

2. Prepare the eluent according to the procedure in section (2.1.2).

3. Start the chromatographic pump according to Appendix B.

4. Prepare the triphenylphosphine solutions, see section (2.1.1.).

5. Mount the photochemical reactor, section (2.1.3.).

6. Take a sample of the reaction mixture, perform the chromatographic analysis and store it in the dark.

7. Turn the lamp on and wait for the thermocouple to mark a constant temperature.

8. Insert the solution into the photoreactor and start the chronometer.

9. Perform the chromatographic analysis of the reaction mixture at intervals of 10-15 min for at least 2h 30min.

10. Analyze the concentration of $P(C_6H_5)_3$ in the previously reserved non-irradiated sample.

3. Calculations and Results

1. Calculate the area of the peaks corresponding to $P(C_6H_5)_3$ for each of the chromatograms. Use the `Azur` program for this.

2. From the area of the chromatographic peaks of $P(C_6H_5)_3$, determine the α fraction for each of the reaction times.

3. Calculate *ln α* and (*1/α*) for each of the reaction times.

4. From the graph of the values of α vs. time, determine the reaction order with respect to $[P(C_6H_5)_3]$ and the value of $k^\star$ with its corresponding error. Calculate the value of k from the value of $k^\star$.

5. Determine the amount of $P(C_6H_5)_3$ consumed in the dark from the values of the areas of the non-irradiated sample.

6. Based on the post-laboratory questions below, discuss the obtained results. Check the feasibility of the reaction mechanism proposed in question 5. Indicate the approximations and relate the experimentally determined k to one or more rate constants in the proposed mechanism.

4. Questions

4.1 Preliminary Questions

1. Before starting the laboratory session, carefully read the articles cited in references [2] and [3].

4.2 Post-laboratory Questions

1. Why was the observation wavelength chosen as 265 nm? At which wavelength is the equality $\frac{[P(C_6H_5)_3]}{[OP(C_6H_5)_3]} = \frac{A_{P(C_6H_5)_3}}{A_{OP(C_6H_5)_3}}$ fulfilled? Why don't we analyze at this second wavelength?

2. Deduce equation (3) from equation (2).

3. Find the literature value for the solubility of oxygen in CH_3CN and estimate its concentration in the reaction mixture. How much $P(C_6H_5)_3$ would it take to

consume all the oxygen if the reactor were closed? What is the limiting reagent? Assume that the reactor volume is 500 mL.

4. Which reactant do you think is excited, oxygen or triphenylphosphine? Why?

5. Assume the reaction mechanism shown below.
¿Does this mechanism explain the observed order with respect to the intensity and concentration of $P(C_6H_5)_3$? What order do you predict with respect to the concentration of oxygen?

$$P(C_6H_5)_3\ (S_0) \xrightarrow{h\nu} P(C_6H_5)_3^*\ (S_1)$$

$$P(C_6H_5)_3^*\ (S_1) \xrightarrow{k_{1,ci}} P(C_6H_5)_3\ (S_0)$$

$$P(C_6H_5)_3^*\ (S_1) \xrightarrow{k_{1,cis}} P(C_6H_5)_3^*\ (T)$$

$$P(C_6H_5)_3^*\ (T) \xrightarrow{k_{2,cis}} P(C_6H_5)_3\ (S_0)$$

$$P(C_6H_5)_3^*\ (T) + O_2 \xrightarrow{k_1} Ph_3PO_2$$

$$Ph_3PO_2 \xrightarrow{k_2} P(C_6H_5)_3\ (S_0) + O_2$$

$$Ph_3PO_2 + P(C_6H_5)_3\ (S_0) \xrightarrow{k_3} 2OP(C_6H_5)_3$$

6. What are the main differences between the proposed mechanism for tertiary phosphine photooxidation proposed in reference [2] and the mechanism proposed in question 5?

Appendix A. Using the UV100 Detector

To prepare the UV-100 detector follow the instructions given below:

1. Connect the detector.

2. Connect the chromatographic pump (eluent flow 1 mL/min).

3. Select the working wavelength (265 nm) by gently turning the corresponding knob. You must select the wavelength from a length shorter than the working length.

4. Select the maximum absorbance value to be measured by the device (3 a.u.)

5. Select the sensitivity in the absorbance measurement (0.001 a.u.).

6. Once the detector and the chromatographic pump have been running for 15-20 min, press the `zero` key.

Once the detector has been started, turn the computer on (user: `hpclab`, password: `cromat01`). Start the `azur` program. Once launched, you will see the welcome message of the program. Select `instrument`. You will see a

screen where the absorbance value is continuously plotted as a function of time. [1] At the left side there are three buttons. Press the `acquisition` button; a form will appear asking for information to control the data acquisition. Fill in the following fields:

- `length`: acquisition time, 6 min.
- `name`: name of the data collection file.[2]
- `information`: comment to identify the chromatogram; for example, indicate the order number and the time and temperature at which the sample was collected.

Make sure that the `from instrument` button is selected in the `start mode` button group. Once the form is completed, press the `signal` button; A screen that displays data acquisition will appear. Now press the data acquisition button located on the toolbar at the top of the screen. You will see two stopwatches at the top of the graph: one stopped at zero and the other at 6 min. Insert the sample into the injector and place it in the `inject` position; at this time the data collection will start automatically. You will see that the screen changes to display only the current signal, and the stopwatches will start.[3] After six minutes, the program will automatically save the chromatogram and show the signal recorded over the last 30 minutes. Do not forget to return the injector to the `load` position. The program is ready to acquire and register a new chromatogram.

To integrate the files follow the instructions given below:

1. Select the data icon. A list with the name of all the registered files is displayed on the left side.
2. Select the chromatogram you want to integrate. The chosen chromatogram graph will be shown. [4]
3. Press the `add peak` button (manual integration toolbar). Select the start time of the integration by clicking with the mouse on the chromatogram line and drag the mouse to select the final time of the integration. The operation is performed automatically: you will see that the peak is identified by its retention time and the baseline of the integration is drawn.
4. Apply the procedure to both the oxide peak and the triphenylphosphine peak.
5. On the left side of the chromatogram you will see a set of buttons. Click the one identified as `results`. A table presenting elution time and area, among other properties, for each peak will appear.
6. Exit the `results` screen by pressing the `chromatogram` button. You will return to the integrated chromatogram. Now press the `print` button

[1] The program does not save this signal
[2] This name will be given to all files generated from this moment on, in such a way that these will differ only in a three-digit suffix that identifies each particular chromatogram.
[3] The first marks the current elution time, while the second indicates the remaining time to complete the data collection.
[4] You can switch between the current signal and a chromatogram by pressing the tab at the bottom of the graph.

(on the toolbar) and choose the `normalize` option: a report of the integrated chromatogram will be printed.

Appendix B. Starting the HPLC Pump

Because the HPLC columns are densely packed, a precision pump is required to develop a large pressure difference between the head and the end of the column. The pressure must remain stable for the eluent to circulate at constant speed, so that the retention times are reproduceable.

An H_2O:CH_3CN 10:90 v/v solution will be used as eluent circulating through the column at 1.5mL/ min. This flow rate is achieved, depending on the state of the column, at more than 140 bar. In any case, you must check that the pressure reading remains constant (±5 bar) and stable before starting the chromatogram recording. Stable readings are achieved only with degassed eluents and in the absence of air inside the pump. To connect the pump to the chromatographic circuit, follow the instructions given below:

a) Priming the pump. The priming of the pump is intended to eliminate air that enters the injection circuits each time the eluent is finished. With the pump stopped, insert the plastic syringe into the priming hole. Turn the priming handwheel 1/4 turn and remove 5 to 10mL of eluent with the syringe slowly. This operation removes air from the circuit. Close the wheel by turning it clockwise and remove the syringe.

b) Once the pump primed. press the edit button. By repeatedly pressing this button you can access the various digits of the LCD screen that allow you to select the flow rate in mL/min. Once placed on a certain digit, it can be modified by pressing the cursor keys. Select flow rate of 1.5 mL/min.

c) Press the menu button and then `run`. The pump starts working and the pressure stabilizes after a few minutes. If this is not the case, repeat the priming process again or de-gas the solvent again.

d) After the laboratory session, the flow must be stopped. To this end, stop the pump by pressing the `stop` key, change the flow to 0.01mL/min and press the run button again. This residual expense prevents the chromatographic column from drying out.

Appendix C. Apparatus

1. For each pair of students:

- One photochemical reactor with hydrogen lamp and power supply.
- One magnetic stirrer and magnet.
- One support.
- Two clamps with clamp holder.

- One digital thermometer with thermocouple.
- One 2.5-mL syringe .
- 30 cm of 1 mm diameter teflon tube.
- One stopwatch.
- One funnel.
- One 100-mL volumetric flask.
- Two 50-mL beakers.
- Twelve vials.
- One vial rack.
- Two pairs of UV protection glasses.

2. Material shared between four couples:

- Two thermostatic baths.
- Two “cold fingers”.
- silicone tube and "T" tubes for thermostatic assembly.
- One 1000-mLvolumetric flask.
- One 1000-mL graduated cylinder.
- One 100-mL graduated cylinder.
- One Büchner flask.
- One filter plate.
- One vacuum pump.
- One ultrasonic bath.
- Two 25-µL syringes.
- One 5-mL plastic syringe.
- Two sets of chromatography equipment (pump, injector and UV detector).
- Aluminium foil.

3. Reagents:

- HPLC quality CH_3CN.
- low conductivity water.
- triphenylphosphine.

Appendix D. Safety in Laboratory

Organic solvents. In the experiment, CH_3CN is used. As it is absorbed through the skin, wear gloves to handle organic solutions and keep the laboratory well ventilated.

UV radiation. In the experiment, sources of UV radiation are used. They are extremely dangerous for the retina and can cause permanent blindness. Therefore, never uncover or open the reactor while the lamp is on and always wear protective glasses near it.

References

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