INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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COMMISSION ON PHOTOCHEMISTRY*

A COLLECTION OF EXPERIMENTS FOR TEACHING PHOTOCHEMISTRY

(Technical Report)

Prepared for publication by

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A collection of experiments for teaching photochemistry (Technical Report)

Abstract - A selection of experiments in photochemistry, appropriate for first-year undergraduate level students is presented. An extensive bibliography to further reading is provided.

CONTENTS

INTRODUCTION

This collection of experiments in photochemistry is designed to assist teachers of the subject at first-degree (undergraduate) level or its equivalent. The material is selected from a more extensive set provided by practising teachers of photochemistry, in response to a request from the IUPAC Photochemistry Commission through Professor Katsumi Tokumaru. We are grateful to those colleagues who provided the manuscripts and to those who commented on the selection and on the details. We are also grateful to Ace Glass Inc. (Vineland, NJ), who gave support for the original experimental development at West Virginia University, and to the Open University (Milton Keynes, UK) for permission to use material from their course on photochemistry.

The collection represents a variety of source material for use in different situations. Some experiments require little other than standard laboratory equipment and materials; some need additionally a water-cooled source of ultraviolet radiation for preparative experiments; for a few there is a need for additional equipment.

There is a similar variation in the expected level of involvement by the teacher. Some of the experiments are written so that the student can work by himself, given proper laboratory preparation and general supervision; others require an input from the teacher to make them workable and effective.

In editing the material supplied, a balance has been attempted between retaining the style of individual authors and providing some harmony to the collection. Terminology, symbols and units have been harmonised to some extent, but sometimes the preference of an author for more convenient forms has been respected. The result is intended to be a workable document for photochemists, and other chemists, who want to incorporate simple experimental photochemistry into their laboratory teaching.

A bibliography is also provided, listing photochemical experiments described in J. Chem. Ed. and similar journals over several decades.

A GUIDE TO EXPERIMENTAL ORGANIC PHOTOCHEMISTRY

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Life on this planet would be impossible without photochemical reactions! This is most evident if we examine the food we eat. The growth of fruits and vegetables involves direct utilization of the sun's energy. It is the driving force behind the chemical reactions which produce edible commodities. Even the meat that we eat comes indirectly to us through plant life. However, food alone is not enough to sustain modern man. We are creatures accustomed to comforts: warm houses, automobiles, electricity, and so on. A flip of the switch or a turn of the key results in a warm house, or a car that starts off for work or vacation, or a light that goes on so that we can study. The list of modern creature comforts is a long one. Not much thought occurs about where the energy comes from to perform these simple tasks. If we stop and think, we realize that the coal and natural gas used to keep us warm during the winter, or the gasoline used to propel our cars, has its origin in the photochemical reactions responsible for life on this planet millions of years ago. Although these solar reactions refer to the process of photosynthesis, solar energy is employed in other important functions such as direct electricity production or heat production, and most of the information each of us receives from the external world is photochemically mediated through vision.

Even though photochemical reactions perform such an important function on planet Earth, we know relatively little about how to harness the energy of light. Early photochemical research relied upon the sun as a source of photons. It should be no surprise to learn that the early reports of photochemical reactions come from Egypt and Italy, since these countries have many cloudless days each year. If the sun were the only light source available to photochemists, the science of photochemistry could be practised in only a few locations. This could have grave implications, given the importance of finding new energy sources to replace or augment the finite amount of fossil fuel in the world. Another problem with solar irradiation is that the light intensity reaching earth from the sun varies widely as clouds pass overhead. This makes it very difficult to reproduce reaction conditions. Fortunately, photochemistry as a science has progressed rapidly in recent years due to the availability of higher quality, more stable light sources. Through the use of appropriate light filters or lasers, any wavelength of light can now be selected to provide precise control. High intensity lamps or lasers can also be used to supply a large number of photons to shorten the overall time required to perform a photochemical experiment. These developments have contributed to a modern science of photochemistry which has become very diverse, including applications such as synthetic chemistry, sophisticated laser analysis of the mechanistic details of reactions, and the application of photoresists for integrated circuit development.

Laboratory experiments

Photons of visible or ultraviolet light contain a vast amount of energy. The amount of energy may be found by using the equation:

$$E = h\nu = (12 \times 10^4)/\lambda$$

where E is the energy in kJ mol^{-1} and λ is the wavelength in nm. Light of 360 nm has the equivalent of 330 kJ mol^{-1} of energy, and 254 nm light has 470 kJ mol^{-1}. In order to break chemical bonds, it is necessary to provide an amount of energy greater than the bond dissociation energy. For C-C bonds, this energy is about 380 kJ mol^{-1}. Thus, the energy of ultraviolet light may cause the cleavage of bonds in an organic compound, which may result in the formation of radical intermediates or rearrangement of the carbon skeleton of the compound.

The most important rule in photochemistry is that the compound must absorb light! Although this seems obvious, experimentally the novice may have some problems. For example, ethylene absorbs only at wavelengths less than 200 nm. Since the *cis-trans* isomerization of olefins is discussed in photochemical textbooks and review articles, the unwary may be surprised when their attempted isomerization of *cis*-2-butene fails after hours of irradiation with a low-pressure mercury lamp. The reason for the failure of the reaction is obvious. The output of the mercury lamp is most intense at 254 nm. The *cis*-2-butene would be expected to absorb similarly to ethylene, only at wavelengths less than 200 nm. Thus, no light has been absorbed by the *cis*-2-butene, and no reaction can occur. It is a cardinal rule that before a photochemical experiment is attempted, a UV absorption spectrum should be obtained, perhaps from a standard source or collection of spectra. An even better procedure is to measure the UV spectrum of the solution to be irradiated both before and after the irradiation. This will ensure proper selection of the wavelength for irradiation as well as ensuring that photochemical reactions are not stopped due to the production of light-absorbing side-products.

The preparative organic photochemical reactions described in this collection can be carried out using equipment provided by any of the major suppliers. The descriptions refer to Ace Glass, Hanovia or Applied Photophysics lamps and glassware, but equivalent experiments can be designed around any medium-pressure mercury arc with appropriate water-cooling and sample holding system.

General operating suggestions

Hundreds of photochemical reactions have been studied, and it should come as no surprise that a great variety of reaction conditions have been developed in order to perform a specific photochemical task or chemical transformation. Thus, it is rarely possible to give a single set of conditions or procedure for performing a photochemical reaction. However, we have found the following guidelines to be generally applicable for obtaining good results in a photochemical reaction:

1.   Oxygen usually has negative effects upon photochemical reactions. Best results are normally obtained by purging solutions with nitrogen for fifteen minutes prior to, and also during, irradiation.

2.   The reaction solution should be stirred during irradiation to ensure an even progress of the reaction.

3.   The progress of reaction should be carefully monitored, particularly during exploratory experiments. The photoproducts may themselves absorb light and be reactive, resulting in the formation of secondary products. The secondary products may also be reactive and result in the formation of tertiary products. The appearance of these secondary and tertiary products may make the analysis of a reaction mechanism difficult, or may lead to much reduced chemical yields.

4.   Quartz glassware should be handled with care. Oils from the skin gradually reduce the transparency of the surface, reducing the number of photons available to the solution.

Safety considerations

Ultraviolet light sources give out radiation that is potentially damaging to exposed skin and especially eyes. There is also a lot of heat generated, and some ozone may be produced by the source. Thus, we emphasize the following minimal safety procedures for the protection of operators and of the equipment:

1.   A waterflow-sensing device should be used with the photochemical reactor to ensure proper cooling of the lamp. This device is most effective if it is placed on the water outlet side of the immersion well to ensure that a water-line breakage will be detected and the electrical power to the lamp disengaged. For a 450-watt lamp, we recommend that a flow rate of at least five litres per minute of water be maintained while the lamp is in operation and continued for two or three minutes after the lamp is turned off. Serious damage may result if these precautions are not followed, such as lamp and/or immersion well breakage, as well as fire.

2.   The output of the lamp includes intense ultraviolet light. Never look directly at the light source while it is in operation. In our laboratory, the reaction assembly has been enclosed in a reaction box. The door to this box operates a microswitch which allows the lamp to operate only when the door is closed. Any operator opening the door immediately disengages the power to the lamp, protecting against accidental blinding. Dark-coloured eye protection is also recommended.

ABSORPTION AND EMISSION OF LIGHT

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When light interacts with matter, it can be reflected, refracted, scattered, transmitted or absorbed. The absorption of light by matter is the first step in photochemistry; only absorbed light can induce photochemical change, but the absorption of light does not necessarily result in any photochemical event. Only if the absorption of light initiates some chemical event are we observing photochemistry.

What is absorption of light?

Light can be described in terms of particles called photons. The energy E_p of a photon is determined by the frequency of the oscillation of the electromagnetic field of which it is made:

$$E_p = h\nu = hc/\lambda$$

where h is Planck's constant. The energy of the photon can also be expressed in terms of its wavelength λ,

since $v\lambda = c$, where c is the velocity of light. When we see a change in colour of light it is because different amounts of the various wavelengths of photons are involved. When matter absorbs light, it is actually absorbing energy; so in the instant a molecule absorbs a photon of energy E_p, it increases its own energy by the same amount E_p. Having suddenly all this extra energy makes the molecule M electronically excited:

$$M \quad + \quad photon \quad \rightarrow \quad M^*$$

The star on M^* indicates that the molecule is excited. We say that the molecule is in an excited state M^*. The molecule with all this extra energy can do one of three things:

- relax back to the original state it was in and lose the energy it absorbed by releasing heat
- relax and lose energy by releasing light
- use the energy to undergo a chemical reaction

How is light absorbed?

There are two basic conditions for a molecule to absorb a photon: first the photon must meet the molecule, and secondly the molecule must then absorb it.

The more molecules there are on the path of the photon, the more likely it is (the higher the probability) that an encounter between the photon and a molecule will occur. Therefore the probability of a photon-molecule encounter depends on how many molecules there are in the path, i.e. the concentration (c) of molecules, and the length of the path, known simply as pathlength (l).

Even when a photon meets a molecule, the molecule is not necessarily capable of absorbing the photon. To absorb the photon, a number of conditions must be met which are of a quantum chemical nature. For example, the energies which a molecule may have are well defined as quantum chemistry predicts. The energies come in steps as illustrated in Figure 1. If the energy of the photon is not equal to one of these steps, the molecule cannot absorb the photon. In other words, for the ground state (S_O) of a molecule to absorb a photon, a necessary condition is:

(Energy of photon) = (Energy of an excited state) - (Energy of ground state)
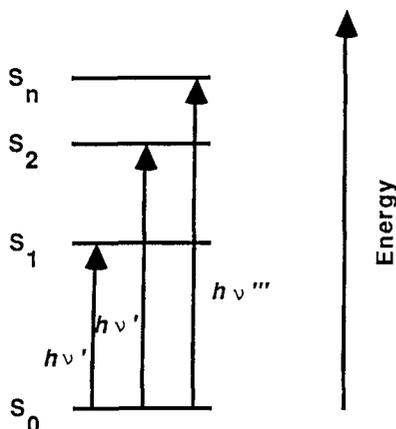
or $\quad E_p = hv = E(S_n) - E(S_o)$

Figure 1. The energies that a molecule may have are well described by the theory of quantum chemistry. S_0 is the ground state, the lowest possible energy the molecule may have. S_1 to S_n are known as excited states which the molecule can reach only with the supply of energy such as photons, e.g., hv', hv'' or hv'''.

Although this energy condition is necessary for the absorption of light, it is not always sufficient. There also exists a number of other quantum chemistry rules that must be satisfied, for example related to the changes in the symmetry or to the conservation of electron spin of the molecule that the absorption of light might induce.

Thus, the probability that an individual molecule will be able to absorb a photon, upon encounter, depends mainly on its internal properties. This probability is commonly symbolized by ε. The higher the value of ε the more likely it is that a photon will be absorbed when it meets a molecule. For example, if E_p is not equal to $E(S_O)-E(S_n)$, then $\varepsilon = 0$. Therefore ε is clearly a function of the energy of photons, or the wavelength of the light λ.

In summary, the absorption of light of wavelength passing through a solution depends on: the concentration of molecules c, the probability ε of absorption by the molecule at wavelength , and the pathlength l of the light through the solution. Let us now see how this is expressed theoretically.

The law of absorbance: Beer–Lambert law

If light of wavelength and intensity I_0 is made to pass through a solution of molecules, then the intensity of the light coming out (the light transmitted, I_t) is given by:

$$I_t = I_0 \ 10^{-\varepsilon \ c \ l}$$

where c, the concentration of molecules, is expressed in moles dm^{-3}, l is in cm, and ε , known as the molar decadic absorption coefficient, must then be in units of $dm^3 \ mole^{-1} \ cm^{-1}$. The absorbance A of the solution is defined as:

$$A = \varepsilon \ c \ l = \log (I_0/I_t)$$

This is known as the Beer-Lambert Law.

The light flux I_a absorbed by the solution is then:

$$I_a = I_0 - I_t = I_0 \ (1 - 10^{-A})$$

It is important not to confuse absorbance and the amount of absorbed light. The relationship between the fraction of light absorbed (I_a/I_0) and the absorbance A is not linear, as Figure 2 clearly shows.
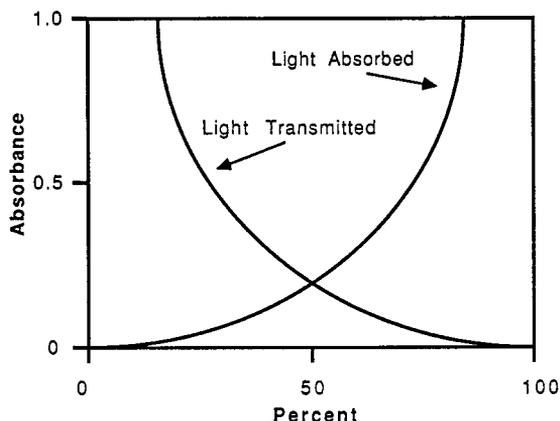

Figure 2. Relationship between the absorbance and the percentages of light intensity absorbed (I_a/I_0)and transmitted (I_t/I_0).
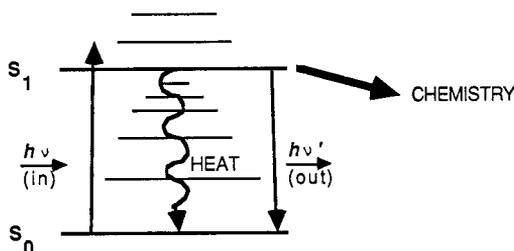

Figure 3. Events that may occur after a molecule is excited: emission of light (hv'), release of heat (wavy line) and chemistry (heavy arrow).

What happens when a photon is absorbed by a molecule?

After absorption of a photon, a molecule is in an excited state, for example S_1, as shown in Figure 3:

$$M(S_0) \quad + \quad hv \ \rightarrow \ M^*(S_1)$$

Typically, an excited molecule stays in the state S_1 for between 1 and 100 nanoseconds (1 nanosecond = 10^{-9} s). Then it may return to the ground state S_0 by emitting light (fluorescence):

$$M^*(S_1) \ \rightarrow \ M(S_0) \quad + \quad hv'$$
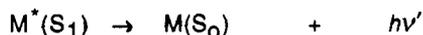
The energy hv' of the photons emitted is always smaller than, or equal to, the energy hv of the photons absorbed, because both the absorption and the emission processes involve vibrational and rotational energy levels as depicted in Figure 3. These small energy steps in each state arise because molecules can increase in energy by vibrating and rotating. The molecule may go, for example, from one vibrational level to another by releasing or absorbing heat. So although $hv' < hv$, the law of energy conservation is respected; for example, fluorescence may also be accompanied by some heat release.

These small vibrational energy steps may also enable the excited molecule to return to the ground state by just releasing heat.

Like a ladder, these steps avoid the big energy jump involved in light emission:

$$M^*(S_1) \rightarrow M(S_0) + heat$$
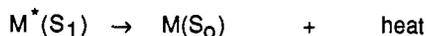
Finally, from the excited state the molecule may undergo a chemical reaction. The excited molecule, having a lot of extra energy, may undergo reactions which don't occur in the ground state due to endothermicity. For example, in photosynthesis, the energy basis of life on Earth, the absorption of photons turns a reaction which is endothermic in the ground state into an exothermic reaction from the excited state. Thereby, some of the energy in the photon can be stored through the synthesis of energy-rich compounds.

## Absorbance spectra and demonstration of light emission

Since ε depends on the wavelength of the light, it is useful to analyze the absorbance A of a molecule as a function of the wavelength λ, at fixed concentration c and pathlength 1. A plot of A versus λ is known as an absorbance spectrum and represents the variation in ε . The coefficient ε reflects mainly the internal properties of the molecule, and each molecule has a distinct absorbance spectrum, like a fingerprint. The absorbance spectrum can therefore be useful in identifying a molecule.

In this experiment, we will analyze the absorbance spectrum of a very colorful group of molecules known as porphyrins. Porphyrins are very similar to the chlorophyll molecule which makes plants green. Sunlight absorbed by the chlorophylls is the source of energy for life on Earth.

The two porphyrins to be studied are the following:
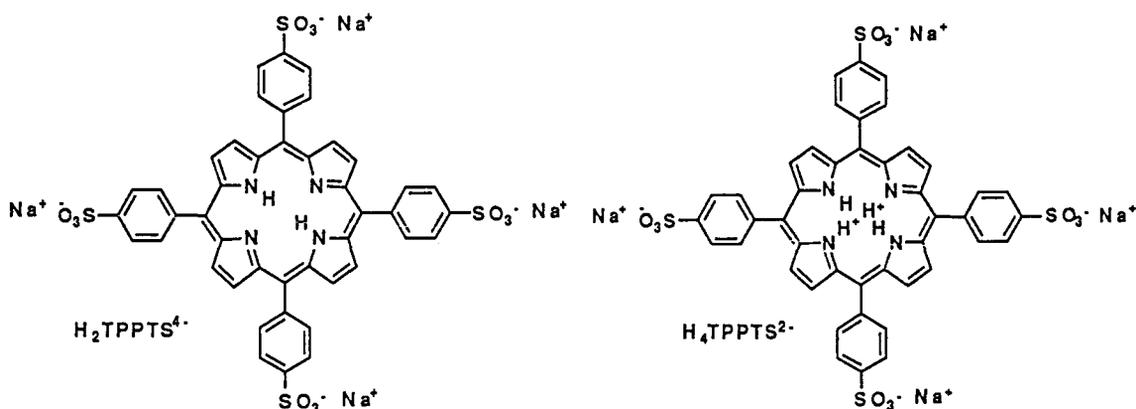
These water-soluble porphyrins may be interconverted by changing the pH of the solution:

$$H_2TPPTS^{4-} + 2H^+ \rightleftharpoons H_4TPPTS^{2-}$$
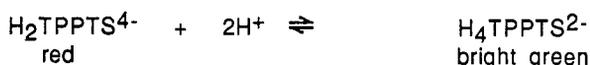
red   bright green

Therefore by adding acid to a slightly basic solution (pH 8) of H_2TPPTS^{4-} the solution will go from red to bright green. The absorbance spectra of these two species are shown in Figure 4.
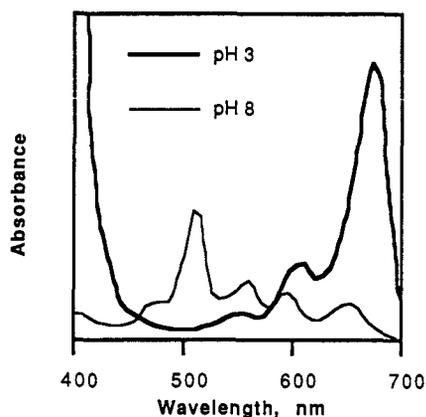
Figure 4. Absorbance spectra of H_2TPPTS^{4-} at pH 8 (light line) and H_4TPPTS^{2-} at pH 3 (heavy line).

The following are some suggestions for both a classroom demonstration and a laboratory experiment.

Materials required

50 cm^3 beaker	hydrochloric acid (0.1 mol dm^{-3})
100 cm^3 beaker	hydrochloric acid (0.05 mol dm^{-3})
50 cm^3 burette	aqueous sodium hydroxide (0.1 mol dm^{-3})
50 cm^3 measuring cylinder	tetraphenylporphyrintetrasulphonate, tetrasodium salt
pH-meter	phosphate buffer
ultraviolet visualisation source (366 nm)	
ultraviolet-visible spectrometer with cuvettes	

Preliminary experiment (or demonstration)

Prepare ca. 3 x 10^{-5} mol dm^{-3} solution of H$_2$TPPTS^{4-} at pH 8, enough to half-fill a 100 cm^3 beaker. Using a burette filled with ca. 0.1 mol dm^{-3} HC1, slowly add this acid to the beaker until the solution turns bright green. This can be reversed by adding some base (ca. 0.1 mol dm^{-3} aqueous sodium hydroxide), which proves that the two species are in equilibrium.

The visible part of absorbance spectra (which relates to the colors) of the initial and final species can be shown (Figure 4). The species that looks green absorbs the red light, and vice versa. Furthermore the small individual peaks indicate the presence of vibrational levels in the excited state. For example, in the case of H$_4$TPPTS^{2-}, the peak at about 650 nm indicates that a photon of 650 nm has enough energy for the molecule to go from S$_0$ to the lowest vibrational level in S$_1$. The small peak at about 590 nm indicates that a photon of 590 nm has enough energy for the molecule to go from S$_0$ to the second vibrational level in S$_1$. The strong absorbance appearing below 450 nm is due to the excitation of the molecule to S$_2$.

The emission (fluorescence) of the initial and final species can be shown by irradiating the samples with a 366 nm ultraviolet light source, such as the hand-held devices used to monitor paper chromatography.

The emission (fluorescence) of the initial and final species can be shown by irradiating the samples with a 366 nm ultraviolet light source, such as the hand-held devices used to monitor paper chromatography. Both porphyrins emit red fluorescence. The emission is not so strong, so that this experiment or demonstration should be done in the dark. The fact that the emission is of one color and not white indicates that molecular energies come in discrete levels. Thus both absorption and emission of light are very good and simple illustrations of the validity of quantum chemistry.

Further experiments

(i)   Absorption Spectrum of H$_2$TPPTS^{4-}:

Record the initial spectrum of H$_2$TPPTS^{4-} between 480 nm and 700 nm. A convenient concentration is 2 x 10^{-5} mol dm^{-3}; the solution should be at pH 8 and should also be slightly buffered (phosphate buffer ca. 10^{-2} mol dm^{-3}). The buffer avoids drastic changes in pH in the neutral region when HC1 is added in the next stage.

(ii)   Determination of K_a:

Place about 25 cm^3 of the solution in a 50 cm^3 beaker. Partly fill a burette with 0.05 mol dm^{-3} HC1. Measure the pH of the solution and the absorbance at 650 nm. Add the acid drop by drop until the pH reaches about 7. Record the pH and the absorbance value at 650 nm. Repeat this at approximately the following pH values: 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5 and 3.0. Remember to allow for the dilution of the solution due to the added HC1. It is not recommended to bring the solution to a pH much lower than 3, because degradation is observed in a very acid environment.

Show how to calculate K_a or pK_a from the data. NB a common mistake is to forget the fact that there are two protons involved in the equilibrium.

(iii)   Absorption Spectrum of H$_4$TPPTS^{2-}:

Measure the absorption spectrum of the final green solution between 480 nm and 700 nm.

Remarks: The equilibrium between the two porphyrins involves two protons, so there are in fact two pK_a values, but they are so close that it is very difficult to determine them separately. By measuring the absorbance at 650 nm, only one K_a is observed.

RADIATIVE AND NON-RADIATIVE PROCESSES

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The purpose of this experiment is to help you: understand the relationship between energy, frequency and wavelength of electromagnetic radiation; understand the meaning of luminescence; know some of the more important luminescent materials and their structures; be able to describe the effects of non-radiative decay of excited molecules; know some of the applications of luminescence.

Introduction

Light, and other forms of electromagnetic radiation, possess energy which can be absorbed by atoms and molecules in spectroscopic transitions. The energy (E) of a photon is related to the frequency (v) or wavelength (λ) of the light by:

$$E = hv = hc/\lambda$$

where h is the Planck constant (6.626×10^{-34} J s) and c is the speed of light (2.998×10^8 m s^{-1} in vacuo). According to quantum theory, molecules exist in discrete energy states and are normally in the state of lowest energy (the ground state). Following absorption of electromagnetic radiation they are promoted to excited states. The energy of the radiation must equal the energy difference between the two states

$$(E_e - E_g) = hv$$

Photochemistry is mainly concerned with the behaviour of excited electronic states, which can be produced by absorption of visible or ultraviolet light. The energy of electromagnetic radiation in this region is similar to that of many chemical bonds. Light absorption in the visible region leads to the characteristic colours of many species, such as blue $CuSO_4.5H_2O$ or orange $K_2Cr_2O_7$.

Excited states must lose their excess energy. This they can do either by re-emitting it as light (luminescence) or by losing it as heat to the system (non-radiative processes). Light absorption and emission are both termed radiative processes.

A	+ hv	→	A*	light absorption
ground state			excited state	

A*	→	A + hv	luminescence

A*	→	A + heat	non-radiative process
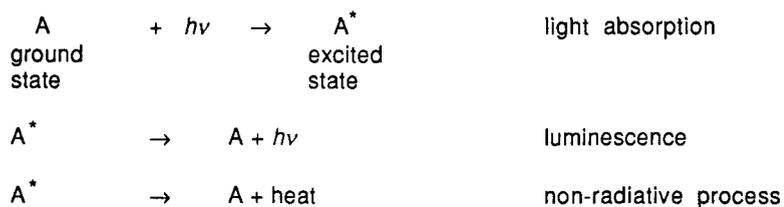
The light emitted by excited molecules when they relax back to the ground state is given the general name *luminescence*. It is convenient to distinguish between two types of luminescence. *Fluorescence* is short-lived luminescence (typically on a time scale of ns) observed when molecules relax in an allowed radiative transition, (usually singlet→singlet), whereas *phosphorescence* is a long-lived luminescence, which may persist for several seconds, and arises from a forbidden process (usually triplet→singlet). The slow decay of the image when you switch off a television is mainly due to the phosphorescence of materials in the screen.

Both fluorescence and phosphorescence normally occur at longer wavelengths than light absorption. The differences in the wavelengths of maximum absorption and luminescence are associated with the fact that absorption is from the lowest vibrational level of the ground state to various vibrational levels of the excited state, whereas fluorescence is from the lowest vibrational level of the excited state to the various vibrational levels of the ground state. The fact that fluorescence occurs at longer wavelengths than absorption can be used to convert ultraviolet to visible light. This has important applications in optical brighteners, which are present in many detergents, plastics, and paper, and also in fluorescent markers in such items as postage stamps and security documents.

Other important applications of fluorescence include luminescent paints and dyes, for example, as "reflective" components of policemen's jackets, or on dials on wristwatches, in analytical chemistry for detection of trace amounts of compounds, and in fluorescent probes of biological structure.

Materials required

Red, yellow and blue colour filters
Ultraviolet lamp, such as those used in thin-layer chromatography (Warning! Follow the manufacturer's instructions as ultraviolet light can be hazardous)
Tungsten filament lamp
Thermometer reading to 0.1° C (preferably a digital thermometer)
Unglazed earthenware trays for solid samples
Test tubes
Beakers
Anthracene
Pyrene
Uranyl nitrate hexahydrate
Potassium hydroxide
Postage stamps
Various detergents, including some containing optical brighteners
Standard optical brightener
Potassium dichromate solution
Copper sulphate solution
Fluorescein solution
Rhodamine B or 6G solution
Quinine sulphate in dilute sulphuric acid
2-Naphthol in 30% methanol/water (5mg in 50 cm^3)
POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene), or other scintillator, in ethanol
1-Anilinonaphthalene-8-sulphonate (ANS), ammonium salt, solution
Cetyltrimethylammonium bromide (0.05 mol dm^{-3})
Methylene blue, in alkaline solution
Phenolphthalein in alkaline solution

Warning! Many of the compounds are potential health hazards both by skin contact and by ingestion, and great care should be exercised in their use. 2-Naphthol can be particularly hazardous.

Experimental procedure

1.   The visible spectrum

        Examine the visible spectrum (Appendix 1), and look at the magnitude of the wavelength, frequency and energy of radiation in this region. Compare these values with the dissociation energies of chemical bonds.

        Hold the tubes of (i) potassium dichromate solution and (ii) copper sulphate solution in front of the tungsten lamp.

        In what region of the visible spectrum do these solutions absorb? What wavelength and energy do these correspond to?

2.   Luminesence

        (i)   Switch on the ultraviolet lamp and hold the tray containing luminescent samples in the path of the emitted light. Note that the luminescence is at longer wavelength than the absorption. Remove the tray.

        (ii)   Hold tubes of water and of solutions of fluorescein, rhodamine, quinine sulphate, POPOP and 2-naphthol under the lamp.

        Note those cases in which you observe emission. Also note how the emission intensity varies with position in the tube.
        Explain this in terms of the Beer-Lambert law.

        Add a pellet of KOH (caution: corrosive) to the 2-naphthol solution and note what you see. Given that 2-naphthol is an acid, explain your observations.
        Remove the tubes.

        (iii) Introduce the tray containing detergents under the lamp. Which of these contain optical brighteners?
        Compare the emission with that of the standard optical brightener.
        Remove the tray.

(iv) Examine the postage stamps under the lamp. Which of these contain fluorescent markers?

(v) Look at the solution of ANS under the lamp. Can you detect any emission?
Add two drops of detergent solution and note what you see. Suggest possible applications of this effect.

3. Non-radiative Processes

(i) Irradiate the beakers containing water and methylene blue solution for 10 minutes. Using the thermometer, determine the change in temperature during this period. In what ways might this arise?

(ii) Examine the solutions of phenolphthalein and fluroescein under the ultraviolet lamp. Look up the structures of these molecules and suggest why excited fluorescein decays radiatively but phenolphthalein does not.

Appendix 1: The Visible Spectrum

The energy of light in the visible and ultraviolet regions is similar to that of many chemical bonds.

ULTRAVIOLET	violet	blue	green	yellow	orange	red	INFRARED
wavelength (nm)	420	470	530	580	620	700	
frequency (THz)	714	638	566	517	484	428	
energy (kJ mol^{-1})	285	254	226	206	193	171	
typical bond dissociation energies (kJ mol^{-1})		Cl-Cl 243	Br-Br 194	I-I 53			

HOW PHOTOEXCITED STATES ARE CREATED AND DECAY – SIMPLE EXPERIMENTS WITH A CAMERA FLASH

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Introduction

When we look around carefully, we will soon see that a tremendous number of things are influenced by light. After realizing the importance of light, we may ask what changes occur when substances are irradiated and how can we follow them as a function of time. What is in the scientist's mind is not only the permanent chemical changes which might be observed readily, for instance by a change in color, but also the intermediate states generated by light absorption. Many sophisticated apparatuses are now available which allow experienced researchers to follow intervening photophysical and photochemical events. For less experienced students, however, if these events can only be seen through instrumental readings, rather than with the naked eye, they appear less impressive and persuasive than direct visual observations. In fact fluorescence itself is very important and attractive because of its variety of clean colors, but when we talk of "the lifetime" of the created (emitting) singlet species, it suddenly becomes inaccessible.

From the educational point of view, therefore, the triplet state provides better examples in order to understand how transient species are generated upon photoexcitation and decay through various processes including chemical reaction. Since the time range of concern is often longer than one millisecond (triplet-state lifetimes in solid matrixes), a camera flash will provide an ideal pulse excitation source. However, we cannot expect that an apparatus which can measure the decay time (e.g. conventional flash photolysis equipment) is readily available for anyone. Therefore, it is the purpose of this experiment to present simple experiments to measure decay times of transient species, especially triplet states.

Materials required

phenanthrene in PMMA[*]
camera flash
three neutral glass filters (10%)
stopwatch

[*] A mixture (5-10 cm^3) of methyl methacrylate, phenanthrene (10^{-5} to 10^{-4} mol dm^{-3}) and 0.1 wt % 2,2'-azobis-(2-methylpropiononitrile) is placed in a Pyrex tube (i.d. = 15 mm), whose open end is covered with aluminium foil. The tube is held in a 70° C hot-water bath for 2 days, until the sample has solidified, and then the temperature is raised to 90° C to complete the polymerization. Alternative solutes are naphthalene or perdeuterated naphthalene, which have even longer lifetimes under these conditions.

Experimental procedure

For the simplest experiment described here, we need no sophisticated equipment except for a commercially available camera flash, three pieces of neutral glass filter whose transmittance is known, say 10%, and a stopwatch. Two of the glass filters (or homogeneously developed photographic films) are superposed on a half of the third one, as illustrated in Figure 5. In this way we made a simple set of eye glasses, each of which has a different but known transmittance, F_1 and F_2. When the emission intensity observed through F_2 disappears, the stopwatch is started, and it is stopped when the intensity through F_1 goes below the detection limit of the observer's eyes. Thus the time interval during which the initial emission intensity from the sample reaches a certain value, 1/100 in the present case, is measured. Such measurements are repeated many times until the observer is well accustomed to the procedure. In order to reduce observer influence of the result, the measured intervals should also be recorded by another person.
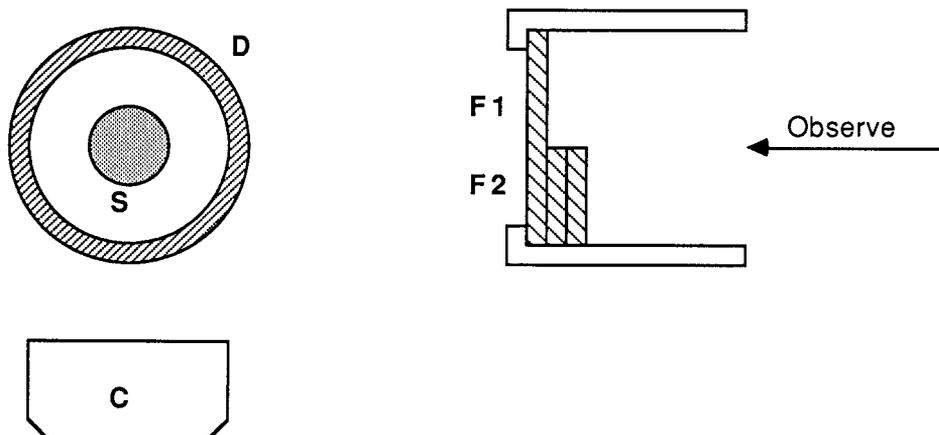

Figure 5. Experimental setup to measure phosphorescence lifetimes with neutral filter sets:
C = camera flash; S = sample; D = Dewar vessel; F1 and F2 = filter sets.

Since in solid matrixes such as poly(methyl methacrylate) (PMMA) or organic glasses at low temperatures, phosphorescence often lasts longer than a second, its lifetime can be measured in the manner described above. In the present experiments phenanthrene imprisoned in PMMA is used. If liquid nitrogen is available you can use quite a lot of solutions which form transparent glasses at 77 K so as to study triplet state behavior more extensively.

Results and Discussion

The experimental set-up for phosphorescence lifetime measurements is illustrated in Figure 5. When an emission follows an exponential decay, the important quantity characterizing the equation is the lifetime τ :

$$I(t) = I_0 \; \exp(-t/\tau) \qquad\qquad (1)$$

The lifetime τ is defined as the duration that elapses until the emission intensity is reduced to 1/e of its initial value.

The question asked here is how we are able to obtain a value with physical significance. This is not difficult if we can record a decay curve, but for this we need a certain amount of instrumentation which we are trying to avoid. However, eq.(1) contains only two parameters, so that if we know the emission intensities, or more simply their ratio at two different times, we can calculate τ from the following equation:

$$I(t_1)/I(t_2) = \exp(-t_1/\tau)/\exp(-t_2/\tau) \qquad (2)$$

$$\text{or } \ln (I(t_1)/I(t_2)) = -(t_1 - t_2)/\tau \qquad (3)$$

The quantity on the left-hand side of eq.(2) can easily be obtained by visual observation of the emission intensities viewed through an appropriate set of filters such as those given in Fig.1. In our case the ratio should be 1/100, and the interval $t_1 - t_2$ is the difference between the times at which the emission intensities through F_1 and F_2 disappear from view. In Table 1 are exemplified some such measurements, from which the phosphorescence lifetime is calculated using eq.(3). The calculated lifetimes are comparable with those obtained with more sophisticated apparatus.

These experiments were carried out in a dark room until the naked eyes became well adapted. It may be a little difficult to say when the emission intensity reaches your eyes' detection limit. In spite of this, the scatter in the values obtained is not great. Compared with the correct value of τ, you will see the values obtained are excellent when you consider the primitive nature of the experiment. Without filter sets like those used here, you cannot tell how long the emission decay time is. This is because the duration of emission depends on the light intensity of an excitation source. Because of this you may feel that the emission appears to endure for much longer than its true lifetime.

Table 1. Time interval (seconds) during which the initial emission intensity of phenanthrene decreases to 1/100 of the original value.

Room Temp.(23 °C) t/s	77 K t/s	EPA (77 K) t/s
11.23	17.68	15.37
12.06	17.69	16.91
11.15	19.70	16.04
9.85	17.83	16.53
12.30	16.84	17.03
10.26	18.70	17.37
11.97	17.99	16.50
11.79	19.28	17.40
13.20	17.80	
11.54	18.00	
11.71	18.29	
means:		
11.5	18.2	16.6
τ /s		
2.5	3.9	3.6

Interesting systems to study at 77K are:

1. anthraquinone in ethanol (ca.10^{-5} to 10^{-4} mol dm^{-3}) - strongly phosphorescent, but the lifetime is too short to measure by this method;

2. indole in ethanol - blue phosphorescence, with a long lifetime (2.4 s);

3. naphthalene in ethanol ($\tau = 2.3$ s).

CHEMILUMINESCENCE

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Introduction

Chemiluminescence is the emission of light during the course of a chemical reaction. Recently, intense emission from the oxidation of oxalyl[1] and oxalate[2] compounds with H_2O_2 in the presence of appropriate fluorescers, and from air oxidation of tetrakis(dimethylamino)ethylene[3], has been reported to be useful for demonstration. In the first part of this experiment is described chemiluminescent emission from the air-oxidation of 9-methylacridine, which can be prepared by a relatively simple technique. (NB The preparative stage may be carried out by the demonstrator).

It is usually difficult to detect the excited triplet species at room temperature by photophysical methods. In the second part of this experiment is described a simple method to detect the species by indirect chemiluminescence, owing to the fact that a molecule with heavy atoms such as 9,10-dibromoanthracene (DBA) is capable of accepting the energy of chemiexcited triplet products by triplet-singlet energy transfer, and the energy is released in the form of fluorescence.

Materials required

test tube
  25 cm^3 conical flasks
100 cm^3 conical flask
250 cm^3 round-bottomed flask, fitted with
    reflux condenser
100 cm^3 measuring cylinder
  10 cm^3 measuring cylinder
graduated pipette (1 or 2 cm^3)
Buchner filter funnel and flask
conical filter funnel

heating bath with thermometer (to 250° C)
diphenylamine
acetic acid
zinc chloride
toluene
N,N-dimethylformamide
potassium t-butoxide in t-butanol (0.02 mol dm^{-3})
benzoin methyl ether
9,10-diphenylanthracene
9,10-dibromoanthracene

Experimental procedure

1.   Direct chemiluminescence:

A mixture of diphenylamine (5.0 g), acetic acid (5.0 g), and zinc chloride (2.0 g) is heated under reflux at 210-220° C (bath temperature) for 10 hours. While warm, 100 cm^3 of water is added to the reaction product. The mixture is stirred and filtered by suction, and then washed with water to remove the water-soluble materials. The crude product is dissolved in about 50 cm^3 of toluene and filtered to remove the insoluble materials. Evaporation of the toluene gives 9-methylacridine as pale yellow needles, which can be dissolved in N,N-dimethylformamide (DMF) (ca. 1×10^{-4} mol dm^{-3}). For the purpose of this experiment, the DMF solution may be prepared by diluting the toluene solution with DMF.

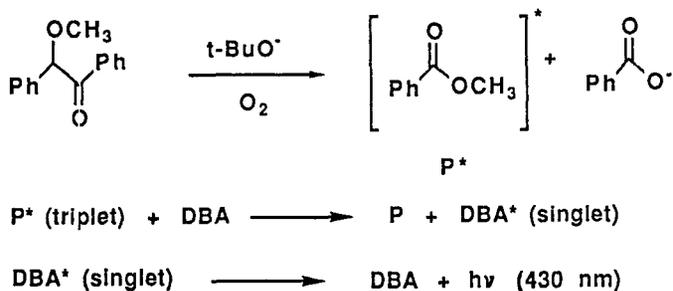Chemiluminescence arises when 0.3 cm^3 of t-BuOK solution in t-BuOH (2×10^{-2} mol dm^{-3}) is added to 2 cm^3 of aerated DMF solution of 9-methylacridine at 40° C.
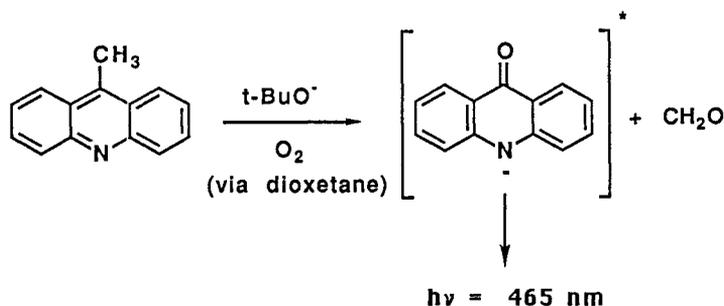
$$h\nu = 465 \text{ nm}$$

The apparent first-order rate constant at 40° C is 1.0 min^{-1}, the activation energy is 65 kJ mol^{-1}, the chemiluminescence quantum yield is 6.3×10^{-3}, and the peak of the emission is at 465 nm (fluorescence from the acridone anion).

2. Indirect chemiluminescence:

Four solutions are prepared: benzoin methyl ether in DMF (1×10^{-3} mol dm^{-3}), 9,10-diphenylanthracene (DPA) in DMF (3×10^{-3} mol dm^{-3}), DBA in DMF (3×10^{-3} mol dm^{-3}), and t-BuOK in t-BuOH (2×10^{-2} mol dm^{-3}). When 1 cm^3 of the *t*-BuOK solution is added to each of the following three mixed solutions: (A) 5 cm^3 of the benzoin solution and 5 cm^3 of DMF, (B) 5 cm^3 of the benzoin solution and 5 cm^3 of the DPA solution, and (C) 5 cm^3 of the benzoin solution and 5 cm^3 of the DBA solution at 40° C in a dark room, no appreciable emission is observed from A and B, but an intense emission is observed from C.

$$P^* \text{ (triplet)} + DBA \longrightarrow P + DBA^* \text{ (singlet)}$$

$$DBA^* \text{ (singlet)} \longrightarrow DBA + h\nu \text{ (430 nm)}$$

References

1. F.F. Bramwell, S. Goodman, E.A. Chandross and M. Kapran, *J. Chem. Educ.*, 1976, 56, 111.

2. A.G. Mohan and N.J. Turro, *J. Chem. Educ.*, 1975, 51, 528;
   B.Z. Shakhashiri, L.G. William, G.E.E. Dirreen and F. Francis, *ibid*, 1981, 58, 70.

3. S.K. Gill and L.K. Brice, *J. Chem. Educ.*, 1984, 61, 713.

PHOTOCHEMICAL IMAGE FORMATION BY A SILVER HALIDE PROCESS

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Introduction

This imaging experiment with the silver halide process[1], including development and toning, is useful for understanding the following photochemical concepts:

(i) Photochemical reaction proceeds only with absorbed light.

(i i) The final imaging yield is amplified nearly 10^9 times, though the primary quantum yield of AgX photolysis is less than unity.

(iii) Development and toning processes involve redox reactions.

Materials required

Photographic black and white printing paper (any commercial type)
Glass plate or transparent plastic plate (about 10 cm x 10 cm)
60 W tungsten lamp
Red filter (Kodak Wratten No. 25, or any dark red transparent sheet)
Tweezers
Glassware and plain vessels

Chemicals and solutions:

    A.   Developer

Water (about 50° C)	750 cm^3
Hydroquinone	4.8 g
Sodium sulfite (Na_2SO_3)	12 g
Sodium carbonate (Na_2CO_3)	30 g
Potassium bromide (KBr)	0.8 g
Water to be added	1000 cm^3

The chemicals should be added in the above order, allowing each chemical to dissolve completely before adding the next.

    B.   Stopper

Water	1000 cm^3
Acetic acid (28%)	48 cm^3

    C.   Fixer

Water	600 cm^3
Sodium thiosulfate ($Na_2S_2O_3$)	120 g
Sodium sulfite	7.5 g
Acetic acid	28 cm^3
Boric acid (H_3BO_3)	3.8 g
Water to be added	1000 cm^3

    D.   Toning solution

D-1	Water	425 cm^3
	conc. HC1	75 cm^3
D-2	Water	100 cm^3
	Potassium permanganate($KMnO_4$)	0.5 g
D-3	Water	700 cm^3
	Sodium sulfide (Na_2S)	9 g

Experimental procedure

1.   <u>Image Formation By Light</u>

Note that procedures 2 to 5 of this experiment should be done in a dark room.

    1.   Pattern making: Make patterns out of paper, and paste the patterns on a glass plate (Figure 6a).

    2.   Preparing for exposure: Put the glass plate on a sheet of photographic printing paper (Figure 6b). Be sure to have the emulsion layer facing up.

    3.   Exposure: Expose the prepared plate to the 60 W lamp from a height of about 50 cm for 10-15 seconds. Remove the exposed photographic paper (Figure 6c).

    4.   Development: Pour the developer (solution A) into a plain vessel. Dip the exposed paper and develop for 3-4 minutes. During the development, vibrate the vessel occasionally to ensure mixing (Figure 6d).

    5.   Stopping: Pour the stopper (solution B) into a plain vessel. Dip the developed paper for 15 seconds.

    6.   Fixing: Pour the fixer (solution C) into a plain vessel. Dip the developed paper for 10 minutes, vibrating occasionally. Patterned black images appear on the paper (Figure 6e).

    7.   Washing: Wash the paper in the plain vessel with running water for 10-15 minutes (Figure 6f).

    8.   Drying: Dry the washed printing paper naturally at room temperature. The image formation by the silver halide process is complete.

2. <u>Wavelength Dependence of Photosensitivity</u>

9. Exposing through a filter: Expose a photographic paper to the 60 W lamp and another paper through a red filter (Figure 6g), for the same period of time as in part 1-3 above, and process both papers under the conditions used for the previous experiment. Compare the images produced with or without the red filter, and account for the differences.

3. <u>Color Image Formation By Toning</u>

10. Bleaching of silver image: Mix 100 cm^3 of solution D-1, 100 cm^3 of solution D-2, and 600 cm^3 of water. Pour the mixed solution into a plain vessel. Dip the washed paper for 4-6 minutes. After complete bleaching, wash the paper with running water for 1 minute.

11. Toning of sepia color: Immerse the washed paper in the toning solution (solution D-3) for 3-7 minutes. After toning, wash the paper with running water for 10-15 minutes, and then dry it. Sepia colored images appear by toning.
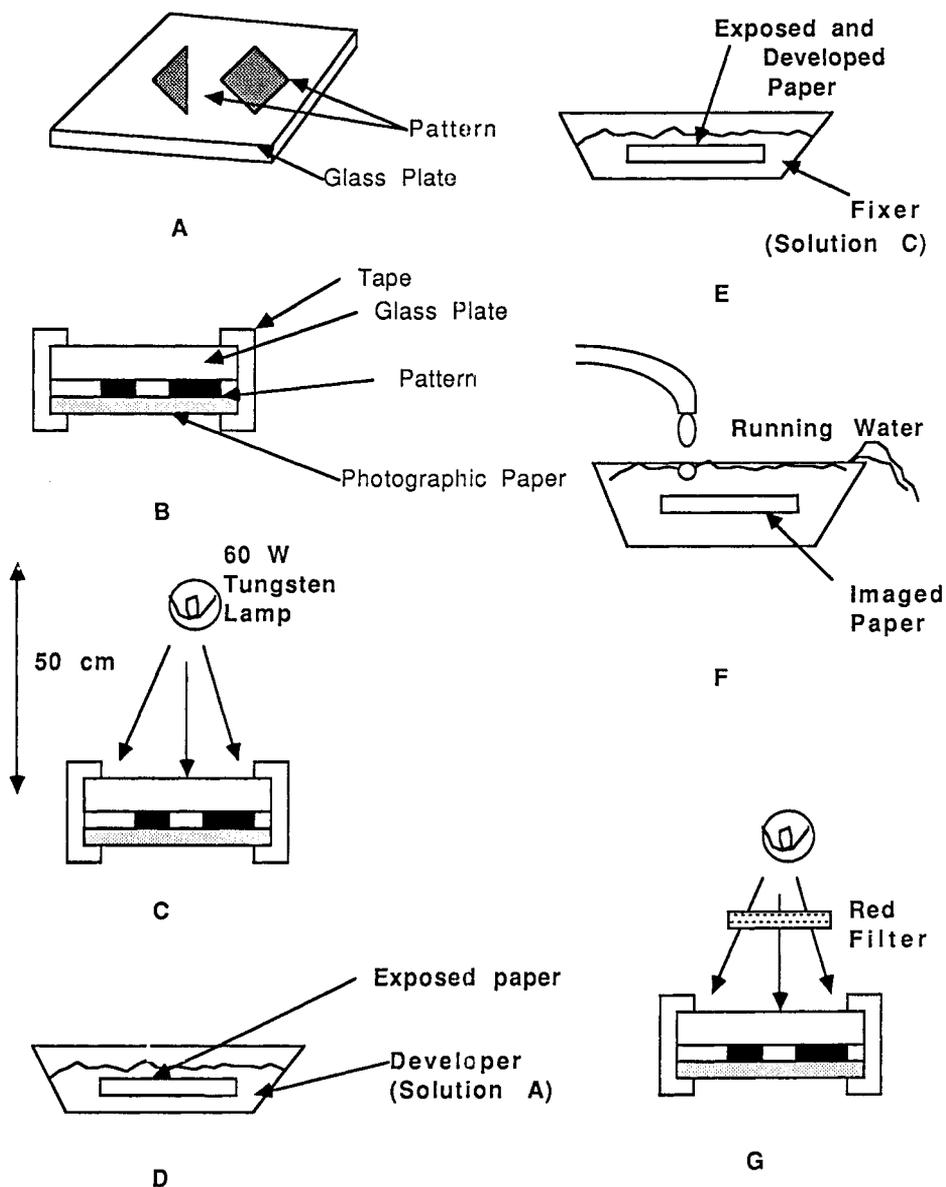
Figure 6. See the description above of the image formation process. Parts A-G of this Figure illustrate the process.

Discussion

Silver halide is photolyzed by visible light of wavelength <550 nm.[2]

$$AgBr \rightarrow Ag + 1/2 Br_2$$

The photolyzed Ag forms a latent image.[3] In the development reaction, dissociation of hydroquinone is necessary to reduce AgX to Ag, because electrons are released by the following reactions.


$$Ag^+ + e^- \longrightarrow Ag^0$$
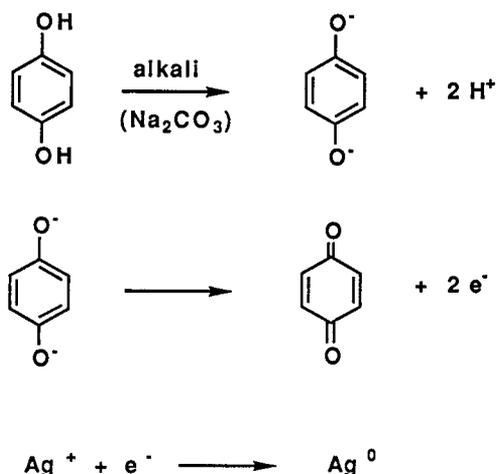
The reduction of Ag^+ does not progress without the latent image. The quantum yield of latent image formation is less than unity, though the redox development reaction amplifies the final imaging yield, and the reduced Ag forms a black image. Hydroquinone is not dissociated under acidic condition, and so acetic acid is effective in stopping the development.
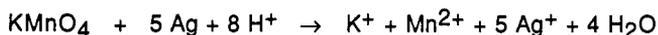
Sodium thiosulfate dissolves non-reduced AgX (fixing):

$$2 AgBr + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2 NaBr$$

The toning reaction is as follows:

$$2 Ag^+ + Na_2S \rightarrow Ag_2S + 2 Na^+$$
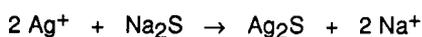
Consequently, the developed silver image (reduced silver) must be oxidized before the toning process, and the toning reaction is effected by the oxidized Ag.

$$KMnO_4 + 5 Ag + 8 H^+ \rightarrow K^+ + Mn^{2+} + 5 Ag^+ + 4 H_2O$$

In the development reaction, silver halide is reduced to metallic silver and the main chemicals of the developer are oxidized. When p-phenylenediamine is applied to the development, the following reaction occurs:
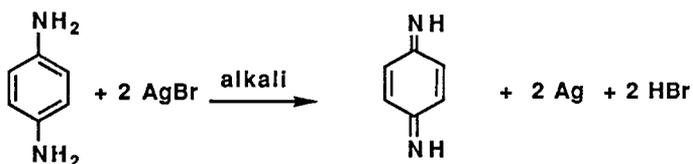
When naphthol is added to the developer solution, a coupling reaction of the oxidized diamine takes place:
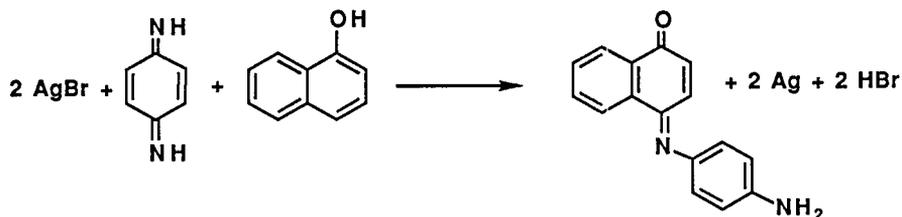
The product is an organic dye. This process occurs only near the latent image (exposed area) and it is similar to the toning reaction. Therefore, a selected catalytic dyeing reaction takes place only in the exposed area. This scheme is similar to that of the chromogenic process of color film. When catechol is used as the main chemical of development, o-benzoquinone will be produced:

The o-benzoquinone has a high chelating reactivity towards gelatin, the main component in the emulsion layer of photographic paper. The chelating reaction causes crosslinking, and the crosslinked polymer is difficult to dissolve in any solvent because of its network structure. Therefore, after developing with catechol, washing with hot water gives relief images on a paper. Though the crosslinked parts are insoluble in hot water, non-crosslinked gelatin is soluble. The above relief imaging process finds applications in microcircuit patterning in the electronics industry and in plate-making in the printing industry.

References and notes

1. The light sensitivity of silver halides was first established scientifically by a German physicist, Johann Heinrich Schulze, in 1727 (reported in Beaumont Newball, "History of Photography," The Museum of Modern Art, New York, 1964, 11). Thomas Wedgewood attempted to make permanent prints "by the agency of light" in 1802 (J. Royal Institution, I, 1802, 170).

2. Panchromatic negative films are sensitized to all of the visible region, but photographic printing paper is sensitive to light of wavelength <550 nm. Therefore, printing paper is not sensitive to light through a red filter.

3. The latent image is composed of silver specks, aggregates of more than three Ag atoms.

4. Details of photographic theory can be found in:
T.H. James, "The Theory of the Photographic Process", 4th ed., MacMillan, New York, 1977.

Notes for teachers

1. All the chemicals used in this experiment are non-toxic. However, strong alkali, acidic and oxidizing solutions are used. For disposal, these solutions should first be neutralized by the acid-base reaction: developer solution (strong base), stopper (strong acid) and bleach solution (strong acid) should be carefully treated.

2. Mitsubishi Gekko SP MR-3 No. 3 photographic printing papers were used in our experiments. All the exposure and treating conditions were determined for these papers. The light intensity of exposure was 300 lux on the paper in the experiment. The conditions may vary depending on the printing papers you use.

3. We suggest the toning experiment need not be carried out in the dark room. During the toning reaction, a little hydrogen sulfide may be produced.

4. The color produced by the toning depends on the reaction time. The longer the reaction time, the deeper the color. Therefore, you can control the color tone by the reaction time.
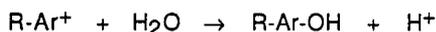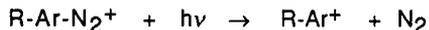
# PHOTOCHEMICAL DECOMPOSITION OF AROMATIC DIAZONIUM SALTS

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Introduction

This experiment demonstrates that the energy of light is high enough to break organic chemical bonds. In this example, the C-N bond in an aromatic diazonium salt is broken by irradiation with ultraviolet light. As a result, the diazonium salt decomposes into nitrogen and a carbenium ion, and this ion reacts for instance with water or another solvent to form a phenol or other products.

$$R\text{-}Ar\text{-}N_2^+ \; + \; h\nu \; \rightarrow \; R\text{-}Ar^+ \; + \; N_2$$

$$R\text{-}Ar^+ \; + \; H_2O \; \rightarrow \; R\text{-}Ar\text{-}OH \; + \; H^+$$

Aromatic diazonium ions react with certain substances to form azo dyes, and this reaction can be used as a test for diazonium salts. Thus, aromatic diazonium salts react in alkaline medium with 2-naphthol. The naphtholate anion is the reactive species.
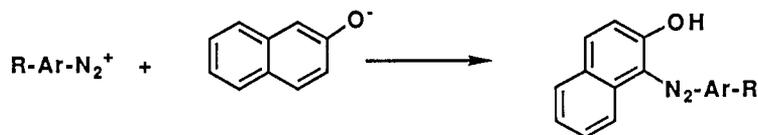
However, in an acidic medium azo dyes are not formed. Therefore diazonium salts and 2-naphthol can be dissolved together in an acidic solution or in an acidic polymer layer without any azo-coupling reaction. The azo-coupling is initiated only by the addition of bases. The experiment combines the photochemical decomposition of diazonium salts and the formation of azo dyes. It is also an example of a simple silver-free image-recording material.

Materials required

20 cm³ conical flasks	p-anisidine
100 cm³ conical flask	sodium nitrite
20 cm³ measuring cylinder	2-naphthol
Buchner filter funnel and flask	40% fluoroboric acid
filter paper	methanol
ice-salt bath	ether
thermometer	dilute sulfuric acid
ultraviolet visualisation source (366 nm)	aqueous ammonia

Experimental procedure

1.   Synthesis of p-methoxybenzenediazonium tetrafluoroborate

3 g (0.025 mol) of p-anisidine are dissolved in a mixture of 12 cm³ of 40% HBF_4 and 10 cm³ of water and cooled to 0° C (ice-NaCl mixture). To this mixture a solution of 1.8 g $NaNO_2$ in 3.6 cm³ water is added slowly with stirring and cooling to 0-5° C. After 10 minutes the precipitate is separated by suction, and washed with cooled 5% HBF_4, methanol and ether. The product obtained is recrystallized from methanol in subdued light conditions.

2.   Photochemical decomposition of the diazonium salt

30 mg 2-naphthol are dissolved in 5 cm³ methanol. Some drops of diluted sulfuric acid are added, and in darkness 50 mg of the diazonium salt are dissolved in this solution. Two or three pieces of white filter paper (10 cm x 10 cm) are impregnated with the solution, and the papers are dried for one hour in darkness. These papers are irradiated under an UV-lamp for about 20 minutes, or in bright sunlight for about an hour. During the irradiation some non-transparent objects (scissors, coins) may be located on the papers. After irradiation the development can be initiated by exposing the paper to ammonia vapour, when a red azo dye is formed. In the irradiated areas of the paper, the colour is much more intense than in the parts which were not exposed to irradiation. The reason for this difference is the photochemical decomposition of the diazonium salt during the irradiation.

PHOTOCHROMISM

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Introduction

A photochromic compound is one that undergoes a reversible colour change on irradiation. Usually the original compound (A) is pale in colour (or colourless), and on irradiation with ultraviolet or visible light it changes to a more deeply coloured compound (B). The reverse reaction, "fading", may occur thermally at room temperature or on heating, or it may occur photochemically using a different wavelength of light. In principle, the process can be repeated many times, but "fatigue" may occur as a result of irreversible side-reactions B → C. Photochromic compounds are used in such diverse applications as optical information storage, map-making, protection against light (for example, in sunglasses), security marking, or actinometry.

There are many classes of compound, both organic and inorganic, that undergo a photochromic change on irradiation. In this experiment you will be working with two organic systems of distinctly different chemical nature.

Aberchrome 540* is a particular example of a class of photochromic compound known as fulgides. The rationale behind designing this particular structure lies in the requirements for a highly coloured product, a product that does not fade thermally, and a system that is fatigue-resistant; fading can be effected, however, with white light. Both forward and reverse reactions are examples of 6-electron electrocyclic reaction.
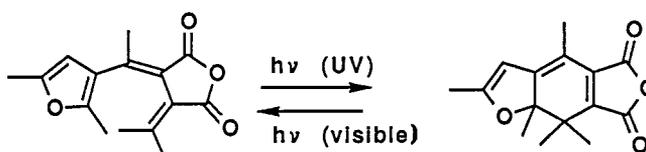
Aberchrome 540

(*Aberchrome photochromic compounds are supplied by Aberchromics Ltd., c/o University College of Wales, Aberystwyth SY23 1NE, U.K.).

Malachite Green is an intensely coloured dye of the triphenylmethane class. The coloured species is the organic cation, and the covalent hydroxide is colourless. However, irradiation of the hydroxide (a substituted triphenylmethanol) causes heterolytic cleavage of the carbon-oxygen bond; the reverse process accounts for the fading of the green colour.
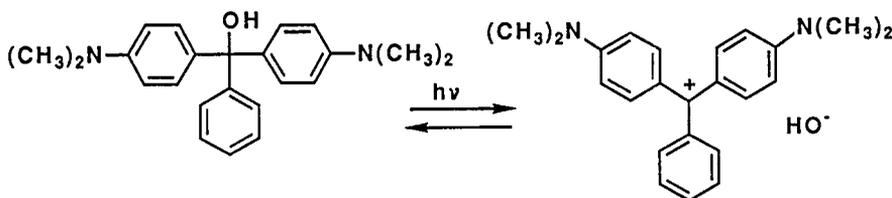
Materials required

25 cm^3 volumetric flask	desk lamp with 60-watt tungsten bulb
5 cm^3 graduated pipette	ultraviolet visualisation source (254 and 366 nm)
25 cm^3 conical flask	ultraviolet-visible spectrometer with cuvettes
50 cm^3 conical flask	toluene
10 cm^3 measuring cylinder	methanol
filter papers, Pasteur pipettes	sodium hydroxide solution (0.1 mol dm^{-3})
weighing bottle	Aberchrome 540 solution in toluene (480 mg dm^{-3})
hot-air blower	Malachite Green hydrochloride

Experimental procedure

1.   Aberchrome 540

Dilute a sample of the stock solution by a factor of ten, by placing 2.5 cm^3 of it in a 25 cm^3 volumetric flask and filling the flask to the mark. Fill a u.v. spectrophotometer cell with the diluted solution, record the absorption spectrum (300-600 nm), and note the colour of the solution.

Remove the cell from the spectrophotometer and irradiate it for 30 seconds with 366 nm radiation from the hand-held u.v. lamp.

Now record the absorption spectrum again on the same piece of chart paper. Repeat this procedure at suitable intervals to give a series of spectra, until no further change occurs (typical total irradiation times in the series might be 0.5, 1, 2, 5, 10 and 15 minutes). If at any stage you have to wait, make sure that your sample is protected from visible (room) light. Note the colour of the final solution.

Finally, irradiate the coloured solution for 2 minutes with light from a 60-watt tungsten bulb, and record the spectrum again. Repeat this irradiation for a further 2 minutes, and once more record the spectrum.

2.   Malachite Green

Make a solution of Malachite Green hydrochloride (about 0.01 g) in methanol (10 cm^3), and add sodium hydroxide solution (0.01 mol dm^{-3}) drop by drop until the colour is just discharged. Note that the neutralisation reaction is not instantaneous, and you should carry it out slowly and carefully so as to avoid ending up with excess hydroxide ions. Put some of the solution on a filter paper, and dry the paper, using a hot-air blower if necessary. Place a suitable mask (for example, a coin) on the impregnated area, and irradiate with 254 nm radiation from the lamp used for t.l.c. visualisation. When the colour change has occurred, switch off the lamp, remove the mask, and put the paper to one side for a while. Note your observations.

It is possible to carry out an experiment with Malachite Green in fluid solution analogous to that described for Aberchrome 540, making appropriate modifications to allow for neutralisation, the longer-wavelength absorption of the green dye, the shorter wavelength needed for effective photochromism, and the thermal (rather than photochemical) fading.

Discussion

1.   Aberchrome 540

Given that the molar absorption coefficient of Aberchrome 450 at its wavelength of maximum absorption is 6000 dm^3 mol^{-1} cm^{-1}, calculate the molar absorption coefficient of the coloured isomer as its absorption maximum. State the assumptions that you have to make in order to do this.

Is the photochromic reaction completely reversed using the tungsten light bulb? If not, can you suggest why, and can you also suggest how a more complete reversal might be achieved? On the basis of your results, devise a procedure for using Aberchrome 540 as an actinometer to measure ultraviolet light intensity. What further information would you need to operate the system, and what limitations would the system have?

2.   Malachite Green

Many triarylmethane salts are used in inks and for copying-paper. Do your results suggest a potential drawback in such applications?


Acknowledgment

pH DECREASE DUE TO PHOTOPRODUCTION OF AN ACID

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Introduction: aciditropic reactions

An interesting class of photochemical reactions which yield changes in the pH of the reaction medium has recently been studied. These have been termed aciditropic reactions.[1] The pH of the solution can decrease if a more acidic product is formed in the reaction. Alternatively, the pH of the solution can increase if a more basic product is formed. To illustrate this, dihydrocoumarin, when irradiated in aqueous solution, yields first a ketene, followed by reaction with water to yield an acid:[2]
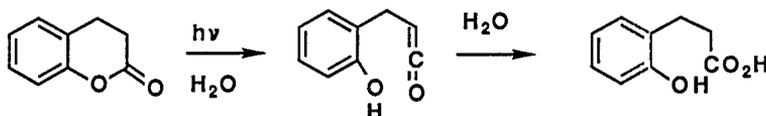
The photoreaction of cyclohexanone may also be considered to be a reaction of this type, starting with an example of a Norrish Type 1 cleavage. Disproportionation of the radical centres results in ketene formation, which adds to water to yield hexanoic acid, or in the formation of an unsaturated aldehyde:
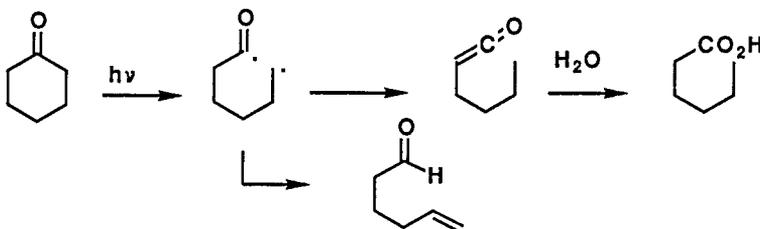
Materials required

1000 cm^3 beaker
50 cm^3 beaker
pH-meter

photochemical reactor with 450-watt medium-pressure mercury arc and Pyrex filter
sodium hydroxide
cyclohexanone

Experimental procedure

In a 1000 cm^3 beaker, dissolve one pellet (ca. 0.15 g) of NaOH in 1000 cm^3 of water. Weigh out 5 g of cyclohexanone and add it to the NaOH solution. Stir the solution (not all of the cyclohexanone will dissolve), and record the pH of the solution. Pour 500 cm^3 of the solution into a photochemical reaction assembly, and irradiate the solution for fifteen minutes with light from a 450-watt mercury arc lamp. Remove a sample of the solution from the apparatus, and record the pH to verify that a chemical reaction has taken place.

(Note that the quantities can be scaled down according to the type of photochemical equipment available).

The pH of the solution may be followed as a function of irradiation time, to illustrate the principles of product yield as a function of reaction time and photobleaching (reduced absorption of light as the substrate is used up).

References

1. F.A. Carroll, J.M. Hain, R.H. Lee and D.K. Green, 189th National ACS Meeting, Miami Beach, Florida, ORGN 94.

2. (a) C.D. Gutsche and B.A.M. Oude-Alinke, J.Amer. Chem. Soc., 1968, 90, 5855; (b) O.L. Chapman and C.L. McIntosh, J.Amer.Chem.Soc., 1969, 91, 4309.
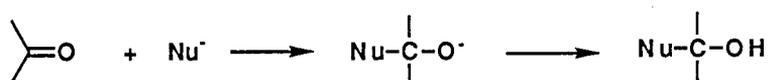
PHOTOREDUCTION OF BENZOPHENONE

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Introduction

The carbon-oxygen bond in ketones such as benzophenone ($Ph_2C=O$) is polarized, and the unsymmetrical distribution of charge, together with the unsaturation represented by the π -bond, is a major consideration in rationalising the thermal (ground-state) reactions of such compounds. Many reactions of ketones can be represented in terms of initial attack by a nucleophile at the partially positively charged carbon atom of the carbonyl group. Nucleophilic attack produces an oxygen-centred anion, which often goes on to abstract a proton in yielding the observed product. The proton source may be present in the reaction medium, or it may be made available in the work-up procedure.

$$\rangle\!\!=\!\!O \;+\; Nu^- \;\longrightarrow\; Nu\!-\!\overset{|}{\underset{|}{C}}\!-\!O^- \;\longrightarrow\; Nu\!-\!\overset{|}{\underset{|}{C}}\!-\!OH$$

Reduction of ketones with metal hydride-type reagents is an example of such reaction, and conventional reduction of benzophenone using sodium tetrahydroborate (sodium borohydride) leads to diphenylmethanol:

$$Ph_2C=O \;\xrightarrow{\;NaBH_4\;}\; \longrightarrow\; Ph_2CH\text{-}OH$$

Ultraviolet irradiation of benzophenone leads to photochemical reaction originating in an electronically excited state, an (n,π^*) triplet state, rather than in the ground state. This excited state does not have such a large polarisation of electrons in the C=O bond. Instead, its chief electronic feature is the odd-electron character of the oxygen atom, and the photochemistry of benzophenone can be rationalised on the basis of processes derived from an oxygen-centred radical-like species. Like radicals, this type of excited state is also much more susceptible to involvement in electron transfer processes than is the corresponding ground state.

It follows that effective reducing agents for the photochemical reduction of benzophenone are hydrogen atom donors rather than hydride ion donors. Primary and secondary alcohols are examples of good hydrogen atom donors, since the radical obtained by hydrogen abstraction from the carbon atom carrying the hydroxyl group is stabilised relative to a simple alkyl radical:

$$Ph_2C=O \;+\; (CH_3)_2CH\text{-}OH \;\xrightarrow{\;h\nu\;}\; Ph_2\overset{\bullet}{C}\text{-}OH \;+\; (CH_3)_2\overset{\bullet}{C}\text{-}OH$$
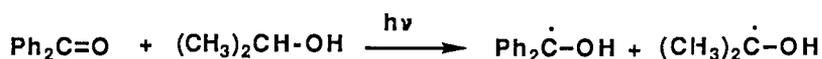
The purpose of this experiment is to demonstrate the effectiveness of an alcohol as reducing agent for the excited state of benzophenone, and by comparison with the product of thermal reduction to see if the overall chemical reaction is similar or different.

Materials required

50 cm^3 conical flask
250 cm^3 conical flasks (2)
10 cm^3 measuring cylinder
100 cm^3 measuring cylinder
250 cm^3 separating funnel with stopper
filter funnel and papers
250 cm^3 round-bottomed flask
Pyrex test-tube (40 cm^3 capacity) with cork
Buchner flask and funnel
Pasteur pipettes
400-Watt medium-pressure mercury arc, with
   Pyrex cooling jacket

rotary evaporator
infrared spectrophotometer
benzophenone
sodium borohydride
propan-2-ol
ethanol
ether
aqueous HCl (2 mol dm^{-3})
anhydrous magnesium sulfate
glacial acetic acid

Experimental procedure

1. Thermal reduction

In a 250 cm³ conical flask prepare a solution of benzophenone (1.0 g) in aqueous ethanol (8 cm³ ethanol and 2 cm³ water). Add sodium borohydride (0.25 g), and swirl the flask to assist solution. After about 30-40 minutes add iced water (100 cm³), and extract the product into ether (2 x 50 cm³). Wash the combined ether extracts with aqueous hydrochloric acid (2 mol dm⁻³, 50 cm³) and then with water (50 cm³). Dry the solution with anhydrous magnesium sulfate, filter off the drying agent, and isolate the crude reaction product by distilling off the ether using a rotary evaporator. Record the infrared spectrum of the product.

2. Photochemical reduction

Dissolve benzophenone (4.0 g) in propan-2-ol (35 cm³) by shaking in a 50 cm³ conical flask and warming gently in a water-bath. Add one drop of glacial acetic acid, to neutralise alkaline impurities on the surface of the glass, and fill a Pyrex test-tube with the solution to within 2 cm of the top. Cork the tube loosely and support it as close as possible to the Pyrex water-cooling jacket around the medium-pressure mercury arc. When the apparatus has been properly enclosed in its protective surround, switch on the lamp and irradiate for 3-4 hours.

After switching off the lamp, filter the precipitated product from the solution using a Buchner flask and funnel, wash it with a little cold ethanol, and suck the crystals as dry as possible. Record the infrared spectrum of the product.

Discussion

By comparison of the infrared spectra, and from other observations, you should be able to determine whether the overall product of photoreduction is the same as, or different from, that obtained by thermal reduction using a metal hydride. If the photoproduct is different, can you suggest a likely structure for it?

PHOTODIMERIZATION OF ANTHRACENE

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Introduction: cycloaddition reactions

The photodimerization of anthracene was the first photochemical reaction to be studied. In 1867, the German chemist Fritzche discovered that benzene solutions of anthracene would yield an insoluble substance upon exposure to the sun's rays. He called the substance "paraphoten" and concluded that it was a polymer of anthracene, after observing that melting "paraphoten" yielded only anthracene. Many years later, studies by other scientists revealed that "paraphoten" was not a polymer, but instead was a dimer of anthracene. This conclusion was based largely on the following observations:

(a) The photoproduct had a melting point of 244° C, much higher than anthracene's melting point (214° C), but anthracene was produced upon melting.

(b) An elemental analysis of the photoproduct yielded an empirical formula of C_7H_5, the same as anthracene.

(c) The photoproduct had a molecular weight which was twice the molecular weight of anthracene.

The structure of the dimer was correctly proposed by Charles Linebarger as having bond formation across the 9- and 10- positions of the reacting anthracenes. The proof that Linebarger had correctly elucidated the structure has been derived from recent three-dimensional X-ray crystal structure data.
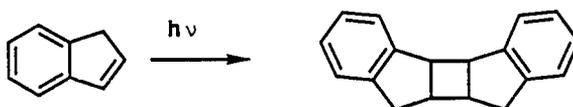
The reaction is:
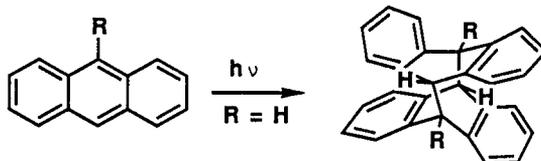
The classification of cycloaddition reactions follows that of Woodward and Hoffman[1], emphasized more recently by Turro[2]. In this definition, a cycloaddition reaction is a ring-forming reaction of m participating electrons of one group to n participating electrons of another group. In most cases, new σ -bonds are formed in the products with a corresponding loss of π -bonds in the starting material(s):
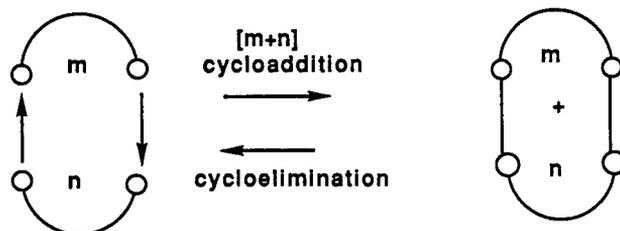
Using this scheme, a large number of dimerizations can be classified into a single group. The most common type of photodimerization involves m = 2 and n = 2 in the classification scheme. These reactions are termed [2+2] cycloaddition reactions, and the example of indene is shown below. The [2+2]-cycloaddition has been found to be extremely versatile, as shown by its recent use in the synthesis of a large number of natural products.[3]

Cycloaddition reactions are not confined to [2+2]-reactions. The dimerization of anthracene illustrates a case in which six electrons from one anthracene molecule react under photochemical excitation with six electrons from another anthracene to yield the dimeric structure shown. In this example, m = 4 and n = 4 in our general classification scheme.

Materials required

750 cm^3 conical flask
250 cm^3 measuring cylinder
filter funnel
Buchner filter funnel and flask
melting-point apparatus
photochemical reaction with 450-watt medium-pressure mercury arc and Pyrex filter
anthracene
hexane or cyclohexane

Experimental procedure

Dissolve 0.7 g of anthracene in 500 cm^3 of hexane or cyclohexane. If all of the anthracene does not dissolve, filter the solution to remove any excess anthracene. Transfer the solution to a photochemical reaction assembly equipped with a 450-W mercury lamp. Bubble nitrogen through the solution for 15 minutes, and then irradiate for approximately two hours. As the irradiation proceeds, white crystals will precipitate from the solution. Collect the precipitate by vacuum filtration using a Buchner funnel. Allow the crystals to dry and determine their melting point. Allow the melted liquid to cool and form crystals again. Redetermine the melting point. Record the weight of the precipitate as well as the two melting-point determinations. A typical yield is 0.45 g of the dimer.

A modification of this experiment, using microscale photochemical equipment, has been published.[4]

References

1.   R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie (Weinheim), 1970.

2.   N.J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings (Menlo Park), 1978.

3.   S.L. Schreiber, Science, 1985, 227, 857.

4.   J.H. Penn and R.D. Orr, J.Chem. Ed., 1989, 66, 86.

PHOTOPOLYMERIZATION OF ACRYLAMIDE

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Introduction

Few developments have changed day-to-day life as much as the discovery of polymers. The history of polymers goes back to Egyptian mummies. Before the mummies were wrapped, the cloth was soaked in a solution of oil of lavender. When the cloth was dried by exposure to the sun's rays, the oil was converted into a protective polymer.[1] Polymers are involved in almost all aspects of our lives. A few examples of the infusion of polymers into everyday life include the clothes we wear, the building materials we use, and the packages we store food in.

The most common method of polymer formation is radical-chain addition polymerization. The reaction steps comprise an initiation reaction, propagation reactions, and termination reactions. An important method for controlling the properties of a polymer is the initiation step. Light, heat, and chemical additives have all been used to generate radicals which may begin the polymerization process.[2] The major advantage of using light to initiate polymerization is its controllability. The wavelength and intensity can be adjusted to select which radicals may be formed when several are possible. Additionally, light can be focused onto a particular site, thus forming a polymer network only in desired places.
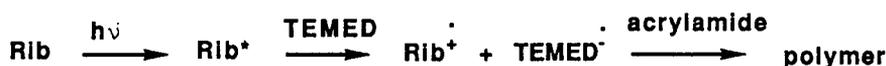
The flexibility is illustrated by the ability to make photoresists which are important in modern electronics. In this process, a film of material is placed on a surface and a laser is focused on the areas in which a polymer covering is desired. After polymerization has occurred, the unpolymerized material can be washed away, leaving the photopolymer intact. Since lasers are able to be focused to two millionths of an inch, "lines of polymer" can be drawn onto a silicon wafer or printed circuit board. The polymer-covered areas then "resist" chemical etching, resulting in integrated circuit formation or printed circuit board construction. This technology has allowed billions of transistors to be placed on a single integrated circuit.

Another example of the use of polymers today is in gel electrophoresis.[3] Electrophoresis is a method for separating proteins based on the charge on the enzyme surface. Application of an electric field causes charged particles to migrate towards the electrodes. Thus, enzymes may be separated on the basis of the relative charge on their surface, with a greater charge giving a faster migration rate. Further, negatively charged species will migrate in the opposite direction from the positively charged species.

A gel is a polymer "fishnet" in which chemical bonds form the ropes which are interwoven to catch chemical fish (i.e. the enzymes). The size of the holes can be varied by changing the amount of cross-linking agent in the polymer network. Small enzymes or proteins are able to move easily through the gel, while larger enzymes have more difficulty moving through the pores of the gel. Thus, separation of enzymes is accomplished on the basis of size, with smaller enzymes being able to move faster and farther through a gel than larger enzymes.

The combination of these two principles results in the technique of gel electrophoresis, which is a powerful technique for the separation of enzymes and proteins.

Polyacrylamide is a polymer which is used commonly in the separation of proteins by gel electrophoresis. To initiate the polymerization in our experiment, we begin by exciting riboflavin (Rib) molecules with light. The excited riboflavin molecule undergoes a charge-transfer reaction, taking an electron from the tetramethylethylenediamine (TEMED). This produces a riboflavin radical anion and a TEMED radical cation. These species then serve as initiators for polymerization. The structure of the final polymer is given below, along with a representation of the reaction mechanism.

$$\text{Rib} \xrightarrow{\text{h}\nu} \text{Rib}^* \xrightarrow{\text{TEMED}} \text{Rib}^{\cdot +} + \text{TEMED}^{\cdot -} \xrightarrow{\text{acrylamide}} \text{polymer}$$

The product polymer is fine and threadlike when formed. To obtain a product which is easily seen and isolated, bisacrylamide (BIS) is added as a cross-linking reagent. BIS has two double bonds to which the radical may add. If one radical adds to one double bond and another radical adds to the other double bond, the two chains of polymer are joined by a cross-link. This causes the threads to become joined like a fishnet. The size of the fishnet may be varied by changing the amount of BIS which is added to the prepolymer mix.
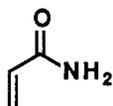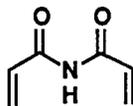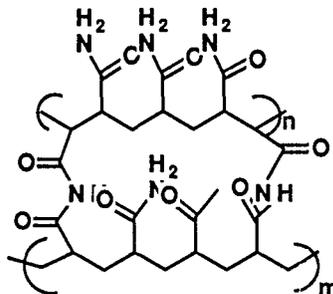
Acrylamide   **Bis-acrylamide**
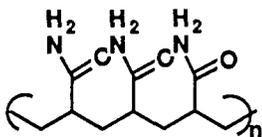
Homopolymer   **Crosslinked Polymer**

Materials required

250 cm^3 beaker
100 cm^3 measuring cylinder
450-watt medium-pressure mercury arc with Pyrex filter
acrylamide
bisacrylamide
riboflavin
tetramethylethylenediamine

Experimental procedure

Prepare a solution of 6 g of acrylamide, 0.0005 g of riboflavin, 0.1 g of bisacrylamide, and 0.05 cm^3 of N,N,N',N' - tetramethylethylenediamine in 100 cm^3 of water. Place the solution in a beaker. Position the beaker approximately three inches from the immersion well of a 450-watt medium pressure mercury lamp, with the center of the beaker being near the centre of the lamp. Irradiate for one-and-a-half hours. The polyacrylamide formed will have a gel-like consistency.

References

1.   G.A. Delzenne, J. Macromol.Sci., Revs. Polymer Technol., 1964, D1(2), 185.

2.   Kh.S. Bagdasar'yan, Theory of Free-Radical Polymerization, S. Monson, Jerusalem, Israel.

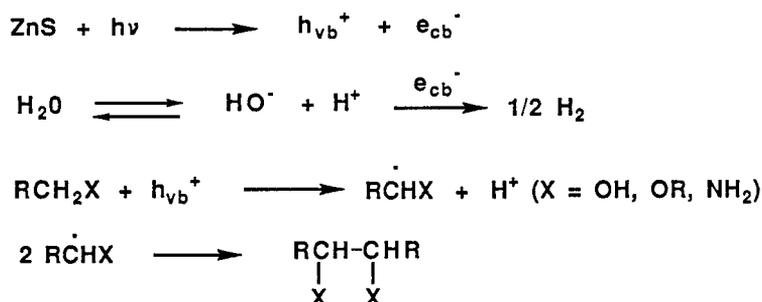3.   B.J. Davis, Annals of the New York Academy of Sciences, 1964, 404.

PHOTOCATALYTIC HYDROGEN EVOLUTION ON ZINC SULFIDE DISPERSION

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Introduction

In photocatalytic systems consisting of photocatalysts, water, and organic electron donors, hydrogen evolution and selective carbon-carbon bond formation by oxidation of the electron donors are of great interest, since this provides a method for energy conversion and storage and is significant in view of organic synthesis and prebiotic chemistry. Such photocatalytic redox reactions are based on photophysical separation of electrons and holes on semiconductors. Zinc sulfide is an efficient semiconductor photocatalyst and works without platinum. When a heterogeneous mixture of an aqueous ZnS dispersion and an organic substrate is irradiated in a Pyrex vessel using a high-pressure mercury arc lamp, hydrogen is evolved in fairly high quantum yield and selective alpha carbon-carbon bond formation occurs in the oxidation of the organic substrate:

$$ZnS + h\nu \longrightarrow h_{vb}^{+} + e_{cb}^{\cdot}$$

$$H_2O \rightleftharpoons HO^{-} + H^{+} \xrightarrow{e_{cb}^{\cdot}} 1/2\ H_2$$

$$RCH_2X + h_{vb}^{+} \longrightarrow R\dot{C}HX + H^{+}\ (X = OH, OR, NH_2)$$

$$2\ R\dot{C}HX \longrightarrow \underset{X\quad X}{RCH\text{-}CHR}$$

Further oxidation to RCH(OH)X occurs concurrently through a carbocation:

$$R\dot{C}HX + h_{vb}^{+} \longrightarrow R\overset{+}{C}HX \xrightarrow{HO^{-}} \underset{OH}{R\text{-}CHX}$$
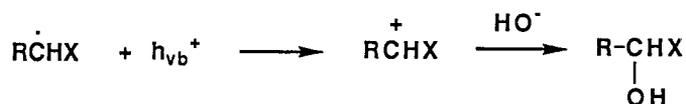
Typical examples of the one-hole and two-hole oxidation products from tetrahydrofuran and triethylamine are shown below:
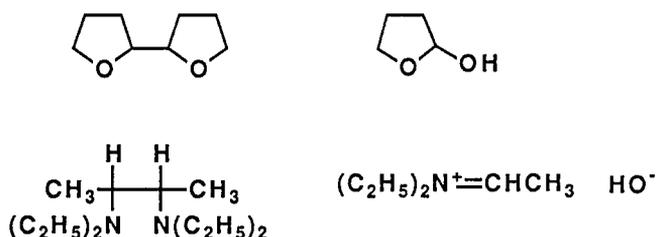
When an appropriate substrate is chosen, i.e. a reducing RCH_2X or inorganic substrates such as sulfide or sulfite ion, efficient hydrogen evolution on ZnS particles can be observed when uv irradiation is carried out through Pyrex glass (cutoff around 290 nm).

Materials required

500 cm^3 conical flask
100 cm^3 measuring cylinder
500 cm^3 beaker
burette
glass tubing
photochemical reactor with 100-watt high-pressure mercury arc and Pyrex filter
zinc sulfate
sodium sulfide
tetrahydrofuran (THF)

Experimental procedure

The apparatus shown in Figure 7 is constructed from a 1-litre Pyrex vessel and a 100-W high-pressure mercury arc lamp. ZnS suspension is prepared under nitrogen atmosphere by magnetic mixing of 100 cm^3 each of aq. $ZnSO_4$ (0.1 mol dm^{-3}) and freshly prepared aq. Na_2S(0.1 mol dm^{-3}) solutions. The resulting ZnS suspension and 200 cm^3 of tetrahydrofuran are placed in the apparatus and purged with nitrogen, then irradiated at room temperature (ca. 20° C) under magnetic stirring. After a few minutes induction, gas is evolved constantly and can be trapped in a gas burette. After 4 hours irradiation, 150-200 cm^3 of the gas are evolved and the gas is confirmed to be hydrogen by gas chromatography using an active carbon column (3mm x 2m). The reaction products in the vessel can be

Hg Lamp

Pyrex Filter

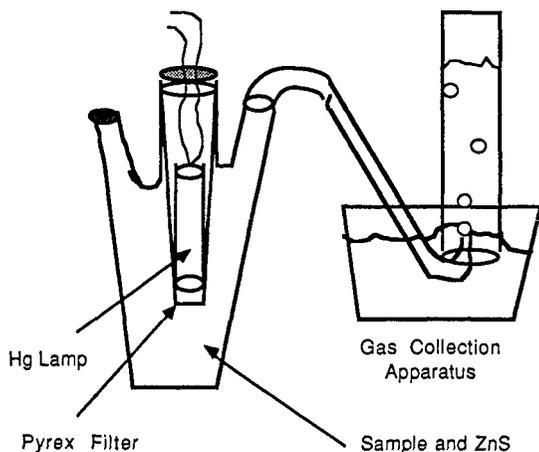Gas Collection Apparatus

Sample and ZnS

Figure 7. A schematic of a photochemical reactor for irradiation of ZnS suspensions and collection of gases produced.

analyzed by using a gas chromatograph with FID and Ucon oil 50LB 550X on Uniport (15%) column (3mm x 2m). The supernatant reaction mixture contains the following products: 2,2'-bi(tetrahydrofuryl) and oligomers of tetrahydrofuran as major components, and 2-hydroxytetrahydrofuran and butane-1,4-diol as minor components.

Problems

1.   The formation of hydrogen and the THF-derived products was monitored as shown in Figure 8. Explain the mechanism for formation of butane-1,4-diol. Also explain the formation of oligomers of THF (ref. J. Chem. Soc., Perkin Trans 2., 1985, 1487; J. Phys. Chem., 1989, <u>93</u>, 2576 and 1990, <u>94</u>, 3104).
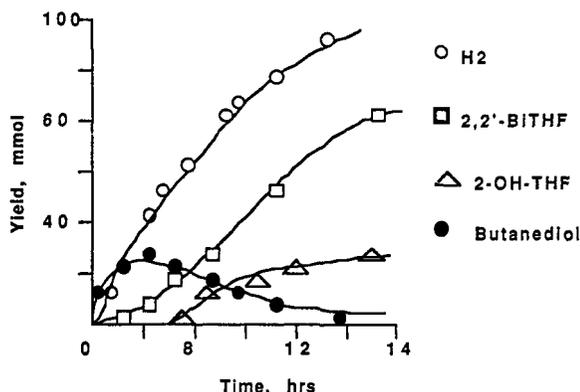
Figure 8. ZnS catalyzed photoreaction of aqueous THF solution. Products are hydrogen, bi-tetrahydrofuryl, 2-hydroxy-tetrahydrofuran and 1,4-butanediol.

2.   What can be expected as oxidation products when methanol is used an an organic substrate (ref. J. Chem. Soc., Chem. Commun., 1984, 21)?

3.   Outline a strategy for the reduction of carbon dioxide using ZnS dispersion as photocatalyst and good reducing agents as electron donors (ref. Chem.Lett., 1990, 931; J.Phys.Chem., 1984, <u>88</u>, 5903; Ber.Bunsenges. Phys.Chem., 1984, <u>88</u>, 170).

EXTRACTION OF PHOTOSYNTHETIC PIGMENTS FROM GREEN PLANTS

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Introduction

Green plants play a vitally important role in the conversion of solar energy into material for food and fuel, and the molecular processes involved in photosynthesis provide a wealth of examples of photochemistry and electron transfer. There are several pigments in plants which absorb visible light in the initial step of photosynthesis. Their molecular structures are known, and their isolation from plant material is relatively easy. In this experiment you will isolate a number of photosynthetic pigments from spinach, identify them by a comparison of visible absorption spectral data, and evaluate their colour and fluorescence emission in terms of their visible absorption.

The molecular structures of six common photosynthetic pigments are shown below:

R = CH3, Chlorophyll-a
R = CHO, Chlorophyll-b

Lutein

β-Carotene

Violaxanthin

Neoxanthin
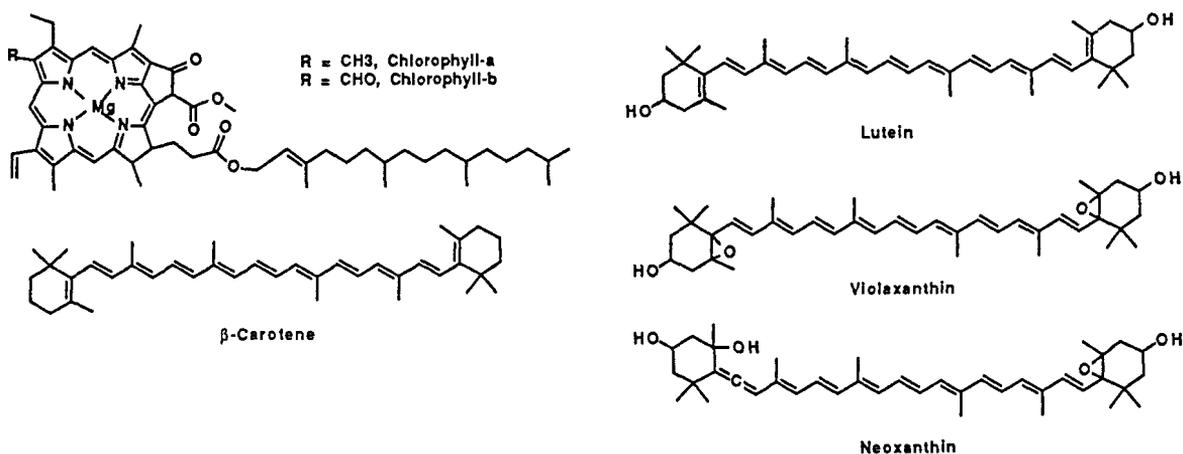
Materials required

spinach leaves (preferably fresh, not frozen)
calcium carbonate
acetone
t.l.c. solvent (15:15:1 methanol: acetone: water)
20 x 20 cm cellulose t.l.c. plates with flexible backing, treated by elution with 4% vegetable oil in
    petroleum ether
mortar and pestle
25 cm^3 conical flask with stopper
filter funnel and paper
t.l.c. applicator pipette
t.l.c. development tank
large filter paper
air blower
long-wavelength (365 nm) uv visualisation lamp
centrifuge and tubes
Pasteur pipettes
uv-visible absorption spectrometer with cuvettes

Experimental procedure

1.   Extraction

Take about 2 g of spinach leaves (free from stalks and large veins) and grind them thoroughly with a small amount of calcium carbonate and acetone (20 cm^3) using a mortar and pestle. Filter the mixture, and transfer the clear solution to a 25 cm^3 conical flask. When not in use, the solution should be stoppered and kept in the dark.

2.   Separation

Take one of the specially prepared cellulose thin-layer plates and apply about 1 cm^3 of the spinach extract to it in the following way:

(i)   Support the air blower above the plate and switch it on so as to have a constant flow of cold air over the plate.

(ii)   Allow some extract to be drawn into a transfer pipette.

(iii)   Discharge this on to the plate by dragging it *lightly* over the line marker. Try to avoid digging into the plate.

(i v)   When the solvent has evaporated, repeat the process until the 1 cm^3 of extract has been applied as a *thin* band of pigment.

Pour into the t.l.c. developing tank sufficient of the solvent mixture (methanol: acetone: water, 15:15:1) to cover the bottom to a depth of between 3 and 5 mm, and insert a large filter paper so that it stands against the wall of the tank with the bottom just dipping into the solvent mixture. Carefully lower the plate inside so that it does not touch the filter paper, replace the tank cover and allow to stand undisturbed until the solvent front is between 2 and 5 cm from the top of the plate (1.5 -2.5   hours). When the elution is complete, remove the plate and dry it using the air blower at room temperature.

3.   Characterisation of pigments

Note the number and colour of the pigments that have been separated on your chromatogram. Examine the plate with a long-wavelength ultraviolet lamp and note the appearance of each band.

Obtain the ultraviolet-visible absorption spectrum of each of the separated pigments in the following way. Carefully cut the band from the plate with scissors and, using a spatula, scrape the cellulose from the strip into a specimen tube containing 5 cm^3 of acetone. Agitate the suspension for a few minutes and separate the solid from the solution using a centrifuge. With a Pasteur pipette, transfer about 2 cm^3 of the supernatant solution to a spectrometer cuvette and, using acetone in the reference beam, record the electronic absorption spectrum from 300 to 800 nm. Record also the spectrum of the original spinach extract, diluting the solution with acetone if necessary.

Conclusions

By comparison of your spectra with the data in Table 2 and with molecular structures, identify as many as possible of the pigments that you have separated. It will help if you remember that under the chromatographic conditions used, which involve a "reverse-phase" system because the cellulose has been impregnated with vegetable oil, more polar compounds elute faster. In each case comment on the relationship between the absorption spectrum and the appearance (colour) of the solution. Comment also on the relationship (if any) between the absorption spectrum and the appearance under the long-wavelength ultraviolet lamp. Can you draw any conclusion about the relative amounts of the various pigments in the original extract?

Table 2. Absorption maxima and extinction coefficients of pigments.

Pigment	λ_{max} /nm (ε_{max} / dm^3 mol^{-1} cm^{-1})
chlorophyll-a	408 (68000), 428 (111000), 577 (7400), 613 (13000), 660 (85000)
chlorophyll-b	430 (sh, 70000), 445 (170000), 600 (13000), 644 (62000)
β-carotene	427 (sh, 127000), 449 (190000), 475 (120000)
lutein	422 (-), 445 (140000), 474 (-)
violaxanthin	417 (115000), 440 (150000), 469 (125000)
neoxanthin	415 (130000), 438 (130000), 467 (100000)

Note

You may find that more than two chlorophylls are present. This could be because stereoisomerisation has occurred, brought about for example by too great an exposure of the extract to room light, or by the blanching process used in preparing frozen spinach.

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