Pilkington Library					
Author/Filing T	itle .	ŀ	UNT	••••••	
 Vol. No	•••••	Clas	s Marl		τ
Please not	e tha	at fin overd	es aro lue ite	e char ems.	ged on ALL
for		টাই জুনাম হাজে ম	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	। জন্ম বিজ মিল	<u>ANU Y</u>



ł ł ł l L ł ł.

ł

Photoreactions of dyes involving radicals in solution and on cotton

By Paula Hunt

A Doctoral Thesis Submitted in Partial Fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

24th March 2001

© Paula Hunt 2001

	Longhi	MOTOU MIY	gh
Date	Ma	i.ibrai 02	ry
Class			
Acc No.	a40250	0776z	<i>,</i>

/

Acknowledgements

Firstly, I would like to thank Professor Frank Wilkinson for all his help and support during the last few years. Also, many thanks are due for his immense patience. Secondly, I would like to thank Dr. Stephen Batchelor of Unilever Research for his suggestions and advice, especially his help with using matlab. Thanks also to Dr. Ian Wilkes for his help with the purification and application of dyes and to Unilever Research for funding this work.

I would also like to thank my parents for their support, especially financial support, which is always very welcome. Thanks also to Howard Yeomans for helping me with formatting this document and taking my mind off work when required and of course tolerating me during this time.

Finally, I would like to thank my co-workers at Loughborough, who have provided both help with problems and understanding when problems arose. They are Jill Crossley, Sian Worrall, David Worrall, David Mandley and Ayman Abdel-Shafi. With Special thanks to Sian for proof reading this thesis, for which I am very grateful.



Abstract

Cellulose is a natural polymer, which is used in many applications, including as clothing fabric. Thermal and photochemical degradation of cellulose is known to involve the production and reaction of radicals, and the degradation of dyes on cellulose fabrics is also thought to occur partially as a result of radical reactions. The radicals produced following hydrogen abstraction from cellulose are likely to be of the α -hydroxy type. The reactions of simple α -hydroxy radicals, as models for cellulose radicals, have therefore been studied here.

Radicals formed from cellulose based polymers such as cotton have been modelled in this work by α -hydroxy radicals, which were formed by photolysis of α -hydroxy ketones. These initiators are molecules that undergo intramolecular cleavage following irradiation, see section 1.10.1.2, the cleavage of which results in the production of benzoyl and α -hydroxy radicals in each case.

Two α -hydroxy radicals were chosen, α -hydroxy cyclohexyl and 2-hydroxy-2-propyl, so as to determine whether steric factors significantly affected the rate constants for the reactions of these radicals. The reaction between the radicals and a series of alkenes was used to determine the difference in rate constants between the two radicals. The reaction rates were determined using a probe molecule to monitor the reaction of the radicals. The reaction between the radicals and the alkenes was monitored by virtue of competition with the probe molecule.

The rate constants for the reaction of these radicals with several dyes have also been determined. The method, validated by the mathematical simulations, was used to determine experimental rate constants for several dyes with radicals using three radical photoinitiators. The rate constants for reaction of some dyes with α -hydroxy radicals have been determined both in methanol and on cotton fabric. These new rate constant values have been determined for both dry and wet cotton fabric samples. Studies were also carried out involving irradiation of dyed cotton linters samples with polychromatic light. In addition, the effect of adsorbing radical photoinitiators onto the cotton samples on the fading rate of these samples was studied, and has been linked to the rate constant data.

1. Introduction	
1.1. Photochemical pro	ocesses
1.2. Electronically exci	ited states7
1.2.1. Molecular or	bitals
1.2.2. Spin multiplic	city 8
1.2.3. Electronic tra	ansitions
1.2.4. Forbidden ele	ectronic transitions10
1.3. Relaxation of elect	tronically excited states11
1.3.1. Intramoleculo	ar processes
1.3.2. Intermolecula	ar processes13
1.4. Quantum yields	
1.5. Flash photolysis	
1.5.1. Light sources	for flash photolysis17
1.6. Lasers	
1.6.1. Population in	iversion
1.6.2. Mirrors	
1.6.3. Q-switching	
1.6.4. Frequency do	publing
1.7. Diffuse Reflectanc	ce
1.7.1. Transient con	acentrations in opaque samples
1.8. Cellulose	
1.8.1. Uses of cellule	ose 27
1.8.2. Structure of co	ellulose
1.8.3. Other species	within cellulose
1.8.4. Cellulose radi	licals
1.8.5. Irradiation of	^c cellulose
1.9. Dyes and pigments	32
1.9.1. Application of	f dyes to fibres
1.9.2. Chemical stru	acture of dyes 34
1.9.3. Azo dyes	

1.9.4.	Photodegradation of dyes
1 .10. I	Radicals
1.10.1	. Radical production
1.10.2	2. Reactions of radicals
1.10.3	B. Determination of radical reaction rates
1.10.4	Detection of radicals
2. Expe	rimental
2.1. Ma	terials
2.1.1.	Azo Dyes
2.1.2.	Non-azo dyes
2.1.3.	Photoinitiators
2.1.4.	Other materials
2.2. Che	mical structures of materials
2.2.1.	Photoinitiators
<i>2.2.2</i> .	Alkenes
2.2.3.	Mono-azo dyes
2.2.4.	Poly-azo dyes
2.2.5.	Non-azo dyes
2.3. Ren	noval of oxygen from solutions
2.3.1.	Nitrogen bubbling
2.3.2.	Degassing
2.4. Puri	fication of dyes
2.5. Prep	paration of solid samples
2.5.1.	Adsorption of materials
2.5.2.	Dyeing of cotton linters
2.6. Gro	und state properties of systems
2.6.1.	Measurement of the absorption of a solution
2.6.2.	Diffuse reflectance measurement
2.7. Dete	ermination of the amount of dye present on dyed cotton linters
2.7.1.	Dyes on solid surfaces

2.8.	Fading of dyes	64
2.8	8.1. Fading of dyed cotton linters	64
2.9.	Laser Flash Photolysis (LFP)	66
2.9	0.1. Transmission mode for studying excited states in solution	66
2.9	0.2. Excitation source	69
2.9	0.3. Monitoring light source	70
2.9	0.4. Detection system	70
3. Ki	netic treatment of data	71
3.1.	Reaction of radicals with crystal violet	71
3.1	1.1. Other dyes	75
3.2.	Radical addition to alkenes	76
3.3.	Mathematical simulation	78
3.3	B.1. Determining the initial concentration of α -hydroxy radicals	79
3.3	8.2. Determination of the termination rate constant, k_1	81
3.3	3.3. Treatment of simulated curves	8 <i>3</i>
3.3	8.4. Varying the initial concentration of dye	87
3.3	8.5. Varying the initial concentration of radicals	<u>89</u>
3.3	6.6. Varying the termination rate constant, k ₁	90
3.3	7. Varying the rate constant of reaction of the dye with the radical	91
3.4.	Summary and conclusions) 2
4. Re	actions of alkenes with radicals) 6
4.1. 1	Kinetics of the reaction between Crystal Violet and radicals	97
4.2.	Determination of the addition rate constant (k _a) of the radical α^{\bullet} to alkenes.) 9
4.3.	Summary and conclusions1	12
5. Re	actions between dyes and radicals11	13
5.1.	Reaction of dyes with α -hydroxy-cyclohexyl radicals11	4
5.1	.1. Reaction of azo dyes	!5
5.1	.2. Reactions of non-azo dyes	?9

5.1.3.	Air saturated solutions	139
5.2. Read	tion of dyes with 2-hydroxy-2-propyl radicals	142
5.2.1.	Photolysis of Irgacure 2959	143
5.2.2.	Photolysis of acetone	148
5.3. Read	tion of dyes with the radicals produced by photolysis of Irgacure	819.153
5.4. Sum	mary and conclusions	
6. Reaction	on of radicals with dyes on cotton and cotton linters	160
6.1. Dete	rmining the concentration of dye on cotton	161
6.1.1.	Dyes on cotton linters	161
6.1.2.	Dyes on cotton fabric and Avicel (microcrystalline cellulose)	164
6.2. Reac	tion of dyes with radicals on wet cotton	165
6.3. Reac	tion of dyes with radicals on dry cotton.	168
6.4. Addi	tion of competing species to the samples	170
6.5. Sum	mary and conclusions	172
7. Steady	state fading of dyes	174
7.1. Fadir	ng of dyes in solution	177
7.2. Fadin	ng of dyes alone on cotton linters and Avicel	178
7.2.1.	Variation in fading rates for different dyes	179
<i>7.2.2</i> .	Effect of dye loading on fading rate	181
7.2.3.	Effect of heat on fading rate	184
7.2.4.	Fading of dyes on Avicel	188
7.3. Light	absorption by photoinitiators	190
7.4. Fadir	ng of dyes on cotton linters with adsorbed photoinitiators	193
7. <i>4.1</i> .	Addition of benzil	193
7.4.2.	Addition of Irgacure 819	194
7.4.3.	Addition of Irgacure 184	196
7.4.4.	Effect of changing the spectral distribution of irradiating light	197
7.5. Sumr	nary and Conclusions	198

.

8. Summary and suggestions for further work	201
8.1. Summary	201
8.2. Suggestions for further work	205
9. References	
10. Appendices	
10.1. Appendix 1	
10.2. Appendix 2	222
10.3. Appendix 3	
10.4. Appendix 4	

Aims and Objectives

Aims:

- To determine the percentage of photofading occurring due to reaction of the dye with radicals
- To determine the importance of a cellulosic substrate on photofading

Objectives:

- To determine the effect of steric factors on the reaction of two radicals, used as a model for possible radicals that may be formed on cellulosic substrate.
 - The difference between the two radicals was determined by studying their reactions with a selection of alkenes.
- To determine rate constants for the reaction of several dyes with the model radicals.
 - The rate constants were determined for some dyes both in methanol and on cotton fabric – In order to note any effects on the reaction of the presence of cotton.
- To investigate the steady state photofading of several dyes on cotton.
 - This was done in an attempt to find a correlation between fading rate and dye structure.

Chapter 1

Introduction

1. Introduction

1.1. Photochemical processes

Light is an important component in many processes¹. The effects of the sun's light can be both beneficial and harmful. For example, excessive exposure of skin to the sun's rays can result in skin cancer. However, life would not exist without the sun, which acts as both a source of heat and of light. Light is a vital component in photosynthesis, the process by which plants make their food. Photosynthesis is an example of what is known as a photochemical process.

A photochemical process is one in which light interacts with matter to produce a chemical change. A photochemical change can only occur when an atom or molecule absorbs a photon of light. The process of absorption of a photon involves the absorbing species gaining the energy of the photon² and becoming an excited state.

1.2. Electronically excited states

A molecule not in its ground state is said to be excited. A molecule may be promoted to an excited state by interaction with a photon (absorption of light). The interaction of visible light with a molecule usually causes the promotion of a π -electron or n-electron into a π^* orbital ($n\pi^*$ or $\pi\pi^*$ transitions).

1.2.1. Molecular orbitals

When two or more atoms combine to form a molecule, that molecule is held together by bonds. These bonds arise from electrons occupying molecular orbitals, which can be considered to be a combination of the atomic orbitals of the two adjoining atoms.

The type of molecular orbital formed depends upon the shape of the two atomic orbitals that go to form it. The two atomic orbitals form two molecular orbitals when they are combined. One of these is a bonding orbital and the other an anti-bonding orbital. In a ground state species in which there is only one bond, the bonding orbital is occupied and the anti-bonding orbital is not. If a molecular orbital is created by the combination of two s-type atomic orbitals it is known as a s σ orbital (or s σ^* orbital in the case of the anti-bonding orbital). The combination of two p-type atomic orbitals results in the production of p σ and p σ^* or p π and p π^* orbitals. The distinction between σ and π orbitals is that σ orbitals are symmetrically distributed about the bond between the two atoms and π orbitals lie above and below the plane containing this bond. Any outer atomic orbital that is not combined with an orbital from another atom is known as a non-bonding orbital, n.

1.2.2. Spin multiplicity

Most molecules in the ground state are in a singlet state, a notable exception being molecular oxygen. A singlet state has a spin multiplicity, which is related to the overall electronic spin in the molecule as shown in Equation 1.1, of one.

Spin multiplicity = 2S + 1

(1.1)

where,

S is the total spin angular momentum quantum number.

If the same number of electrons have negative spin as have positive spin, then S = 0, the spin multiplicity is one and the molecule is defined as being in a singlet state.

The spin multiplicity can also take other values. If the outer two electrons in the system are in degenerate orbitals then they will have the same spin (Hund's rule). This means that the overall spin (S) of the molecule is 1. In this case the spin multiplicity is 3, therefore the molecule is in a triplet state. Figure 1.1 shows the configuration of the outer two electrons in ground state and excited singlet and triplet states.



Figure 1.1 Ground and excited state singlet and triplets.

Free radicals, which have one unpaired electron, have ground states that are doublet states. Radicals may also have more than one unpaired electron.

1.2.3. Electronic transitions

Interaction of light with an absorbing species may cause an electronic transition. This involves the promotion of an outer electron into a higher energy orbital, which is usually an anti-bonding orbital. Electronic transitions are rapid in comparison with nuclear motion. Therefore, nuclei remain in the ground state configuration throughout an electronic transition. This is represented in Figure 1.2 and is known as the Franck-Condon principle. The most probable configuration of the nuclei is likely to change for the excited state. Structural changes, for example an increase in internuclear distance often occur following the transition.



Figure 1.2 Franck-Condon principle

1.2.4. Forbidden electronic transitions

As mentioned previously, an electronic transition can occur by absorption of radiation only if the energy of the photons is the same as the energy gap between two states of the molecule. However, this is not the only requirement for a transition to take place. The differences between the two states need to be such that interaction with a photon can induce the necessary changes in all the properties. This leads to selection rules and transitions can be classified as being allowed or forbidden.

An example of a forbidden transition is one in which a singlet state is transferred to a triplet state and the spin of the molecule changes. The photon interacting with the singlet molecule does not possess any spin and therefore cannot change the spin of the electron that is excited.

However, forbidden transitions do take place. Spin forbidden transitions can occur due to the fact that singlet and triplet states are not entirely pure. A singlet state has a small amount of triplet character and a triplet state has a small amount of singlet character³. This mixing of spin states is known as spin-orbit coupling. A spin forbidden transition will occur due to spin-orbit coupling, but it is far less probable than a fully allowed transition.

1.3. Relaxation of electronically excited states

An excited state may decay, losing its excess energy via many different processes. These processes may be due to spontaneous decay of the excited state, which are known as intramolecular processes. The possibility also exists for the excited state to lose this energy via interaction with other species in the system (intermolecular processes). These processes can be classified as radiative or non-radiative in nature. Radiative relaxation involves the emission of a photon to lose excess energy. Nonradiative processes involve the conversion of electronic energy into vibrational energy.

1.3.1. Intramolecular processes

A state diagram may be used to represent the electronic states of a molecule. Figure 1.3 shows a typical state diagram. The spin multiplicity of the system is represented by placing singlet states on the left of the page and triplet states on the right.





If a molecule is excited from its singlet ground state (S_0) into a higher singlet state (e.g. S_1) then the intramolecular processes that can occur are numerous:

Radiative transitions occur by loss of energy from the excited state by emission of a photon of light.

1.3.1.1. Fluorescence

 $^{1}A^{*} \rightarrow ^{1}A + h\nu$

The excited singlet state $({}^{1}A^{*})$ may lose its excess energy by emission of a photon of light. Fluorescence emission occurs between two states with the same spin multiplicity, and fluorescence is a spin allowed radiative process. The emitted photon has the same energy as the gap between the excited and ground states of the molecule. This process is usually only efficient between S₁ and S₀ states since the energy gap is often large and internal conversion, see later, can not compete successfully. For higher electronic states S_n, the energy gap between S_n and S_{n-1} is usually small and internal conversion competes with fluorescence effectively, so emission from higher singlet states is rarely seen. An exception to this is azulene, which fluorescence from its second excited singlet, S₂.

1.3.1.2. Phosphorescence

 $^{3}A^{*} \rightarrow {}^{1}A + h\nu$

An excited triplet can be formed by intersystem crossing, see section 1.3.1.5. This triplet can decay to the singlet ground state and lose its excess energy by emission of a photon of light. Phosphorescence emission occurs between two states with different spin multiplicities. This means that phosphorescence is a spin forbidden radiative process. Despite being formally forbidden, spin orbit coupling allows it to occur. The excited triplet state is longer-lived than the excited singlet state due to its decay to the ground state singlet being a spin forbidden transition. It is often necessary to lower the temperature of a sample in order to see phosphorescence emission as this decreases competing thermal deactivation processes and diffusional quenching by solvent molecules.

1.3.1.3. Thermally activated delayed fluorescence

Occasionally, the triplet may also intersystem cross, given that the energy gap is small enough for a thermally activated transition to take place, back to a lower energy singlet to occur state which may then fluoresce. If this happens it is known as delayed fluorescence and has a far greater lifetime than prompt fluorescence.

$${}^{3}A^{*} + heat \rightarrow {}^{1}A^{*} \rightarrow {}^{1}A + hv$$

Non-radiative pathways occur where electronic energy is converted into other types of energy and light is not emitted:

1.3.1.4. Internal conversion (IC) and vibrational relaxation (VR)

$$^{1}A^{*} \rightarrow ^{1}A + heat$$

Internal conversion involves the relaxation of a molecule into a lower electronic energy state without loss of energy. Electronic energy in one state is converted to vibrational energy in a lower energy state. The two states have the same spin multiplicity, and the process is a spin allowed non-radiative process. In solution or in the gas phase at normal pressures, the vibrational energy is soon lost as heat in collisions with other molecules (vibrational relaxation).

1.3.1.5. Intersystem crossing (ISC)

$$^{1}A^{*} \rightarrow ^{3}A^{*}$$

This process occurs between states of different spin multiplicities. This is a spin forbidden non-radiative process. Intersystem crossing takes longer to occur than internal conversion due to being spin forbidden. The efficiency of the process is dependent on the magnitude of the energy gap between the states. In ketones, where the gap between S_1 and T_n is small, ISC is highly efficient.

1.3.2. Intermolecular processes

In addition to loss of energy by internal decay, an excited molecule can also lose its excess electronic energy by transfer to neighbouring molecules. This transfer

proceeds via different mechanisms, which can be either radiative or non-radiative. For energy transfer to take place the vibronic levels in the donor, D, must be close in energy to the vibronic levels in the acceptor, A. Any small difference in energy between these levels can be dispersed in the solvent by rotational and translational motion. Energy can be transferred from D* to A if the excited state D* has a higher energy than the excited state A*.

$$D^* + A \rightarrow D + A^*$$

Transfer of energy from D* to A, will lead to quenching of D* by A.

1.3.2.1. Radiative energy transfer

This process involves the emission of a photon by the excited molecule. However, unlike other emission processes, the photon does not leave the system. Instead, the photon is re-absorbed by another molecule in the system to produce a new excited state. In order for this process to occur the emission spectrum of D* and absorption spectrum of A should have considerable overlap. The emission of a photon by the donor is spontaneous and is not influenced by the presence of the acceptor. Therefore, the distance separating the donor and acceptor is unimportant.

> $^{1}D^{*} \rightarrow ^{1}D + hv$ $^{1}A + hv \rightarrow ^{1}A^{*}$

1.3.2.2. Non-radiative energy transfer

Non-radiative energy transfer, as its name suggests, does not involve the emission of a photon from the excited molecule. Two basic types of non-radiative transfer, which are described below can occur.

1.3.2.2.a. Collisional (exchange) energy transfer

For this type of transfer to occur the molecules need to be sufficiently close to one another that their electron clouds overlap. This allows the exchange of electrons between the donor and acceptor molecules as illustrated in Figure 1.4. This type of energy transfer is limited by the rate at which the donor and acceptor collide. The rate of electron transfer falls off⁴ with the distance, R_{DA} , between the donor and acceptor. For this deactivation mechanism to be effective, the energy gap between the ground and exited state of D should be equal to or larger than the energy gap between the states of A. If both transitions are favourable, then the electrons move together. In some cases, one electron may move before the other forming an intermediate species.

Triplet-triplet energy transfer usually occurs via a collisional mechanism, due to the low extinction coefficient of the $S_0 \rightarrow T_1$ transition, on which the coulombic mechanism, see Figure 1.4, is dependent.



Figure 1.4 An illustration of the electron exchange transfer mechanism.

1.3.2.2.b. Coulombic (induced dipole) mechanism

This process takes place between a well-separated donor and acceptor. The donor can induce a change in the acceptor at a distance. This will only occur if there is sufficient superposition of the electronic and nuclear vibrational levels in both donor and acceptor⁵. The oscillation of the excited electron in the donor induces an oscillation in the highest energy electron in the acceptor. This will lead to the relaxation of the excited electron in the acceptor in the acceptor in a co-ordinated step. A depiction of this type of energy transfer is shown in Figure 1.5. The rate of this step is dependent on the extinction coefficient of the acceptor transition and on the probability of fluorescence by the donor, even though no emission occurs.



Figure 1.5 An illustration of the coulombic energy transfer mechanism.

1.4. Quantum yields

The efficiency of a photochemical or photophysical process, for example the breakdown of an excited molecule, I*, into two radicals, A[•] and B[•], is represented by the quantum yield. The quantum yield of production of radical B[•] can be defined as the number of B[•] radicals formed for each photon absorbed by initiator molecules.

Quantum yield for	==	no. of B [•] radicals produced
the production of B*		no. of photons absorbed by the initiator

1.5. Flash photolysis

Porter⁶ developed flash photolysis in the 1950's. The use of this technique was revolutionary, as it allowed the observation of transient species. Initially the technique was restricted to the milli-second timescale, but quickly extended to the microsecond range. The observation of fairly long-lived species was possible. Both the excitation and analysing light sources were flash lamps. Flash photolysis led to an increase in the understanding of organic photochemical reactions and photophysical processes.

The spectral and kinetic characteristics of transient species can be observed by this technique. Transient difference spectra can be obtained, which show the difference in spectral absorption of the original species and the transient species. The development of lasers in the 1960's allowed flash photolysis to be carried out on ns to fs timescales.

Flash photolysis was originally used to study the transients produced in gaseous systems or solutions. In the 1980's, this was extended to opaque samples. The transients produced in an opaque sample could be studied by monitoring the changes in the diffusely reflected analysing light^{7,8,9}. This has led to the ability to study the behaviour of dyes and other substances on cellulose⁹.

1.5.1. Light sources for flash photolysis

1.5.1.1. 'Hot' light sources

A hot light source is one that gives out light due to spontaneous emission. Arc lamps involve a potential between two electrodes in an enclosed system, or bulb. The bulb contains gas molecules, which become excited by interaction with the electrons travelling between electrodes. These excited gas molecules relax into the ground state, spontaneously emitting light. Pulsed xenon arc lamps can be used to excite samples. The xenon arc lamp, which is used in this work, contains xenon at a high pressure. The high pressure broadens the emission bands of the molecule. The broadened emission of xenon can be used to simulate sunlight.

1.5.1.2. 'Cold' light sources

A cold light source involves the stimulated emission of light. The principle of these light sources, lasers, is described below.

1.6. Lasers (Light Amplification by the Stimulated Emission of Radiation)

As previously mentioned, excited molecules may lose their excess energy through many processes including the emission of radiation. The energy jump between the excited state and ground state, ΔE , is equal to the energy of the photons emitted by the excited molecule. Let us consider a simple two-level electronic system where atoms can be in either the ground state or an excited state (Figure 1.6).

In this simple two level system there are three ways in which the system can move between the two energy levels:

Stimulated absorption

Absorption must be stimulated, as it is the result of the molecule using the energy of the incident photon to move into a state of higher energy. The photon absorbed must have the same energy as the gap between the two levels. The incident photon is consumed in this process.

Spontaneous emission

The excited molecule has excess energy, and can lose this energy, as previously mentioned, by spontaneous emission of a photon. This process does not require any external source of light and many molecules emit photons spontaneously when they are in an excited state.

Stimulated emission

Emission from the upper energy level may be stimulated by a photon of light of the same energy as the energy gap. The incident photon stimulates return to the ground state. The emission of a photon occurs when this electron returns to the ground state. The incident photon is not consumed in this process as it is in the absorption process. The photon has to be of equal energy to the energy gap between the two energy states. Interaction of the excited state with this photon leads to the emission of a further photon as the excited state is stimulated into its ground state.



Figure 1.6 Absorption and emission in a two level system.

As shown in Figure 1.6, emission of radiation can be spontaneous or stimulated and can occur in any region of the electromagnetic spectrum. Emission will only be stimulated from an excited state if the photon interacting with the excited state has the same energy as the energy gap between the two states.

The stimulating photon can go on to either stimulate further excited states into emitting photons or be absorbed by a ground state molecule. Also, the emitted photons are capable of stimulating emission from excited molecules. If there are more molecules in an excited state than there are molecules in their ground state, a population inversion exists, and the amount of light in the system can be amplified.

Stimulated emission has three unique properties which spontaneous emission does not have. These unique properties arise from the fact that the emission is stimulated by the interaction with the excited molecule with the electromagnetic field of a photon.

- It is collimated. This means that the stimulated emission travels in the same direction as that of the light that interacted with the excited state.
- It is in phase. As the emission is caused by the interaction of an oscillating electrical field, the emitted radiation will have its maximum in the same place as the stimulating radiation.
- It is of a specific wavelength. The emitted light has exactly the same wavelength as the light that stimulated its emission.

1.6.1. Population inversion

The amount of light absorbed is directly related to the proportion of atoms or molecules that are in the ground state. Also, the amount of light that stimulates emission is directly proportional to the proportion of molecules in the excited state. If fifty per cent of the atoms or molecules are in the ground state and fifty per cent in the excited state, then the probability of a photon stimulating emission is equal to the probability of the photon being absorbed.

In order to get more light energy out of a system than is put in it is necessary for there to be more molecules in the excited state than in the ground state. This situation is known as a population inversion and is essential for laser action. In two level systems a population inversion is not possible by optical pumping of the ground state. The Boltzmann distribution, Equation 1.2, demonstrates that the proportion of molecules in the excited state at equilibrium will always be lower than those in a lower energy state.

$$\frac{N_{upper}}{N_{lower}} = exp\left(\frac{-\Delta E}{kT}\right)$$
(1.2)

Therefore, before optical pumping begins there are many less molecules in the excited state than in the ground state. Optical pumping between two levels can not lead to a population inversion. This is because, when $N_{upper} = N_{lower}$, there is an equal probability of absorption or stimulated emission.

The required population inversion can be obtained by using systems with more than two energy levels. If more than two energy levels are used, then the laser transition is not the same as the transition involving the initial excitation of the molecule. There are examples of both three and four level systems in lasers that are commercially available¹⁰. Diagrammatic representations of three and four level systems are shown in Figure 1.7.

An example of a 3-level system is a ruby laser. Ruby is an aluminium oxide crystal with chromium ions present as impurities. It is the small proportion of chromium ions, which emit the light and allow ruby to function as a laser. Neodynium lasers are 4-level systems. The system is optically pumped by wavelengths around 800 nm, and the laser transition emits light with a wavelength of 1064 nm. Nd³⁺ ions can be doped into silicate, phosphate or other glasses. Nd³⁺ ions can also be added as an impurity (displacing Y^{3+}) to crystalline yttrium aluminium garnet (YAG). Although the doped glass lasers have a higher conversion energy input to laser output, the Nd:YAG crystalline laser is more stable to heat.



Figure 1.7 Three and four level systems.

1.6.2. Mirrors

A laser crystal, such as ruby, is a light amplifier as previously explained due to the interaction of photons with excited molecules. Once a photon leaves the laser crystal there can be no further stimulation of emission by that photon. To increase the gain of the laser, mirrors are used at either end of the laser crystal so that the light produced is continuously used to induce more emissions¹¹ (see Figure 1.8). An output is obtained, as one of the mirrors is slightly transparent. The mirrors must not be absorbing or scattering, as this will produce an unacceptable loss.



Figure 1.8 A laser crystal between two mirrors.

1.6.3. Q-switching

Q-switching is used to get a pulse of very high energy from a laser. The Q-switch is placed between the laser crystal and the output mirror. If the Q-switch is off it will prevent the laser oscillating by blocking off the light between the mirrors. While the Q-switch is off the laser material is continuously pumped^{11,12} so that a large population inversion of the activator molecules in the excited state is produced.

At some point, usually determined by a timing device, the Q-switch is turned on. This allows the light to resonate in the laser cavity as if the Q-switch were not there. The excited state activator atoms all emit within a short space of time, which produces a high power laser, pulse.

1.6.4. Frequency doubling

When light passes through a material its electromagnetic field can change the distribution and alignment of atoms¹². These changes are dependent on the energy of the incident light. If the molecules in a crystal have a dipole then the interaction with light may cause the dipole to oscillate¹¹. This dipole oscillation leads to the emission of light. The frequency of the oscillation of the dipole has harmonics, the strongest of which being the second. The oscillation dipole will emit light of the same wavelength as the incident and light with half that wavelength (the second harmonic).

The alignment of the doubling crystal is critical to the efficiency of the frequency doubling. Dispersion of oscillation energy within the crystal can cause the second harmonic to be produced out of phase with the incident radiation. This causes destructive interference of the light, which can be minimised by correct alignment of the crystal.

1.7. Diffuse Reflectance

When a beam of light arrives at a surface it can be reflected or refracted (transmitted). Reflection of light from a surface can be either specular (regular) or diffuse.

Specular reflection generally occurs from a surface into which the light does not penetrate to any great extent¹³. It involves light meeting the boundary between two

media with different refractive indices. The amount of specularly reflected light depends on the angle of the incident light, the direction of the electric field vector and the relative refractive indices of the two media. The Fresnel equations can be used to find the total amount of specularly reflected light¹⁴. Specular reflection has not been investigated here so it will not be discussed in further detail.

Diffuse reflection occurs when the incident light penetrates beneath the surface of the sample and is absorbed and scattered by the particles therein⁸. The diffusely reflected light is unpolarised and distributed symmetrically at all angles to the surface. The absorption and scattering coefficients, K and S respectively, determine the amount of diffusely reflected light.

These coefficients can be found by applying Mie theory¹⁴, considering the sample to consist of identical spherical particles. The reflecting and absorbing properties of each individual particle are calculated, and the contributions from all particles summed to obtain coefficients for the whole sample.

When light passes into an absorbing scattering sample, its intensity is reduced as when it passes through absorbing non-scattering samples. The reduction in intensity is given by the Bouguer-Lambert law¹⁵:

$$I = I_0 \exp(\varepsilon'\delta) \tag{1.3}$$

where,

 $\boldsymbol{\epsilon}'$ is the molar naperian extinction coefficient, and

 δ is the mean penetration depth



Figure 1.9 Light reflection from a diffusely scattering sample.

The effect of the sample on the incident, I(0), and generated, J(0), fluxes can be determined by considering the fraction of light which is absorbed and scattered in the sample^{13,16} The result of this consideration is shown in the following equations:

$$dI(x) = (-I(x)(K+S) + J(x)S)dx$$
(1.4)

$$dJ(x) = (J(x)(K+S) - I(x)S)dx$$
(1.5)

where,

I is the flux of the incident light, J is the flux of the reflected light, S is the scattering coefficient, and K is the absorption coefficient

Also, the measurable quantities, the reflectance and transmittance are related to the fluxes, thus:

$$R = \frac{J_0}{I_0}$$
(1.6)
$$T = \frac{I_d}{I_0}$$
(1.7)

where,

 I_d is the light intensity at a distance d from the front face of a sample of thickness d.

The reflectance and transmittance of the sample are related to the absorption and scattering coefficients. This relationship can be found¹⁴ by solving equations 1.4 and 1.5, followed by insertion of the resultant into equations 1.6 and 1.7.

The solution of these equations for an optically thick sample can be shown^{14,15} to give equations 1.8 and 1.9. An optically thick sample is one in which an increase in the value of d does not affect the reflective properties of the sample.

$$I(x) = I(0)e^{-bSx}$$
 (1.8)

$$J(x) = RI(0)e^{-bSx}$$

$$(1.9)$$

where,

$$b = \frac{\sqrt{K^2 + 2KS}}{S}$$
(1.10)

Equations 1.8 and 1.9 can be treated in many ways, depending on the assumptions made. One of the approximations is known as the Kubelka-Munk treatment. This treatment is a good approximation for the following conditions^{15,16}.

- Optically thick sample
- · Dimensions of the particles are much smaller than the thickness of the layer
- Specular reflection is comparatively small
- Incident radiation is diffuse or rapidly become diffuse on penetration into sample
- · Uniform distribution of inhomogenities

Kubelka-Munk treatment results in the following equation for the remission function, F(R):

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$
(1.11)

For an ideal diffuser it can be shown⁷ that:

$$\mathbf{K} = 2\varepsilon'\mathbf{c} \tag{1.12}$$

where,

c is the concentration of absorbing species

It is assumed for the experiments mentioned here that S is constant for all wavelengths. This approach is valid, as the particle size is much greater than the wavelength of light used (250 - 1100 nm). Therefore, there exists a linear relationship¹⁷ between the remission function and the concentration of absorber present in the sample.

1.7.1. Transient concentrations in opaque samples

In an opaque sample usually the absorbing species are distributed randomly and uniformly. This is an assumption upon which the Kubelka-Munk and other mathematical treatments are based.

Photoexcitation of the ground state absorbers leads to the production of non-randomly distributed transients. There are two limiting possibilities⁸ for the concentration profile of transients:

- Homogeneous plug profile. All the ground state absorbers are converted into transients up to a certain depth. Any deeper into the sample than this and there will be no transients present. This extreme occurs with a low concentration of ground state absorbers and a high laser energy.
- Exponential decrease with increasing penetration depth. This extreme occurs with a high concentration of ground state absorbers and a low laser energy. The equations (7) and (8) have been solved by Lin and Kan¹⁷ when K varies exponentially with x. The result of this is a converging series. They showed that kinetic analysis of transient absorption is possible for a low percentage absorption⁷. Under these conditions the change in reflectance is proportional to the transient concentration if it is less than 10%.

1.8. Cellulose

Cellulose is of vast economic importance, being used in the production of paper and textiles and to feed livestock. Cellulose is a natural, abundant polysaccharide, which is produced in the cell walls of plants. It is found in nature either in a nearly pure form, from the seeds of the cotton plant, or in combination with lignin and other polysaccharides in the cell walls of woody plants.

Wood consists of approximately forty per cent cellulose, the remainder of the cell walls being composed of a complex polymer, lignin. The production of paper involves breakdown of lignin by physical and chemical methods. The most pure natural form of cellulose is cotton, which consists of greater than ninety per cent cellulose. Cotton can be woven into fabrics, which are used widely in the textile industry.

1.8.1. Uses of cellulose

Cellulose is a natural polysaccharide, the structure of which is more fully described below, and forms a valuable source of food for herbivores. Bacteria that are present in the bowels of cows and other mammals produce cellulase, an enzyme that causes the breakdown of cellulose. Therefore, cellulose has a high nutritional value for these animals. Humans do not possess the cellulase-producing bacteria and therefore can not digest cellulose. Cellulose in the human diet is known as dietary fibre, which assists with digestion and helps to keep the bowel healthy.

Cellulose is a strong polymer both in terms of the individual macromolecular chain structure and due to the high strength of the inter-chain hydrogen bonds. It has been widely used as a construction material for many centuries, both by the plants that produce it and mankind. Cellulose obtained from plants is used in the production of paper and textiles and also in the form of untreated wood.

Paper is produced by treatment of wood involving the chemical breakdown of the lignin impurities, which involves the use of alkalis and bleaches. The specific way in which the wood is treated varies depending on the requirements of the final product. The production of paper using alkalis and bleaches can lead to partial degradation of the cellulose present in addition to the required degradation of the lignin.

Raw natural materials containing cellulose are also used to produce textiles. Once fibres are obtained from the plant, they are cleaned and then spun. Spinning involves the twisting together of several fibres to form strong threads, which are then woven into sheets of fabric. The fibres obtained from the stems of flax are used to produce linen and those from the cotton plant to form cotton fabric.

Cellulose can also be treated chemically to produce artificial cellulose-based derivatives. Cellulose nitrate, a type of cellulose ester, is produced by the nitration of cotton. Fully nitrated cellulose, or gun cotton, has been used in the past as an explosive, and partially nitrated cellulose was used in the early part of the twentieth century as a plastic. Partially nitrated cellulose is highly flammable, therefore was replaced by cellulose acetate, a non-flammable cellulose ester. Cellulose acetate is used to make transparent films, which are used in photography.

1.8.2. Structure of cellulose

The structure of cellulose is complex and consists of three structural levels: The macromolecular supramolecular and morphological structures. These structures are discussed below and further information can be found in the literature¹⁸.

1.8.2.1. Molecular structure

The structure of cellulose consists of chains of cellobiose units, the number of units depending largely on the source of the cellulose. A cellobiose unit is a glucose dimer, the two glucose units being linked by a β -glycosidic bond, see Figure 1.10.



Figure 1.10 Cellobiose unit.

Cellulose fibres, the structure of which is shown in Figure 1.11, are strong, durable and no branching of the chain occurs. The free hydroxy groups on the backbone have been found to be positioned equatorial to the six-membered ring using X-ray diffraction and NMR measurements.



Figure 1.11 Cellulose polymer structure.

In treated cellulose, carboxylic acid and carbonyl groups are often detected. The proportion of these groups is small for cotton – less than 10 mmol of these groups per kg of material. The bond angles and lengths of the β -glycosidic bonds determine the backbone conformation, which is assumed to be a linear zigzag shape.

The number of glucose units in a chain, the degree of polymerisation of the cellulose chains, varies depending on its source and subsequent treatment. Natural cotton can

contain chains with up to 12,000 units, whereas bleached cotton and wood pulp contain chains with approximately half this number of glucose units.

1.8.2.2. Supramolecular structure

The large number of hydroxy groups present on the backbone of the cellulose fibres leads to efficient hydrogen bonding between fibres. The sites at which hydrogen bonding can occur are regularly spaced throughout the chains. This regularity leads to good cohesion between chains. The hydrogen-bonding network includes all three hydroxy groups on the glucose unit. Formation of these inter-fibre bonds determines the strength of the material. The order of the macromolecules is not uniform throughout the structure and regions of high crystalline order are interspersed with less ordered regions. This bonding can lead to the formation of either crystalline or amorphous structures; the proportion of these two structures depends on the source of the cellulose.

1.8.2.3. Morphological structure and pore structure

The morphology of cellulose exists as a well-organised aggregation of fibrillar elements. Natural and regenerated types of cellulose have different morphological structures. Microfibrils have a diameter in the range 2-20 nm and the macrofibrils formed by their aggregation have a diameter in the range 10-50 nm. The aggregation of microfibrils leads to the formation of larger fibrils, macrofibrils, which are then aligned parallel and densely packed to form a helix spiral in the case of cotton. The fibre is composed of layers of differing thickness.

In addition to the fibril arrangements there is a system of pores and capillaries, which are random in their size and shape. The total pore volume and average pore size can be determined, but information is not available about the size distribution or the shape of pores. Information about average pore size can be obtained by using small angle X-ray scattering for small pores and mercury porosimetry for larger pores and also by size exclusion chromatography.

Total pore volume and pore size distribution are affected by swelling and drying treatments of samples. Drying of cellulose can lead to irreversible reduction of the
pore size. Interfibrillar swelling in liquids such as water and methanol leads to an increase in the pore volume, which can be preserved by drying techniques, such as freeze-drying.

The volume of pores as a percentage of the volume of the cellulose differs depending on the source and treatment of the cellulose samples. The surface area of these pores can be determined by the sorption of either inert gases or water. It has been found by these methods that the pores in amorphous regions of cellulose have a larger internal surface area than the crystalline regions.

1.8.3. Other species within cellulose

As previously mentioned, natural forms of cellulose are often mixed with other polysaccharides. Other foreign components, which include metal cations such as iron and calcium, are also found in the raw cellulose products. The presence of these cations can cause problems in the spinning processes of threads.

The adsorption of species to cellulose depends on the availability of groups on the inner surface. Water is able to penetrate into the amorphous regions and destroy weak hydrogen bonds holding these regions together. It has been shown by D_2O exchange experiments that water can not penetrate into the crystalline regions of cellulose¹⁹. Cellulosic fibres have a high affinity for water due to hydrogen bonding between the water and hydroxy groups on the cellulose backbone. This affinity leads to cellulose readily absorbing moisture from the atmosphere and being readily wetted. Fibres of cellulose undergo swelling on saturation with water. Swelling involves fibres becoming shorter and fatter and leads to an increased strength of the fibres²⁰.

1.8.4. Cellulose radicals

As shown in Figures 1.10 and 1.11 the backbone of cellulose contains many hydroxy groups and radicals can be formed on the cellulose backbone by abstraction of hydrogen as outlined below. The site of this abstraction will depend on the strength of the bond linking the hydrogen to the cellulose backbone. If we consider a glucose unit in the polymer chain, the weakest C–H bonds are expected to be those alpha to a hydroxy group for reasons explained later, as shown in Figure 1.12. The abstraction of

these hydrogen atoms leads to the formation of α -hydroxy radicals, which are represented in Figure 1.12. Radicals formed by hydrogen abstraction from cellulose are therefore expected to be of the α -hydroxy type.



Figure 1.12 Hydrogen abstraction from cellulose backbone.

The hydrogen is likely to be abstracted from carbon atoms attached to hydroxy groups because the C–H bond is expected to be weaker for these hydrogens. The strength of the central C–H bond in propane and 2-propanol, shown below²¹, gives evidence for this view.

Bond involved	ΔH / kJ mol
(CH ₃) ₂ HC–H	401
(CH ₃) ₂ (OH)C-H	381

The central C–H bond in propane is stronger than that in propanol, therefore it is likely that the hydroxy groups in cellulose reduce the strength of the bond between the α -hydrogen and the carbon atom to which they are both attached.

1.8.5. Irradiation of cellulose

The irradiation of cellulose can lead to the degradation of the polymer. This is characterised by a change in the light absorption by the polymer, which is known as yellowing. Yellowing is thought mainly to be due to the photooxidation of the cellulose. This is reinforced by the finding²² that yellowing is more pronounced in the presence of oxygen.

The radiolysis and photolysis of sugars results in the production of radicals²³. ESR studies have also been carried out on irradiated cellulose. These studies found evidence²² for the formation of a number of radicals on irradiation. The addition of dyes to the system results in a wider spectral range that may cause photodegradation. It has been suggested²⁴ that the free radicals generated from the fibre go on to react with the textile azo dye present. Also, on the addition of dyes it is thought that singlet oxygen may play a role²⁵ in the cellulose photooxidation mechanism.

1.9. Dyes and pigments

Colorants can be divided into dyes and pigments. Pigments are generally insoluble in the medium in which they are applied, whereas dyes are soluble. The most important property of a colorant is the absorption of visible light, but it must also have other properties besides this to be commercially viable. The dyes must be applicable to the system that is to be coloured and have good fastness properties. Fastness to both light and water are important properties of dyes if the system to which they are applied will come into contact with light and water.

Dyes can be classified either in terms of their chemical structure or their method of application to a fibre. Those working in the dyeing industry generally use the latter classification method, whereas chemists classify dyes according to their chemical structure. There are many classes of dyes other than azo dyes despite azo dyes being the most widely used for many years. Since some of this work has involved non-azo dyes a brief overview of some studies on these dyes is given here. In this work, studies have been carried out on the photofading of a phthalocyanine dye, see section 7.2. Also, the reaction rates of several non-azo dyes with α -hydroxy-cyclohexyl radicals have been determined, and are described in section 5.1.

1.9.1. Application of dyes to fibres

Several methods of applying a dye to a fibre can be used. These vary depending on the properties of the fibre and the dye to be used and also on the final method of use of the dyed product.

1.9.1.1. Disperse, ionic and Vat dyes

Disperse and ionic dyes are usually applied to fibres other than cellulosics. Therefore, these dyeing methods have not been applied in this work. The most common application of disperse dyes is to polyester. This can be carried out using a high temperature in a pressurised vessel. Under these conditions it is possible for the dye to enter the structure of the polyester. Once this has been achieved, the wet fastness of the dyed polyester is high due to its hydrophobic structure. Ionic dyes interact with charged groups on the fibre to which they are applied. These dyes can be applied to wool, nylons and acrylics.

Vat dyes can be applied to cellulosic materials although this has not been done in this work. A vat dye is applied to the fibre in the following way. The dye is originally insoluble in water, but can be solubilised by addition of sodium sulphite. It is then possible for the dye to enter the polymer. The dye is then returned to its insoluble state and has high wet fastness.

1.9.1.2. Direct and reactive dyes

Direct dyes have a high affinity for cellulosic polymers and are attached to the fibre via hydrogen bonding. Direct dyes are usually long polyazo dyes and contain sulphonic acid groups, which facilitate dissolution in water. They are applied as an aqueous solution with no need for 'the addition of' extra reagents as in the case of other dyes. The wash fastness of fibres dyed with direct dyes is often low. Wash fastness can be improved by the addition of finishers, which limit the diffusion of the dye in the fibres. These finishers, however, may lead to an adverse effect²⁶ on the light fastness of the dyed fibre.

Reactive dyes have groups in their structure that are capable of reacting with the cellulose. Thus chemical bonds are formed between the dyes and the fibre. The reactive group used to reactively dye cellulosics in this work was the chlorotriazinyl group. The production of a reactive dye is shown in Figure 1.13. The reaction of this grouping with the fibre is shown in Figure 1.14. Both direct and reactive dyes have been applied to cellulosic fibres in this work.



Figure 1.13 Formation of a triazinyl reactive dye.



Figure 1.14 Application of a monochlorotriazinyl reactive dye to a cellulosic fibre.

1.9.2. Chemical structure of dyes

Many synthetic dyes have a similar structure to naturally occurring dyes. For example, phthalocyanines have a similar structure to porphorins, e.g. haemoglobin and chlorophyll. Alizarin is a natural dye with an anthraquinone structure, synthetic dyes with similar structures are an important class of dyes. Indigo, which is a naturally occurring dye, is still used today but is now manufactured synthetically. The first synthetic dye, Mauveine²⁷, which was produced by Perkin in 1856, was an azine dye. The most common type of dye used today, which was studied in this work is the azo dye. Azo dyes have no natural counterparts.

1.9.3. Azo dyes

Organic azo dyes absorb in the visible due to the presence of a low lying $^{1}(n\pi^{*})$ state. The spectral position of this state is dependent on the groups attached to the azo group. The intensity of the transition, and therefore the observed colour, is generally greater for cis isomers than the trans isomers. Substituted aromatic azo compounds are widely used as dyes.

Emission from azo compounds is not usually observed, and neither is absorption or emission from excited triplet states except in a few cases where the molecule is highly substituted^{28,29}. Discussions of many spectroscopic properties exhibited by azo compounds can be found in the literature³⁰.

The most widely studied of the properties of azo compounds are those of cis-trans isomerisation and photodecomposition, which are discussed here.

1.9.3.1. Cis-trans isomerisation of azo compounds

Azo compounds are known to undergo cis \leftrightarrow trans isomerisation, the rate of which is dependent on the structure of the compound and the viscosity of the media. The cis \leftrightarrow trans isomerisation of a simple aromatic azo compound is shown in Figure 1.15. This phenomenon and the effect of many factors on it has been investigated over many years and by many workers³¹⁻³⁵.



Figure 1.15 Cis-trans isomerisation of an azo compound.

The mechanism of cis \leftrightarrow trans isomerisation has also been studied widely and been the subject of much discussion³⁶⁻³⁹. It has been suggested that the cis \rightarrow trans isomerisation may proceed⁴⁰⁻⁴³ via a hydrazone form, which is described in the following section. Cis \leftrightarrow trans isomerisation is also well known for the C=C group³⁷, for example in stilbenes⁴³ and fumaronitrile⁴⁴.

1.9.3.2. Azo-hydrazone tautomerism

Azo compounds containing a hydroxy group ortho or para to the azo group, may exist as two tautomers. These tautomers are the azo and hydrazone forms and are depicted in Figure 1.16 for a simple aromatic azo compound. Azo-hydrazone tautomerism is of interest due to the differing properties of the two tautomers⁴⁵. The nature of the medium and the substituents play an important role in determining the position of the azo-hydrazone equilibrium. The hydrazone form is dominant for compounds that contain electron-withdrawing substituents⁴⁶. Aryl-azo-naphthols exist primarily in the hydrazone form in most solvents^{47,48}. The hydrazone tautomer is known to be an intermediate in the thermal cis-trans isomerism of hydroxy azo compounds^{49,50}. The hydrazone tautomer has also been found to be more susceptible than the azo tautomer to reaction with singlet oxygen^{51,47}. Studies of the azo-hydrazone tautomerism of azo compounds can be found in the literature⁴¹.



Figure 1.16 Azo-hydrazone tautomerism of an azo compound.

1.9.4. Photodegradation of dyes

The understanding of photodegradation mechanisms is important since the fading of clothing dyes due to sunlight is a noticeable problem. The photodegradation of dyes

has been studied by many workers, and several reviews on these studies can be found in the literature⁵²⁻⁵⁶. Azo dyes undergo permanent discoloration via both oxidative and reductive routes⁵⁷. The fading mechanisms of azo dyes in solution have been studied extensively^{24,57,58}, but the mechanism of dye fading on cotton is not well understood. The environment in which the dye exists is an important factor determining the dominant fading pathway.

Some investigations on the photodegradation of dyes on substrates similar to cotton, e.g. cellulose acetate films, have been carried out⁵⁸⁻⁶¹. Studies of photodegradation have also been carried out⁶²⁻⁶⁵ on substrates used to model other fibres. Films are often used as a model for fibres due to their transparency, which facilitates optical measurements. Many workers⁶⁶⁻⁷⁵ have investigated the effect of the substrate nature on photodegradation of dyes. The presence of a substrate was invariably found to increase the rate at which photofading occurred. The effect of substrate varied depending on the type of dye used, these effects are discussed in the review paper by Tennett et. al.⁶⁶, where proposed mechanisms are also given.

Other environmental factors also influence the rate and mechanism of photodegradation. It has been found that the presence of water leads to an increased rate of fading⁷⁶⁻⁸¹. Histidine has been used in several studies as a model for perspiration and has been found to increase the fading rate⁸²⁻⁸⁴. Residual washing powder on dyed fabrics has been found to increase photodegradation, but it is unclear which components of the washing powder are responsible^{76,85-87}.

The chemical⁸⁸⁻⁹¹ and physical^{92,93} nature of the dye also affects the photodegradation pathway. It has been found that dyes tend to have higher stability at high concentrations^{72,73,94}, when aggregation occurs. The nature of the dye-fibre bond has also been found to influence the photofading rate^{67,69,76,95,96}.

The fading⁹⁷⁻¹⁰¹ and other photochemical properties¹⁰²⁻¹⁰⁶ of non-azo dyes has been studied, but is only briefly considered in this work. The fading of azo dyes has been studied in this work because this class of dye is the most commonly used to dye textiles. A short review of photooxidation and photoreduction processes occurring in azo dyes is given below.

1.9.4.1. Photooxidation

Photooxidation of azo dyes has been widely studied¹⁰⁷ and is thought to be due in many cases to reaction with singlet oxygen. Molecular oxygen exists as a triplet in its ground state. Singlet oxygen, an excited state of molecular oxygen, can be formed by energy transfer from a sensitiser in its triplet state, as displayed in Equations 1.15 and 1.16. Singlet oxygen is a highly reactive species and is important in the photooxidation of organic dyes.

$$^{1}S \xrightarrow{hv} {}^{3}S^{*}$$
 (1.13)

$${}^{3}\mathrm{S}^{*} + {}^{3}\mathrm{O}_{2} \longrightarrow {}^{1}\mathrm{S} + {}^{1}\mathrm{O}_{2}^{*}$$
 (1.14)

Reactive quenching of singlet oxygen by the dye^{108,109} has been shown to occur, resulting in the oxidation of the dye. The hydrazone form of an azo dye has been found to be a more effective singlet oxygen quencher, and dyes that exist predominantly in the hydrazone form are found to be more susceptible to photooxidation^{110,111}. Incorporation of known singlet oxygen physical quenching groups into the structure of the dye leads to an increase in photodegradation¹¹², due to an increase in the reactivity of the dye with radicals. The quenching of singlet oxygen by dyes has been shown to occur both in solution and when then dyes are adsorbed onto microcrystalline cellulose¹¹³.

The oxidation of azo dyes has also been found to occur via electron transfer from the dye into the conduction band of a semiconductor¹¹⁴⁻¹¹⁶. These studies were carried out in an attempt to solve the problem of dyes in waste water from factories.

1.9.4.2. Photoreduction

It is thought that radicals play an important role in the photoreduction of azo dyes on cotton^{23,58}. It has been shown that simple radicals, for example ketyl radicals¹¹⁷⁻¹²⁰, can reduce azo dyes. This results in the production of hydrazyl radicals^{121,122}, which have been detected by EPR¹²³ and Laser Flash Photolysis (LFP)¹²⁴. These hydrazyl radicals can then break down via N-N fission, see Figure 1.17, resulting in the formation of amines¹²⁵⁻¹²⁷.



Figure 1.17 Reduction of azo dyes.

Many workers have analysed the products formed following irradiation and found amines present in this mixture^{127,128}.

1.10. Radicals

Radicals are highly reactive species containing an unpaired electron and can be either neutral or charged.. Radical polymerisation occurs when the initial reactive species is a radical. This radical then reacts with the monomer in an addition reaction. The adduct radical formed is able to add to further monomer molecules. The chain continues growing in this way until two radicals react with each other in a termination reaction. Studies¹²⁹ have been carried out in an attempt to improve the efficiency of radical photopolymerisation. In this work, radicals have been created in the same way as for the initiation of polymerisation.

1.10.1. Radical production

A photoinitiator must be able to absorb light in order to be promoted into an excited state¹³⁰. Once the excited state of the photoinitiator has been formed it can decay by intramolecular processes, quenching reactions or breaking down into a reactive species. A radical photoinitiator produces a radical (\mathbb{R}^{\bullet}) from a photoexcited state.

This occurs via two main processes, intermolecular hydrogen abstraction or intramolecular bond cleavage³.

1.10.1.1. Production of radicals by hydrogen abstraction by a photoexcited carbonyl

The reactions of excited carbonyl compounds have been studied extensively by many workers¹³¹⁻¹³⁴. Photoexcited carbonyl compounds undergo reactions^{134,135} with other species in the system. This reaction can lead to the production of radicals^{26,136} as shown in Figure 1.18. Benzophenone and benzil are examples of this type of photoinitiator and some of the studies carried out on their reactions are listed below.



Figure 1.18 Hydrogen abstraction by a photoexcited ketone resulting in a ketyl radical derived from the ketone.

1.10.1.1.a. Photoexcitation of benzophenone

Benzophenone has long been known to undergo photoreduction in the presence of amines^{133,137,138}. The process is thought to occur, as illustrated in Figure 1.18, via hydrogen abstraction from the amine¹³⁹ or from the solvent¹⁴⁰. It has also been suggested that the ground state benzophenone can abstract hydrogen from the amine radical¹⁴¹. Triplet benzophenone is also known to react with solvent molecules¹⁴⁰ to form radicals.

The mechanism of radical formation has been the subject of considerable discussion¹⁴²⁻¹⁴⁴. Studies have even been carried out on photoexcitation of the ketyl radical¹³², the excited form of which was found to be more reactive than the lowest state. Studies of benzophenone on silica and microcrystalline cellulose⁹ found that the energy of the triplet benzophenone can be transferred to further adsorbed species, which results in the formation of a triplet. In these studies of adsorbed benzophenone, hydrogen abstraction from the excited state was not found to occur.

1.10.1.1.b. Photoexcitation of benzil

The photoreactions of benzil have also been studied widely and some examples of these studies are given below. It is found that, similar to benzophenone, photoexcited benzil reacts with amines¹⁴⁵⁻¹⁴⁸ to produce a ketyl radical. This involves the abstraction of a hydrogen atom from the amine by the excited carbonyl. It has been suggested that hydrogen abstraction competes¹⁴⁹ with cleavage of the excited molecule. It has been shown that triplet benzil will also react with other species, for example the solvent¹⁵⁰.

Also, in studies of photopolymerisation initiated by benzil^{148,151,152}, it was found that triplet benzil can react with the monomer to form radicals. The mechanisms of ketyl radical formation from photoexcited benzil have been investigated and discussed¹⁵³. However, in studies of pure crystalline benzil^{154,155} no evidence of radical formation was found.

1.10.1.1.c. Photoexcitation of acetone

Acetone is a well-known ketone, which absorbs light below 280 nm. Its extinction coefficient is not very high, but it is sufficiently soluble in many solvents for this not to cause a problem. Triplet acetone¹⁵⁶⁻¹⁵⁷ and 2-hydroxy-2-propyl radicals¹⁵⁹⁻¹⁶¹ have both been observed in studies of acetone photolysis.

Both these species were found to absorb with a very low extinction coefficient above 300 nm. Therefore, the detection of either species is difficult. The triplet of acetone was found, by studies of energy transfer to a naphthalene group, to have a lifetime less than 2us.¹⁵⁶

1.10.1.2. Production of radicals by intramolecular bond cleavage of a photoexcited species

Many excited photoinitiator species (RA^{*}) break down into two or more small radicals³ when light is absorbed. The photoinitiator molecule is usually thermally stable, but may have a bond with a lower dissociation energy than the excitation energy of the triplet state. Cleavage takes place with a greater efficiency, as the triplet has a short lifetime and there is little competition between bimolecular quenching and intramolecular bond cleavage. For example, iodoketones¹⁶² undergo homolytic bond cleavage under irradiation.

Some molecules undergo bond cleavage thermally. Azobisisobutyronitrile (AIBN), the structure of which can be seen in Figure 1.19, can undergo intramolecular bond cleavage by the absorption of light (photolysis) or by heat activation (thermolysis).



Figure 1.19 Thermolysis / photolysis of AIBN.

Its instability is due to the fact that its breakdown yields nitrogen, which is extremely stable¹³¹. Other photoinitiators also yield stable products, such as carbon dioxide or carbon monoxide.

Aryl alkyl ketones and acylphosphine oxides are examples of photoinitiators that undergo intramolecular bond cleavage following excitation¹⁶³⁻¹⁷³. The quantum yield of production of radicals is high and the triplet state of these molecules, from which cleavage occurs, has a very short lifetime of less than one nanosecond^{3,170}. Examples of the way in which these photoinitiators break down are given below:



Figure 1.20 Benzoin ether bond cleavage.





1.10.1.3. Production of radicals by pulse radiolysis

Pulse radiolysis of aqueous solutions produces electrons that react with species in the solution. This reaction leads to the formation of radicals^{25,174-176}, which then go on to react with other species in solution. The reaction of radicals produced by pulse radiolysis with dyes¹⁷⁶ has been studied. In these studies, the rate constants for the reaction of the dyes with the radicals was determined, and is discussed further in chapter 5.

1.10.2. Reactions of radicals

Radicals are highly reactive species, which can react either with other radicals or non-radical species. The reactions of radicals are discussed in general below, with the specific example of 2-hydroxy-2-propyl radicals used to illustrate the reactions. The reactions of this simple α -hydroxy radical have been studied extensively due to its use as for example in polymerisation reactions.

1.10.2.1. Radical-radical reactions

Radical-radical reactions are important and must be considered in any system in which radicals are involved. These reactions are usually very exothermic with a low activation barrier. Therefore, the rate of these reactions is usually determined by the diffusion rate of the radicals. Radical-radical reactions result in either coupling or disproportionation occurring as represented in Figure 1.22 for the 2-hydroxy-2-propyl radical. These reactions can be between two identical radicals, self-termination, or between two different radicals, cross-termination.



Figure 1.22 Self-termination and cross-termination of 2-hydroxy-2-propyl radicals. Spin traps, which are stable free radicals, are used to intercept radicals^{177,178}, the stable products of whose reactions can be investigated. These spin traps, for example 2,2,6,6,-tetramethyl-1-piperidinyloxy (TEMPO) shown in Figure 1.23, can also be used to prevent degradation caused by radicals.



Figure 1.23 A stable nitroxide type radical, TEMPO.

It should also be remembered that oxygen is a bi-radical and as such is highly reactive towards radicals. This reaction leads to the formation of a peroxy radical, as shown in Figure 1.24. The peroxy radical is usually less reactive than the parent radical. The presence of oxygen in radical reactions can lead to a decreased rate of the desired radical reaction due to competition with oxygen. Figure 1.24 The reaction of the 2-hydroxy-2-propyl radical with oxygen to give a peroxy radical.

1.10.2.2. Radical-molecule reactions

It is well known that radicals add to π -systems, and this type of reaction has been thoroughly studied since it is the basis for radical polymerisation. Radical addition to a π -system depends on the strength of the π -system and of the new σ -bond. Aromatic π -systems are therefore less reactive towards radicals as the reaction will destroy the aromatic stabilisation. The studies carried out on radical addition to alkenes have shown that addition at the less substituted carbon atom of the alkene is preferable^{179,180}.

OH

Figure 1.25 The addition reaction between 2-hydroxy-2-propyl radicals and alkenes.

1.10.2.2.a. Hydrogen abstraction reactions

Radicals are also known to abstract hydrogen from compounds. For 2-hydroxy-2propyl radicals this reaction is much slower than the reactions discussed above. Peroxy radicals are less reactive than the parent radical, both in terms of the addition reactions discussed above and in terms of the abstraction of hydrogen¹³⁰.

1.10.3. Determination of radical reaction rates

Many methods are used to determine the rate of reaction of radicals¹⁸¹. The observation of the disappearance of the reacting radicals¹⁷¹, disappearance of other reacting species or the formation of adduct radicals are all possible ways of determining the reaction rate of radicals.

1.10.4. Detection of radicals

Radical reactions can be studied either directly or indirectly. Descriptions of direct and indirect methods of studying radical reactions are given below. Only optical studies have been carried out in this work. Many other methods of study are possible and have been used by other workers.

1.10.4.1. Optical detection of radicals

Direct observation of radicals via their optical characteristics is possible^{182,183}. Radicals can be observed directly by the light they absorb¹⁸⁴⁻¹⁸⁶ and in some cases by emission from the excited radical¹⁸⁷.

There are problems concerned with the detection of radicals by optical techniques. One of the problems concerning the optical observation of radicals is that characterisation is not easy. Radicals used in this study, namely α -hydroxy alkyl radicals, absorb light with a low extinction coefficient at wavelengths¹⁸⁴ below 300 nm. This makes detection difficult due to other species absorbing in the same region of the spectrum. Recently radicals have been detected and characterised by their absorption of IR radiation¹⁶⁹.

1.10.4.2. Detection of radicals by electron paramagnetic resonance (EPR) spectroscopy

Direct detection of radicals by EPR spectroscopy allows the characterisation of the structure of the radicals^{188,189}. The expected spectra can be simulated mathematically and compared to the spectra obtained.

Changing the isotopic composition of the components of the solution to be photolysed leads to a change in the isotopic composition of the radicals formed on photolysis. Radicals having different isotopic composition which are otherwise identical have different EPR spectra^{190,191} but the same optical characteristics. The change in EPR spectra on isotopic composition can be used to assist in the characterisation of radicals.

1.10.4.3. Chemically induced dynamic nuclear/electron polarisation (CIDNP/CIDEP)

This technique is used to study the radicals by looking at the polarisation of products formed by the reaction of radicals. This method, and its use alongside EPR is described in the literature¹⁹²⁻¹⁹⁴. This method has been used extensively to study the reactions of acyl phosphine oxides^{173,194}, which have been used in this work.

The photoinitiators and the radicals produced on their irradiation have been previously studied using these methods. However, EPR and CIDNP were not used in this work and are only mentioned so as to give a fuller picture as to the methods that are used to detect radicals.

Chapter 2

Experimental

2. Experimental

2.1. Materials

The materials listed in this section were chosen for the following reasons: The azo dyes were selected by structure, in order to determine how small structural changes affect their behaviour. The structures of the selected azo dyes, are shown in section 2.2.3, page 53, with the simplest structure shown first, and increasingly complex structures then displayed. The rate constants for the reaction of many of these azo dyes have been determined and this will be discussed in chapter 5 and related to the structures of these dyes.

The steady state fading of the azo dyes on cotton linters has also been studied, for which reason a number of direct and reactive dyes were chosen. The steady state fading of the more simple azo dyes and the non azo dyes (except for Reactive Blue 15) has not been studied. The non-azo dyes were selected in order to compare their reaction rate constants with those found for azo dyes. The commercial lightfastness values, taken from the colour index¹⁹⁵ for the azo dyes are all very similar (4-6 using ISO standards). This is because the dyes studied in this work were all commercially used textile dyes and as such have high lightfastness values.

A number of commercial radical photoinitiators were also chosen in order to produce radicals to react with the dyes. Three of these photoinitiators produce radicals via intramolecular bond cleavage, as described in section 1.10.1.2, page 41. By contrast, the photoinitiator benzil produces radicals by hydrogen abstraction from a secondary species, as shown in section 1.10.1.1, page 40.

The alkenes were selected as their reactions with radicals has been studied previously¹⁹² and a wide range of rate constant values for their reactions has been found. It was thought that using these alkenes, the difference between the reactivity of two radicals could be determined.

The nitroxide radical, 4-hydroxy TEMPO, was chosen to intercept radicals and interupt their reaction with the dyes. This was chosen as similar species are used commercially to prevent photoreactions.

2.1.1. Azo Dyes

Name	Supplier
Direct Red 75	Aldrich
Direct Red 80	Aldrich
Orange II (Acid Orange 7)	Aldrich
Disperse Orange 3	Aldrich
Reactive Black 5	Aldrich
Orange I	Aldrich
Procion Orange MX-2R	Kemtex
Procion Orange H-ER	Kemtex
Reactive Red 120	Unilever
Reactive Red 3	Unilever
Direct Green 26	Unilever
Orange G	Unilever
Amaranth	Aldrich
Red MX	Unilever
Solophenyl Red 4G	Ciba

2.1.2. Non-azo dyes

Name	Supplier
Crystal Violet	Aldrich
Brilliant Green	Aldrich
Azure B	Aldrich
Methylene Blue	Aldrich
Safranine O	Aldrich
Basic Blue 3	Aldrich
Acid Green 25	Aldrich
Solvent Blue 35	Aldrich
Indocyanine Green	Aldrich
Reactive Blue 15	Unilever

2.1.3. Photoinitiators

Name	Supplier
Benzil	Aldrich
1-hydroxy-cyclohexyl-phenyl ketone (Irgacure 184)	Ciba
bis(2,4,6-trimethylbenzoyl)- phenyl phosphine oxide (Irgacure 819)	Ciba
2-hydroxy-2-methyl-1- phenylpropanone (Irgacure 2959)	Ciba

2.1.4. Other materials

Name	Supplier
Methanol	Aldrich (spectrophotometric grade)
Isopropyl alcohol	Aldrich
Acetone	Aldrich
N,N-dimethyl formamide	Aldrich
cotton linters	Fluka
fumaronitrile	Aldrich
1,1-diphenylethylene	Aldrich
dimethyl maleate	Aldrich
Acrylonitrile	Aldrich
Styrene	Aldrich
Methyl methacrylate	Aldrich
Methacrylontrile	Aldrich
Cotton	Unilever
4-hyroxy-TEMPO	Aldrich

2.2. Chemical structures of materials

2.2.1. Photoinitiators



Irgacure 184

Irgacure 2959



Irgacure 369

Irgacure 819

2.2.2. Alkenes



N

Fumaronitrile



Acrylonitrile



Methacrylonitrile

Dimethyl maleate



Methyl methacrylate

2.2.3. Mono-azo dyes





Disperse Orange 3



Orange I



Amaranth

Orange G







Red MX

53













2.2.4. Poly-azo dyes



Procion Orange HER



Solophenyl Red 4G



Reactive Red 120





2.2.5. Non-azo dyes



Acid Green 25



Solvent Blue 35





Reactive Blue 15

2.3. Removal of oxygen from solutions

It was often desirable to remove oxygen from samples due to the sensitivity of radicals to oxygen. Oxygen was removed in two distinct ways, which are described below.

2.3.1. Nitrogen bubbling

The sample was sealed with a rubber suba-seal, fitted with inlet and outlet syringe needles. Nitrogen was passed into the solution through one of these needles. The solution was saturated with nitrogen, thus removing the oxygen present. The needles were then removed and the sample remained oxygen free for approximately one hour. However, for these experiments, the solution was flashed once and then discarded so the time during which the solution is kept oxygen free was not considered.

2.3.2. Degassing

Degassing involves the removal of air from the system using a vacuum pump. The air is removed using three or more freeze-pump-thaw cycles. The solution is frozen in liquid nitrogen and the air is then 'sucked' out of the sample using a vacuum pump. The frozen solution is then isolated from the pump and thawed. The air dissolved in the solution is then released into the surrounding vacuum. The sample is again frozen, subjected to the vacuum pump and thawed. This cycle continues until there is no change in the pressure in the sample container. The solution is then closed off with a vacuum tap and the vacuum can last for in excess of 24 hours.

2.4. Purification of dyes

The commercial dyes used are typically only about forty percent dye. The remainder of the material consists of water-soluble salts to help with the dyeing process. When dyeing the cotton linters, the un-purified dyes were used. The impurities in the system were rinsed away due to their high water solubility.

For experiments carried out in solution it is necessary that the dyes are pure. Therefore, the following purification procedure was employed. A small amount of the impure dye was dissolved in dimethyl formamide (DMF) and heated to 40°C then filtered to remove the insoluble salt impurities. The DMF was then partially evaporated, and the crystals formed were rinsed with isopropyl alcohol.

2.5. Preparation of solid samples

Solid samples were prepared either by adsorbing material to the surface or, in the case of some dyes, by dyeing the solid. These methods are described below.

2.5.1. Adsorption of materials

Both cotton fabric and cotton linters have had materials adsorbed to their surface during these studies. A solution of the adsorbate was added to the substrate and the solvent allowed to evaporate slowly. The solvent used for this adsorption process was usually methanol. Methanol is a good swelling agent for cotton, so the adsorbate can penetrate into the sample.

All of the adsorbates used, except direct Green 26, were sufficiently soluble in methanol. Direct Green 26 was added to cotton or cotton linters as an aqueous solution. Water is a better swelling agent than methanol so it is possible for direct Green 26 to penetrate into the sample.

2.5.2. Dyeing of cotton linters

The rate of fade of these adsorbed dyes in a wet state cannot be determined as the dyes are highly soluble in water. An accurate study of their light fastness in the wet state could not be made, because they can be rinsed off the cotton.

Therefore, it was clearly necessary to fix the dyes onto the cotton linters in a more permanent way so that no physical removal of the dye was possible. Two types of dyeing method were used for the two different dye types. These two methods, for direct and reactive dyes, are described below.

2.5.2.1. Direct dyeing

Direct dyes attach to the cotton via hydrogen bonding with the hydroxy groups on the surface. The un-purified dye was mixed with the cotton linters, water and sodium sulphate at 40°C. Once mixing was complete the temperature was raised to 100°C and kept at this temperature for 1 hour. The dyed cotton linters were then filtered and rinsed.

2.5.2.2. Reactive dyeing

Reactive dyes attach themselves to cotton linters via covalent bonds to reactive groupings on the surface, as described in chapter 1. The un-purified dye was mixed with the cotton linters, water and sodium sulphate at 40°C as before. The temperature was then slowly raised to 60°C at which point sodium carbonate was added. The temperature was then raised to 80°C and kept at this temperature for 1 hour.

All the prepared samples were rinsed with water until there was no colour visible in the water after rinsing.

2.6. Ground state properties of systems

2.6.1. Measurement of the absorption of a solution

For this type of measurement a Hewlett Packard diode array spectrophotometer, model HP8453, was used. This system measures all wavelengths of light, 190 nm -1100 nm, simultaneously. A low power light source, which is an internal component of the system, is used. This light source consists of two lamps, a deuterium and a tungsten lamp.

The sample, usually a solution in a glass or quartz cell, is placed between the light source and the detector. The light transmitted through the sample is detected. The machine is set to zero by placing the pure solvent in a cell in the sample compartment. This gives the value of I_0 and the absorbance or transmission at all wavelengths for every sample that is subsequently measured can be determined.

The spectrophotometer is connected to a computer, which displays the spectra as either absorbance or transmission. The spectra can then be saved for further analysis.

2.6.2. Diffuse reflectance measurement

2.6.2.1. Perkin Elmer Lamda Bio 40 Spectrophotometer

The diffuse reflectance of a sample was measured using a Perkin Elmer Lambda Bio 40 spectrophotometer fitted with an integrating sphere to ensure that all the diffusely reflected light is collected. As with the Hewlett Packard diode array a low intensity light source consisting of two lamps is contained within the apparatus.

The diffuse reflectance of a sample was not measured using a diode array system, instead each wavelength is measured sequentially.

The reflectance is determined as a percentage of the intensity of light reflected from a white surface. The white surface used was a sample of barium sulphate tightly packed into a 10 mm pathlength quartz cell. A quartz cell was used so that reflection can be measured below 300 nm, as glass absorbs a significant amount of light for wavelengths shorter than this.

The remission function can be determined using equation 1.13. This function can be used to determine the molar absorption coefficient of the absorbing substance. The remission function should vary linearly with the concentration of absorber, as the absorbance of a solution should. If the reflectance of the sample is low, below 10%, there is a large error associated with the remission function as only a small amount of light is detectable.

2.6.2.2. Photodiode array system

The reflected light was collected via a fused-silica bundle in contact with the entrance slit of a photodiode array system (EG & G Princeton Applied Research, Model 1235 digital grating spectrograph, gratings blazed for 300 and 500 nm, with a Model 1455 peltier cooled linear photodiode array detector and a Model 1461 detector controller) interfaced to an IBM-compatible PC.

The fading of cotton linters samples was, as will be mentioned in chapter 7, monitored by recording the reflectance spectra at intervals in the irradiation. This interupts the irradiation for the time it takes to measure the spectra. It is possible to determine the reflectance of the sample following irradiation periods during the irradiation. This was achieved by looking at reflected arc lamp light. The arc lamp beam is very powerful so it was necessary to use a number of neutral density filters. These filters block out approximately the same proportion of light at all wavelengths. The intensity of light received by the system can be recorded for a range of wavelengths over a short period of time. The data can then be displayed as light intensity versus wavelength giving time dependent spectra.

2.7. Determination of the amount of dye present on dyed cotton linters

Although a known amount of dye is added to a known amount of cotton linters, some of the dye is not dyed onto the cotton linters and is rinsed away. Therefore, the amount of dye present may be very different to what is expected. It may be useful to know what percentage of the dye has been faded during irradiation rather than simply looking at the change in reflectance. To achieve this it is necessary to be able to directly compare a F(R) value at a certain wavelength with the dye loading. This was done by preparation of samples with known amounts of dye adsorbed onto their surface.

The reflectance spectra of the samples were measured both wet and dry. The reading for the wet sample may be subject to errors due to the dye dissolving in the water. However, it was necessary to take these readings as the sample is irradiated and measured when wet. A calibration graph could then be made and the loading of dye on the dyed samples could be determined.

The molar absorption coefficient, ε , of dyes in solution can be determined easily. The concentration of the dye is varied and the absorption of each solution measured. Equation 2.1 is used, which relates the absorbance of a solution to the concentration of absorbing species. The molar absorption coefficient is constant for a particular species in a given solvent at a given wavelength. The absorption coefficients measured here are all measured in methanol and at λ_{max} , the wavelength of maximum absorption of the species.

$$\frac{I}{I_0} = 10^{-\varepsilon cl}$$

where,

 I_0 is the intensity of the radiation that has passed through a blank sample,

I is the intensity of the radiation after it has passed through the sample,

c is the concentration of the absorbing species,

l is the pathlength of the cell (the distance the light must travel through the absorbing solution) and

 ε is the extinction coefficient of the absorbing substance. This is a constant for each molecule and wavelength.

The quantity ccl is known as the absorbance of the solution.

2.7.1. Dyes on solid surfaces

For an opaque sample, the absorption coefficient can not be determined by the transmission of the sample. It must be determined instead by the light reflected from

63

(2.1)

the sample. As can be seen by equations 1.11 and 1.12, there is a linear relationship between the remission function and the concentration of absorbing species in a solid sample. The absorption coefficient of dyes on cotton and cotton linters was, therefore, determined in the following way:

When a molecule is adsorbed to a surface the mass of cotton linters and the mass of adsorbate is known. The concentration of the adsorbate can therefore be determined in units of either percentage by weight or μ mol g⁻¹. In order to determine the concentration of dye in mol dm⁻³, the more usual units of concentration, it is necessary to know the density of cotton and cotton linters. These values were not measured in this work; the values used here were taken from previous results, see Chapter 6, page163.

2.8. Fading of dyes

The fading of dyes was studied on cotton linters and in solution. The fading of dyes in solution was investigated by irradiating the solution in a cell and then at intervals during the irradiation measuring the absorption spectrum. The fading of dyes can be followed by plotting the change in absorbance at the wavelength of maximum absorption. The fading of the dyes can also be plotted as percentage fade, the percentage of dye originally present that has reacted after irradiation for time t. This is determined simply using Equation 2.2.

$$\Delta(\%) = 100 \left(\frac{A_0 - A}{A_0}\right) \tag{2.2}$$

2.8.1. Fading of dyed cotton linters

Once the cotton linters had been dyed and rinsed thoroughly, 0.08 g samples were measured into powder holders and dampened. The powder holder was then closed and immersed in a glass vessel filled with water as shown in Figure 2.1. This vessel was then placed in front of the arc lamp at a known distance. A cell with a 10 mm pathlength was filled with water and placed between the sample and the arc lamp in an attempt to filter out IR radiation, which reduced the heating of the sample. Reflectance spectra were recorded before irradiation and at intervals in the irradiation.


Figure 2.1 Illustration of the set-up used for fading of dyed cotton linters.

The fading of dyes on cotton linters is plotted as the loss of dye versus time or percentage fading versus time. Other workers, using transparent samples, have used percentage loss to quantify the fading of the dye⁵⁵. The percentage fading is easy to determine for either solutions or solid samples. Equation 2.3 shows how this is calculated for solid samples.

$$\Delta(\%) = 100 \left(\frac{F(R)_0 - F(R)}{F(R)_0} \right)$$
(2.3)

This type of plot can be obtained without a need to calculate the concentration of dye present. If this plot is linear, which most of the fading curves in this study are, then the gradient is hereafter known as the rate of fade.

The gradient of a plot of loss of dye versus time gives a different rate, which is here called the rate of dye loss. The rate of fade has units of s^{-1} , whereas the units of the rate of dye loss are concentration s^{-1} . The exact units will depend on the units used for the concentration of the dye. For these experiments, the units of concentration of the dye were μ mol g^{-1} . This is the number of μ mol of dye present per gram of cotton linters.

2.9. Laser Flash Photolysis (LFP)

2.9.1. Transmission mode for studying excited states in solution

LFP provides a method of monitoring excited states of a molecule which have been produced by an intense flash of laser light. The solution is placed in the path of a laser beam. An arc lamp beam passes through the solution perpendicular to the laser light and crossing the laser pulse at a point in the sample. The laser pulse, which for the lasers used here lasts for a few nanoseconds, excites the molecules in the solution. These excited molecules have different optical properties to the parent molecule, which allows them to be detected.

When a transient absorption spectrum is recorded it is necessary to look at both the emission and absorption changes due to the laser pulse at several monitoring wavelengths. To obtain a single trace four measurements need to be taken, these are listed below and a representation of the traces is shown in Figure 2.2.

- Topline Neither of the shutters is open. This gives the signal with zero analysing light.
- Baseline The Arc lamp shutter is opened and the solution is monitored in an unexcited state without any scattered light.
- Emission The laser shutter is opened but the Arc lamp shutter is closed. This gives a trace of emission by the excited state and any scattered light.
- Absorption Both the Arc lamp and laser shutters are open. The arc lamp
 monitors the sample after the laser has excited it. This trace shows the extra
 absorption of the solution due to the excited species present. This trace may be
 negative which may be due either to loss of ground state molecules that absorb at
 this wavelength or to a large emission by the excited state.



Figure 2.2 The traces recorded in LFP experiments.

These traces are then converted into a corrected trace which represents either the change in transmittance (ΔT) (or the change in reflectance (ΔR), see later). The corrected trace is obtained by using all four recorded traces as follows.

$$\Delta T = 1 - \left(\frac{A - E}{B - T}\right)$$
(2.4)

$$\Delta A = \log_{10} \left(\frac{1}{1 - \Delta T} \right)$$
 (2.5)

Therefore,

$$\Delta A = \log_{10} \left(\frac{B - T}{A - E} \right)$$
(2.6)

where,

A is the absorption trace

- E is the emission trace
- B is the baseline
- T is the topline

The set-up for measurement of diffuse reflectance changes and transmittance changes are the same except for the geometry of the systems (Figures 2.3, 2.4 and 2.5). For solids the diffuse reflectance of the sample is detected in the same way that the transmitted light is detected in solution experiments. The reflectance change, ΔR is determined in the same way as the transmission change:



Figure 2.3 The set up used to measure the change in absorbance of a solution due to laser excitation.



Figure 2.4 Representation of the change in geometry when using 1 mm cells.



Figure 2.5 The change in geometry when studying solid samples.

2.9.2. Excitation source

The excitation sources used were Q-switched Nd:YAG lasers: An HY200 Nd:YAG (Lumonics) with a pulse lasting 8 ns and a JK2000 Nd:YAG (Lumonics) with a longer pulse time of 20 ns. The fundamental output wavelength of these lasers is in the infrared at 1064 nm. This wavelength is not very useful for photochemical measurements, so the fundamental wavelength is changed in the following ways:

The 1064 nm laser beam is passed through a doubling crystal to give an output in the visible region with a wavelength of 532 nm. The doubling crystal is deuterated caesium dihydrogen arsenate. Frequency mixing of 532 nm and 1064 nm in a potassium dihydrogen phosphate crystal produces an output at 355 nm. The 532 nm output can also be frequency doubled, using an ammonium dihydrogen phosphate crystal, to achieve an output at 266 nm.

2.9.3. Monitoring light source

The monitoring light source used is a 300W xenon arc lamp (LOT Oriel). Filters are used to prevent damage to the sample. The filters most commonly used are those which cut out UV light, as this tends to be the most damaging to the samples used. The monitoring light is sent through a converging lens and directed onto the sample, so as to overlap with the laser beam. The spot of analysing light must be converged to such an extent that only the portion of the sample that has been irradiated with the laser is observed.

2.9.4. Detection system

The monochromator, into which the analysing light is directed, is connected to a photomultiplier tube (R928 Hamamatsu). A high voltage supply (Brandenburg 412B Fluke) was used to provide the accelerating voltage for the PM tube. The output voltage from the photomultiplier is directed into a digitising oscilloscope (Tektronix TDS420) with a single shot digitising rate of 4 ns/point. Each trace on the oscilloscope has 512 data points, 28 of which are pretrigger points, used to make sure that the baseline has not moved. The oscilloscope is connected, via a GPIB cable, to an IBM computer. The data is then stored and analysed on the computer.

The shutters are controlled through the computer. The triggering of the oscilloscope is achieved by reflection of the laser beam into a fibre optic cable connected to a channel of the oscilloscope. The timing unit consists of a quartz oscillation system and a series of analogue delays.

Chapter 3

Kinetic treatment of data

3. Kinetic treatment of data

In the following chapters the reactions of radicals are studied, and a brief outline of these experiments and their purpose is given below. In chapter 4, a method developed by Turro¹⁹⁶ is applied to determine the rate of reaction of radicals with alkenes using crystal violet as a probe. This method is extended to include the reaction of dyes other than crystal violet in chapter 5. The method employed makes use of certain assumptions, which are justified in this chapter.

Kinetic analysis of the reactions occurring, which were simplified by the assumptions made, has been carried out. The equations resulting from this kinetic analysis have been applied in later chapters to experimental data. These equations have been tested here by applying the same methods to simulated data.

The simulated data are presented prior to the bulk of the experimental data in order to demonstrate that the method used in the following chapters is adequate. Several assumptions were required in order to simplify the solution of the kinetic analysis and simulations were carried out to determine the validity of the method, which is based on these assumptions.

Mathematical simulations were carried out to determine whether it was possible to find quantitative rate constants using the method chosen following kinetic analysis. These simulations, see section 3.3, have shown that at least one of the assumptions made in the kinetic analysis is often incorrect. Despite these incorrect assumptions, it can be shown using the simulated data, that it is still possible to determine the rate constants quite accurately.

3.1. Reaction of radicals with crystal violet

The determination of rate constants was carried out by observation of one of the reactants involved. The reactions involved are set out below along with the kinetic analysis that was carried out.

If a radical initiator, I, is considered, the following reaction scheme can be written for its photo-induced breakdown and the subsequent reaction of radicals with the crystal violet probe. Reactions occurring:

Reaction 3.1	I $\xrightarrow{h\nu}$	$\alpha^{\bullet} + R^{\bullet}$
Reaction 3.2	$\alpha^{\bullet} + \alpha^{\bullet} \xrightarrow{k_0}$	products
Reaction 3.3	$\alpha^{\bullet} + R^{\bullet} \xrightarrow{k_1}$	products
Reaction 3.4	$R^{\bullet} + R^{\bullet} \xrightarrow{k_2}$	products
Reaction 3.5	$\alpha^{\bullet} + CV^{+} \xrightarrow{k_{c}} \rightarrow$	CV•

Where the symbols used in the equations represent the following species:

 $R^{\bullet} \rightarrow$ the benzoyl radical, $\alpha^{\bullet} \rightarrow$ the α -hydroxy radical, $CV^{+} \rightarrow$ the ground state crystal violet cation, and $CV^{\bullet} \rightarrow$ the crystal violet radical.

The following assumptions are then made in order to simplify the kinetic analysis.

Reaction 3.1 is instantaneous with respect to the other reactions.

This assumption is acceptable, because these molecules are known to breakdown in nanoseconds³. The laser pulse lasts for 8 ns; therefore, the initiator molecules will breakdown in the duration of the laser pulse. It is important that the initiator does breakdown quickly, as this means that Reaction 3.1 need not be considered in the subsequent kinetic treatment.

• R[•] does not react with CV⁺.

This assumption was validated using a phosphorus initiator, Irgacure 819, the structure of which is shown in section 2.2.1. Photolysis of this initiator is known^{167,168} to lead to the formation of benzoyl and phosphinoyl radicals. The benzoyl radical produced by this photolysis along with the benzoyl radicals formed on photolysis of the two α -hydroxy ketones, Irgacure 184 and Irgacure 2959, is shown in Figure 3.1.

It was found that photolysis of Irgacure 819 in the presence of crystal violet did not result in the formation of the crystal violet radical. Figure 3.2 shows the traces obtained at a monitoring wavelength of 405 nm following 355 nm excitation of crystal violet solutions containing different initiators. The initiators Irgacure 2959 and Irgacure 184 both produce α -hydroxy radicals on photolysis, whereas Irgacure 819 does not. Turro et. al.¹⁹⁶, using a slightly different phosphorous initiator, also demonstrated that this assumption is valid.



Figure 3.1 Benzoyl radicals produced by photolysis of various initiators.



Figure 3.2 Absence of crystal violet radical signal using Irgacure 819 as the radical precursor.

One can be confident that the benzoyl radical produced does not react with the crystal violet and that the crystal violet radical is produced only through the reaction of crystal violet with the α -hydroxy radicals produced. It follows that the crystal violet radical production can be used to monitor the reactions of the α -hydroxy radicals.

• [CV⁺] can be considered to be constant throughout the reaction.

The crystal violet cation reacts with the radicals in the system. Its concentration is, therefore, not constant throughout the reaction. However, the percentage change in the crystal violet cation concentration is not significant.

• Self-reaction of α[•] is discounted.

The concentration of the α -hydroxy radical is small. The self-termination reaction rate involves the square of this concentration, which will therefore be very small. Also, the concentration of these radicals is decreasing very quickly due to their reaction with other species in the system. Therefore, the $[\alpha^{\bullet}]^2$ term is small and rapidly decreasing and the self-termination reaction, Reaction 3.2, can be ignored.

[R[•]] is constant and is equal to [α[•]]₀.

The concentration of benzoyl radicals is considered to be constant as it is changing much more slowly than the concentration of the α -hydroxy radicals. This alone is not sufficient for this assumption to be validated. The assumption leads to Equation 3.4, which fits the data well, and thus the assumption is justified.

The above assumptions result collectively in Reactions 3.1, 3.2 and 3.4 being ignored in the following analysis.

From Reaction 3.5 the following equation can be determined:

$$\frac{d[CV^{\bullet}]}{dt} = k_{c}[CV^{+}][\alpha^{\bullet}]$$
(3.1)

and from Reactions 3.3 and 3.5:

$$\frac{\mathrm{d}[\alpha^{\bullet}]}{\mathrm{d}t} = -k_1[\alpha^{\bullet}][R^{\bullet}] - k_c[\mathrm{CV}^{+}][\alpha^{\bullet}] \qquad (3.2)$$

Integration of Equation 3.2 gives:

$$[\alpha^{\bullet}] = [\alpha^{\bullet}]_{0} \exp(-k_{obs}t)$$
(3.3)

where,

$$k_{obs} = k_1 [\alpha^*]_0 + k_c [CV^*]$$
 (3.4)

Therefore, from equations 3.1 and 3.3:

$$\frac{\mathrm{d}[\mathrm{CV}^{\bullet}]}{\mathrm{dt}} = k_{\mathrm{e}} [\mathrm{CV}^{+}][\alpha^{\bullet}]_{0} \exp(-k_{\mathrm{obs}} t)$$
(3.5)

Integration of equation 3.5 gives:

$$[CV^{\bullet}] = \frac{k_{e}[CV^{+}][\alpha^{\bullet}]_{0}}{k_{obs}} (1 - \exp(-k_{obs}t))$$
(3.6)

Each curve was found to fit reasonably well to a first order rate equation. The value of the observed rate constant, k_{obs} , can therefore be determined for each trace. The bimolecular rate constants can then be determined by plotting the observed rate constant against the concentration of one of the reacting species, crystal violet cations or α -hydroxy radicals.

3.1.1. Other dyes

The rate constants for the reaction between radicals and dyes were determined by monitoring the disappearance of the dye, see chapter 5. Reactions 3.1, 3.2, 3.3 and 3.4 are occurring as in the case of crystal violet solutions. Additionally reactions 3.6 and 3.7, below, must also be considered.

Reaction 3.6
$$\alpha^{\bullet} + dye \xrightarrow{k_d} products$$

Reaction 3.7 $R^{\bullet} + dye \xrightarrow{k_3}$ products

Reaction 3.7 is considered to be, and in section 5.3 is shown to be, much slower than

Reaction 3.6. Therefore, Reaction 3.7 is ignored along with Reactions 3.1, 3.2 and 3.4. Only Reactions 3.3 and 3.6 are considered in this analysis.

In the case of crystal violet, the overall equation, Equation 3.6, was obtained by considering the change in the concentration to be zero. Equation 3.6 relates the crystal violet radical concentration to the rate constants involved. The concentration of the crystal violet radical is equal to the change in concentration of the crystal violet cation. Therefore, Equation 3.6 can be modified to get Equation 3.7, below:

$$\Delta[CV^+] = \frac{k_c[CV^+][\alpha^{\bullet}]_0}{k_{obs}} (\exp(-k_{obs}t) - 1)$$
(3.7)

Reaction 3.6 is similar to Reaction 3.5. The following equation, which is a modified form of equation 3.7, shows how the concentration of dye changes following photolysis:

$$\Delta[dye] = \frac{k_d [dye][\alpha^{\bullet}]_0}{k_{obs}} (exp(-k_{obs}t) - 1)$$
(3.8)

where,

$$\mathbf{k}_{obs} = \mathbf{k}_1 [\alpha^{\bullet}]_0 + \mathbf{k}_d [dye] \tag{3.9}$$

3.2. Radical addition to alkenes

In the presence of alkenes, reactions 3.8 and 3.9, below, are occurring along with Reactions 3.1, 3.2, 3.3, 3.4, and 3.5. It is assumed that the reaction of the benzoyl radical with the alkene, Reaction 3.9, is much slower than the reaction of the α -hydroxy radical with the alkene, Reaction 3.8. Therefore, the assumption made for the system in the absence of alkene, that the benzoyl radical concentration does not change, can still be made despite the additional reaction, Reaction 3.9.

Also, Reaction 3.9 is expected to have little effect on the concentration of alkene, which is high to begin with, even in the case of the most reactive alkenes.

Reaction 3.8 $\alpha^{\bullet} + A \xrightarrow{k_a}$ products

Reaction 3.9 $\mathbf{R}^{\bullet} + \mathbf{A} \xrightarrow{\mathbf{k}_4} \mathbf{products}$

The alkene competes with the crystal violet for the α^{\bullet} radicals. This competition results in the increase in the rate of rise of the crystal violet radical and a decrease in the amount of crystal violet radical formed. Equation 3.10 shows this effect on the crystal violet radical rise kinetics.

The kinetic analysis of the reactions is similar to the case in the absence of alkene. The equation resulting from Reaction 3.5, Equation 3.1, is unchanged.

$$\frac{d[CV^{\bullet}]}{dt} = k_{c}[CV^{+}][\alpha^{\bullet}] \qquad (3.1)$$

Equation 3.2 is modified slightly because Reaction 3.8 must be considered along with Reactions 3.3 and 3.5. The modified form of equation 3.2, equation 3.10, is shown below.

$$\frac{d[\alpha^{\bullet}]}{dt} = -k_1[\alpha^{\bullet}][R^{\bullet}] - k_c[CV^+][\alpha^{\bullet}] - k_a[\alpha^{\bullet}][A] \qquad (3.10)$$

Integration of equation 3.10 gives equation 3.3, where k_{obs} is different to that of the integrated equation 3.2.

$$[\alpha^{\bullet}] = [\alpha^{\bullet}]_{0} \exp(-k_{obs}t)$$
(3.3)

In this case, as opposed to equation 3.4,

$$k_{obs} = k_1 [\alpha^*]_0 + k_c [CV^+] + k_a [A]$$
 (3.11)

Therefore, from equations 3.1 and 3.3:

$$\frac{d[CV^{\bullet}]}{dt} = k_{c} [CV^{+}][\alpha^{\bullet}]_{0} \exp(-k_{obs} t)$$
(3.5)

Integration of equation 3.5 gives.

$$[CV^{\bullet}] = \frac{k_{c}[CV^{+}][\alpha^{\bullet}]_{0}}{k_{obs}} (1 - \exp(-k_{obs} t))$$
(3.6)

Note: Equations 3.5 and 3.6, above, have the same form as the equations used in the absence of alkenes but the value of k_{obs} differ in each case, see Equations 3.4 and 3.11.

3.3. Mathematical simulation

Equation 3.8, above, is not calculated analytically, but merely taken from the analytical solution of the crystal violet case, Equation 3.6, which is obtained assuming that the concentration of dye does not change. The percentage change in crystal violet concentration is small so this assumption is valid, but the percentage change in the dye concentration is larger.

For the other dyes studied, the initial concentration of dye is lower than that of crystal violet. The concentration is reduced so that it is possible to detect the change in concentration of the dye, which would not be possible if the absorbance of the solution was high. Equation 3.8 needs validation to determine whether Equation 3.9 can be used to determine the rate of reaction of the dye.

This validation was carried out by simulation using the reaction equations below, Reactions 3.10, 3.11, 3.12 and 3.13, in a Matlab program.

Reaction 3.10	α	+	α	$\xrightarrow{2k_1}$	products
Reaction 3.11	α.	+	R•	$\xrightarrow{k_1}$	products
Reaction 3.12	R•	+	R•	$\xrightarrow{2k_1}$	products

Reaction 3.13 $\alpha^{\bullet} + dye \xrightarrow{k_d} products$

The equations given to the computer, Equations 3.12, 3.13 and 3.14, are based on the above mechanisms. The rate constant values, k_1 and k_d , are set at a known value. The initial concentrations of the radicals and the dye are also set at the beginning of each calculation.

$$\frac{d[\alpha^{\bullet}]}{dt} = -2k_1[\alpha^{\bullet}]^2 - k_1[\alpha^{\bullet}][R^{\bullet}] - k_d[\alpha^{\bullet}][dye] \qquad (3.12)$$

$$\frac{d[R^{\bullet}]}{dt} = -k_1[R^{\bullet}][\alpha^{\bullet}] - 2k_1[R^{\bullet}]^2 \qquad (3.13)$$

$$\frac{d[dye]}{dt} = -k_d[\alpha^{\bullet}][dye] \qquad (3.14)$$

Given these equations, the values of k_d and k_1 and the initial concentrations of the radicals and the dye, the computer calculated the concentration of each of these species at various times.

The dye concentration was varied in a similar way as it was experimentally. The concentration of dyes used in the experimental studies was in the range of 8 - 300 μ mol dm⁻³. Therefore, this was the range of concentrations used in the simulations carried out using Matlab. The initial concentration of the radicals α^{\bullet} and R[•] are always set at the same value as each other, as this would be the case in reality. In the following sections both the initial concentration of radicals and the termination rate constant, k₁ are calculated.

3.3.1. Determining the initial concentration of α -hydroxy radicals

For experiments to determine rate constants, cells with a pathlength of either 10 mm or 1 mm were used. The concentration of initiator was 8.9×10^{-3} mol dm⁻³ in the 10 mm cell and 0.108 mol dm⁻³ when in the 1 mm cell giving absorbances of 0.44 and 0.54 respectively. The initial concentration of radicals using the full power of the laser was estimated by consideration of the light absorbed by the sample. Shown here is an example of how this was estimated for solutions in 1 mm cells with values calculated for 10 mm cells in blue type.

Number of photons entering the system.

The laser was set at 355 nm with a pulse energy of 18 mJ. Using equation 3.15 it is possible to calculate the number of photons entering the system per pulse.

$$E = \frac{nhc}{\lambda}$$
(3.15)

where,

n is the number of photons entering the system per pulse

Thus,

n =
$$\frac{1.8 \times 10^{-2} \times 3.55 \times 10^{-7}}{6.62618 \times 10^{-34} \times 2.997925 \times 10^8} = 3.22 \times 10^{16}$$

There are 3.22×10^{16} photons per pulse, which is the same value regardless of the concentration of absorber.

The quantum efficiency of breakdown of both Irgacure 184 and Irgacure 2959, ϕ_I , is approximately 0.3. This approximation is based on values given by Turro¹⁹⁷ for the quantum yield of radicals from similar ketones.

The absorbance of the solution at 355 nm was 0.54

The fraction of light transmitted is $\frac{I}{I_0} = 10^{-0.54}$ The fraction of light absorbed is $1 - 10^{-0.54} = 0.71$

Therefore the number of α -hydroxy radicals produced per pulse is:

$$n_{\alpha \bullet} = n (1 - 10^{-A}) \phi_{I}$$

$$n_{\alpha \bullet} = (3.22 \times 10^{16}) \times (0.71) \times (0.3) = 6.85 \times 10^{15}$$

$$n_{\alpha \bullet} = 6.18 \times 10^{15}$$

 The radicals are produced in the volume of solution irradiated by the laser pulse. Assuming that the radicals do not move from this volume during the reaction time, the concentration of radicals can be determined.

Area of sample irradiated $= 70 \text{ mm}^2$.

Pathlength of cell = 1 mm.

Therefore, the volume of irradiation is 70 mm³ = 7×10^{-5} dm³. (7×10^{-4} dm³)

Assuming that the radical concentration is constant within this volume, with a laser power of 18mJ, $[\alpha^{\bullet}]_{0}$, is

$$[\alpha^{\bullet}]_{0} = \frac{(6.85 \times 10^{15})}{(7 \times 10^{-5}) \times (6.02 \times 10^{23})} = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$$

 $[\alpha^{\bullet}]_0 = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$

This is not strictly the case, especially for the 10 mm cell as the light is not of the same intensity at the far end of the sample as it is at the front face. This adds a large error to the calculation. The simulations described in the following sections use radical concentrations in the region 5×10^{-4} to 5×10^{-7} mol dm³.

3.3.2. Determination of the termination rate constant, k1

The termination rate constant was determined in the following way. The initial concentration of radicals was varied by attenuation of the power of the laser beam using aqueous solutions of sodium nitrite. The percentage transmission of these solutions at 355 nm was measured, and the solution was then placed in the laser beam to attenuate the light reaching the sample.

For the determination of the termination rate constant, cells with a 10 mm pathlength were used and the concentrations of Irgacure 2959 ($8.9 \times 10^{-3} \text{ mol dm}^{-3}$) and crystal violet ($7.3 \times 10^{-5} \text{ mol dm}^{-3}$) were kept constant. The time-dependent rise in absorption due to the crystal violet radical was affected by the initial concentration of radicals and therefore also by the power of the laser. This dependence is shown in Figure 3.3, together with the first order fittings of these curves. The percentage laser power was converted into initial radical concentration using the value calculated in the above section for 100% laser power. Figure 3.4 shows the linear plot of the observed rate constant versus the initial radical concentration and the laser power.



Figure 3.3 The dependence of the production of crystal violet radicals on the laser power.



Figure 3.4 The relation between the observed rate constant and the initial concentration of radicals.

A linear fit for this plot gave an equation similar to equation 3.4:

$$k_{obs}/s^{-1} = 6.2 \times 10^4 + (2.8 \times 10^9) [R^{\circ}]_0$$

Therefore, by this method it can be concluded that:

$$k_{c} [CV^{+}] = 6.2 \pm 0.3 \times 10^{4} s^{-1}$$
 and

$$k_e = \frac{6.2 \times 10^4}{7.35 \times 10^{-5}} = 8.43 \pm 0.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \text{ and that}$$

$$k_1 = 2.8 \pm 0.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

3.3.3. Treatment of simulated curves

The curves created by the program were treated in the same way as the experimental curves. This involved fitting the curves with a first order rate equation then plotting the observed rate constant values against the dye concentration values. Some of the fits were not good, but this was ignored even for the very bad fits to see the effect on the determined rate constant of very bad fits.

The plot of observed rate constant against dye concentration was fitted to a linear equation, as would be done for experimental data. The gradient of this linear fit, for experimental curves, would have been taken as the reaction rate of the dye with the radical, k_d . Here, the exact value of k_d is known, as it has been set prior to simulation. The value found for k_d by the linear fitting of the rate constant data is here referred to as the experimental rate constant, k_{exp} .

The variables are changed and the effect of these changes on the experimentally determined rate constant determined. For many of the cases, the experimentally found value, k_{exp} , was very close to the actual value of k_d . The case shown in Figure 3.5, below, gives good exponential fits and a good linear fit. The value of the experimental rate constants found for simulations where the exponential fits were very good were within 3 % of the value set for k_d .





Even for simulations in which the fits were not good, the value of k_{exp} was fairly close to the value set for k_d . For reasonable, though not excellent fits, similar to those found for most dyes in the experimental sections (chapter 5), the value of k_{exp} was within 10% of the value set for k_d . For slightly worse exponential fits, as in the case of disperse orange 3 (see page 116), the determined values were within 25% of the set value. Figure 3.6 shows the fitting of curves and determination of the rate constant for a simulation in which the fits were bad, in fact worse than the fits of any of the experimental curves. All of the fits to experimentally obtained curves were better than the fits shown in Figure 3.6. The value determined for k_{exp} using these bad fits is not very far from the true value, k_d . For the simulations in which the fits were bad, the determined rate constant was never found to be lower than the set value, k_d .



Figure 3.6 A simulation with bad exponential and linear fits in which $k_d < k_{exp}$.

3.3.4. Varying the initial concentration of dye

A decrease in the concentration of dye leads to a worse fit to a first order rate equation. This is shown in Figure 3.7, which illustrates the first order fittings for various initial dye concentrations. The other variables used by the computer for simulation are the same for all of these curves.



Figure 3.7 The effect of initial dye concentration on the exponential fit of the loss of

It can be seen quite clearly from Figure 3.7 that the fits are increasingly bad as the initial dye concentration decreases. It should also be noted that, as the concentration of dye increases, the % loss of dye increases. In the simulation in which the initial concentration of dye is 8 μ mol dm⁻³, 90% of the original dye is lost, whereas for an initial concentration of 300 μ mol dm⁻³ only 25% is lost. This is a significant percentage, which would invalidate the assumption that the percentage loss of dye is low. The fact that this assumption has been invalidated does not appear to matter, as the fit is still very good.

Also, the linear fit for the plot of observed rate constant versus dye concentration gives a value very close to the value set as k_d , and the linear fit is a good one, see Figure 3.8.



Figure 3.8 The linear fit for simulated curves that do not fit well to a first order rate equation.

3.3.5. Varying the initial concentration of radicals

An increase in the concentration of radicals leads to a worse first order fit. In general, an increase in the concentration of radicals also leads to a less accurate determination of k_d . An example is given in Figure 3.9 of the determination of the rate constant with initial concentrations of radical being 5×10^{-7} , 5×10^{-6} , 5×10^{-5} and 5×10^{-4} mol dm⁻³. It can be seen that the high concentration of radicals leads to a large error in the experimentally found rate constant.

It should also be noted, that if fits are generally bad, then the experimentally determined rate constant will be less accurate. Therefore, if the fits for experimental data are very bad then the determined rate is assumed to be less reliable. The plots of observed rate constant also tend to be less linear for a less accurate experimental rate constant.



Figure 3.9 Experimental rate constants found for simulated systems with varying initial radical concentration with the same k_d .



Figure 3.10 The effect on the curve fitting of the initial concentration of radicals.

3.3.6. Varying the termination rate constant, k1

In these simulations, the termination rate constant was varied, although for most of the experiments a value of 3×10^9 was used. This value was used because it was the value found experimentally using crystal violet, see section 3.3.2.

For one set of simulations, the value for the termination rate constant was set at 5×10^8 . The rate constant found for the reaction of the dye with the radical was more accurate for the lower termination rate constant.

3.3.7. Varying the rate constant of reaction of the dye with the radical

The variation of the rate constant of reaction of the dye, k_d , was also investigated. The rate constant of reaction of the dye varies for different dyes and also for different photoinitiators. Changing the rate constant k_d was designed to investigate if a fast and slow reaction of dyes could be distinguished. As the value of k_d increases the accuracy of the value of k_{exp} increases.



Figure 3.11 The effect of the value of the rate constant, k_d on the accuracy of the determined rate constant, k_{exp} .

3.4. Summary and conclusions

In this chapter the reactions occurring following photolysis of solutions containing photoinitiators has been considered. These photoinitiators are known to break down into two radicals following photolysis. This cleavage is known to occur in less than 1 ns³, therefore there is no need to include this cleavage in the subsequent analysis. The reaction of the radicals created with each other and other components of the solution are considered.

A probe molecule, which can be easily monitored spectrophotometrically, crystal violet, will be used in the following chapter to follow the reaction of the α -hydroxy radicals with alkenes. In the kinetic analysis, the reactions of the α -hydroxy radicals with crystal violet are considered in addition to the reactions of the radicals with other radicals.

The radicals created on photolysis of α -hydroxy ketones are benzoyl and α -hydroxy radicals. Benzoyl radicals are known to be less reactive than α -hydroxy radicals^{52,53}. Thus, the assumption was made that the crystal violet probe used does not react with the benzoyl radicals. This assumption was shown to be true by Turro et. al.¹⁹⁶ and in this work, page 73, using an acyl phosphine oxide photoinitiator.

Several other assumptions were made, which led to a simplified analysis of the mechanisms involved. These assumptions result in some of the steps in the mechanisms being ignored in the analysis. The validity of these assumptions has been discussed and justified in the case of crystal violet. By kinetic treatment of these equations it has been shown that the rate constants for these reactions can be determined. The rate constants for the reaction between α -hydroxy radicals and crystal violet, k_c, and the reaction between α -hydroxy and benzoyl radicals, k₁, can be determined using Equation 3.4.

$$k_{obs} = k_1 [\alpha^*]_0 + k_c [CV^+]$$
(3.4)

In considering addition of alkenes to the system, similar assumptions were made. These assumptions are still valid in this case. Although it is known that the alkenes react with both the α -hydroxy radicals and the benzoyl radicals, the reaction with the benzoyl radicals can be ignored due to the lower reactivity of benzoyl radicals. In the kinetic analysis only the change in concentration of the crystal violet and the α -hydroxy radicals are considered.

The reaction between the alkene and the benzoyl radicals is slow, therefore the assumption that the concentration of the benzoyl radicals is constant is not unreasonable. Also, it can be assumed that the change in the concentration of alkene due to its reaction does not affect the observed reaction of the α -hydroxy radicals with crystal violet. This assumption is valid as the concentration of alkene is high in all cases, therefore, even if the reaction with benzoyl radicals was fast there would not be a significant change in the concentration of alkene.

It is therefore possible to determine the rate constants for the reaction between these radicals and alkenes by observing the change in the crystal violet rise on addition of alkenes. By kinetic analysis of mechanisms including the reaction of α -hydroxy radicals with alkenes, Equation 3.11, below, resulted. It is therefore possible to determine the rate of reaction of these alkenes by varying their concentration.

$$k_{obs} = k_1 [\alpha^{\bullet}]_0 + k_c [CV^+] + k_a [A]$$
 (3.11)

Consideration has also been given here to the possibility of determining the rate constants for the reaction between these radicals and dyes. This was done by observing the disappearance of the dye. The same assumptions were made for the case of the dye as were made for the crystal violet probe. These assumptions led to Equation 3.9, which is a modified form of Equation 3.4.

$$\mathbf{k}_{obs} = \mathbf{k}_1 [\alpha^{\bullet}]_0 + \mathbf{k}_d [dye]$$
(3.9)

This equation is based on the assumptions made for the case of crystal violet, which include the assumption that the concentration of the dye does not change. This is not the case, therefore, simulations were carried out to determine whether the rate constant could be determined using Equation 3.9 despite the inaccuracy of assumptions made.

Numerical calculation of the kinetics of reactions has been carried out. Rate constants for the reaction between the radicals and the dyes were obtained following treatment

of the numerically simulated data using the same method as for experimental data. These calculations have shown that the value for the rate constant of reaction between the dyes and the radicals is still accurate, despite some of the assumptions being incorrect.

These simulations have shown that an incorrect rate constant tends to be larger than the actual rate constant. Therefore, if the fits are poor, the determined rate constant may be larger than the true value, but it appears that the determined value will not be lower than actual value. In simulations the determined rate constants are within 10% of the set values for reasonable fits and within 25% for fits that are poor.

It has also been found that if the initial concentration of dye is high, then a first order exponential will fit better to the data. Therefore, for experiments it is desirable to have a high concentration of dye. In experiments carried out it is necessary that sufficient analysing light reaches the detector. Therefore, the sample must be reasonably transparent. The concentrations of dye used in the experiments in Chapter 5 were such that the change in the dye concentration was as high as 50% in many cases (the absorbance of the solution was less than or close to 1).

In simulations varying the initial concentration of radicals it was found that the first order fits were poorer for a higher initial concentration of radicals. The determined rate constants were less accurate for high radical concentration. Experimentally, a high concentration of radicals could be avoided using a low laser power. A low laser power, however, would lead to smaller signals. These small signals have a larger proportion of noise and therefore any fitting of these curves could be less accurate.

Determination of the rate constants for the reaction of dyes with radicals on cotton fabric has also been carried out and these results are displayed in chapter 6. The rate constants for the reactions on cotton linters are calculated assuming that the cotton fabric behaves as a liquid solvent¹⁸³, and therefore the concentration of species in the cotton fabric can be quantified.

In experiments involving cotton, there is a large concentration of dye, which would lead to a more accurate fit. A high concentration of adsorbed photoinitiator, which is present in the samples used, will give rise to a large concentration of radicals following photolysis. A large concentration of radicals has been shown above to result in worse fits to the experimental curves and less accurate values for rate constants. The availability of these radicals is unknown, and therefore the effective concentration (i.e. those available for reaction with the dye) is also. It was hoped that the high radical cocentration would not adversely affect the cotton fabric experiments.

In general, it was found that the experimental data, treated using the same method as the simulated data, can be trusted to yield results within 25% of the true value if the exponential fits to the data curves are not excessively bad, e.g. as shown in Figure 3.6. This is not a bad percentage error as far as the determination of absolute rate constants is concerned¹⁸⁴.

Chapter 4

Reactions of alkenes with radicals

4. Reactions of alkenes with radicals

Cellulose is known to form radicals following irradiation, which lead to 'yellowing'²² and the photoreactions of dyes on cotton are thought to involve radicals. Chapter 7 shows how the photodegradation of dyes is affected by the presence of cellulose. This effect may be due to the formation and subsequent reaction of cellulose radicals.

Since α -hydroxy radicals are the types of radical most likely to result following hydrogen abstraction from cellulose, they were used as models for radicals formed from cellulose. These radicals were produced by photolysis of two α -hydroxy ketones, which are used widely as radical photoinitiators. The photoinitiators used in this study were Irgacure 184 and Irgacure 2959, the structures of which are shown in section 2.2.1 and below. Photolysis of these initiators, represented in Figures 4.1 and 4.2, results in the production of α -hydroxy radicals and benzoyl radicals in each case.



Figure 4.1 Photolysis of Irgacure 2959.



Figure 4.2 Photolysis of Irgacure 184.

In the experiments carried out here, the reaction of the α -hydroxy radicals, not the benzoyl radicals, was studied. It was hoped that, in comparing the reactivities of the two α -hydroxy radicals, the effect of extra steric hindrance on the reactions of the cyclic radical could be determined.

These radicals absorb in the UV region of the spectrum, as do the initiators and the alkenes. Therefore, it is not practical to directly detect these radicals using the laser

flash photolysis set-up. Instead, a highly absorbing probe, Crystal Violet, was used here as in work carried out by Turro et. al.¹⁹⁶, to follow the reaction of the α -hydroxy radicals.

4.1. Kinetics of the reaction between Crystal Violet and radicals

Solutions of the photoinitiator and the probe molecule, Crystal Violet, were photolysed with the frequency tripled output of a Nd:YAG laser at 355 nm. Oxygen was removed from these solutions due to the high reactivity of radicals with oxygen. The oxygen was removed either by nitrogen bubbling or degassing, both of which are described in section 2.3. For most solutions, nitrogen bubbling was sufficient. However, for the samples containing volatile components, i.e. some of the alkenes, degassing using a vacuum pump was necessary in order to avoid the evaporation of these components.

The absorption of light at 355 nm is almost all a result of absorption by the initiator, because the extinction coefficient of Crystal Violet at this wavelength is relatively small. This is illustrated in Figure 4.3, which shows the ground state absorption spectra of solutions containing Irgacure 184 and Crystal Violet.



Figure 4.3 Ground state absorption of solutions of Crystal Violet and Irgacure 184.

The above figure also shows the high absorption of Crystal Violet at its wavelength of maximum absorption. This high absorption makes it difficult to directly observe the disappearance of the Crystal Violet cation at these concentrations. The disappearance of the Crystal Violet cation due to reaction with the radicals has been monitored in these experiments, but not at its wavelength of maximum absorption. The wavelength used to determine the loss of the Crystal Violet cation was 620 nm.

The α -hydroxy radicals produced by photochemical breakdown of the initiator react with the Crystal Violet cations, CV⁺, to produce Crystal Violet radicals, CV[•]. These Crystal Violet radicals absorb visible light and can be monitored at 405 nm. Figure 4.4 shows the rise of the Crystal Violet radical at 405 nm and the loss of the Crystal Violet cation, at 620 nm. These samples both contained Irgacure 2959 (8.9 × 10⁻³ mol dm⁻³) and Crystal Violet (7.3 × 10⁻⁵ mol dm⁻³) in acetonitrile. In all experiments mentioned here, a new sample was used for each set of traces.

The first order fitting for these events is also shown. The rate of loss of the Crystal Violet is seen to be the same as the rate of rise of the Crystal Violet radical. This is consistent with the radical being directly produced from the cation. The loss of the Crystal Violet is a much smaller signal than that of the rise of the Crystal Violet radical. Therefore, in all future studies, the reaction of the Crystal Violet was monitored via the rise of the Crystal Violet radical.



Figure 4.4 Traces showing the loss of Crystal Violet and the rise of the Crystal Violet radical.
4.2. Determination of the addition rate constant (k_a) of the radical α^{\bullet} to alkenes

It has been shown in the previous chapter that the observed rate constant, k_{obs} , for the rise of the Crystal Violet radical can be related to the rate constants of reaction of the radical α^{\bullet} with the radical R^{\bullet} , k_1 , and with Crystal Violet, k_c , Equation 3.4. These rate constants can be determined by varying the concentration of either the Crystal Violet or the initial radical concentration.

$$k_{obs} = k_1 [\alpha^*]_0 + k_c [CV^+]$$
 (3.4)

The rate constant for addition of α^{\bullet} to the alkene may be obtained by varying the concentration of alkene and plotting the observed rate constant versus alkene concentration, using Equation 3.11.

$$k_{obs} = k_1 [\alpha^{\bullet}]_0 + k_c [CV^+] + k_a [A]$$
 (3.11)

Turro¹⁹⁶ used this method to determine the reaction rates of n-butylacrylate with many different radicals. Here, the method has been used to determine the rate constants for reaction of the two α -hydroxy radicals with several alkenes.

Rate constants for reactions between these radicals and alkenes are displayed below along with the linear fits of the plots of the observed rate constant versus the alkene concentration, and the values found are discussed for each alkene separately. The rise in absorption at 405 nm, due to the formation of the Crystal Violet radical is shown in Figure 4.5 for different concentrations of dimethyl maleate. These traces were fitted with a first order exponential as were the similar traces obtained for the other alkenes. These traces shown in Figure 4.5, are displayed normalised, to their maximum ΔA , in Figure 4.6, which clearly demonstrates the change in rate of the rise on addition of the alkene at the maximum absorbance change. A plot of the observed rate constant versus the concentration of dimethyl maleate is given in Figure 4.7.



Figure 4.5 Effect on the rise of Crystal Violet radical of the concentration of dimethyl maleate.



Figure 4.6 Normalised spectra from Figure 4.5.



Figure 4.7 The effect of dimethyl maleate concentration on the observed rate constant.

In the following figures, the rise traces of the Crystal Violet radical are shown for solutions containing various alkenes, along with the exponential fits for these traces. The linear plots of the observed rate constant versus the alkene concentration are also shown in these figures. The range of concentrations of alkenes used was selected on the basis of previously determined rate constants^{184,192}. The figures are organised displaying the most reactive alkene, fumaronitrile first and the least reactive, styrene, last. Although, the reaction rate constants for the reaction of these alkenes with 2-hydroxy-2-propyl radicals has been determined previously, this was repeated here in order to validate the method. Also, the determination of the reaction rate constants for both α -hydroxy radicals in the same way allows comparison of the two values. Systematic error in the method may be such that comparison of values determined by separate methods may be flawed¹⁸⁴.

It should be noted that the errors displayed in the figures below are errors for the linear fit only. The overall error on the determined rate constant is given in the summary table, page 109.





Fumaronitrile is known to be very reactive towards 2-hydroxy-2-propyl radicals^{184,192} and was assumed to also be reactive towards α -hydroxy cyclohexyl radicals. Therefore, in the experiments to determine the reaction rate constants for the reaction between this alkene and the two radicals, the concentration of alkene was kept below 5 mmol dm⁻³.

The rate of reaction of this alkene with the two radicals was found, as expected, to be close to diffusion controlled. This alkene is particularly reactive towards these

radicals due to the two electron-withdrawing cyano groups at either end of the double bond. Addition of the radical is equally likely at either end of the C=C double bond, because the molecule is symmetrical about this bond. The strong electronwithdrawing cyano group is well known¹⁹⁶ to increase the rate of reaction of the alkene with nucleophilic radicals.



Figure 4.9 The effect of the concentration of acrylonitrile on the reaction between Crystal Violet and α -hydroxy radicals.

The concentration of acrylonitrile was greater than that used for fumaronitrile in order to allow effective competition for radicals with the Crystal Violet. The concentration was set in the range of 3 to 70 mmol dm⁻³. When the concentration of acrylonitrile

was as low as 3 mmol dm⁻³, very little change in the Crystal Violet radical signal was observed. The concentration of acrylonitrile was raised as far as 65 mmol dm⁻³, at which value the amount of Crystal Violet radical produced becomes very small and is difficult to observe.

Acrylonitrile has been shown¹⁹² to be less reactive towards nucleophilic radicals than fumaronitrile, because it has only one electron-withdrawing cyano group in comparison to the two in fumaronitrile. Therefore, the reaction rate constants are expected to be less for acrylonitrile than for fumaronitrile.





Methacrylonitrile is expected to be only slightly less reactive than acrylonitrile, therefore the range of concentrations used was similar to that used for acrylonitrile. Methacrylonitrile is less reactive again, due to the presence of a methyl group not present on the acrylonitrile molecule. This methyl group is not expected to affect the reaction by steric hindrance as the reaction is expected to take place at the non-substituted end of the molecule¹⁹⁶. It is thought that this alkene reacts more slowly than acrylonitrile due to the electron-donating methyl group counteracting, to a limited extent, the electron-withdrawing effect of the cyano group.



Figure 4.11 The effect of the concentration of methyl methacrylate on the reaction between Crystal Violet and α -hydroxy radicals.

Methyl methacrylate was expected to react more slowly than the alkenes previously mentioned. It was found to be possible to raise the concentration of methyl methacrylate to almost 300 mmol dm⁻³ and still gain a signal large enough to fit.

Methyl methacrylate contains an electron-withdrawing group (methyl ester - CO_2Me), which is less electron withdrawing than the cyano group. The reaction of this alkene with the nucleophilic α -hydroxy radicals is therefore slower than the reaction of the cyano-containing alkenes. The reaction rate constants for the reaction of methyl methacrylate (CH₂=CHCO₂Me) is also smaller than the reaction rate constants for dimethyl maleate (trans-MeO₂CHC=CHCO₂Me), Figures 4.5, 4.6 and 4.7 show traces and a linear fit relating to the reaction of dimethyl maleate. The reason for this difference is similar to that given for the difference in the values for acrylonitrile and fumaronitrile.







The phenyl groups present in both diphenylethene and styrene are slightly electron withdrawing. This effect, however, is much less than the electron-withdrawing effect of the substituents previously mentioned. The reaction rate constants of these two alkenes are lower than those of the other alkenes. The rate constant for the reaction of 1,1-diphenylethene is significantly larger than that for styrene, due to its possessing two phenyl groups on the substituted carbon atom. A wide range of reaction rates was found for the various alkenes studied. This was expected and has been found by other workers^{180,184,192}.

For the experiments carried out on styrene, a high concentration of alkene was required in order to see the effect on the Crystal Violet radical rise. The rate constant for styrene was found to be 5.4×10^5 dm³ mol⁻¹ s⁻¹. This is considered to be the lower limit of rates that can be found by this method. Other methods of finding radical reaction rate constants¹⁸⁰ have different ranges that can be found accurately.





Vinyl acetate was also studied, but its reaction with the radicals was too slow to monitor using this method. Although the concentration of vinyl acetate was raised to 3 mol dm⁻³, only a very small change in the rise kinetics of Crystal Violet was noticed. This was also a problem for styrene, which required a high concentration in order to compete effectively with the Crystal Violet. Table 4.1 summarises the reaction rate constants found for the alkenes studied along with values found by other workers for 2-hydroxy-2-propyl radicals. If a probe molecule that reacted more slowly with the

108

radicals was found, then slower reactions could also be studied. A search for a probe of this nature has not been carried out.

 $k_{\alpha p}$ is the rate constant of reaction of the alkene with 2-hydroxy-2-propyl radicals, and $k_{\alpha c}$ is the rate constant of reaction of the alkene with α -hydroxy cyclohexyl radicals.

Alkene	$k_{\alpha p}$ / dm ³ mol ⁻¹ s ⁻¹	$k_{\alpha c}$ / dm ³ mol ⁻¹ s ⁻¹
Fumaronitrile	$3.1 \pm 1.0 \times 10^9$ $(1.4 \times 10^9)^{192}$	$2.3 \pm 0.9 \times 10^9$
Acrylonitrile	$\begin{array}{c} 1.1 \pm 0.4 \times 10^{8} \\ (1.1 - 1.5 \times 10^{8})^{184} & (2.2 \times 10^{8})^{192} \end{array}$	$8.3 \pm 2 \times 10^7$
Methacrylonitrile	$5.0 \pm 1.8 \times 10^{7}$ $(3.1 - 3.4 \times 10^{7})^{184} \qquad (7.7 \times 10^{7})^{192}$	$2.9 \pm 1 \times 10^7$
Dimethyl maleate	$2.9 \pm 1 \times 10^{7}$	$8.8\pm1.7\times10^6$
Methyl methacrylate	9.2 \pm 3 \times 10 ⁶ (6.2 \times 10 ⁶) ¹⁹²	$8.5 \pm 2.5 \times 10^{6}$
1,1-diphenyl ethene	$\begin{array}{c} 1.3 \pm 0.5 \times 10^{6} \\ (7.2 \times 10^{5})^{184} & (4.1 \times 10^{6})^{192} \end{array}$	$2.3\pm~0.8\times10^{6}$
Styrene	$(4 - 7 \times 10^5)^{184}$ $(4.2 \times 10^2)^{192}$	$5.4 \pm 3 \times 10^5$

Table 4.1 Rate constants of reaction of alkenes with α -hydroxy radicals in methanol.

Values found by other workers, shown in brackets in the above table, were determined using methanol¹⁸⁴ and propanol¹⁹² as solvents. These values are close enough to the values found in this work to allow the conclusion that the method used here is valid.

The difference between the values found for 2-hydroxy-2-propyl radicals and α hydroxy cyclohexyl radicals appears to be quite small. A plot of the rate constants for the reaction of both alpha-hydroxy radicals with various alkenes is shown in Figure 4.14.



Figure 4.14 The relationship between the rate constants for the reaction between alkenes and the two α -hydroxy radicals.

The linear fit shown on the above plot has a gradient of 0.76, which shows that the rate of reaction of the α -hydroxy cyclohexyl radical is slower than the reaction of the 2-hydroxy-2-propyl radical.

Attempts to relate the rate constants of the reactions of the various alkenes with each radical with the electron affinity of the alkene have been made. Given the small number of data points available from these results, it was difficult to determine this relationship. An attempt to relate the electron affinity, values for which were taken from the literature¹⁹⁸, of the alkene with the rate constant determined for its reaction with each radical is shown in the figure below. The values included in the linear fit are those found for methyl methacrylate, acrylonitrile, methacrylonitrile and fumaronitrile. Values determined for 1,1-diphenylethene are displayed in the plot, but are not included in the fits. Alkenes containing aryl groups are usually excluded from such fits due to their reactivities being affected by electron delocalisation in the transition state formed.

The values of log (k_a) for the reaction of 2-hydroxy-2-propyl found by Fischer et. al.¹⁹² are also shown for these alkenes along with the linear fit for these alkenes alone (red line) and the linear fit for these and other less reactive alkenes (black line). The linear fits shown in green and blue are those found using data obtained in this work for the reactions of 2-hydroxy-2-propyl and α -hydroxy cyclohexyl radicals respectively. Despite the gradient of these fits being significantly different to that found by Fischer et. al.¹⁹², the gradients are identical given that only values for these four alkenes is included. From this it is concluded that these two α -hydroxy radicals have identical nucleophilicity. Since both radicals are assumed to be equally nucleophilic, only their size affects their reactivity. Radicals formed on the backbone of cellulose are expected to react in a similar way to the above radicals. Their reactions are expected to be much slower due to the increased steric hindrance.



Figure 4.15 The relationship between the rate constants for reaction and the electron affinity of the alkene.

4.3. Summary and conclusions

Turro et. al.¹⁹⁶ determined the rate constant of the reaction of many radicals with nbutylacrylate. Here, the same method has been used to determine the reaction rate constants of several alkenes with two separate α -hydroxy radicals. The rate constants for the reaction of 2-hydroxy-2-propyl radicals have been determined previously by other workers using different methods. The method of determining the rate constants of reaction of these radicals with alkenes has been shown to be adequate based on the fact that the values for 2-hydroxy-2-propyl radicals are close to values found by other workers^{184,192}.

The rate constants for the reactions of the two α -hydroxy radicals vary similarly depending on the electron affinity of the alkenes, which indicates that these radicals have a similar nucleophilicity. Although efforts have been made to determine the relationship between the electron affinity of the alkene and the rate constant for the reaction, this has been found to be difficult, due to the small number of values obtained. A linear fit of alkene electron affinity versus log (k_a) gave the same gradient for both the radicals. However, the fit for the 2-hydroxy-2-propyl radical was different to that found by other workers using a greater number of values.

The rate constant values found in this work have shown that there is a significant difference in the reactivities of the two α -hydroxy radicals. This indicates that the size of the radicals hinders the reaction at the radical centre. It is possible that similar radicals on the polymer backbone of cellulose materials have a slower reactivity and that the bulk of the polymer has a significant effect. The increased size of the polymer backbone compared to the two radicals studied here may not lead to greatly increased steric hindrance as the polymer backbone may not be spatially close to the radical sites.

It is noted that it is a large leap to extrapolate this conclusion from the comparison of two small radicals. Effects other than that of blocking access to a reactive site must be considered. Radicals on a polymer backbone will not be mobile as are the radicals studied here, and therefore, the reaction rate is expected to decrease as a result.

Chapter 5

Reactions between dyes and radicals

5. Reactions between dyes and radicals

The rate constants for the reaction of dyes with radicals were determined both in methanol solution and when dyed on cotton linters, see chapter 6. These rate constants were determined using a similar approach to that for alkenes using Crystal Violet as a probe. There was no need to use a probe molecule, because the disappearance of the dye can be monitored directly. Instead of the use of a probe, the sample was monitored at the wavelength of maximum absorption of the dye, λ_{max} .

For most solutions, oxygen was removed by nitrogen bubbling. For solutions containing acetone however, this resulted in a substantial loss in the acetone from the sample due to its low boiling point. These samples were degassed using the freeze pump thaw technique as for samples containing alkenes with low boiling points. LFP of these solutions was carried out in a 1 mm pathlength cell set up at 45° to both the laser and arc lamp beams, as shown in Figure 2.4. When using a 1 mm cell, the absorbance of each solution is decreased compared to the 10 mm cell used in experiments in chapter 4. This decrease in the absorbance of the solution allows the dye concentration to be raised whilst it is still possible to analyse the solution at λ_{max} of the dye. Section 3.3 shows that an increase in the initial dye concentration leads to the dye depletion approaching first order behaviour. The closer to first order decay each trace is, the closer the rate constant found by plotting k_{obs} versus dye concentration is to the actual rate constant.

Using a 1 mm cell at 45° to the laser beam results in the absorbance of the laser light by the sample being greater than that measured on the Hewlett Packard diode array. The pathlength of the laser beam, as illustrated in Figure 5.1, through the sample is $\sqrt{2}$ mm. Therefore, the absorbance of the solution measured using the diode array equipment should be multiplied by $\sqrt{2}$ in order to obtain the actual absorbance of the laser beam by the solution.



Figure 5.1 Illustration of the increased pathlength of the cell due to its position relative to the laser beam.

5.1. Reaction of dyes with α-hydroxy-cyclohexyl radicals

The reaction of dyes with α -hydroxy-cyclohexyl radicals was studied in order to determine which factors affect the rate of the reaction. The majority of the studies involved the reaction of the α -hydroxy cyclohexyl radical as a model for cellulose radicals. In this section, only reactions of the α -hydroxy cyclohexyl radicals are considered. The reactions, in methanol solution, of both azo and non-azo dyes with this radical have been studied. The reactions of dyes with other radicals, including the 2-hydroxy-2-propyl radical, have also been studied to a limited extent, and are given in the following sections.

The α -hydroxy-cyclohexyl radicals were produced by photolysis, exciting at 355 nm, of methanol solutions of Irgacure 184, see Figure 4.2, page 96. For each solution used the concentration of Irgacure 184 was 0.108 mol dm⁻³. This concentration gave an absorbance of 0.54 at 355 nm. This means that the absorbance of the solution at 45⁰ to the 355 nm laser beam is 0.76. This absorbance rises slightly, although not significantly, on addition of dyes to the solution.

5.1.1. Reaction of azo dyes

The depletion of several azo dyes due to the photolysis of Irgacure 184 in nitrogen saturated methanol solution is shown in Figures 5.2-5.12. Again, the other radical produced is assumed to be much less reactive than the α -hydroxy-cyclohexyl radical. Therefore, the reaction rate constant of this radical with the dyes can be easily determined, which is achieved using a similar method to that used for the alkenes.

Similar assumptions were made for these reactions as were made for the Crystal Violet samples. The rate constants, k_d , are obtained in a similar way to the determination of k_a in chapter 4, using equation 3.9, which was determined in chapter 3.

$$k_{obs} = k_1 [\alpha^{\bullet}]_0 + k_d [dye]$$
(3.9)

The observed rate constant of dye depletion is plotted against the dye concentration and the gradient taken as the rate constant for reaction of the dye with the radical, k_d . Linear plots of the observed rate constant of dye depletion versus the dye concentration are shown, along with the observed depletion of the dye, in the following Figures. The data displayed in these Figures begin with the simplest dye, Disperse Orange 3, which also has the lowest rate constant of the dyes studied. Following Disperse Orange 3, other simple dyes are shown and the change in structure is related to the change in rate constant.

Disperse Orange 3 has a relatively simple structure, being a di-substituted azobenzene, the structure is shown along with the plots. This dye is not capable of azo-hydrazone tautomerism, and it is therefore the azo form that reacts with the radicals resulting in the loss of absorption of the solution. The exponential fits to the experimental data are fairly poor, therefore the determined value of k_d may be slightly higher than the true value. In chapter 3 worse fits than these have been shown to give values determined for the rate constant only a factor of two different to the set value.

Again, as with the alkene reactions, the error displayed in the figures is only the error for the linear plot. The overall error for the rate constant values is given in the summary tables, pages121, 127, 128, 138, and 157.



N=N.

NH.

Figure 5.2 The depletion of Disperse Orange 3 shown along with its structure and the linear fit used to determine k_d .

Orange I, shown below, has a slightly more complex structure. Unlike Disperse Orange 3, this dye is capable of azo-hydrazone tautomerism. It is therefore possible for the dye to exist in either the azo or hydrazone form although it is most likely to be in the hydrazone form when dissolved in methanol^{46,47}, the solvent used in this set of experiments.

Despite the difference in structure between the two dyes, Disperse Orange 3 and Orange I, the reaction rate constants determined for the two dyes are very close in value (2.5 and 2.8×10^8 dm³ mol⁻¹ s⁻¹). The exponential fits for the depletion traces of orange I were better than those for Disperse Orange 3. There may, therefore, be a difference in the reaction rate constants of the two dyes due to their differing structures, which has not been detected here.

116



Figure 5.3 The depletion of Orange I, shown along with its structure and the linear fit used to determine k_d .

The structure of Orange G differs from that of Orange I in the position of the hydroxy group, and the position of sulphonate groups in the two dyes differs. This difference in structure makes a small, but not necessarily significant difference in the rate constant. The dye with the hydroxy group in the ortho position, Orange G, has a slightly larger reaction rate constant $(3.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ than that of the dye with the hydroxy group in the para position, Orange I $(2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$.



Figure 5.4 The depletion of Orange G, shown along with its structure and the linear fit used to determine k_d .

The difference in structure between Acid Orange 7 and Orange G consists only of the position of sulphonate groups. Acid Orange 7 differs from Orange I only in the position of the hydroxy group. The rate constants for the reaction of Acid Orange 7 was found to be higher $(4.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ than the rate constants for the reaction of either Orange I $(2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ or Orange G $(3.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$. The position of the hydroxy group appears to affect the rate constants, the hydroxy group in the ortho position leading to an apparently larger reaction rate constant. It is possible that Orange G is less reactive towards the radicals than acid orange 7 due to the sulphonate groups on the naphthalene ring, which may block a route of attack for the radicals.



NaO,S

Figure 5.5 The depletion of Acid Orange 7, shown along with its structure and the linear fit used to determine k_d .

Amaranth, which has an extra benzene ring and more sulphonate groups, has a larger rate constant than the other simple dyes $(4.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ as opposed to values ranging from } 2.5 - 4.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The rate constant for Amaranth is not significantly different from the rate constant found for Acid Orange 7 $(4.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, so the difference in their structures is not thought to affect the reaction rate constants.

The comparisons made above show that there is a possible difference in the rate constants for various dye structures. However, the error on the results is a similar magnitude to the differences observed, making definitive conclusions difficult.

119



Figure 5.6 The depletion of Amaranth, shown along with its structure and the linear fit used to determine k_d .

In summary, for the simple dyes it appears that several factors can be thought of as affecting the rate constants. Firstly, the absence of a hydroxy group, and therefore ability to exist in a hydrazone form, leads to a lower rate constant possibly due to the lower reactivity of the azo form towards radicals. Hydroxy groups either ortho or para to the azo group lead to an increase in the rate constants and dyes with the hydroxy group ortho to the azo group have a larger reaction rate constant. Other factors, such as the blocking of radical attack by substituents may have an affect on the rate constant. It should be noted that the conclusions made here are based only on the limited data obtained by the study of a small number of dyes. The rate constants found for these simple azo dyes are summarised in Table 5.1.

120



Table 5.1 Rate constants for the reaction of several simple azo dyes with α -hydroxycyclohexyl radicals in methanol at 20^{0} C.

Levanon et.al.²⁰⁰ observed the formation of azobenzene radicals, which were formed by reaction of azobenzene with 2-hydroxy-2-propyl radicals formed by pulse radiolysis of aqueous propanol, by virtue of their absorption in the near UV region of the spectrum. In their work, Levanon et. al.²⁰⁰ found rate constant values of 4×10^8 dm³ mol⁻¹ s⁻¹ (in water) and 3×10^7 dm³ mol⁻¹ s⁻¹ (in neat isopropanol) for the reaction between azobenzene and 2-hydroxy-2-propyl radicals. These values are in agreement with those found here and displayed in the above table. The dyes that are shown in the following figures, procion orange MX-2R, procion orange H-ER and Reactive Red 120, are more complex than the dyes examined previously. These dyes have larger variety of groups attached to the benzene rings than the simpler dyes. Some of the dyes discussed below contain chlorotriazine groups, which allow their attachment to fabric through covalent bonds.



[Procion Orange MX-2R] / umol dm-3 23 43 $k_a = 2.9 + -0.5 \cdot 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 100 0.8 140 170 0.00 0.6 -0.02 / 10⁵ s-1 ∆A_{490 nn} 04 -0.04 0.2 150 200 0 50 100 100 200 Delay time / us [Procion Orange MX-2R] / µmol dm⁻³

Figure 5.7 The depletion of Procion Orange MX-2R, shown along with its structure and the linear fit used to determine k_d .

The structure of Procion Orange MX-2R is far more complex than that of the dyes discussed above. Despite this, the rate constant of its reaction with α-hydroxy cyclohexyl radicals is close to that found for the simple dyes. This is also the case for Direct Red 75, the rate constant for which is displayed in the Table above. The two dyes Red MX and Reactive Red 3, the structures of which are shown in the figures below, are simpler than Procion Orange MX-2R in terms of their overall structure. All three of these dyes have one azo group and contain chlorotriazinyl groups in their

structure. However, the rate constants for the reaction of the two dyes shown below are larger than those found for Procion Orange MX-2R.



 $k_d = 6.9 \pm 0.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Figure 5.8 The structure of Red MX, shown along with the rate constant of its reaction with α -hydroxy cyclohexyl radicals.



 $k_d = 6.7 \pm 1.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Figure 5.9 The structure of Reactive Red 3, shown along with the rate constant of its reaction with α -hydroxy cyclohexyl radicals.

Reactive Red 3 and Red MX have one particular structural feature in common, which is not shared with Procion Orange MX-2R. This is the position of an amino group on the naphthalene ring of the molecule. For Reactive Red 3 and Red MX the amino group is attached at the 8 position, whereas Procion Orange MX-2R has an amino group attached to the 7 position. The numbering is shown in Figure 5.10 for both the azo and hydrazone tautomers.



Figure 5.10 Azo-hydrazone tautomerism of amino-hydroxy-azo dyes showing the numbering used to define the positioning of substituents.

The position of this group clearly has a great effect upon the rate of reaction of the dyes with radicals. A possible explanation for this difference in rate may be that the dye radicals formed following reaction may be stabilised or destabilised by the position of the amino group. This same difference in rate constant was also observed in the polyazo dyes discussed below.

The following dyes are polyazo dyes and include both reactive dyes, Reactive Red 120 and Procion Orange H-ER, and a direct dye, Solophenyl Red 4G. Procion orange H-ER is effectively the dimer of Procion Orange MX-2R and a rate constant of the reaction of this dye is approximately twice that of Procion Orange MX-2R.



[Procion Orange H-ER] / µmol dm⁻³



Figure 5.11 The depletion of procion orange H-ER, shown along with its structure and the linear fit used to determine k_d .



$$k_d = 6.0 \pm 1.0 \times 10^8 \,dm^3 \,mol^{-1} \,s^{-1}$$

Figure 5.12 The structure of solophenyl red 4G, shown along with the rate constant of its reaction with α -hydroxy cyclohexyl radicals.

The rate constant for the reaction of Solophenyl Red 4G ($6.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is very close to that for Procion Orange H-ER ($5.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Both these dyes have two azo groups, but their structures are quite different in terms of the additional features in the molecule. Both Procion Orange H-ER and Solophenyl Red 4G have two azo groups attached to naphthalene rings, on which amino groups occupy the 7 position.

Similar to Solophenyl Red 4G and Procion Orange H-ER, Reactive Red 120 contains two azo groups. The amino groups on the naphthalene rings in Reactive Red 120 are attached in the 8 position. In the figure below, the structure of Reactive Red 120 is displayed, and the rate constant for its reaction with α -hydroxy cyclohexyl radicals is considerably higher than that found for Procion Orange H-ER and Solophenyl Red 4G $(1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$. This is further evidence in addition to the reaction rate constants for the reaction of the mono-azo dyes for the effect of the position of this amino group.



Figure 5.13 The depletion of Reactive Red 120, shown along with its structure and the linear fit used to determine k_d .

It is thought that reaction of the azo dyes with the radicals occurs at the azo group^{54,55}. Reactive Red 120, which is the dimer of Reactive Red 3, has a rate constant double that of the monomer $(1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as opposed to $6.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Procion Orange MX-2R and Procion Orange H-ER are also similar, and here also the dye with two azo groups reacts twice as fast as that with only one $(5.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$. The reaction rate for each pair of dyes in terms of per mole of azo groups is the same; which is consistent with the idea that the azo group is the reactive site. The values obtained for the rate constants, k_d , for the more complex azo dyes are summarised in Table 5.2.



Table 5.2 Rate constants for the reaction of several azo dyes with α -hydroxycyclohexyl radicals in methanol at 20^oC.

In work carried out by Jansen²⁰¹, the reaction of dyes, some of which have been studied here, with singlet oxygen was studied. Singlet oxygen (¹O₂), an exited state of molecular oxygen can be formed by energy transfer from many excited species. Singlet oxygen undergoes unimolecular decay and can be observed by its phosphorescence emission at 1270 nm. Decay can also occur via non-radiative processes resulting from interaction with other species, with which it may also react chemically. In the case of dye degradation resulting from the production of singlet oxygen, Jansen considered the three reactions shown below.

$${}^{1}O_{2} \xrightarrow{k_{decay}} {}^{3}O_{2}$$

$${}^{1}O_{2} + dye \xrightarrow{k_{phys}} {}^{3}O_{2} + dye$$

$${}^{1}O_{2} + dye \xrightarrow{k_{r}} {}^{3}O_{2} + products$$

Only the chemical reaction of the dye with singlet oxygen, and not physical quenching, results in the degradation of the dyes. The value of the rate constant, k_r , for the chemical reaction between singlet oxygen and several dyes was determined, and the table below displays values for the rate constants for reaction of dyes with singlet oxygen²⁰¹ and α -hydroxy cyclohexyl radicals.

Dye	$k_d / dm^3 mol^{-1} s^{-1}$	$(k_r / dm^3 mol^{-1} s^{-1})^{201}$
Orange G	$3.6 \pm 2.0 \times 10^8$	$1.4 \pm 0.2 \times 10^{5}$
Acid Orange 7	$4.0 \pm 0.7 \times 10^8$	$1.5 \pm 0.2 \times 10^{5}$
Amaranth	$4.9 \pm 0.6 \times 10^8$	$1.3 \pm 0.1 \times 10^{5}$
Reactive Red 120	$1.4 \pm 0.1 \times 10^9$	$2.8 \pm 0.3 \times 10^3$

Table 5.3 Rate constants for the reaction of azo dyes with α -hydroxy-cyclohexyl radicals (k_d) and singlet oxygen (k_r)²⁰¹ in methanol at 20⁰C.



Figure 5.14 The relationship between the rate constants for the reaction of azo dyes with α -hydroxy cyclohexyl radicals and singlet oxygen.

It appears, from the plot shown above, that there is a negative relationship between the two rate constants, although it is not clear why this is so. The reaction rate constant for the reaction between Reactive Red 120 and singlet oxygen is significantly lower than the values for the other dyes, this may be an error in the results as no explanation was attempted²⁰¹ as to why this was so. Due to the small number of points on the above plot, no clear relationship can be determined.

Jansen²⁰¹ also looked at the photodegradation of these dyes in methanol solution with various singlet oxygen sensitisers and found that Reactive Red 120 was less susceptible to degradation than the more simple dyes studied. This is opposite to that found in the work carried out here, which will be discussed in chapter 7, on the photodegradation of dyed cotton linters. These results indicate that the involvement of singlet oxygen in the photofading of dyes on cellulosic substrates is not as great as the involvement of radicals.

5.1.2. Reactions of non-azo dyes

The reaction of non-azo dyes with the α -hydroxy cyclohexyl radicals was also surveyed. This study was carried out in order to determine whether other types of dye were more or less susceptible to radical attack than azo dyes.

Two dyes of the same type were chosen so as to determine the rate of reaction of both dyes. This was done to ensure that additional groups attached to the main structure did not affect the reaction rate significantly. The dyes used were chosen on the basis of their solubility in methanol and low extinction coefficient at 355 nm. A low extinction coefficient at this wavelength is necessary so that the initiator, and not the dye, absorbs a large proportion of the laser light.

Two anthraquinone dyes, Solvent Blue 35 and Acid Green 25, were studied, but only one phthalocyanine dye, Reactive Blue 15, was used because other commercially available phthalocyanine compounds were found to be insufficiently soluble in methanol. The triphenylmethane dye Brilliant Green was chosen in order to compare its rate of reaction with that found in section 5.2.1 for the reaction between 2-hydroxy-2-propyl radicals and Crystal Violet.

The reaction rate constants were determined in the same way as for the azo dyes. In general, these dyes were found to be more reactive than the azo dyes towards α -hydroxy cyclohexyl radicals. The loss of absorption at λ_{max} of these dyes at different concentrations is shown in Figures 5.17-5.24 together with the linear plots of observed rate constant versus dye concentration.





Figure 5.15 The depletion of Acid Green 25, shown along with its structure and the linear fit used to determine k_d .

For the anthraquinone dyes, Acid Green 25 and Solvent Blue 35, the rate constants for their reaction with the α -hydroxy radicals are not much different to those found for the azo dyes examined. The reaction rate constant for Acid Green 25 is smaller than that for Solvent Blue 35. This may be due to the steric hindrance of the phenyl groups, which may restrict the access of the attacking radical, in the Acid Green 25 structure as opposed to the smaller groups in Solvent Blue 35.



Figure 5.16 The depletion of Solvent Blue 35, shown along with its structure and the linear fit used to determine k_d .



Me

NH,

Me

H₂N

Figure 5.17 The depletion of Safranine O, shown along with its structure and the linear fit used to determine k_d .

Safranine O, an azine dye, and Basic Blue 3, an oxazine dye, have similar strutures. The main difference in the structure being the replacement of a nitrogen atom (Safranine O) with an oxygen atom (Basic Blue 3). This difference, and perhaps the phenyl group present in Safranine O, leads to the rate constant for the reaction of Safranine being lower than that of Basic Blue 3.

132



Figure 5.18 The depletion of Basic Blue 3, shown along with its structure and the linear fit used to determine k_d .


Figure 5.19 The depletion of Indocyanine Green, shown along with its structure and the linear fit used to determine k_d .

There are many sites in Indocyanine Green where radical attack is possible. Attack at one of the C=C bonds would discolour the molecule if it occurred. The reaction rate constant is fairly high for an alkene, see Table 4.1, probably because there are four alkene groups available for radical attack.



Figure 5.20 The depletion of Brilliant Green, shown along with its structure and the linear fit used to determine k_d .

The rate constant for the reaction between Brilliant Green and α -hydroxy cyclohexyl radicals was very close to that found for the reaction between 2-hydroxy-2-propyl radicals and Crystal Violet, section 5.2.1.



Figure 5.21 The depletion of Methylene Blue, shown along with its structure and the linear fit used to determine k_d .

There appears to be no significant difference in the rate constants for the reaction of Methylene Blue and Azure B with the radical. The structures differ only in the extra methyl group on methylene blue as opposed to a hydrogen in Azure B, so this is not surprising.



Figure 5.22 The depletion of Azure B, shown along with its structure and the linear fit used to determine k_d .



Table 5.4 Rate constants for the reaction of non-azo dyes with α -hydroxy-cyclohexyl radicals.

Hayon et. al.²⁰² reported values for the rate constants of the reaction of dyes with 2-hydroxy-2-propyl radicals, which were produced by pulse radiolysis. They reported values of 2.3×10^9 dm³ mol⁻¹ s⁻¹ for Crystal Violet and 4.4×10^9 dm³ mol⁻¹ s⁻¹ for Methylene Blue, which are in agreement with the values displayed in the table above. Hayon et. al.²⁰² followed the reaction by monitoring the loss of visible absorption at the λ_{max} of the dye, as was done in this work.

In general, the dyes that react with α -hydroxy cyclohexyl radicals at the fastest rate are positively charged, whilst the lowest rate constants are found for the azo and anthraquinone dyes, which are neutral species. This small difference in rate constants may be due to the nucleophilic nature of the radicals.

5.1.3. Air saturated solutions

A limited number of studies were carried out on the reactions of dyes with radicals in air saturated solutions. Only photolysis of Irgacure 184 in the presence of dyes and oxygen was carried out. The presence of oxygen resulted, as expected, in the reduction of the amount of dye degradation. Examples of this are shown in Figures 5.23 to 5.25. No attempt was made to control the oxygen concentration, only the two cases of air saturation and degassing / nitrogen bubbling were studied.



Figure 5.23 The depletion of Amaranth due to the photolysis of Irgacure 184 in the presence and absence of oxygen.



Figure 5.24 The depletion of Procion Orange H-ER due to the photolysis of Irgacure 184 in the presence and absence of oxygen.



Figure 5.25 The depletion of Procion Orange MX-2R due to the photolysis of Irgacure 184 in the presence and absence of oxygen.

Oxygen is expected to react with α -hydroxy radicals to produce peroxy radicals. The dye depletion decreased in the presence of oxygen, which indicates that the oxygen competes with the dye for the radicals. It was hoped to be possible to determine the rate constants of reaction of the dyes with peroxy radicals, produced by reaction of the radicals with oxygen, but this was found not to be possible with the data obtained. The reactions thought to be occurring in the presence of oxygen are listed below:

 $\begin{array}{l} \alpha^{\bullet} + \ dye & \stackrel{k_{d}}{\longrightarrow} \quad products \\ \alpha^{\bullet} + \ O_{2} & \stackrel{k_{ox}}{\longrightarrow} & \alpha O_{2}^{\bullet} \\ \alpha O_{2}^{\bullet} + \ dye & \stackrel{k_{per}}{\longrightarrow} \quad products \end{array}$

The rate constant for the reaction of these radicals with oxygen, k_{ox} , is expected to be close to diffusion controlled, due to the high mobility of oxygen within solutions and its high reactivity with radicals. The rate constants for the reaction of oxygen with phenyl and tertiary-butyl radicals have been found to be 4.4×10^9 and 4.9×10^9 dm³ mol⁻¹ s⁻¹ respectively²⁰³. Following the initial depletion thought to be due to the initial α -hydroxy radical, no evidence of a further depletion, due to the peroxy radical, is apparent. Neither of the rate constants, k_{ox} or k_{per} , have been determined due to the large amount of noise on the depletion signals obtained in the presence of oxygen.

Figure 5.26 shows the effect of oxygen on the depletion of Methylene Blue, which is found to be different than for the other dyes. The effect of oxygen on the dyes previously shown is simply to decrease the depletion, but two effects are noticed in the case of Methylene Blue, both decreased depletion, as with the other dyes, followed by recovery of absorption by the dye.

It is believed that the initial depletion is lessened due to competition for the radicals, as with the depletion of other dyes. The recovery of the dye could be due to the self-reaction of Methylene Blue radicals to form the hydroquinone and regenerate the methylene blue cation. The hydroquinone, which was not observed due probably to the high absorption of the Methylene Blue ground state, may then react with oxygen to form the ground state, as shown in Figure 5.27.



Figure 5.26 The depletion of Methylene Blue due to the photolysis of Irgacure 184 in the presence and absence of oxygen.



Figure 5.27 The possible effect of oxygen on the reaction of Methylene Blue with radicals.

5.2. Reaction of dyes with 2-hydroxy-2-propyl radicals

In most cases, the reaction of dyes with the 2-hydroxy-2-propyl radicals was studied by following the loss of the dye at the wavelength of maximum absorption. In the case of Crystal Violet, the reaction with the radical was monitored, as described below, by following the rise of the absorption of the Crystal Violet radical. The production of 2hydroxy-2-propyl radicals was achieved in two different ways, either by photolysis of Irgacure 2959 or acetone; the results achieved using these methods are shown below.

5.2.1. Photolysis of Irgacure 2959

The photolysis of Irgacure 2959, see Figure 4.1 page 96, leads to the formation of a benzoyl radical and a 2-hydroxy-2-propyl radical. As mentioned above, the reaction of the benzoyl radical is much slower than the reaction of the 2-hydroxy-2-propyl radical. The disappearance of the dye is, therefore, attributed to its reaction with the 2-propyl-2-hydroxy radical.

Firstly, the reaction of Crystal Violet with 2-hydroxy-2-propyl radicals was studied. This reaction is observed in a different way to that for the other dyes in that the loss of the dye was not observed directly. The reaction was followed by observation of the Crystal Violet radical produced, as for the alkene measurements in chapter 4. A set of solutions containing the same concentration of Irgacure 2959 (1.8×10^{-1} mol dm⁻³), with varying concentrations of Crystal Violet between 20 and 130 µmol dm⁻³ were prepared. Each of these solutions was bubbled with nitrogen and several traces were taken with separate samples of each solution.

The traces recorded for the solutions containing different concentrations of Crystal Violet are shown in Figure 5.28. This figure also shows the first order rate equation fitted to the data. A plot of the observed rate constant versus Crystal Violet concentration is displayed in Figure 5.29.







Figure 5.29 The relationship between the observed rate constant and the concentration of Crystal Violet.

A linear fit of the above plot gives: $k_{obs} / s^{-1} = 3.4 \times 10^5 + (1.8 \times 10^9) [CV^+]$

Therefore, from this method: $k_c = 1.8 \pm 0.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

The disappearance of other dyes due to the photolysis of Irgacure 2959 is shown in a series of plots in Figure 5.30, below.



144







Figure 5.30 Depletion of various dyes due to the photolysis of Irgacure 2959.

Dye	$bye k_d / dm^3 mol^{-1} s^{-1}$	
Reactive Blue 15	$2.3 \pm 0.2 \times 10^9$	
Reactive Red 120	$1.6 \pm 0.1 \times 10^9$	
Solophenyl Red 4G	$9.0 \pm 1.0 \times 10^8$	
Reactive Red 3	$7.7 \pm 0.6 \times 10^8$	
Red MX	$5.1 \pm 0.7 \times 10^8$	
Amaranth	$5.8 \pm 0.8 \times 10^8$	

Table 5.5 Reaction rates of dyes with 2-hydroxy-2-propyl radicals.

The values displayed here and for α -hydroxy cyclohexyl radicals are of the same order of magnitude and vary with dye in the same way - i.e. dyes with two azo groups react twice as quickly than those that have only one. At first glance these values are similar to the values found for the α -hydroxy cyclohexyl radical. However, a plot of $k_{\alpha h}$ (rate constants for the reaction with α -hydroxy cyclohexyl radicals) versus k_{2h} (rate constants for the reaction with 2-hydroxy-2-propyl radical), which is shown below, shows that they are not the identical. In fact, the relationship between the two values is similar to the relationship found between these two rate constants for the reaction of the radicals with alkenes, see Figure 4.14.



Figure 5.31 The relationship between the rate constants for the reaction between dyes and two α -hydroxy radicals.

5.2.2. Photolysis of acetone

Acetone can be photolysed with 266 nm light, which results in the production of 2hydroxy-2-propyl radicals. Other reactive species are also produced, but it is thought that the dye reacts with the 2-hydroxy-2-propyl radicals only. The reaction rate constants of the dyes with the photolysed acetone is similar to the rate for reaction of the dyes with photolysed Irgacure 2959.

Therefore, the photolysis of acetone in an aqueous solution of a dye can be used to determine the reaction rate of that dye with 2-hydroxy-2-propyl radicals. This method has been applied to Direct Green 26, which has a low solubility in methanol. The traces recorded of the depletion of Direct Green 26 are shown in Figure 5.32. Plots of the observed rate constant versus dye concentration are shown for three dyes in Figure 5.33.



9 0.000 18 36 54 -0.002 72 ∆A_{643 nm} -0.004 -0.006 -0.008 0 50 100 150 Delay time / us

[Direct Green 26] / µmol dm-3

Figure 5.32 The depletion of Direct Green 26 due to the photolysis of acetone, displayed along with its molecular structure.



Figure 5.33 Reaction rates of dyes with photolysed acetone.

Dye	$k_{d} / dm^{3} mol^{-1} s^{-1}$	$k_{\rm d} / {\rm dm}^3 {\rm mol}^{-1} {\rm s}^{-1}$	
	(Irgacure 2959)	(acetone)	
Solophenyl Red 4G	$9.0 \pm 3.0 \times 10^8$	$9.8 \pm 4.0 \times 10^8$	
Reactive Red 120	$1.6 \pm 0.5 \times 10^9$	$1.1 \pm 0.5 \times 10^9$	
Direct Green 26	_	$2.2 \pm 0.9 \times 10^8$	

Table 5.6 The rate constants for reaction of dyes with 2-hydroxy-2-propyl radicals produced by the photolysis of Irgacure 2959 and acetone.

The table above illustrates that the rate constants found using the two methods are not widely different. However, a study of a greater number of dyes, which has not been carried out here, would be needed to confirm this. The reaction rate constant found for Direct Green 26 is significantly lower than would be expected for a dye with three azo groups in its structure. This low value, similar to the values found for monoazo dyes, may be explained by consideration of the nature of the azo groups. Of the three azo groups in Direct Green 26, only two have a hydroxy group close by and so may exist as the hydrazone tautomers. It may be that the reaction of the hydrazone groups take place in preference to the reaction with the other azo group. Another reason may be that Direct Green 26 has two chromophores in its structure, and therefore the reaction

of Direct Green 26 with the radicals may not be detected by observation at 643 nm only. This observation may lead only to a rate constant for the reaction of part of the molecule. Other regions of the molecule may react and not affect the absorption at the observed wavelength.

Another advantage of using acetone as opposed to the photoinitiators previously used is that the transient absorption spectrum can be measured over a larger wavelength range. The photoinitiators may be photolysed by the analysing light if this light includes wavelengths lower than 410 nm. This problem does not arise for acetone due to the fact that it does not absorb above 300 nm. The transient absorption spectra, Figure 5.34, show the depletion of the dye and, most noticeably in the case of Solophenyl Red 4G, a small transient absorption below 400 nm.



Figure 5.34 Transient absorption spectra of dyes and acetone.

The transient absorption below 400 nm is thought to be due to the hydrazyl radical of the dyes. The hydrazyl radical was expected to absorb here, due to the fact that the hydrazyl radical of azobenzene²⁰⁴ and of azobenzene derivatives^{66,74} have been observed in this region. The formation and decay of these hydrazyl radicals is

depicted in the following figure. The lifetime of these species was found to be less than 200 μ s for three of the dyes. For amaranth, no decay of the signal was seen over the timescale used.



Figure 5.35 Rise and decay of species formed on photolysis of acetone.

5.3. Reaction of dyes with the radicals produced by photolysis of Irgacure 819

A disadvantage in this work is that the disappearance of the dye is not due to only one of the radicals produced. Using the Crystal Violet probe, one can be confident that the Crystal Violet radical is produced only by reaction of the probe with one radical. This was shown by Turro¹⁹⁶ et. al. and in this work, page 73, using a photoinitiator that produces benzoyl and phosphinoyl radicals.

Therefore, in an attempt to show with which radical the dye reacts, the reaction of the dyes with benzoyl and phosphinoyl radicals was studied. Photolysis of a benzoylphospine oxide, which is known to produce benzoyl and phosphinoyl radicals, was carried out. The benzoylphosphine oxide used here was Irgacure 819, the structure and photolysis of which is illustrated in Figure 5.36.



Figure 5.36 Photolysis of Irgacure 819

The photolysis of Irgacure 819 was carried out in the presence of dyes. From these studies the rate constants for reaction between the dye and these radicals can be determined. This rate constant is either an average of the reaction rate of the dye for both radicals or the rate of reaction of the most reactive radical. The most reactive radical is assumed to be phosphinoyl radical as other workers have found^{171,173,203} this to be the case for its reaction with alkenes. The reaction of the dyes with photolysed benzoylphosphine oxide has been found to be approximately a thousand times slower than the reaction with photolysed α -hydroxy ketones. The plots in Figure 5.37 display the loss of dye due to the photolysis of Irgacure 819 for four dyes.





Figure 5.37 The depletion of dyes due to the photolysis of Irgacure 819 in methanol saturated with nitrogen at 20° C.

The photolysis of Irgacure 819, see Figure 5.36, leads to the formation of benzoyl and phosphinoyl radicals. The disappearance of the dye upon photolysis of Irgacure 819 has not been attributed to either one of the radicals produced, although it is assumed to be the phosphinoyl radical that is reacting, resulting in the loss of dye.

These results contrast with work carried out on the reaction rate of alkenes with similar radicals. Kamachi et.al.¹⁷² found, by time-resolved EPR measurements, rate constants, some of which are displayed in Table 5.7 below, in the region $10^6 - 10^7$ dm³ mol⁻¹ s⁻¹ for the addition of diphenylphosphinoyl radicals to many alkenes.

Alkene	$k_a / dm^3 mol^{-1} s^{-1}$	$k_a / dm^3 mol^{-1} s^{-1}$	$k_a / dm^3 mol^{-1} s^{-1}$
	(*C ₆ H ₅ OH)	$(O^{\bullet}PPh_2)^{172}$	$(O^{\bullet}PPh_2)^{173}$
Acrylonitrile	8.3×10^{7}		1.8×10^{7}
Methyl methacrylate	8.5×10^{6}	1.6×10^{7}	6×10^7
1,1-diphenyl ethene	2.3×10^{6}	2.4×10^{7}	
Styrene	5.4× 10 ⁵	1.1×10^{7}	6×10^7
Vinyl acetate	< 10 ⁵	2.7×10^{7}	



The above table displays the difference in rate constants depending on the alkene electronegativity found for the reaction of the α -hydroxy cyclohexyl radical, as discussed in chapter 4. The rate constants for the reaction of the diphenylphosphinoyl radical are consistently high, but the values do not vary according to the electronegativity of the alkenes. This suggests that the diphenylphosphinoyl radical is not nucleophilic, as opposed to the α -hydroxy cyclohexyl radical.

The rate constants may be high for the diphenylphosphinoyl radical due to other factors, for example a high reaction enthalpy. Kamachi et. al.¹⁷² concluded that the rate of reaction of the diphenylphosphinoyl radical with phenyl substituted alkenes was increased by stabilisation of the adduct radical.

The rate constants for the reaction between the dyes and the phosphinoyl radical used in this work are approximately two orders of magnitude lower than the rate constants displayed in the above table for alkenes. As the reaction of the phosphinoyl radical is not greatly affected by steric factors, the relative orientation of the reacting species may be more important in determining the reaction rate. The phosphinoyl radical used in this work is also slightly different to the diphenylphosphine radical for which rate constants for the reaction with alkenes are displayed in the above table. The phosphinoyl radical used in this work is slightly larger than that used in the alkene work^{172,173}. Also, the radical includes a carbonyl group, the presence of which may affect the reactivity of the radical. The dyes used in this work are much larger than the alkenes and their bulk may affect the approach of the radical and thus decrease the rate constant value.

The values obtained for the rate constants for the reaction between the phosphinoyl radical and several dyes are summarised in Table 5.8. Again, as with the reactions of the α -hydroxy radicals, methylene blue is more reactive than the azo dyes.

$k_{d} / dm^{3} mol^{-1} s^{-1}$
$9.2 \pm 3.0 \times 10^{6}$
$5.2 \pm 1.5 \times 10^5$
$4.9 \pm 1.5 \times 10^{5}$
$3.3 \pm 1.0 \times 10^5$
$1.9 \pm 1.0 \times 10^{5}$
$6.1 \pm 3.0 \times 10^4$

Table 5.8 Reaction rates of dyes with the radicals produced by photolysis of Irgacure 819 in methanol at $20^{\circ}C$ (all azo dyes except for methylene blue).

The rate constants for the reaction of dyes with the photolysis products of Irgacure 819 (phosphinoyl and benzoyl radicals) are approximately one thousand times lower than for the reaction of the dyes with the photolysis products of Irgacure 184 or 2959 (α -hydroxy and benzoyl radicals). Based on this vast difference in rate constants, it is concluded that the results shown in Tables 5.1, 5.2, 5.4 and 5.5 are the rate constants for the reaction between the dyes and the α -hydroxy radicals, as was previously assumed.

5.4. Summary and conclusions

In this chapter the rate constants for the reaction of dyes with radicals have been determined. It was found that the rate of reaction of azo dyes was slower than that of other dye types. The rate of reaction of azo dyes was linked to the number of azo groups in the molecule, in that the rate constant doubled for two azo groups as opposed to one. This supposition fits in with the work of van Beek et.al.¹²³, who found that in photoreduction of azo dyes the azo group was attacked.

Other structural factors in the azo dyes were also found to have an effect on the reaction rate. It has been suggested here that the position of an amino group in the molecule may affect the reactivity of the dyes. It is not known why the amino group has such an effect, but it was suggested that the stability of the adduct radical may be affected by the position of the amino group, which in turn affects the rate constant for the reaction.

For other types of dye no link has been made between the rate of reaction and the structure of the dye as only a small number of dyes were studied. The thionin type dyes (Methylene Blue and Azure B) are the most reactive dye type studied here, but the reason for this is unclear. It is possible that the dyes with an overall positive charge are more reactive towards the α -hydroxy cyclohexyl radicals than the neutral dyes because of the nucleophilic nature of the radical.

The reaction of dyes with the smaller α -hydroxy radical, 2-hydroxy-2-propyl, was studied to a limited extent. The reaction rate constants for the reaction of several dyes was determined in methanol solution by the photolysis of Irgacure 2959. These values were found to differ significantly from those found for α -hydroxy cyclohexyl radicals, the ratio between the rate constants being identical to that found for the alkenes ($k_{\alpha c} / k_{2h} = 0.76$).

Attempts were also made to determine the rate of reaction of dyes that could not be dissolved in methanol, using acetone in water. This method shows a similar rate of reaction for Reactive Red 120 and Solophenyl Red 4G to that found using Irgacure 2959 to produce the radicals. Using acetone to produce 2-hydroxy-2-propyl radicals allows the detection of transient species that absorb light in the near UV region of the

spectrum. For the four dyes studied some evidence for transients absorbing below 400 nm was found. These transient species are assumed, based on the results found for azobenzene²⁰⁴, to be the hydrazyl radicals of the azo dyes. These transient signals were found to have a lifetime of less than 200 μ s for three of the dyes – Solophenyl Red 4G, Direct Green 26 and Reactive Red 120.

The reaction of dyes with photolysed Irgacure 819 was also studied and it was found that the dyes reacted one thousand times slower than for the other radicals. These rate constants were assumed to be for the reaction of the phosphinoyl radicals and not the benzoyl radicals, due to the known greater reactivity of the phosphinoyl radicals¹⁷¹. The low rate constants found for the dyes are in contrast to the reaction of phosphinoyl radicals with alkenes studied by other workers^{172,173}.

Chapter 6

Reaction of radicals with dyes on cotton and cotton linters

6. Reaction of radicals with dyes on cotton and cotton linters

The steady state fading of dyes on cotton and how that fading is affected by the addition of photoinitiators to the system is discussed in chapter 7, and in chapter 5 the reaction of radicals with dyes in solution is reported. In this section attempts to study the reaction of dyes with radicals on cotton, in order to get a fuller picture are outlined. The experimental technique used was diffuse reflectance laser flash photolysis, which is discussed in section 2.9.

Both dyed cotton fabric and dyed cotton linters were used in this study. The reaction rates were determined as for solutions, plotting the observed rate constant versus dye concentration. The dye concentration of these samples was determined by the method shown below. Rate constants have been measured only for the cotton fabric samples. These samples, although more difficult to dye evenly, are much easier to rinse. Therefore, the unfixed dye can be removed easily, so a wider range of dye concentrations were obtained.

The photoinitiators were adsorbed to the cotton by adding a methanol solution of the photoinitiator and allowing the methanol to evaporate slowly. Initially, the intention was to use 355 nm light, so the loading of the photoinitiator added to the solution was large (200 μ mol g⁻¹). Using 355 nm light was not very successful, so 266 nm was used instead because the photoinitiator absorbs a greater proportion of light in this region. Excitation at 266 nm was not used with solutions because some of the dyes were found to photodegrade on absorption of 266 nm radiation in the absence of a photoinitiator. This was found also, but only to a limited extent, on cotton. For all experiments mentioned here, 266 nm light has a very small effect on the dye alone on cotton.

These experiments were carried out on both dry and wet cotton using both Irgacure 2959 and Irgacure 184. Also, 4-hydroxyTEMPO, which is a stable free radical, was added in some cases in order to compete with the dye for the radicals. This was adsorbed onto the fabric in the same manner as the initiators.

6.1. Determining the concentration of dye on cotton

The process of dyeing cotton linters or cotton fabric results in a loss of some of the dye originally added. Therefore, the amount of dye present on the solid is less than the amount added, and can be determined by the reflectance of samples at the wavelength of maximum absorption. It is necessary to know the concentration of the dyes in the cotton in order to determine the rate constants for their reaction with radicals in this medium.

The absorption coefficients of dyes in solution can be easily determined using the method described in chapter 2. The determination of the absorption coefficients of dyes on cotton linters or fabric is more complex and only relative values have been measured here. This is all that is required as the only purpose was to find the 'concentration' of dye present on dyed samples. The experiments carried out are described below.

6.1.1. Dyes on cotton linters

Figure 6.1 shows reflectance spectra for Reactive Red 3 at different loadings on dry cotton linters. It can be seen that the shape of the curve does not change significantly and there is no shift in the λ_{max} value. Both of these indicate that there is no aggregation of the dye on the surface. This was also found for the other dyes studied.







Figure 6.2 Remission function plots of varying dye loading on cotton linters. Figure 6.2, above, shows the remission function plots of Reactive Red 3 at differing loadings. It is the value of the remission function and not the reflectance that is expected to change linearly with concentration. The reflectance spectra for several dyes at various loadings and the corresponding remission function plots are shown in Appendix 1.

The linear relationship expected between remission function and dye loading was found for all dyes studied. However, at higher loadings this linear relationship breaks down. This is thought to be due to the error in the measurement of highly absorbing samples. It is also possible that a certain amount of aggregation has taken place. Therefore, when considering the fading of samples that reflect little light, it is important to take note of the compounding errors involved.

Plots of remission function versus dye loading for several dyes are shown in Figure 6.3. It can be seen that the relationship is definitely linear. The linear fits pass through zero. Therefore, the concentration of dye on the surface can be determined by dividing the remission function at a given wavelength by the gradient of these plots. It is noted that in these plots the concentration of dye has units of μ mol g⁻¹. The more usual units for concentration are mol dm⁻³.

The absolute extinction coefficients can not be obtained because S is unknown. Using equations 1.11 and 1.12, page 25, one can get equation 6.1.

$$F(R) = \frac{2\varepsilon' c}{S}$$
(6.1)

Therefore, the gradient of the plots of remission function versus concentration is $2\epsilon'/S$. In Appendix 2, the determined value of ϵ'/S for several dyes on cotton fabric and cotton linters are displayed in a table.



Figure 6.3 Relationship between remission function and dye loading on cotton linters.

The concentration of absorbing species in units of μ mol g⁻¹ can be determined using plots similar to that shown above. Once a concentration has been determined in these units, conversion to mol dm⁻³ is achieved in the case of cotton fabric, using the value for the density of cotton²⁰⁵ of 1.50 g cm⁻³.

6.1.2. Dyes on cotton fabric and Avicel (microcrystalline cellulose)

The reflective properties of cotton are different to those of cotton linters. Cotton linters exists as a powder of small particles, whereas, cotton fabric is woven strands of fibre. Therefore, the scattering coefficient is expected to differ between the two substrates.

Cotton and cotton linters both have amorphous and crystalline regions in their structure. Avicel, which is a type of microcrystalline cellulose, has no amorphous structure. Also, the particle size of avicel is much smaller than that of cotton linters. This leads to a change in its reflecting properties. Figure 6.4 shows the reflectance spectra for Direct Red 75 on cotton fabric, cotton linters and avicel. If one looks at the region of the spectrum in which the dye does not absorb, it can be seen that the reflectance of the samples increases as the particle size decreases. The change in the particle size changes the scattering coefficient of the material, which in turn affects the reflectance of the material, equation 1.11, page 25.



Figure 6.4 Reflectance spectra of various cellulose samples with Direct Red 75 adsorbed.

6.2. Reaction of dyes with radicals on wet cotton

Unfortunately, the rate constants for reactions on cotton linters were not obtained, as mentioned above, due to the small number of samples that were prepared and the greatly increased preparation time compared to the cotton fabric samples. The depletion of dyes on wet cotton linters is shown in Figure 6.5, and experiments to determine the rate of reaction on wet cotton fabric were subsequently carried out.



Figure 6.5 Depletion of dyes on cotton linters.

The depletion of four dyes on cotton fabric was studied. The depletion of these dyes, due to adsorbed Irgacure 184 or Irgacure 2959, is shown below.



Figure 6.6 Depletion of Procion Orange MX-2R on wet dyed cotton fabric due to the photolysis of adsorbed Irgacure 2959.



Figure 6.7 Depletion of Direct Green 26 on wet dyed cotton fabric due to the photolysis of adsorbed Irgacure 2959.



Figure 6.8 Depletion of Reactive Red 3 on wet cotton fabric due to the photolysis of adsorbed Irgacure 2959 and Irgacure 184.



Figure 6.9 Linear relationship between k_{obs} and the dye concentration on cotton fabric.

6.3. Reaction of dyes with radicals on dry cotton.

The depletion of the dye on dry cotton is very small. It is difficult to determine the rate of this depletion. It can be seen in Figure 6.10 that this depletion is almost indistinguishable from the noise on the signal. However, it was possible to fit the curves, although not very accurately, and the rate constants found for the reactions on dry cotton were not very reliable.



168


Procion Orange MX-2R / mmol dm⁻³





Figure 6.10 The effect of photolysis of adsorbed Irgacure 2959 or Irgacure 184 on dyed dry cotton fabric.

The rate constants found for the reaction of dyes with radicals on cotton fabric are ten times smaller and involve larger errors than those found in methanol. This may be due to several factors, including the immobility of the dyes, which have been fixed onto the cotton fabric, but were free to move in solution. Also the radical may have decreased mobility in the cotton fabric, as compared to methanol¹⁸³. Table 6.1 shows the rate constants found for the reaction of dyes with radicals on cotton and the corresponding value found in methanol.

	$k_{d} / dm^{3} mol^{-1} s^{-1}$				
Dye / Radical	Cotton	Methanol			
	wet	dry			
Procion Orange MX-2R / 2-hydroxy-2-propyl	$4.5 \pm 1 \times 10^7$	$1.9\pm0.5\times10^7$			
Procion Orange MX-2R / α-hydroxy cyclohexyl	$5.4 \pm 0.8 \times 10^{7}$	$1.7 \pm 0.9 \times 10^7$	$2.9\pm0.5\times10^8$		
Reactive Red 3 / 2-hydroxy-2-propyl	$1.4\pm0.2\times10^7$	$3.7 \pm 2.5 \times 10^7$	$7.7 \pm 0.6 \times 10^8$		
Reactive Red 3 / α-hydroxy cyclohexyl	$2.0 \pm 0.2 \times 10^{7}$	$0.9 \pm 1.7 \times 10^{7}$	$6.7 \pm 1 \times 10^8$		
Direct Green 26 / 2-hydroxy-2-propyl	$9.6 \pm 2 \times 10^7$	$4.0 \pm 1.5 \times 10^{7}$	$2 \pm 0.6 \times 10^8$ (water)		
Direct Green 26 / α-hydroxy cyclohexyl	$5.6\pm0.6\times10^7$	$7.7 \pm 3.3 \times 10^7$			

Table 6.1 Rate constants for the reaction of dyes with radicals.

6.4. Addition of competing species to the samples

The process of radical depletion of dyes on cotton has been found to be a dynamic, rather than static, process. Given this, it should be possible to interrupt this reaction using a species that reacts with radicals at a fast rate. The stable free radical 4-hydroxy-TEMPO was added to the system because the reaction between two radicals, even stable ones, is known to be fast. 4-hydroxy-TEMPO is often used as a radical trap in order to study indirectly the structure of short-lived radicals.

Figure 6.29, below, shows the decrease in the depletion of dyes due to the addition of 4-hydroxy-TEMPO. The fact that the depletion can be reduced shows that addition of species that react with radicals can reduce the magnitude of the other reactions occurring.







Figure 6.11 The effect of 4-hydroxy-TEMPO on the depletion of dyes on cotton.

6.5. Summary and conclusions

The rate constants for the reaction between these dyes and the α -hydroxy radicals have been determined on cotton fabric. Photoinitiators, α -hydroxy ketones, were adsorbed onto dyed cotton fabric and the depletion of the dye due to photolysis of the α -hydroxy ketones was monitored both when the fabric was wet and dry.

The magnitude of this depletion was greater on the wet cotton than the dry, due to the greater penetration depth in the wet samples. Due to the greater magnitude of the depletion, the fits of the curves were better for the wet samples. The rate constants found for dry cotton were slightly lower than the rates found on wet cotton, although the errors on the dry values were large. The mobility of radicals may be slightly increased in the wet cotton fabric, due to a slight solubility. The errors on the values for dry cotton are large so there may not be any true difference in the wet and dry values.

Comparison of the values found on cotton linters and in methanol shows that the rate constants for reaction between the radicals and dyes are approximately ten times lower when the dye is immobilised on cotton linters. This could be due to the decreased mobility of both the dye and the radicals. Reactive dyes have no mobility within the fabric as they are attached to the cotton via covalent bonds. Direct dyes only have a decreased mobility as they are fixed to the cotton fabric only by hydrogen bonds. The orientation of the dyes, especially the reactive dyes will be limited. This may hinder the approach of the radical to the reactive site on the dye.

The addition of 4-hydroxy TEMPO to the samples led to a decrease in the loss of dye following the laser flash. This shows that the reactions on cotton fabric can be interrupted by using species that consume radicals. Therefore, it is possible that undesired radical reactions on cotton can be slowed by the use of such species.

Chapter 7

Steady state fading of dyes

7. Steady state fading of dyes

The work presented in this chapter is aimed at forming a link between the findings in other chapters with practical problems involving cellulose. The practical problem chosen for study was the fading of dyed cotton textiles. The fading of several dyes has been studied on wet cotton linters both in the presence and absence of photoinitiators.

Radical producing photoinitiators were used in this work due to the thought that radical species may be involved in the photoreactions of dyed polymers. This idea was first suggested by Egerton²⁰⁷, following work carried out on anthraquinone-dyed polymers. Egerton suggested that an exited state of oxygen could be formed via quenching of the excited state of the dye by oxygen, which could then go on to react and form destructive peroxy radicals. It should be noted that the suggestions of Egerton were made long before the major work carried out concerning the now well-known excited state of oxygen, singlet oxygen.

Cotton linters was chosen in these experiments as opposed to cotton fabric as its source is well-defined and it is easier to work with. The dyes studied in this work are similar to those whose reaction with radicals was studied in the previous chapters. This work seeks to determine whether a direct link can be made between the reaction rate constants of the dyes with α -hydroxy radicals and the rate of fade of dyes when irradiated on cotton linters.

The fading of dyes due to continuous irradiation with light has been investigated. The dyes were studied both in solution and dyed onto cotton linters surfaces. The light source used was a xenon arc lamp, the emission spectrum of which, shown in Figure 7.1, is similar to that of the sun⁵¹. The emission spectrum was measured via reflection of light from a barium sulphate sample. The barium sulphate was behind glass, as the dyed sample was, so the emission spectrum shown is that which reached the sample. The detection of this emission was achieved using the photodiode array system described in section 2.6.2.2.



Figure 7.1 Emission spectrum of the xenon arc lamp uncorrected for the response of the detector.

The spectral distribution of light reaching the sample was varied using filters. The transmission spectra of these filters are shown in Figure 7.2. The filters are numbered according to their cut-off wavelengths for ease of reference in further sections. The 'normalised' emission spectra, shown in Figure 7.3, were obtained by multiplying the 'normalised' emission spectra of the arc lamp by the fractional transmission of each filter. Most experiments were carried out using the full range of the arc lamp, filtered only by glass.



Figure 7.2 Transmission spectra of filters used for fading experiments.





Many dyes have been studied, these were mainly azo dyes. The relative extinction coefficients of these dyes on the cotton were determined, see chapter 6, and the amount of dye lost during fading could be found. In addition, the effect on the fading rate of the presence of photoinitiators has been investigated.

7.1. Fading of dyes in solution

Dyes in solution were not extensively studied. The irradiation, using the full spectrum of the arc lamp, of dyes alone in solution resulted in no observable fading. The addition of photoinitiators, which was only investigated for Amaranth solutions, resulted in a very fast rate of fade. Figure 7.4 shows a plot of the fading of Amaranth in methanol with Irgacure 184 present. It can be seen from the plot that the rate of fade is increased by approximately ten times by the exclusion of air from the sample. This effect is caused by the reaction of oxygen with the radicals produced, leaving less radicals available for reaction with the dye.





7.2. Fading of dyes alone on cotton linters and Avicel

As mentioned in chapter 1, it is thought that radicals play an important part in the fading of dyes on cellulosic textiles. Therefore, studies of the fading rate of dyes on cotton linters were carried out. Several factors affecting the rate of fade were studied. These being, the effect of heat, spectral distribution of irradiation and adsorbed photoinitiators. These effects were studied in combination and for many dyes. The fading of some dyes on Avicel was also investigated, although photoinitiators were not added to these samples.

Dyes adsorbed on cotton linters were first irradiated in the dry state, but fade rates were slow and experiments took many hours. The fading of Amaranth on cotton linters is illustrated in Figure 7.5. Samples of cotton linters with adsorbed dyes were dampened with distilled water, which increased the rate of fade; this has also been found by other workers⁷⁶⁻⁷⁸. The dampening of samples containing adsorbed dyes resulted in the dye being rinsed from the surface. Therefore, for further experiments, dyes were fixed more permanently onto the cotton linters so that fading could be carried out in the wet without the dye being rinsed off. This lead to a limit on the dyes that could be studied, the more simple dyes being excluded due to an inability to fix them to the cotton linters. The only dyes studied in this way are direct and reactive dyes, which were fixed onto the cotton linters as described in section 2.5.2.



Figure 7.5 Fading of Amaranth adsorbed on dry cotton linters by irradiation using a xenon arc lamp at 20° C.

Fading of samples was quantified either as the loss of dye or as percentage loss of dye as described in section 2.8. The quantum yield of fading was not determined, as this is difficult to do due to the following factors:

- A polychromatic light source is used and it is, therefore, more difficult to determine the number of photons absorbed than when a monochromatic light source is used.
- The wavelengths of light that induce dye degradation are unknown.

An attempt to determine the relative number of photons absorbed for various samples is given in section 7.3.

7.2.1. Variation in fading rates for different dyes

Many dyes were studied and their fading rates have been compared. Most of the dyes were azo dyes, although one was a copper phthalocyanine. This dye is Reactive Blue 15, the structure of which can be seen in chapter 2. It should be noted that the change in fading rate might be due to the difference in concentration of the dyes and not the dye structure. This problem is difficult to avoid, as it is not possible to determine the amount of dye in the sample when preparing it.

It was found in general that the reactive dyes faded much faster than the direct dyes. This leads to the thought that the fading is influenced greatly by the interaction of the dye with the cotton. The reactive dyes interact with the surface through a covalent bond joining the two. The direct dyes, however, are more weakly attached with noncovalent bonds. It may be that the greater interaction of the reactive dyes with the cotton linters leads to an increase in the fading rates. Figure 7.6 shows the remission function plots of cotton linters dyed with reactive and direct dyes before and after twenty minutes irradiation. The difference in photodegradation between the direct and reactive dyes is a very obvious one.



Figure 7.6(a) The remission function plots of direct dyes on cotton linters before and after 20 min irradiation at 20° C.



(b) The remission function plots of reactive dyes on cotton linters before and after 20 min irradiation at $20^{\circ}C$.

7.2.2. Effect of dye loading on fading rate

For some dyes, the original dye concentration was varied. The effect of this on the fading rate of the dye was studied. As mentioned in chapter 1, it is often found that the fading rate changes depend on dye concentration. The rate of fade may be either decreased or increased by an increase in the concentration of dye²⁰⁶.

A decrease in fading rate with increasing dye concentration is thought to be due to the aggregation of the dye in higher concentrations. This is due to that fact that the light interacts with and degrades dye molecules on the surface of an aggregate. The overall appearance of the collection of aggregates is not altered by a change in the surfaces of aggregates. This increased light stability in aggregated samples may also be due to an aggregates greater efficiency, as compared to the monomer, at dissipating energy non-radiatively.

Dyes that readily form aggregates are often found to have a higher stability to light³⁴. It is therefore possible that a sample with a high loading of dye may initially fade much more slowly than a sample containing a lower amount of dye. This effect should, therefore, not be seen for the reactive dyes. Reactive dyes are not expected to give aggregates as they are covalently bound to the linters. The direct dyes used, however, may form aggregates, as they are not covalently attached to the cotton linters.

An increase in fading rate with increasing dye concentration may simply be due to a larger amount of light being absorbed. Obviously, if more dye is present, then more light will be absorbed.

Any difference in fading rate between samples with differing dye content may be explained in another way. The samples with a high dye content reflect very little light at the wavelength of maximum absorption. Since the spectra of the wet samples are measured this reflectance is decreased further. With a very small percentage reflectance, there is a large error involved. Therefore, the apparent fading rate may be altered by these errors.

Figure 7.7 shows the remission function plots of two samples containing different initial concentrations of the same dye. It can be seen that the difference in initial concentration is large and that the sample with the lower dye concentration loses its

colour more quickly. The plots of loss of dye and percentage change versus irradiation time are shown in Figure 7.7b. The dye loss and percentage change were determined using the method described in section 2.6.2.



Figure 7.7(a) The remission function plots showing the fading of two Reactive Red 3 dyed cotton linters samples.



(b) Plots showing the change in the remission function and the percentage change in the amount of dye present due to irradiation of cotton linters dyed with Reactive Red 3.

The gradients for the plots of $\Delta F(R)$ versus time do not differ significantly for two dye loadings. Reactive red 3 is typical in that the rate of loss of dye appears to be independent of the initial concentration of dye. Table 7.1 shows the rate of dye loss for several other dyes at two loadings and the differences are not large. Obviously, overall the sample with more dye will lose more, but the rate of dye loss is independent of initial concentration. The percentage fade is therefore different for samples of different dye loading.

These results appear to suggest one of the following possibilities:

1. Both of the effects of increased dye concentration mentioned above occur and cancel each other.

2. The fading is caused primarily by the absorption of light by the cotton linters and not by the dye.

3. The measured fading rate of the two samples may not differ significantly as the difference in the light absorbed (1-R) of the two samples before irradiation is not great.

The first possibility is highly unlikely, mainly because it is believed that the reactive dye is not present in aggregates. Given that this is the case, the fading rate would be expected to be faster for the sample with a higher dye loading.

Therefore, the second possibility must be seriously considered. The light is passed through a glass cell containing water before it reaches the sample. Therefore, the wavelengths of light to which the sample is exposed are limited. The sample will not receive light of wavelengths lower than 310 nm. The cotton linters alone will not absorb a large amount of light above this wavelength. Figure 7.8 shows the reflectance spectra of dry and wet cotton linters. The amount of light absorbed by the cotton linters alone may be sufficient to cause the fading of the dye.



Figure 7.8 Reflectance spectra of dry and wet cotton linters.

The wet sample reflects less light overall due to less scattering in the wet sample. It is also noticeable that there is an extra absorbance in the IR region of the spectrum due to the presence of the water.

7.2.3. Effect of heat on fading rate

Most experiments were carried out at room temperature, but for some samples the temperature was raised to 70°C. Temperature was found to have a small, but noticeable effect on the fading rate of the dyed cotton linters samples. The effect of temperature on fading rate is shown in Figure 7.9.



Figure 7.9 (a) Remission function plots showing the fading of Reactive Blue 15 on cotton linters at two different temperatures.



(b) Change in the fade rate of Reactive Blue 15 due to the increase in temperature.

The temperature rise from 25 to 71^oC resulted in a slightly increased rate at which the dye fades. This was found for all dyes studied, some of which are displayed in the Table below. This increase in rate is not surprising as many processes speed up at higher temperatures. Table 7.1 shows the effect of all of the above mentioned factors (dye concentration, method of attachment to the surface and heat) on the fade rate.

Dye	[dye]	Temperature	Rate of dye loss	Rate of fade (%)
	/ µmol g ⁻¹	/ °C	/ µmol g ⁻¹ s ⁻¹	/ s ⁻¹
Reactive Red 3	2.18	20-25	1.9×10^{-4}	8.9×10^{-3}
Reactive Red 3	0.31	20-25	1.3×10^{-4}	4.1×10^{-2}
Procion Orange MX-2R	3.05	20-25	2.1 × 10 ⁻⁴	6.8×10^{-3}
Procion Orange MX-2R	1.60	20-25	2.3×10^{-3}	1.4×10^{-1}
Direct Red 75	0.57	20-25	2.8×10^{-5}	4.8×10^{-3}
Direct Red 75	0.07	20-25	3.8 × 10 ⁻⁵	5.7×10^{-2}
Direct Green 26	3.55	20-25	8.3 × 10 ⁻⁵	2.3×10^{-3}
Direct Green 26	0.46	20-25	7.8×10^{-5}	1.6×10^{-1}
Solophenyl Red 4G	0.47	20-25	1.8 × 10 ⁻⁵	3.8×10^{-3}
Solophenyl Red 4G	0.20	20-25	1.8 ×10 ⁻⁵	7.3×10^{-3}
Solophenyl Red 4G	0.20	71	1.46 ×10 ⁻⁴	7.3×10^{-2}
Reactive Blue 15	0.14	20-25	6.95 ×10 ⁻⁶	5 × 10 ⁻³
Reactive Blue 15	0.14	71	1.27×10^{-5}	9.6 × 10 ⁻²
Red MX	0.22	20-25	8.67 × 10 ⁻⁵	3.6 × 10 ⁻²
Red MX	0.22	71	1 × 10 ⁻³	5 × 10 ⁻¹

(Errors 10 %)

Table 7.1 The fading rate of various samples containing no adsorbed additives.

7.2.4. Fading of dyes on Avicel

Avicel, as mentioned previously, is a form of microcrystalline cellulose. The particles it is composed of are smaller than the fibres of cotton linters. Also, there is no amorphous region present in Avicel. Therefore, it is possible that these factors cause a difference in the fading rate of dyes. However, there does not appear to be a great difference between the fading rates of a dye on cotton linters and on Avicel. Figure 7.10 shows the fading of two dyes on cotton linters and Avicel. There were other differences between the samples, such as dye loading, so any differences may not be due entirely to the substrate used. The few samples studied showed that there was not a significant difference in the fading rate of dyes on cotton linters and Avicel.





Figure 7.10 Remission function plots of dyed cotton linters and avicel at intervals in irradiation.

189

7.3. Light absorption by photoinitiators

The amount of light absorbed by the samples was determined as a value relative to other samples. This was carried out in the following way.

The photodiode array equipment described in section 2.6.2.2 was used to determine the emission spectrum of the arc lamp, which is shown in Figure 7.1. The emission spectrum of the arc lamp was normalised at the wavelength of maximum output. These normalised spectra were then multiplied by (1-R) - the light absorbed by the sample - for the samples used. The resultant curve was then integrated over the range 300-600 nm. This value was taken as the amount of light absorbed by the sample.

The spectra of various samples displayed as (1-R) versus wavelength are displayed in Figure 7.11. These samples only contain an adsorbed photoinitiator and no dye so the spectra shown are representative of the light absorbed by the cotton linters and photoinitiator only. The loading of each photoinitiator was 50 µmol g⁻¹, which is the same loading as was added to the dyed samples.



Figure 7.11 Wet cotton linters with various photoinitiators adsorbed.

Dye	No additive	Irgacure 184	Benzil	Irgacure 819
Direct Green 26	37	37	39	40
Direct Red 75	27 50 29 29	28	32 51 30 37	34 52 32 45 37
Procion Orange MX-2R		51 29		
Procion Orange H-ER				
Reactive Red 3		31		
Reactive Blue 15	33	33	36	

Table 7.2 The change in the amount of light absorbed due to the addition of photoinitiators

The values of the integral found for dyed cotton linters samples containing the three photoinitiators are shown in Table 7.2. Figure 7.12 shows the spectra for Solophenyl Red 4G samples as an example of these calculations. The spectra of 1-R versus wavelength, hereafter known as absorption spectra, are shown in Figure 7.12(a). From these spectra it can be clearly seen that the samples with adsorbed photoinitiators absorb more light than the initiator free sample.

The spectra shown in Figure 7.12(b) show the result of combining the normalised arc lamp emission spectrum with the absorption spectra of the samples. The difference in the integral value on addition of Irgacure 184 is very small and not noticeable from the curves in Figure 7.12(b). This initiator absorbs less light than the others used. The light it does absorb is at the lower end of the spectrum, in which region the arc lamp emits less light. The integral value is increased more noticeably by the addition of benzil and Irgacure 819. This can be seen in Figure 7.12(b). The detector response, as mentioned earlier in the chapter, page174, falls off at higher and lower wavelengths. This, however, does not affect the results displayed below as they are for comparison with each other only, so the absolute values are not necessary.



Figure 7.12(a) Absorption spectra of samples dyed with Solophenyl Red 4G



(b) Combination of emission of the arc lamp and absorption of the samples dyed with Solophenyl Red 4G.

7.4. Fading of dyes on cotton linters with adsorbed photoinitiators

The initiators used in this study, as mentioned in the previous section, were benzil, Irgacure 184 and Irgacure 819. The rate of fade of each dye studied increased on the addition of each of the photoinitiators. The increase in the rate of fade was dependent on the photoinitiator used. The results obtained for each photoinitiator are reported separately.

7.4.1. Addition of benzil

Benzil is a photoinitiator that is known to produce radicals via reaction with a second species, see Figure 1.18, page 40. Its addition to the samples increased the fading rate for all the dyes studied except Reactive Blue 15. Reactive Blue 15, as previously mentioned, is a phthalocyanine dye, whereas the other dyes studied were azo dyes. This difference in basic structure may be responsible for the different effect that benzil has on the fading rate.

For the azo dyes studied an increase in fading rate between five and ten times the fading rate of the dye alone was achieved. Figure 7.13 shows an example of the effect of addition of benzil with reference to Reactive Red 3 samples.



Figure 7.13(a) Remission function plots showing the effect of benzil on the fading of Reactive Red 3.



(b) Fading of Reactive Red 3 on cotton linters alone and in the presence of benzil.

7.4.2. Addition of Irgacure 819

The production of radicals by photolysis of Irgacure 819 occurs via breakdown of the initiator. This is a different method to that of benzil, see Figure 1.18, page 40. An equal number of radicals is expected to be produced for all samples, provided that there is not too much filtering of the light reaching the photoinitiator by the dye. The dyes absorb in the same region as the initiator as well as in the visible, but this effect is similar for all samples. This is shown in section 4.4 and has not been considered further. The increasing fade rate of Direct Green 26 due to adsorption of Irgacure 819 is shown in Figure 7.14.



Figure 7.14(a) Increase in fading rate due to the presence of Irgacure 819.



(b) Fading of Direct Green 26 on cotton linters alone and in the presence of Irgacure 819.

7.4.3. Addition of Irgacure 184

The addition of Irgacure 184 to samples increased the rate of fade considerably. This is illustrated in Figure 7.15, which shows the fading of a sample of cotton linters dyed with Procion Orange MX-2R. The fading rate for all dyes studied was increased by at least a hundred times on the addition of Irgacure 184. This is a much greater increase in fading rate than that which is achieved by addition of either benzil or Irgacure 819 to the samples. It appears from these studies that the radicals produced by photolysis of Irgacure 184 are more reactive towards the dyes than the radicals produced from the other initiators.



Figure 7.15(a) Remission function plots showing the altered fade rate on addition of Irgacure 184 to a sample of cotton linters dyed with Procion Orange MX-2R.



(b) Fading of Procion Orange MX-2R on cotton linters alone and in the presence of Irgacure 184.

7.4.4. Effect of changing the spectral distribution of irradiating light

For samples not containing photoinitiators, the use of filters considerably slowed the rate of fade of the dye. This can be seen in Figure 7.16, which shows the remission function plots for cotton linters dyed with reactive red 3 and Reactive Red 120 following twenty minutes irradiation. This shows, as was previously thought, that the fading of the dyes occurs mainly due to the absorption of ultraviolet light.



Figure 7.16 The influence of filters on the fading of Reactive Red 3 and Reactive Red 120 alone on cotton linters.

The samples with adsorbed photoinitiators were also affected by the use of filters. The transmission spectra of the filters used are shown in Figure 7.2. The effect of the filter used depended, as expected, on the absorption spectrum of the photoinitiator, which can be seen in Figure 7.11. The effect of these filters on the fading of dyes in the presence of photoinitiators following irradiation for twenty minutes is illustrated in appendix 3.

7.5. Summary and Conclusions

It is clear from these experiments that the presence of cotton linters affects the dye degradation. It was also found that the method of dyeing the linters affected the rate of fade. Reactively dyed samples faded much faster than samples that were directly dyed. This is further evidence that the cotton linters structure is involved in the degradation process, and it seems that a closer association between the dye and the fibres increases the fading rate.

It should be noted that the direct and reactive dyes were not equivalent in structure. It is thought that, given the number of dyes of differing structure, which are both direct and reactive, there is a definite distinction between the two types of dye. A clearer picture would be obtained using reactive dyes, which could be either reactively or directly dyed. A direct comparison would then be possible with the only difference between the dyes being the method of application to the fibre. It is concluded that there are groups in the cotton that facilitate the fading of the dye. Whether this is a result of absorption of light by the cotton linters or by the dye is not clear.

The effect of adsorption of photoinitiators onto the dyed cotton linters surface was also studied. The photoinitiators adsorbed were benzil, Irgacure 184, Irgacure 369 and Irgacure 819. These photoinitiators produce radicals in different ways, the Irgacure compounds by intramolecular bond cleavage and the benzil by reaction of its photoexcited state with a secondary species.

For Reactive Blue 15, a phthalocyanine dye, the addition of benzil to the sample resulted in no observable increase in the rate of fade. For the other dyes studied, all of which were azo dyes, the addition of this initiator led to approximately a four fold increase in the photodegradation rate.

The three Irgacure additives produce radicals by a similar mechanism to each other. The difference in the effect of their presence on the fading of the dyes can be due only to the following three factors. The efficiency of the photoinduced cleavage of the photoinitiators may differ. This is not thought to be the case, it is thought that the quantum efficiency of the breakdown of these photoinitiators are similar to each other. Also, the amount of light absorbed by these initiators is an important factor determining the number of radicals produced, and therefore the effect on the fading rate of the dye. The final factor to be considered is the reactivity of the radicals created with the dyes.

The initiator that absorbs the least light, Irgacure 184, was found to be the initiator that produced the greatest increase in the fading rate. This led to the conclusion that either the efficiency of breakdown of the molecule is larger than for the other two initiators or that the radicals produced are more reactive towards the dye. The efficiency of breakdown, as mentioned above, is not thought to be greater for Irgacure 184 than for the other initiators. Therefore, the great effect of Irgacure 184 on the fading of these samples is concluded to be due to the high reactivity of the radicals produced. This coincides with the results in Chapter 5 where the reaction rate constants for the reactions between radicals and dyes were determined. It was found that the radicals produced from Irgacure 184 were a thousand times more reactive than those produced from Irgacure 819.

The dyes studied were found not to degrade under irradiation in methanol solution. Rapid fading was observed on addition of photoinitiators to the solutions. The above series of experiments show that the presence of cotton leads to an increase in the rate of fading. This increase in rate may well be due to radicals produced from the cotton, which as already mentioned, can be modelled using α -hydroxy radicals.

Chapter 8

Summary and suggestions for further work

8. Summary and suggestions for further work

8.1. Summary

In this work, a study has been carried out on the reactions of α -hydroxy radicals as models for radicals produced on irradiation of cellulose and/or of dyed cotton. These radicals were created by photolysis of α -hydroxy ketones, which breakdown into two radicals, one of which is an α -hydroxy radical. The reaction of these radicals with alkenes as a model reaction was monitored using a visible probe, crystal violet, as used by Turro et. al.¹⁹⁶. The method developed by Turro has been used in this work to determine the difference in the reaction rates of two α -hydroxy radicals.

In order to obtain an equation to determine these rate constants it was necessary to make several assumptions, some of which were of concern. These assumptions and their justification are described in chapter 3. The kinetic analysis of reaction equations, including the consideration of these assumptions, led to the simple equations, shown below, which were used in later chapters to determine rate constants, where k_{obs} was determined by fitting a simple first order equation to the curves.

$$k_{obs} = k_1 [\alpha^{\bullet}]_0 + k_c [CV^+]$$
(3.4)

$$k_{obs} = k_1 [\alpha^*]_0 + k_d [dye]$$
(3.9)

$$k_{obs} = k_1[\alpha^{\bullet}]_0 + k_c[CV^+] + k_a[A]$$
 (3.11)

The initial concentration of radicals for both solutions in 10 mm and 1 mm pathlength cells has been determined so similar values could be used in simulations. The termination rate constants of the radicals have also been determined by varying the laser power, and therefore the initial concentration of radicals. Equation 3.4, determined following kinetic analysis of the reaction equations, was employed to find a value of the termination rate constant, k_1 .

Numerical simulations of the reaction equations have been carried out. In order to carry out these simulations, it was necessary to set the values of the rate constants and for the initial concentrations of the reacting species. The initial concentration of dye

was varied between 8 and 300 μ mol dm⁻³ and the initial concentration of radicals set between 0.5 and 50 μ mol dm⁻³ (in a similar region to the values calculated).

It was found using these simulations that accurate rate constants, within 3 % of the set value, could be found in the majority of cases. The assumption that the concentration of the dye does not change is obviously a fallacy, as the disappearance of the dye is being monitored. The assumption was still made given that the percentage loss of the dye was considered to be low. In simulations it was shown that the percentage change in the dye was not small, but this did not extensively affect the fitting of the curve.

Treatment of these simulated results has shown that, despite the inaccurate assumptions made, the method works well. The determined value was found to be most accurate in the following conditions: High dye concentration, low initial concentration of radicals, low value of the termination rate constant, k_1 , and a high value of the rate constant for reaction with the dye, k_d .

The simulations showed that the fits were better for high dye concentrations. Therefore, in experiments the concentration of dye was kept as high as possible. The simulations also showed that a high concentration of radicals resulted in the curves deviating from first order behaviour. The concentration of radicals could be kept low in experiments by attenuating the laser power. This was not done as a low laser power would lead to small signals where the signal to noise ratio is smaller.

In simulations the value of the determined rate constant was either the same as or greater than the set value. Equation 3.9 was used to determine the rate constant k_d as these simulations have shown that fairly accurate results can be obtained even with badly fitting curves. For curves with reasonable fits, similar to those fits for most experimental curves, the values were found to be correct to within 3 % of the set value. For worse fits, such as those obtained for some experimental curves e.g. Disperse Orange 3 depletion, the determined values remained within 10 % of the true value. It should be noted that the accuracy of determined values depends on the size of the data set, which was large in simulations and considerably smaller for experimental data.

Experiments to determine the reaction rate constants of alkenes with radicals, see chapter 4, were carried out using Equation 3.11 and varying the alkene concentration.
The method was validated since rate constants for reaction of 2-hydroxy-2-propyl radicals and alkenes determined in this way were similar to those found previously^{183,192}. The studies carried out in this work have shown that the rate constant for 2-hydroxy-2-propyl reactions were higher than those found for α -hydroxy cyclohexyl reactions. The rate constants for the reaction of both α -hydroxy radicals were found to vary in the same way according to the electron affinity of the alkene. The difference in the rate constant is believed to be due entirely to the fact that the α -hydroxy cyclohexyl radical is bulkier and therefore its reactions are inhibited.

The work presented in chapter 5 shows the large effect of radicals on dyes in methanol. The reaction of α -hydroxy radicals with azo dyes has been found to be fast both in solution and on cotton fabric, see chapter 6. For most of the azo dyes studied, tautomerism to the hydrazone form was possible, which may affect the reaction rate of the dyes. It appears that the number of azo groups present in the dye molecule affected the rate constant values. The greater the number of azo groups in the molecule, the higher the rate constant value. This was assumed to be due to the azo group being the reactive site.

Other structural variations have also been shown to result in a change in the rate constant. In chapter 5, the explanation for this variation is given in terms of the stabilisation of the adduct radical formed. The reaction of other types of dye with these radicals was generally found to be faster than the reaction of azo dyes. This is thought to be due to the nucleophilic nature of the radical and the positively charged dye molecules.

The reaction rate constants found were similar to those found previously by other workers. The values for the simplest azo dyes were similar to values found by Levanon et.al.²⁰⁰ for the reaction between 2-hydroxy-2-propyl radicals and azobenzene. Values have also been obtained by Hayon et.al.²⁰² for the reaction rate constant of Crystal Violet and methylene blue, along with other dyes not studied here, with 2-hydroxy-2-propyl radicals. These values are similar to the values found here for the reaction of these dyes with α -hydroxy cyclohexyl radicals.

A study of these reactions was then carried out using dyed cotton fabric with initiators absorbed. The depletion of the dyes studied was easily observable when the cotton was wetted and less noticeable for the dry cotton. The traces presented in chapter 6 for these reactions are an average of forty separate traces, as each single trace was not well defined. These average traces were fitted to a first order rate equation as the solution results had been. These new results have shown that the rate of reaction of dye with radicals is approximately ten times slower when on cotton fabric than when in solution. The reaction appears to be slightly slower when the cotton is dry, although this is not clear as the error on these results is high.

There are practical problems associated with cellulose based radicals, one of which is the photofading of dyes on cellulosic textiles. The effect of continuous irradiation of dyes in solution and on cotton linters has been studied here to a limited extent. It was found, for the dyes studied, that photodegradation was much faster when the dye was on cotton linters than when in solution. In fact, no degradation was observed in solution following hours of irradiation. This observation led to the conclusion that the cotton linters structure participates in the degradation of the dyes.

It is not clear what this participation involves, or whether it involves absorption of light by the cotton linters or by the dye. The spectral range of absorption of light by the cotton linters was found to be sufficient to account for the degradation to be due to its absorption of light. The percentage of light absorbed also increased when the cotton linters samples were dampened due to less scattered light, which was the usual state of the samples when irradiated.

In experiments varying the spectral distribution of the irradiation light, which was carried out using filters, it was found that UV light was responsible for most of the degradation that occurred. It is still, however, unclear as to whether this light is absorbed by the dye or the cotton linters.

The addition of radical photoinitiators to the samples resulted in an increase in the rate at which the dye fades. The amount by which this rate is changed varies depending on the initiator used. Irgacure 184 was found to increase the rate of fade of all dyes more than any of the other initiators despite absorbing less of the irradiation light. This fits in with the results presented in Chapter 5, which show that the radicals produced from photolysis of Irgacure 184, α -hydroxy and benzoyl radicals, are more reactive than those produced form photolysis of Irgacure 819, phosphinoyl and benzoyl radicals.

8.2. Suggestions for further work

The determination of rate constants lower than the 5×10^5 dm³ mol⁻¹ s⁻¹ limit for the Crystal Violet technique is possible by observing the radicals directly or using non-optical techniques. However, a coloured probe, which is less reactive than Crystal Violet, if one could be found, could be used to determine the rate of reaction of less reactive alkenes and other radical sensitive species. This may be useful to compare with the results found by other methods.

A bulkier α -hydroxy radical could be used to give more precise information on the effect of size on the reactions of α -hydroxy radicals. It may be possible to create such a radical by pulse radiolysis of an aqueous alcohol. This was the method used by Hayon et.al.²⁰² to produce small α -hydroxy radicals. A photoinitiator cleaving to give a bulkier α -hydroxy radical could also be used, if first synthesised (commercially available photoinitiators were used in this work).

A study of the rate constants for the reaction of similar azo dyes to those studied in this work with methoxy groups in place of hydroxy groups could be carried out. In dyes without hydroxy groups, the hydrazone form can not exist and, therefore, the rate constants will not be affected by tautomerism. A study involving a larger number of commercially available dyes may also prove useful.

The difference found between the rate of degradation of the direct and reactive dyes could be further explored using direct dyes with and without a reactive group. If this was done, the difference between the two dyes would be due mainly to the attachment to the surface and there would be no large structural differences as was the case in this work. This could be used to back-up the finding that the dyes reactively bound to the surface are less stable to light due to their closer link with the surface than the direct dyes.

It would be useful to determine the action spectrum for the photodegradation of dyes on cotton. A very careful study could be carried out to accurately determine what wavelengths of light cause the most damage. These studies could also be used to determine whether the absorption by the dye or the cotton was responsible for the degradation. **Chapter 9**

References

9. References

- Cox,A.; Kemp,T.J., Chapter 1 of 'Introductory Photochemistry' McGraw-Hill London (1971)
- Banwell, C.N., 'Fundamentals of molecular spectroscopy 3rd edition'
 McGraw-Hill London (1983)
- Pappas,S.P., Chapter 13 of 'Handbook of organic photochemistry volume II'
 Ed. Scaiano,J.C. CRC press (1989)
- 4 Dexter, D.L. Journal of Chemical Physics 21(5) (1953) 836
- 5 Forster, Th., Discussions of the Faraday Society 27 (1959) 7
- 6 Porter, G., Proceedings of the Royal Society: London 200 (1950) 284
- Wilkinson, F., Journal of the Chemical Society: Faraday Transactions 2 82 (1986) 2073
- 8 Wilkinson, F.; Kelly, G.P., Chapter 2.2 (p30) 'Laser flash photolysis of solid surfaces.' of 'Photochemistry on solid surfaces' eds. Anpo, M.; Matsuura, T., Elsevier (1989)
- 9 Wilkinson, F., Ferreira, L.F.V., Journal of Luminescence 41 (1988) 704
- Chapter 6 of 'Handbook of Organic Photochemistry Volume I' Scaiano, J.C. CRC press (1989)
- 11 Beesley, M.J., 'Lasers and their applications' Taylor and Francis (1971)
- Brown, R., 'Lasers: a survey of their performance and applications.' Hazell,
 Watson and Viney Ltd. (1969)
- Hecht,H.G., Chapter 1 of 'Modern aspects of reflectance spectroscopy.' Ed.
 Wendlandt,W.W.M. Plenum Press NY (1968)
- Wilkinson, F., Chapter 6 of 'Photochemistry in condensed phases' Ed.
 Scaiano, J.C., CRC Press (1989)

- 15 Wendlandt, W.W.M.; Hecht, H.G., Chapter 3 of 'Reflectance spectroscopy.' Interscience publishers (1966) Eds. Elving, P.J.; Kotthoff, I.M.
- 16 Kubelka, P., Journal of the Optical Society of America 38 (1948) 448-457
- Lin, T-P.; Kan, H.K.A., Journal of the Optical Society of America 60 (1970)
 1252-1256
- 18 Klemm,D.; Philipp,B.; Heinze,T.; Heinze,U.; Wagenknecht,W.,
 'Comprehensive cellulose chemistry Volume 1 Fundamentals and analytical methods' Wiley-VCH (1993)
- 19 Krassig,H.A., 'Cellulose, structure and reactivity.' Gordon and Breach science publishers, Switzerland (1993)
- 20 Doree, C., Chapter V in 'The methods of cellulose chemistry' Chapman and Hall Ltd.(1950)
- 21 'Handbook of Chemistry and physics' CRC Press Boca Raton (1992)
- Hon, D.N.S., Journal of Polymer Science: Polymer Chemistry Edition 17 (1979) 441
- Shkrob, I.A.; Depew, M.C.; Wan, J.K.S., Chemical Physics Letters 202(1,2) (1993) 133
- 24 Sirbiladze,K.J.; Rusznak,I.; Vig,A.; Krichevskiy,G.E.; Anyisimova,O.M.; Anyisimov,V.M., Dyes and Pigments 19 (1992) 235
- 25 Ranby,B.; Rabek,J.F., 'Photodegradation, photooxidation and photostabilisation of polymers.' Wiley Interscience publishers (1975)
- 26 Shoute, L.C.T.; Huie, R.E., Journal of Physical Chemistry : A 101 (1997) 3467
- 27 Meth-Cohn,O.; Smith,M., Journal of the Chemical Society Perkin Transactions I (1994) 5
- 28 Gorner,H.; Gruen,H.; Schulte-Frohilnde,D., Journal of Physical Chemistry 84 (1980) 3031

- 29 Solomon, B.S.; Thomas, T.F.; Steel, C., Journal of the American Chemical Society 90(9) (1968) 2249
- 30 Rau, H., Angewandte Chemie International Edition 12 (1973) 224
- Maack, J.; Ahuja, R.C.; Tachibana, H., Journal of Physical Chemistry 99 (1995) 9210
- 32 Bortolus, P.; Monti, S., Journal of Physical Chemistry 83 (1979) 648
- Kessler, R. W.; Krabichler, G.; Uhl, S.; Oelkrug, D.; Hagan, W.P.; Ayslop, J.;
 Wilkinson, F., Optica Acta 30(81) (1983) 1091
- Tera, F.M.; Abdou, L.A.; Michael, M.N.; Hebeish, A., Polymer Photochemistry
 6 (1985) 375
- 35 Kobayashi, T.; Degenkolb, E.O.; Rentzepis, P.M., Journal of Physical Chemistry 83(19) (1979) 2431
- Rau,H.; Luddecke,E., Journal of the American Chemical Society 104 (1982)
 1616
- 37 Wildes, P.D.; Pacifici, J.G.; Irick, G. (Jn.); Whitten, D.G., Journal of the American Chemical Society 93(8) (1971) 2004
- 38 Ahuja,R.C.; Maack,J.; Tachibana,H., Journal of Physical Chemistry 99 (1995) 9221
- 39 Kuramoto, N.; Kitao, T., Journal of the Society of Dyers and Colorists 96 (1980) 529
- 40 Ball, P.; Nicholls, C.H., Dyes and Pigments 6 (1985) 13
- 41 Sahu, M.; Bikash, S.; Chandra Bera, S., Journal of Photochemistry and Photobiology A: Chemistry 89 (1995) 19
- 42 Fischer, E.; Frei, Y.F., Journal of the Chemical Society (1959) 3159
- 43 Duveneck, G.L.; Sitzman, E.V.; Eisenthal, K.B.; Turro, N.J., Journal of Physical Chemistry 93 (1989) 7166

- Arnold, D.R.; Wong, P.C., Journal of the American Chemical Society 101(7) (1979) 1894
- 45 Griffiths, J., Journal of the Society of Dyers and Colorists 88 (1972) 106
- 46 Jacques, P., Dyes and Pigments 5 (1984) 351
- 47 Griffiths, J.; Hawkins, C., Journal of the Chemical Society: Perkin Transactions II (1977) 747
- 48 Ball, P.; Nicholls, C.H., Dyes and Pigments 3 (1982) 5
- 49 Gabor, G.; Fischer, E., Journal of Physical Chemistry 66 (1962) 2478
- Gabor, G.; Frei, Y.F.; Fischer, E., Journal of Physical Chemistry 72(9) (1968)
 3566
- 51 Griffiths, J.; Hawkins, C., Journal of the Chemical Society Chemical Communications (1972) 463
- 52 Giles, C.H.; Mckay, R.B., Textile Research Journal 33 (1963) 527
- 53 Egerton, G.S.; Morgan, A.G., Journal of the Society of Dyers and Colorists (1971) 268
- 54 Bentley, P.; McKellar, J.F.; Phillips, G.O., Rev. Prog. Colouration 5 (1974) 33
- 55 Allen, N.S., Rev. Prog. Colouration 17 (1987) 61
- 56 Allen, N.S., Polymer Degradation and Stability 44 (1994) 357
- 57 van Beek, H.C.A.; Heertjes, P.M., Journal of Physical Chemistry 70(6) (1966) 1704
- 58 Sirbiladze, K.J.; Vig, A.; Anyisimov, V.M.; Anyisimova, O.M.; Krichevskiy, G.E.; Rusznak, I., Dyes and Pigments 14 (1990) 23
- 59 Okada, Y.; Fukuoko, F.; Morita, Z., Dyes and Pigments 35(4) (1997) 311
- 60 Honma, Y.; Choji, N.; Karasawa, M., Textile Research Journal 60 (1990) 433

- 61 Datyner, A.; Nicholls, C.H.; Pailthorpe, M.T., Journal of the Society of Dyers and Colorists (communications) (1977) 213
- 62 Wang, P.Y.; Wang, I.J., Textile Research Journal 62 (1992) 15
- 63 Giles, C.H.; Shah, C.D.; Johari, D.P.; Sinclair, R.S., Journal of the Society of Dyers and Colorists 88 (1972) 59
- Mallet, V.N.; Newbold, B.T., Journal of the Society of Dyers and Colorists 90 (1974) 4
- 65 Arcoria, A.; Longo, M.L.; Parisi, G., Journal of the Society of Dyers and Colorists 100 (1984) 339
- 66 Allen, N.S.; Binkley, J.P.; Parsons, B.J.; Phillips, G.O.; Tennent, N.H., Polymer Photochemistry 5 (1984) 411
- 67 Krichevskii, G.E.; Vachobov, B.; Ershov, Y.A.; Dovbii, E.B., Textile Research Journal 45 (1975) 608
- 68 Allen, N.S.; Fatinikun, K.O.; Davies, A.K.; Parsons, B.J.; Phillips, G.O., Polymer Photochemistry 1 (1981) 275
- Remi,E.; Horvath,O.; Vig,A.; Rockenbauer,A.; Korecz,L.; Aranyosi,P.;
 Rusznak,I., Radiation Physics and Chemistry 47(3) (1996) 461
- 70 Giles, C.H.; Strevens, E.A., Textile Research Journal 49 (1979) 724
- 71 Wang, P.Y.; Ma, J.F., Dyes and Pigments 37(2) (1998) 121
- Tera, F.M.; Michael, M.N.; Hebeish, A.; Polymer Degradation and Stability 17 (1987) 13
- 73 Giles, C.H.; Rahman, S.M.K., Textile Research Journal 31 (1961) 1012
- Arcoria, A.; Longo, M.L.; Parisi, G.; Allen, N.S., Dyes and Pigments 7 (1986)
 299
- 75 Abdel-hay, F.I.; Etaiw, S.H.; Anwar, M.; El-Morsi, M., Kolorisztikai Ertesito 6 (1977) 365

- 76 Allen, N.S.; Fatinikun, K.O.; Davies, A.K.; Parsons, B.J.; Phillips, G.O., Polymer Photochemistry 1 (1981) 275
- Okada, Y.; Hirose, M.; Kato, T.; Motomura, H.; Morita, Z., Dyes and Pigments
 14 (1990) 113
- 78 Bredereck, K.; Schumacher, C., Dyes and Pigments 23 (1993) 135
- 79 Okada, Y.; Kato, T.; Motomura, H.; Morita, Z., Dyes and Pigments 12 (1990) 197
- 80 Okada, Y.; Fukuoka, F.; Morita, Z., Dyes and Pigments 37(1) (1998) 47
- 81 Okada, Y.; Hirose, M.; Kato, T.; Motomura, H.; Morita, Z., Dyes and Pigments
 14 (1990) 265
- 82 Okada, Y.; Sugane, A.; Watanabe, A.; Morita, Z., Dyes and Pigments 38(1-3) (1998) 19
- 83 Okada, Y.; Asano, M.; Morita, Z., Dyes and Pigments 31(1) (1996) 53
- Okada, Y.; Sugane, A.; Fukuoka, F.; Morita, Z., Dyes and Pigments 39(1) (1998)
 1
- 85 Croud, V.B., Journal of the Society of Dyers and Colorists 112 (1996) 117
- 86 Bevan, G., Journal of the Society of Dyers and Colorists 112 (1996) 209.
- 87 Croud, V.B., Journal of the Society of Dyers and Colorists 112 (1996) 249
- 88 Sartori, M.F., Journal of the Society of Dyers and Colorists (1967) 144
- 89 Shakra, S.; Ghattas, A.A.G., Kolorisztikai Ertesito 5 (1979) 287
- 90 Kamel,M.; Sherif,S.; Abd-El-Hay,F.I., Journal Praktische Chemichte 315(3) (1973) 436
- Okada, Y.; Orikasa, K.; Motomura, H.; Morita, Z., Dyes and Pigments 19 (1992)
 203
- 92 Kissa, E., Textile Research Journal 41 (1971) 715

- Dubini-Paglia, E.; Beltrame, P.L.; Marcandalli, B.; Carniti, P.; Seves, A.;
 Vicini, L., Journal of Applied Polymer Science 31 (1986) 1251
- 94 Irick, G.(Jn); Pacifici, J.G.; Textile Research Journal 41 (1971) 255
- 95 Okada, Y.; Kato, T.; Motomura, H.; Morita, Z., Sen'I Gakkaishi 46(8) (1990)
 346
- Baxter,G.; Giles,C.H., Journal of the Society of Dyers and Colorists 73 (1957)
 386
- 97 Egerton, G.S.; Roach, A.G., Journal of the Society of Dyers and Colorists (1958) 401
- 98 McKellar, J.F., Radiation Research Review 3 (1971) 141
- 99 Bortolus, P.; Monti, S.; Albini, A.; Fasini, A.; Pietra, S., Journal of Organic Chemistry 54 (1989) 534
- Neckers, D.C.; Valdes-Aguilera, O.M., Advances in Photochemistry 18 (1992)
 315
- 101 Yamada,K.; Shosenji,H.; Nakano,Y.; Uemura,M.; Uto,S.; Fukushima,M., Dyes and Pigments 2 (1981) 21
- 102 Jones, G.(II); Goswami, K., Journal of Physical Chemistry. 90 (1986) 5414
- 103 Oelkrug, D.; Uhl, S.; Wilkinson, F.; Willsher, C.J.; Journal of Physical Chemistry 93 (1989) 4551
- 104 Tang, W.Z.; Chen, R.Z., Chemosphere 32(5) (1996) 947
- 105 Chang, I.Y.; Miller, I.K., Journal of the Society of Dyers and Colorists 102 (1986) 46
- Lenhard, I.R.; Cameron, A.D., Journal of Physical Chemistry 97(19) (1993)
 4916
- 107 Stiborova, M.; Asfaw, B.; Frei, E.; Schmeiser, H.H., Collection of Czechoslovakian Chemical Communications 61 (1996) 962

- 108 Ayyangar, N.R.; Srinivasan, K.V., Colorage 36(2) (1989) 47
- Wilkinson, F.; Willsher, C.J.; Pritchard, R.B., European Polymer Journal 21 (1985) 333
- 110 Ball, P.; Nicholls, C.H., Dyes and Pigments 5 (1984) 437
- Griffiths, J.; Hawkins, C., Journal of the Chemical Society Perkin Transactions II (1977) 747
- Griffiths, J.; Hawkins, C., Journal of Applied Chemistry and Biotechnology
 27(1977) 558
- 113 Jansen, L.M.G.; Wilkes, I.P.; Wilkinson, F.; Worrall, D.R., Journal of Photochemistry and Photobiology A: Chemistry 125 (1999) 99
- Peral, J.; Mills, A., Journal of Photochemistry and Photobiology A: Chemistry
 73 (1993) 47
- 115 Vinodgopal,K.; Wynkoop,D.E.; Kamat,P.V., Environmental Science and Technology 30 (1996) 1660
- 116 Nasr,C.; Vinodgopal,K.; Fisher,L.; Hotchandani,S.; Chattopadhyay,A.K.; Kamat,P.V., Journal of Physical Chemistry 100 (1996) 8436
- Gehlen, M.H.; Ferreira, M.; Neuman, M.G., Journal of Photochemistry and Photobiology A: Chemistry 87 (1995) 55
- 118 Blaisdell, B.E., Journal of the Society of Dyers and Colorists 65 (1949) 618
- 119 Pacifici, J.G.; Irick, G.(Jr), Tetrahedron Letters 27 (1969) 2207
- 120 Heijkoop,G.; van Beek,H.C.A., Recueil, Journal of the Royal Netherlands Chemical Society 95 (1976) 6
- 121 Cowan, D.O.; Drisko, R.L.E., Journal of the American Chemical Society 92(21)
 (1970) 6286
- 122 Albini, A.; Fasini, E.; Pietra, S., Journal of the Chemical Society Perkin Transactions II (1986) 681

- 123 Heijkoop,G.; van Beek,H.C.A., Recueil, Journal of the Royal Netherlands Chemical Society 96(3) (1997) 83
- 124 Allen, N.S.; Binkley, J.P; Parsons, B.J.; Phillips, G.O.; Tennent, N.H., Dyes and Pigments 5 (1984) 209
- van Beek, H.C.A.; Heertjes, P.M., Journal of the Society of Dyers and Colorists
 79 (1963) 661
- 126 Rehak, V.; Novak, F.; Cepciansky, I., Collection of Czechoslovak Chemical Communications 38 (1973) 697
- 127 Arcoria, A.; Longo, M.L.; Maccarone E.; Parisi, G.; Perrini, G., Journal of the Society of Dyers and Colorists 100 (1984) 13
- 128 Pacifici, J.G.; Irick, G.(Jr); Anderson, C.G. Journal of the American Chemical Society 91 (1969) 5654
- 129 Buback, M.; Degener, B., Makromolekulare Chemischte 194 (1993) 2875
- 130 Perkins, M.J., 'Radical chemistry' Ellis Horwood Ltd. 1994
- 131 Takeda,K.; Kajii,Y.; Shibuya,K.; Obi,K., Journal of Photochemistry and Photobiology A: Chemistry 115 (1998) 109
- 132 Adam, W.; Schulte Oestrich, R., Chemichte Berichte 125 (1992) 2463
- Kohno, S.; Hoshino, M.; Shizuka, H., Journal of Physical Chemistry 95 (1991)
 5489
- Sakaguchi, Y.; Hayashi, H.; I'Haya, Y.J., Journal of Photochemistry and Photobiology A: Chemistry 65 (1992) 183
- 135 Leigh, W.J.; Lathioor, E.C.; StPierre, M.J., Journal of the American Chemical Society 118 (1996) 12339
- 136 Hutchinson, J.; Ledwith, A., Advances in Polymer Science 14 (1974) 49
- 137 Peters,K.S.; Freilich,S.C.; Schaeffer,C.G., Journal of the American Chemical Society 102 (1980) 5701

- 138 Marshall, J.H., Journal of Physical Chemistry 78(22) (1974) 2225
- Bartholomew, R.F.; Davidson, R.S., Journal of the Chemical Society (C) (1971)
 2342
- Naguib, Y.M.A.; Steel, C.; Cohen, S.G.; Young, M.A, Journal of Physical Chemistry 91 (1987) 3033
- 141 Cohen, C.G.; Baumgaten, R.J., Journal of the American Chemical Society 87 (1965) 2996
- 142 Miyasaka, H.; Kiri, Y.; Morita, K.; Mataga, N., Chemical Physics Letters 199(1,2) (1992) 21
- 143 Viltres Costa, C.; Grela, M.A.; Churio, M.S., Journal of Photochemistry and Photobiology A: Chemistry 99 (1996) 51
- 144 Mustroph, H.; Marx, J.; Epperlein, J., Acta Polymerica 34 (1983) 336
- Shen, T.; Zhao, Z.; Yu, Q.; Xu, H., Journal of Photochemistry and Photobiology
 A: Chemistry 47(2) (1989) 203
- Encinas, M.V.; Scaiano, J.C., Journal of the American Chemical Society
 101(26) (1979) 7740
- 147 Kajii, Y.; Itabashi, H.; Shibuya, K.; Obi, K., Journal of Physical Chemistry 96(18) (1992) 7244
- 148 Okada, Y.; Motomura, H.; Morita, Z., Dyes and Pigments 16 (1991) 205
- Mukai, M.; Yamauchi, A.; Hirota, N., Journal of Physical Chemistry 93(11) (1989) 4411
- 150 Ebihara, K.; Takahashi, H.; Noda, I., Applied Spectroscopy 47(9) (1993) 1343
- 151 Encinas, M.V.; Lissi, E.; Gargallo, L.; Radic, D.; Sigdman, R., Journal of Polymer Science: Polymer Chemistry Edition 22(10) (1984) 2469
- 152 Amat-Guerri, F.; Rivera-Sagredo, A.; Sanz, J., Journal of Photochemistry and Photobiology A: Chemistry 55 (1990) 87

- 153 Dutta, R.; Chowdhury, M., Journal of Photochemistry and Photobiology A: Chemistry 55(2) (1990) 197
- 154 Kohomoto, T.; Fukuda, F.; Kuroda, R.; Hashi, T., Chemical Physics Letters
 119(5) (1985) 438
- 155 Wilkinson, F.; Willsher, C.J., Applied Spectroscopy 38(6) (1984) 897
- Kasama,K.; Takematsu,A.; Arai,S., Journal of Physical Chemistry 86 (1982)
 2420
- 157 Zakharova, T.D.; Solov'eva, V.B.; Zaitseva, V.N. Journal of Applied Chemistry USSR 44 (1971) 2865
- 158 Borkman, R.F.; Kearns, D.R.; Journal of Chemical Physics 44(3) (1966) 945
- Porter, G., Journal of the Chemical Society Faraday Transactions I (1973)
 1462
- 160 Lehmann, M.N.; Bakker, M.G., Journal of the Chemical Society Perkin Transactions II (1997) 2131
- Terazima, M.; Okamoto, K.; Hirota, N., Journal of Physical Chemistry 97 (1993) 13387
- 162 Wagner, P.J.; Waite, C.I., Journal of Physical Chemistry 99(19) (1995) 7388
- 163 Turro, N.J.; Khudgakov, I.V., Chemical Physics Letters 193(6) (1992) 546
- 164 Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J., Journal of the American Chemical Society 118 (1996) 6477
- 165 Chakrovorty, K.K., Applied Optics 32(13) (1993) 2331
- Ottersbach, P.; Lennarz, K.; Bargon, J., Macromolecular Chemistry and Physics
 195 (1994) 3929
- 167 Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J., Journal of the American Chemical Society 118 (1996) 6477

- 168 Sluggett, G.W.; Turro, C.; Gearge, M.W.; Koptyug, I.V.; Turro, N.J., Journal of the American Chemical Society 117 (1995) 5148
- 169 Neville, A.G.; Brown, C.E.; Rayner, D.M.; Lusztyk, J.; Ingold, K.U., Journal of the American Chemical Society 113 (1991) 1869
- 170 Kamachi, M.; Kuwata, K.; Sumiyoshi, T.; Schnabel, W., Journal of the Chemical Society Perkin Transactions II (1988) 961
- 171 Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y., Macromolecules 26 (1993) 7369
- Kajiwara, A.; Konishi, Y.; Morishima, Y.; Schnabel, W.; Kuwata, K.;Kamachi, M., *Macromolecules* 26 (1993) 1656
- 173 Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P., Polymer 26 (1985) 141
- 174 Sumiyoshi, T., Chemistry Letters (8) (1995) 645
- 175 Miller, J.R.; Beitz, J.V.; Huddleson, R.K., Journal of the American Chemical Society 106(18) (1984) 5057
- 176 Das,S.; Kamat,P.V.; Padmaja,S.; Au,V.; Madison,S.S., Journal of the Chemical Society Perkin Transactions II (1999) 1219
- 177 Lane, J.; Tabner, B.J., European Polymer Journal 25(7,8) (1989) 677
- Baugh, P.J.; Hinojosa (?).; Arthur, J.C. (Jr.), Journal of Physical Chemistry
 71(4) (1967) 1135
- 179 Dietliker,K.; Leppard,D.; Kunz,M.; Gatlik,I.; Kolczak,U.; Rzadek,P.; Rist,G., The Spectrum (1997-1999) 13
- 180 Tedder, J.M.; Walton, J.C., Accounts of Chemical Research 9 (1976) 183
- 181 Fischer, H.; Paul, H., Accounts of Chemical Research 20 (1987) 200
- Mukai, M.; Yamauchi, S.; Hirota, N., Journal of Physical Chemistry 96(8)
 (1992) 3305
- 183 Batchelor, S.N., Journal of Physical Chemistry B 103(32) (1999) 6700

- Martschke, R.; Farley, R.D.; Fischer, H., Helvetica Chimica Acta 80 (1997)
 1363
- 185 Salzmann, M.; Tsentalovich, Y.P.; Fischer, H., Journal of the Chemical Society Perkin Transactions II (1994) 2119
- 186 Vinodgopal,K.; Kamat,P.V., Journal of Photochemistry and Photobiology A: Chemistry 83 (1994) 141
- 187 Ohbayashi, K.; Akimoto, H.; Tanaka, I., Journal of Physical Chemistry 81(8) (1977) 798
- Mukai, M.; Yamauchi, S.; Hirota, N.; Higuchi, J., Journal of Physical Chemistry 96(23) (1992) 9328
- 189 Borer, A.; Kirchmayr, R.; Rist, G., Helvetica Chimica Acta 61 (1978) 305
- 190 Tominaga, K.; Yamauchi, S.; Hirota, N., Journal of Physical Chemistry 95 (1991) 3671
- 191 Levstein, P.R.; van Willigen, H., Journal of Chemical Physics 95(2) (1991) 900
- 192 Batchelor, S.N.; Fischer, H., Journal of Physical Chemistry. 100 (1996) 9794
- 193 Craw, M.T.; Depew, M.C.; Wan, J.K.S. Canadian Journal of Chemistry 64 (1986) 1414
- 194 Baxter, J.E.; Davidson, R.S.; Hageman, H.J.; McLauchlan, K.A.; Stevens, D.G., Journal of the Chemical Society Chemical Communications (1987) 73
- 195 Colour Index International, Bradford: Society of Dyers and Colourists: American Association of Textile Chemists (1999)
- Jockusch, S.; Turro, N.J., Journal of the American Chemical Society 121 (1999)
 3921
- 197 Turro, N.J., 'Modern molecular photochemistry' Benjamin/CummingsPublishing Co., 1978

- Lias,S.G.; Bartmess,J.E.; Liebmann,J.F.; Holmes,J.L.; Levin,R.D.;
 Mallard,W.G., Journal of Physical and Chemical Reference Data 17 (1988)
 Supplement 1
- 199 Tedder, J.M.; Walton, J.C., Tetrahedron 36 (1980) 701
- 200 Neta, P.; Levanon, H., Journal of Physical Chemistry 81(24) (1977) 2288
- 201 Jansen, L.M.G., PhD Thesis (1997) Loughborough University
- 202 Rao, P.S.; Hayon, E., Journal of Physical Chemistry 77(23) (1973) 2753
- 203 Fossey, J.; Lefort, D.; Sorba, J., 'Free radicals in organic chemistry' Chichester: Wiley 1995
- 204 van Beek, H.C.A.; Heertjes, P.M.; Hontepen, C.; Retzloff, D., Journal of the Society of Dyers and Colorists 87 (1971) 87
- 205 Billmeyer, F.W.Jr 'Textbook of polymer science' Wiley (1971) 530
- 206 Giles, C.H.; Johari, P.; Shah, C.D., Textile Research Journal 38 (1968) 1048
- 207 Egerton, G.S., Journal of the Society of Dyers and Colorists 63 (1947) 161

Chapter 10

Appendices

10.1. Appendix 1







Kubelka-Munk plots of a range of dyes absorbed on cotton linters.

10.2. Appendix 2

Dye	λ _{max}	$\frac{\varepsilon'}{S} / (\mu \text{mol } g^{-1})^{-1}$		
	/ nm	Cotton linters	Cotton	Avicel
Procion Orange H-ER	493	0.838	1.748	0.811
Procion Orange MX-2R	498	0.375		0.377
Solophenyl red 4G	527	1.079		1.304
Amaranth	532	0.838	0.558	
Safranine O	534	0.272	0.356	
Direct red 80	542	0.298		0.374
Red MX	547	0.324	0.48	
Reactive red 3	553	0.329	0.724	
Reactive red 120	553	0.836		0.90
Direct red 75	566	0.530		0.595
Direct green 26	643	0.259	0.365	0.195
Methylene Blue	659	0.721	1.036	
Reactive blue 15	675	0.825	0.232	

Relative values of the absorption coefficient of dyes on three solid substrates.

10.3. Appendix 3

10.4. Appendix 4



The effect of filters on the fading of dyes in the presence of photoinitiators



Effect of the spectral distribution of light on dye fading in the presence of Irgacure 184.



Effect of the spectral distribution of light on dye fading in the presence of Irgacure 369.



Effect of the spectral distribution of light on dye fading in the presence of Irgacure 819.