Experiment 2

Chemistry with Light – Using Photons as Reagents

The Task

To establish the exposure times required to make contact prints using a photochemical system.

Skills

By the end of the experiment you should be able to:

- weigh out samples accurately,
- make up solutions of known concentration,
- record data clearly and accurately in experimental log sheets.

Other Outcomes

- You will observe a photochemical reaction in solution and on a solid substrate.
- You will observe the difference between radiation absorption and heating on a photochemical process.
- You will produce contact prints.

The Assessment

You will be assessed on your ability to keep a record of your lab work and experimental results in a logbook. See Skill 2 on how to number pages, set up tables of data, record your observations, *etc*.

Introduction

Photochemical reactions involve the absorption of light. An important example of photochemistry in Nature is photosynthesis, where plants and algae use the energy from light to make glucose from carbon dioxide and water. Photodegradation, where sunlight is used to break down plastic bags, is an environmental aspect of photochemistry. Photochemistry can also be found in other areas such as traditional photography and printing.

In traditional black and white photography, silver salts are used to produce the black image. When silver chloride is exposed to light, an electron is transferred from the chloride to the metal ion and silver metal is produced. It is the silver metal made by this photochemical reaction that produces the dark colour on the film.

More than fifty years ago, photochemical reactions were commonly used for printing. Because of their colouring they were called “blueprints”. Architects and engineers used blueprints because they allowed them to reproduce exactly the same thing many times.

Blueprinting works by placing a translucent sheet that contains the diagram on top of sensitised paper and irradiating it with light. The light is obscured by markings on the translucent paper, and the negative image is produced on the sensitised paper. The paper is “developed” and then washed in water. The copy emerges as a light-stable, white-line print on blue paper.

Today you are going to make the ion, $[Fe(C_2O_4)_3]^{3-}$ by adding oxalic acid to iron(III) nitrate. This complex ion is commonly called ferrioxalate and is made *in situ*, so there is no need to isolate and purify it before use. (An explanation of complex ions and all the chemistry involved in today’s experiment can be found in Appendix 2.1 on page E2-9.)

The ferrioxalate complex absorbs light at the blue end of the visible light spectrum resulting in an internal electron transfer reaction in which Fe^{3+} is reduced to Fe^{2+}. Potassium hexacyanidoferrate(III), $K_3[Fe(CN)_6]$, then reacts with the Fe^{2+} ions to produce a component with a deep blue colour called Prussian blue. This allows us to detect if the ferrioxalate complex has undergone photochemical reduction and also gives the blue colour in the blueprint.

Safety

Chemical Hazard Identification

potassium hexacyanidoferrate(III) - Hazardous. avoid contact with your skin.

oxalic acid - Hazardous. Harmful in contact with skin and if swallowed.

iron(III) nitrate - Hazardous. Irritating to the eyes, respiratory system and skin.

Risk Assessment and Control

Low risk.

The lamp used for irradiating solutions generates a lot of heat. **Be careful not to touch it.**

Boiling water baths and Bunsens are potential burn, scald and fire hazards.

Waste Disposal

All of the solutions used today can be washed down the sink with water.

Experimental

This experiment is to be carried out in pairs.

Part A Preparation of $[Fe(C_2O_4)_3]^{3-}$ stock solution and making photosensitive paper

The ferrioxalate is prepared *in situ*. The formation of the ferrioxalate is indicated by the appearance of a bright yellow colour. When you are not using the ferrioxalate solution, place it in your locker with the door closed. The ferrioxalate is **sensitive to light**.

(A1) Using a top loading balance (Skill 3.1), weigh out separately 0.5 g of oxalic acid and 0.5 g of $Fe(NO_3)_3 \cdot 9H_2O$. Mix these solids together in a 400 mL beaker and then dissolve in 12 mL of deionised water. **Protect the solution from light by keeping it in your locker when it is not being used**.

(A2) Write your initials with a lead pencil on the edge of a piece of filter paper and then, using tongs, dip the filter paper in the ferrioxalate solution that you made in step (A1). Prepare 2 such filter papers - one for each student.

(A3) Use paper towel to blot dry the filter paper and place it at the back of your drawer. Keeping it in the dark limits any unwanted photochemical reactions.

(A4) Using a measuring cylinder, pour 100 mL of deionised water into the solution you prepared in step (A1). This is your stock solution. Transfer it to a 250 mL conical flask and place it in your locker with the door closed.

Part B What causes the reaction?

Parts C - G investigate the effect of light on ferrioxalate. As the light source also produces heat, it is vital to establish whether it is indeed light rather than this heat that initiates any chemical change. To do this, the effect of heat and the effect of light are tested separately. It is also important to use a ‘control’ in which both these effects are removed to ensure that any reaction is not simply occurring over time due to the chemicals themselves.

If a reaction is light sensitive, it is important to minimise exposure to light when testing for the effect of heat. Make sure you read through *all* of the following instructions and set up the glassware required *before* you take the ferrioxalate solution made in Part A from your locker. Replace the stock solution in your locker again immediately after use. In steps (B1)-(B3), you investigate the effect of heat with minimum exposure to light. In steps (B4)-(B6), you investigate the effect of light *and* heat. In step (B7), you design a control to determine if any reaction produced by heat or light would have happened anyway.

(B1) Fill a clean test tube with 10 mL of the ferrioxalate solution made in step (A4).

(B2) Protect the solution from light by wrapping the test-tube with aluminium foil and then place it in a beaker of boiling water for 4 minutes. Whilst this is running, you can proceed to step (B4).

(B3) Add 1 mL of 0.1 M $K_3[Fe(CN)_6]$ solution to the test tube and place the test tube in a beaker in your locker.

(B4) Fill a second test tube with 10 mL of the ferrioxalate solution, and place it in a second beaker.

(B5) Using the set up shown in Figure 1 (overleaf), irradiate this test tube under light for 4 minutes. Whilst this is running, you can proceed to step (B7).

(B6) Add 1 mL of 0.1 M $K_3[Fe(CN)_6]$ solution to the test tube and place the test tube in a beaker in your locker.

(B7) Design and carry out a third experiment in which the effects of light and heat are minimised.

(B8) Record all your results in your logbook. Include all relevant observations and any conclusions about whether heat or light energy (or neither) is required for the reaction.

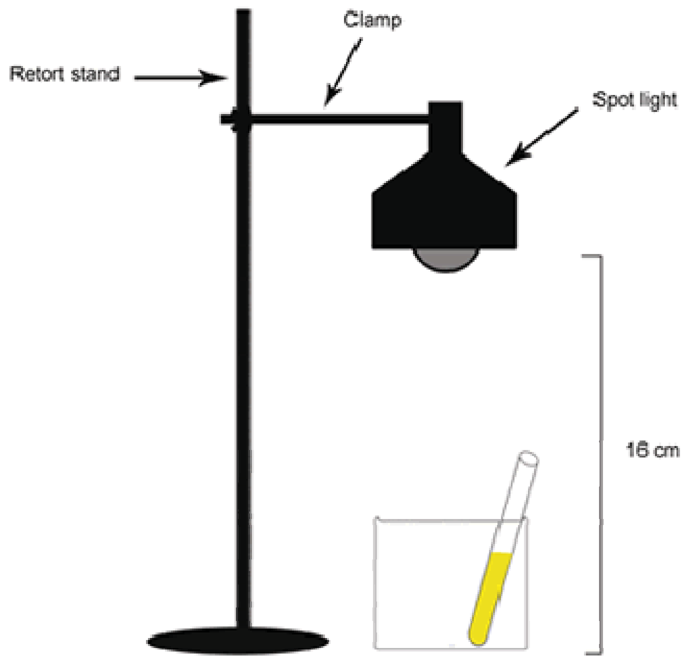


Figure 1: Experimental set-up for irradiating ferrioxalate complex with light.

Part C What time is required for complete reaction?

Read through all of the instructions and set up your glassware before you take your ferrioxalate solution from your locker. Replace the stock solution in your locker again immediately after use. For this part of the experiment you will need two beakers to hold your test tubes - one in your locker and one on your bench for the irradiation with light.

(C1) Label four clean macro test tubes with the numbers 0-3.

(C2) Fill each test tube with 10 mL of the ferrioxalate solution, and place them in the beaker that is in your locker.

(C3) Leave the test tube labelled “0” in the locker as a control.

(C4) Place the remaining test tubes in the other beaker.

(C5) Irradiate these test tubes under the light for 1, 2 and 3 minutes respectively, by removing test tube 1 after 1 minute, test tube 2 after 2 minutes, *etc*. (Irradiation for 4 minutes was investigated in (B5).)

(C6) After irradiation of each test tube, return it to the beaker in your locker.

(C7) Add 1 mL of 0.1 M $K_3[Fe(CN)_6]$ solution to each of the test tubes and record the results in your logbook.

For your logbook.

What is the minimum exposure time required to reach maximum colour?

Part D Does the light intensity affect the photochemical reaction?

(D1) Fill another two test tubes with 10 mL of the ferrioxalate solution.

(D2) Place the test tubes 20 cm and 40 cm away from the centre of the light source respectively and irradiate for 4 minutes.

(D3) Add 1 mL of 0.1 M $K_3[Fe(CN)_6]$ solution to each of the test tubes.

(D4) Record your results in your logbook.

For your logbook.

How does the light intensity affect the rate of the reaction?

Part E What is the effect of the period of irradiation?

(E1) Using a lead pencil, draw four parallel lines on a filter paper so that there are five sections. Prepare 2 such filter papers - one for each student.

(E2) Pour 5 mL of 0.1 $K_3[Fe(CN)_6]$ solution into a 400 mL beaker.

(E3) Pour 20 mL of the ferrioxalate solution into another 400 mL beaker.

(E4) Using your tongs, dip the filter paper into the ferrioxalate solution and blot dry using a paper towel. Return the solution to your locker.

(E5) Cover four of the sections on your filter paper with a tile from your locker and irradiate for 1 minute.

(E6) Move the tile so that the next section is revealed and irradiate for a further minute.

(E7) Continue until the fourth section has been irradiated for 1 minute. The fifth section is the control.

(E8) Using your tongs dip the filter paper into the beaker of 0.1 M $K_3[Fe(CN)_6]$ solution.

(E9) Wash the filter paper in a beaker of deionised water, let the filter paper dry and then attach it to your logbook.

(E10) Record your results in your logbook.

For your logbook.

Did the photochemical reaction of ferrioxalate occur on paper?

What is the minimum exposure time required to reach maximum colour?

Part F Does the wavelength of light affect the reaction?

White light is made up of different colours with different wavelengths. Blue light has the shortest wavelength and red light has the longest wavelength in the visible spectrum.

In this experiment, you will use a coloured checked photo slide divided into red, blue, green and clear sections. The red part acts as a filter and allows red light to pass through (wavelengths ≥ 650 nm). The blue part allows blue light to pass through (wavelengths of light ≤ 450 nm). The green section allows green light to pass through it (wavelengths in between red and blue).

(F1) Obtain a coloured slide from the front bench.

(F2) Using tongs, dip a piece of filter paper in the ferrioxalate solution and blot dry with paper towel. Prepare 2 such filter papers - one for each student.

(F3) Cover the filter paper with the coloured slide and irradiate for the time you determined in Part E to be the minimum exposure for maximum colour.

(F4) Using your tongs, dip the filter paper into the beaker of 0.1 M $K_3[Fe(CN)_6]$ solution.

(F5) Wash the filter paper in a beaker of deionised water, dry and attach it to your logbook. Record its appearance in your logbook.

For your logbook.

What colour light is the most effective?

Part G Making a contact print

You have been experimenting with the photochemical ferrioxalate, determining:

- whether the reaction requires heat or light,
- the irradiation time required for the photochemical reaction to go to completion,
- the irradiation intensity required for the photochemical reaction to go to completion and
- the wavelength of light required.

By now, your photosensitive paper made at the start of the practical session should be dry.

(G1) Lay flat opaque objects (*e.g.* keys, coins, spatula) on your dried photosensitive paper.

(G2) Irradiate the paper for the time required for complete reaction (as you determined from previous parts of the experiment).

(G3) Using tongs, dip the paper into a 400 mL beaker containing about 15 mL of the $K_3[Fe(CN)_6]$ solution. There is one beaker per group - see your demonstrator.

(G4) Remove the developed blueprint and dip in a beaker of deionised water to wash off excess reagent thoroughly. It should be blue and white.

(G5) Blot dry with a paper towel and leave to dry. Once it's dry, staple or paste your blueprint into your logbook.

Group Discussion

Which wavelength of light did you find most effective in causing the photochemical reaction? Can you explain why?

Light intensity has no effect on a photochemical reaction if the wavelength of the light isn't appropriate to the reaction. Can you explain why?

References

1. D. Baker, A Casadavell, H. D. Gafney and M. Gellender, J. Chem. Ed., 57, 314, (1980).
2. "*Laboratory Manual*" School of Physical, Environmental and Mathematical Sciences, University of New South Wales at Australian Defence Force Academy (ADFA), (2006)

Appendix 2.1

Many neutral or negatively charged species, like the oxalate ion, can bond with metal ions. Species that bond to metals in this way are called *ligands*. Water forms quite weak bonds to metal ions. When ligands such as oxalate or ammonia are added to a solution containing a water complex, they are able to replace some or all of the water ligands to form new complexes such as ones you make in this experiment. Figure 2 shows some examples of complex ions.

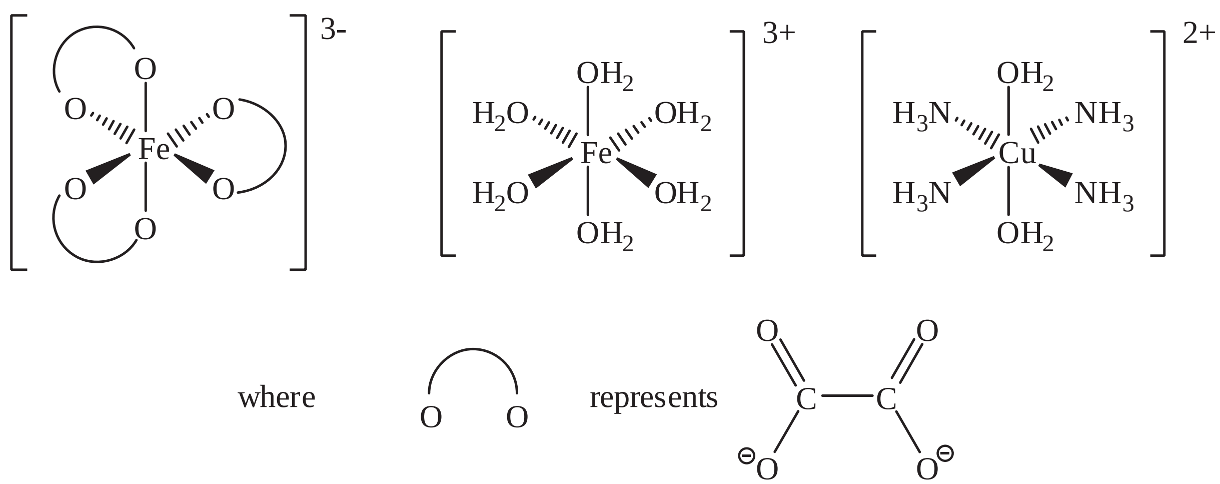


Figure 2: Some examples of oxalate, water and ammonia metal complexes

Each oxalate ion forms two bonds with the iron(III) ion. As it attaches with two 'teeth', the oxalate ion is called a bidentate ligand. Other ligands, such as water and ammonia are called monodentate as they can only form one bond with a metal ion.

Ferrioxalate, the complex ion used in this experiment, has the formula $[Fe(C_2O_4)_3]^{3-}$. Its systematic name is tris(oxalato)ferrate(III) ion and it is synthesised by adding oxalic acid to iron(III) nitrate, as shown in Figure 3.

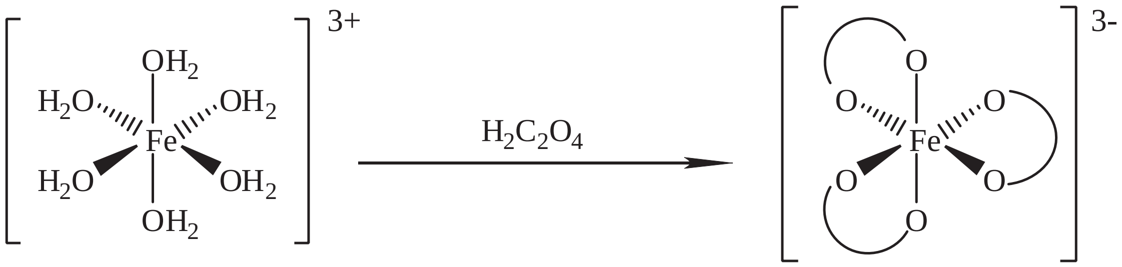
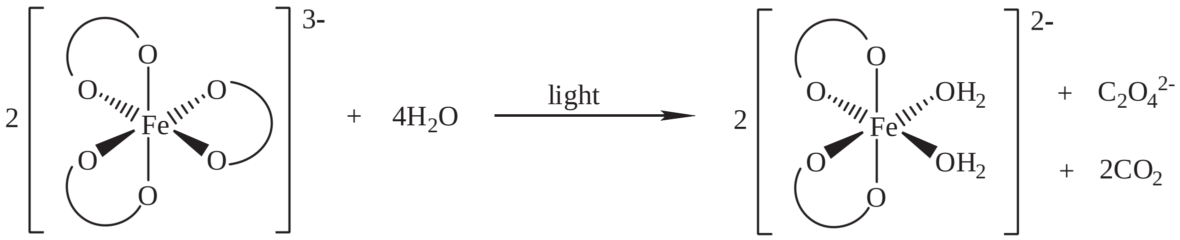


Figure 3: The synthesis of ferrioxalate

When the ferrioxalate complex absorbs light energy, it undergoes photoreduction, where the light causes an internal electron transfer. Iron(III) is reduced to iron(II) and one of the oxalate groups is oxidised to CO_2, as shown in Figure 4.



tris(oxalato)ferrate(III) ion
or ferrioxalate complex

diaquabis(oxalato)ferrate(II) ion

Figure 4: The photochemical reaction of ferrioxalate

Potassium hexacyanidoferrate(III), $K_3[Fe(CN)_6]$, reacts with Fe^{2+} ions to produce a deep blue colour called Prussian blue. This allows us to detect if the ferrioxalate complex has undergone photochemical reduction and also gives the blue colour in the blueprint.