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Study of Mono- and Multiphoton Processes on Pulp and in Model Systems

by

Klára Kónya

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In the Ottawa-Carleton Chemistry Institute
Department of Chemistry
University of Ottawa
Ottawa, Ontario
Canada

Candidate

Supervisor

Klára Kónya

J. C. Scaiano

UNIVERSITÉ  UNIVERSITY
D'OTTAWA OF OTTAWA

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Abstract

The work described in this thesis deal primarily with the ortho-quinone present in high-yield pulp. In the first part of this thesis a sensitive fluorescence method is described using derivatized pyrene compounds, as well as other, more red-emitting fluorescent molecules to detect ortho-quinone structural moieties in high-yield pulp and paper. This method is selective, efficient, and by means of time resolved diffuse reflectance fluorescent spectroscopy and fluorescent microscopy, it is possible to show that, during photoyellowing of high-yield pulp, ortho-quinoid groups form in domains. Furthermore, fluorescence microscopy made it possible to determine that the morphological structures of the high yield pulp, where the quinone formation occurs preferentially, are the fines, broken fibers and aggregates.

The second part of this thesis deals with ortho-quinone formation via multiphotonic processes involving phenoxy radicals. To study multiphotonic processes, laser drop photolysis and two-laser two-color techniques were used. For detection, products were derivatized, and examined by means of fluorescence spectroscopy and a gas chromatograph with mass spectroscopy as detection system (GC-MS). The process was shown to have a very low quantum-yield.

The third part of the thesis describes the photochemistry of 1,3-dichloro-1,3-diphenylpropanes. In apolar solvents, beside the expected monophotonic processes, high-intensity irradiation light leads to the formation of 1,3-diphenylallyl radicals. In polar solvents,

only monophotonic reactions were observed. Further, the 1,3-diphenylallyl cation was also detected. To explain the kinetics of the formation of this cation, a four member cyclic chloronium cation was suggested as a precursor. Both the precursor and the allyl cation were characterized by their quenching with a number of nucleophiles and anions. Irradiation of the 1,3-diphenylallyl cation leads to the appearance of a new transient which was suggested to be its Z-isomer.

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Index

Abstract	
Index	i
List of figures	v
List of tables	xv
List of abbreviations	xvi
Chapter 1- Introduction	
1.1. Historical background	1
1.2. Chemical composition of lignin	2
1.2.1. Structure of lignin	4
1.3. Photochemistry of lignin and lignocellulosic materials	12
1.3.1. Establishing the mechanism for the photo- degradation of lignin	13
1.3.2. Utilization of model compounds	16
1.3.3. Studies on pulp and paper	21
1.3.4. Use of fluorescence spectroscopy to study lignocellulosic materials	22
1.4. Purpose of this thesis	25
Chapter 2- Laser Techniques and General Instrumentation	
2.1. Introduction	26
2.2. Time-resolved fluorescence	26
2.3. Laser flash photolysis	33
2.4. Two-laser-two-color laser flash photolysis	35
2.5. Laser-drop photolysis	36

2.6. Fluorescence microscopy	38
2.7. Steady-state fluorescence spectroscopy	39
2.8. Steady-state irradiation	39
2.9. UV-visible spectra	40

Chapter 3-Development and Application of Fluorescence Techniques for Monitoring Photodegradation of Lignin-Rich Products

3.1. Introduction	41
3.1.1. Effects of molecular structure on fluorescence	41
3.2. Application of pyrene-containing fluorescent probes	45
3.2.1. Method I: pyrene-derivatized phosphites	52
3.2.2. Method II: hydrolysis of cyclic phosphorous compounds	59
3.2.2.1. NMR reactivity studies	60
3.2.2.2. Steady state fluorescence spectroscopy	65
3.2.2.3. Time resolved fluorescence spectroscopy	72
3.3. Application of more red-emitting fluorescent probes	75
3.3.1. Application of Rose Bengal, Fluorescein and Rhodamine B	78
3.3.2. Application of coumarines	81
3.3.3. Application of polycyclic aromatic compounds	84
3.3.3.1. Derivatization of fluoranthene	84
3.3.3.2. Derivatization of rubrene	87
3.4. Fluorescence microscopy	89
3.5. Study of pulp fluorescence applying the synchronous technique	93

3.6. Discussion	98
3.7. Experimental section	102

Chapter 4-High Intensity Laser Generation of *ortho*-Quinones from 2-Methoxyphenols

4.1. Introduction	108
4.2. Results	111
4.2.1. Derivatization of <i>ortho</i> -quinones	111
4.2.2. Choice of starting materials	115
4.2.3. Low-intensity irradiation	116
4.2.4. High-intensity experiments	118
4.2.4.1. Experiments with α -Guaiaoxyacetoveratrone	118
4.2.4.2. Experiments with substituted 2-methoxy phenols	121
4.3. Discussion	131
4.4. Experimental section	132

Chapter 5-Multiphoton Chemistry of 1,3-Dichloro-1,3-diphenyl Propane

5.1. Introduction	135
5.1.1. Photochemistry of bichromophoric systems	135
5.1.2. Photochemistry of carbon-halogen bond	138
5.1.3. Photochemistry of (α,ω)-dihalo- (α,ω)-diphenyl alkanes	141
5.2. Results	144
5.2.1. Studies in apolar solvent	146

5.2.1.1. Laser Flash Photolysis studies	146
5.2.1.2. High intensity product studies	154
5.2.1.3. Laser-Drop Photolysis studies	156
5.2.2. Studies of polar solvents	156
5.2.2.1. Laser Flash Photolysis studies	156
5.2.2.2. Effect of the second laser on the ally lcation	167
5.3. Discussion	169
5.4. Experimental section	173
 References	 174
Claims to original research	182

List of Figures

- Figure 1.1.**
Schematic representation of the structure of wood cells
- Figure 1.2.**
Phenylpropanols which participate in lignin formation (coniferyl alcohol, syringyl alcohol, sinapyl alcohol)
- Figure 1.3.**
Some resonance structures of coniferyl alcohol radicals
- Figure 1.4.**
Reaction of two coniferyl alcohol radicals with resonance structure Rb and Rc to form dehydroconiferyl alcohol
- Figure 1.5.**
Dilignols which can form in the reaction of two coniferyl alcohol radicals
- Figure 1.6.**
Addition of a carbohydrate chain to the quinone methide structure.
- Figure 1.7.**
A structural scheme of spruce lignin as proposed by Freudenberg
- Figure 1.8.**
Role of phenoxy radicals in photoyellowing as proposed by Leary
- Figure 1.9.**
Lignin model compounds examined by Lin et al.
- Figure 1.10.**
Photodecomposition pathway of lignin proposed by Lin et al.
- Figure 1.11.**
Characteristic β -O-4 and β -1 structures in lignin
- Figure 1.12.**
Quinone-hydroquinone redox cycle, and its role in the irreversible yellowing of the carbohydrate framework
- Figure 1.13.**
Ketyl mediated degradation pathway of chromophores in lignin
- Figure 2.1.**
Fluorescence emission intensity as a response to sinusoidal excitation
- Figure 2.2.**
Fluorescence emission upon pulsed excitation

Figure 2.3.

Experimental set-up for the time resolved fluorescence measurements

Figure 2.4.

Built-up of a streak tube

Figure 2.5.

Fluorescence decays and spectra as well as the original streak image

Figure 2.6.

Schematic representation of the laser system in transmission mode

Figure 2.7.

Time-event representation of laser drop photolysis

Figure 2.8.

Laser drop cell

Figure 3.1.

Relevant photophysical processes after absorption of a photon

Figure 3.2.

Cycloaddition of ortho-quinone and trialkylphosphite and hydrolysis of cyclic phosphite esters

Figure 3.3.

Pyrene

Figure 3.4.

Relevant photophysical properties of pyrene

Figure 3.5.

Two possible pyrene excimers

Figure 3.6.

Derivatization of ortho-quinones with 4-pyrenebutyldimethyl phosphite

Figure 3.7.

Fluorescence spectra of irradiated TMP paper with 2 and 6. Excitation wavelength 330 nm

Figure 3.8.

Fluorescence spectra of non-irradiated TMP paper with 2 and 6. Excitation wavelength 330 nm

Figure 3.9.

Difference fluorescence spectrum of irradiated and non-irradiated TMP paper treated with 6 and 2

Figure 3.10.

Difference spectrum between irradiated and non-irradiated TMP pulp treated with 6 and 2

Figure 3.11.

Effect of different excitation wavelengths on the fluorescence of thermomechanical pulp after treatment with 6

Figure 3.12.

Pyrenebutyric acid

Figure 3.13.

Model compounds used in ^{13}C -NMR experiments. p-Benzoquinone (9), 4,6-di-*tert* butyl-orthoquinone (10) and conyferaldehyde (11)

Figure 3.14.

Assignment of ^{13}C -NMR results presented in Table 3.4.

Figure 3.15.a.

^{13}C -NMR spectrum of 10 in CDCl_3

Figure 3.15.b.

^{13}C -NMR spectrum of cyclic phosphite ester of 10 in CD_2Cl_2

Figure 3.15.c.

Cyclic phosphite ester of 10 after reaction with $\text{CH}_3^{13}\text{COOH}$

Figure 3.16.

Four ring opening possibilities for cyclic phosphite ether of 10 upon hydrolysis with $\text{CH}_3^{13}\text{COOH}$

Figure 3.17.

Fluorescence spectra (excitation wavelength 330 nm) of irradiated TMP with and without pyrene as well as the difference spectrum

Figure 3.18.

Fluorescence difference spectrum (excitation wavelength 330 nm) and diffuse reflectance spectra of treated TMP paper, and diffuse reflectance spectrum of untreated TMP paper

Figure 3.19.

Effect of irradiation wavelength on the fluorescence of irradiated and treated TMP (excitation wavelength 330 nm)

Figure 3.20.

Normalized intensity of pyrene fluorescence upon treatment of TMP with different amounts of pyrene

Figure 3.21.

Maximum intensity of pyrene fluorescence (plateau at maximum pyrene incorporation for samples subjected to irradiation)

Figure 3.22.

Effect of bleaching on pyrene incorporation (excitation wavelength 345 nm)

Figure 3.23.

Gated spectra of treated and untreated TMP in different time windows

Figure 3.24.

Time-resolved fluorescence spectra of irradiated TMP treated at high pyrene butyric acid concentration

Figure 3.25.

Decay kinetics of monomer and excimer emission. Detection system was delayed by 30 ns.

Figure 3.26.

Fluorescence spectra after treatment of irradiated and nonirradiated pulp with (13) (excitation: 490 nm)

Figure 3.27.

Fluorescence spectra after treatment of irradiated and nonirradiated pulp with 15 (excitation: 490 nm)

Figure 3.28.

Fluorescence spectra after treatment of irradiated and nonirradiated pulp with 14 (excitation wavelength: 500 nm)

Figure 3.29.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 16 (excitation wavelength: 400 nm)

Figure 3.30.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 18 (excitation wavelength: 400 nm)

Figure 3.31.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 17 (excitation wavelength: 400 nm)

Figure 3.32.

Synthesis of 3-fluoranthanol (19)

Figure 3.33.

Synthesis of the 3-fluoranthanol derivative (20)

Figure 3.34.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 20 (Excitation wavelength: 395 nm)

Figure 3.35.

Difference spectrum of irradiated and non-irradiated pulp after treatment with 20

Figure 3.36.

Friedel-Crafts acylation and alkylation of rubrene

Figure 3.37.

Fluorescence spectra of irradiated and non-irradiated pulp treated with 21, as well as the fluorescence spectrum of 21 in dichloromethane (Excitation wavelength: 400 nm)

Figure 3.38

Fluorescence and phase-contrast microscopic photographs of fibers treated with pyrenebutyric acid according to method II

Figure 3.39.

The fluorescence of a very thin fine is particularly intense

Figure 3.40.

Fluorescence is more intense in damaged fibers

Figure 3.41.

Fluorescence microscopy photograph of one part of the pulp which shows the higher fluorescence of the fine agglomerations and that of the damaged fibers

Figure 3.42.

Model compounds used for synchronous measurements

Figure 3.43.

Synchronous spectra of Whatmann paper

Figure 3.44.

Synchronous spectra of 23 absorbed on Whatmann filter paper

Figure 3.45.

ORTEP diagram of 22

Figure 4.1.

Formation of ortho-quinones from phenols via multiphotonic pathways

Figure 4.2.

Some cycloaddition reactions of ortho-quinones

Figure 4.3.

Thermal decomposition of phenylenediamine in water and in ethanol (Monitored at 395 nm)

Figure 4.4.

Decomposition of 1,2-phenylenediamine in the presence of different acids (Monitored at 395 nm)

Figure 4.5.

Different mechanisms to generate phenoxy radicals

Figure 4.6.

Comparison of the fluorescence of non-irradiated and irradiated (low intensity, 254 nm light) 2-methoxyphenol in hexane (following treatment with 1,2-phenylenediamine) (Excitation wavelength: 420 nm)

Figure 4.7.

Phenoxy radicals formed from α -guaiacoxyacetoveratrone, using the attenuated (45%) pulses from a 308 nm laser

Figure 4.8.

Fluorescence of possible products and the starting materials for the photolysis of α -guaiacoxyacetoveratrone after treatment with 1,2-phenylenediamine

Figure 4.9

Fluorescence spectra of model quinone (3-methoxy-1,2-orthoquinone), and α -GAV after steady state and laser drop irradiation in acetonitrile and treatment with 1,2-phenylenediamine

Figure 4.10

Fluorescence spectra of a model quinone (3-methoxy-1,2-orthoquinone), and α -GAV after steady state and laser drop irradiation in benzene and treatment with 1,2-phenylenediamine

Figure 4.11.

Model phenols

Figure 4.12.

Fluorescence emission spectra of 3-methoxy-quinone, 2,6-dimethoxyphenol and 2,6-dimethoxyphenol after laser drop

photolysis in hexane and treatment with 1,2-phenylenediamine.
Excitation wavelength 420 nm

Figure 4.13.

Fluorescence excitation spectra of 3-methoxyquinone, 2,6-dimethoxyphenol and 2,6-dimethoxyphenol after laser drop photolysis in hexane and treatment with 1,2-phenylenediamine (Fluorescence monitored at 520 nm)

Figure 4.14.

Effect of excitation wavelength on the fluorescence emission of 2,6-dimethoxyphenol after laser drop photolysis and treatment with 1,2-phenylenediamine

Figure 4.15.

Comparison of the results of laser drop photolysis of 2-methoxyphenol in hexane and in acetonitrile to the unphotolyzed starting material in hexane after the usual treatment with 1,2-phenylenediamine (Fluorescence monitored at 520 nm)

Figure 4.16.

Excitation spectra of different substituted 2-methoxyphenols after laser drop irradiation and treatment with 1,2-phenylenediamine (Fluorescence monitored at 520 nm)

Figure 4.17.

Emission spectra of different substituted 2-methoxy phenols after laser drop irradiation and treatment with 1,2-phenylenediamine (Excitation wavelength: 420 nm)

Figure 4.18.

Effect of the leaving group. Fluorescence spectra following laser drop irradiation of 2-methoxyphenol and 2-isopropoxyphenol in hexane followed by treatment with 1,2-phenylenediamine (Excitation wavelength 420 nm)

Figure 5.1.

Multiphoton chemistry of bis-dibenzyl ketones

Figure 5.2.

Multiphoton chemistry of bis(diazomethane)

Figure 5.3.

Photochemistry of the carbon-halogen bond

Figure 5.4.

Photochemistry of geminal alkyl dihalides

Figure 5.5.

Photochemistry of acyclic vicinal dibromides

Figure 5.6.

Photochemistry of 1,8-bis(halomethyl)naphthalene

Figure 5.7.

(α,ω)-dihalo-(α,ω)-diphenyl alkanes studied in our laboratory

Figure 5.8.

Photochemistry of 1,5-dichloro-1,5-diphenylpentane in cyclohexane

Figure 5.9.

Photochemistry of 1,5-diiodo-1,5-diphenylpentane in cyclohexane

Figure 5.10.

Low intensity irradiation of 1,3-dichloro-1,3-diphenylpropane in cyclohexane

Figure 5.11.

Transient absorption spectra of 1,3-dichloro-1,3-diphenylpropane in cyclohexane. (Excitation wavelength 266 nm, recorded 770 ns after the laser pulse)

Figure 5.12.

Decay monitored at 360 nm of 1,3-dichloro-1,3-diphenylpropane in cyclohexane after excitation with 266 nm light

Figure 5.13.

Decay monitored at 320 nm of 1,3-dichloro-1,3-diphenylpropane in cyclohexane after excitation with 266 nm light

Figure 5.14.

Multiphoton chemistry of 1,3-dichloro-1,3-diphenylpropane and 3-chloro-1,3-diphenylpropane in cyclohexane

Figure 5.15.

Transient decay at 360 nm of 1,3-dichloro-1,3-diphenylpropane in cyclohexane under air after excitation with 266 nm light

Figure 5.16.

Transient spectra recorded for 3-chloro-1,3-diphenylpropane in cyclohexane following excitation at 266 nm

Figure 5.17.

Decay at 360 nm of 3-chloro-1,3-diphenylpropane in cyclohexane following excitation at 266 nm

Figure 5.18.

Products of irradiation of 3-chloro-1,3-diphenylpropane under oxygen in cyclohexane

Figure 5.19.

Transient spectra obtained upon irradiation of 1,3-diphenylpropene in 50/50 di-*tert*-butyl peroxide/ benzene at 355 nm

Figure 5.20.

Hydrogen abstraction by *tert*-butoxyl radical

Figure 5.21.

Transient absorption spectra of 1,3-dichloro-1,3-diphenylpropane recorded with and without a diffuser in cyclohexane, under nitrogen. Excitation at 266 nm

Figure 5.22.

Effect of oxygen on the 320 nm band in the absorption spectra of 1,3-chloro-1,3-diphenylpropane upon excitation with 266 nm light in cyclohexane in the presence of a beam diffuser

Figure 5.23.

Transient absorption spectra from 10 in 2,2,2-trifluoroethanol following 266 nm laser excitation; spectrum recorded 850 ns after the laser pulse

Figure 5.24.

Kinetic trace at 490 nm of 10 in TFE following 266 nm laser excitation, showing instantaneous and total signal intensities

Figure 5.25.

Instantaneous/total signal intensity of 1,3-dichloro-1,3-diphenylpropane after irradiation with 266 nm laser light in TFE

Figure 5.26.

Laser power dependence of the initial jump at 490 nm after irradiation of 1,3-dichloro-1,3-diphenylpropane in TFE by 266 nm laser light

Figure 5.27.

Transient absorption spectra of 10 in acetonitrile following 266 nm laser excitation. Recorded 1.2 ms after the laser pulse

Figure 5.28.

Kinetic trace at 490 nm of 1,3-dichloro-1,3-diphenylpropane in acetonitrile after irradiation with 266 nm laser light

Figure 5.29.

Decay at 490 nm from 3-chloro-1,3-diphenylpropane in TFE after irradiation with 266 nm laser light

Figure 5.30.

Photochemistry of 10 in 2,2,2-trifluoroethanol

Figure 5.31.

Quenching of 28 by chloride ion

Figure 5.32.

Transient of 1,3-dichloro-1,3-diphenyl propane after irradiation (266 nm) monitored at 490 nm and its quenching with bromide

Figure 5.33.

Effect of second laser on transient spectrum of allyl cation 30. Irradiation of 10 with 266 nm laser and 490 nm dye laser in TFE

Figure 5.34.

Transient spectra in TFE following production 30 of 266 nm excitation and its photolysis with 490 nm pulses from a dye laser

Figure 5.35.

Transient absorption at 510 nm following two laser excitation (266 nm and 490 nm) of 10 in TFE under air

List of Tables

Table 1.1.

Dilignols which can be built up with the reaction between two coniferyl alcohol radicals of dominant resonance structures A and B

Table 2.1.

Lasers used to perform experiments described in this thesis

Table 3.1.

Principal fluorescence bands of pyrene at 4 K

Table 3.2.

Representative relative intensities of the band I and band III of pyrene fluorescence emission

Table 3.3.

Fluorescence quantum yield (Φ) and singlet lifetime (τ) in brackets for various substituted pyrenes in various solvents

Table 3.4.

Reactions of different functional groups (present in TMP) with trialkyl phosphites

Table 3.5.

^{13}C -NMR results in ppm

Table 3.6.

Red emitting fluorescent compounds used for fluorescent derivatization of ortho-quinones

Table 4.1.

Relative fluorescence quantum yield for substituted phenazines formed by reaction of 1,2-phenyldiamine with various model quinones. Excited at 420 nm

Table 5.1.

Rate constant of quenching of 28 and 30 with different nucleophiles. Monitored at 490 nm, after excitation of 10 with 266 nm light in TFE

List of Abbreviations

- CBH= carbohydrate framework
CCD= charged coupled device
ESR= electromspin resonance
GC-MS= gas chromatograph with mass
spectroscopy as detection system
 α -GAV= α -guaiacoxyl acetovanillone
ISC= intersystem crossing
LDP= laser drop photolysis
LFP= laser flash photolysis
NMR= nuclear magnetic resonance
 Δ OD= change of absorption
OMA= optical multichannel analyser
PMT= photomultiplier tube
TEMPO= tetramethylpiperidineoxide
TFE= 2,2,2-trifluoroethanol
TMP= thermomechanical pulp

Chapter 1

Introduction

1.1. Historical background

The story of papermaking¹ goes back to the beginning of human development. The first paper was made by the Egyptians in 3500 AD, who used a sheet of vegetable fiber (known as papyrus) which could be dried and pressed into thin sheets.

Modern papermaking, which involves producing the pulp and manufacturing the sheets, originated from China. The inventor is reported to be Ts'ai Lun. He manufactured paper in a similar fashion as handmade paper is made today, i.e. a screened mold was dipped into a fluid pulp and the film which remained on the screen was dried. This technology was learned first by the Arabs, and it was then taken to Europe by either the Crusaders or the Moors¹.

However, by the 18th century the demand for paper increased substantially. This increased need was due to, on one hand, the discovery of Guttenberg's printing technique, and on the other, the intellectual revolution of the 18th century. Guttenberg invented a printing machine which facilitated the reproduction of printed text. The intellectual revolution promoted a higher need for written words.

At this stage paper was still made from rags, but the need for a more abundant source for papermaking arose. The utilization of wood had not started before the middle of the last century. The mass production of cheaper paper has had an enormous impact on social

life; it has revolutionized literature, education and the reading habits of the world.

1.2. Chemical composition of lignin

This new, cheaper paper however, was more photosensitive than paper made out of rags. The wood, beside cellulose and hemicellulose (which are both polysaccharides), contains considerable amounts of lignin (up to 40%), a natural wood polymer. Upon exposure to light lignin undergoes photoyellowing. Lignin forms during the aging of the wood cells. It is spread over continuous, wide areas. During the development of the wood cell it impregnates the cell more and more. In this way, lignin acts as a "glue" between cellulose and hemicellulose fibers which, themselves, function as supporting material.

A schematic outline of the wood cells is shown in Figure 1.1. About 25% of the lignin is found in the middle lamella and the primary cell walls². The remainder is mainly in the middle layer of the secondary wall. These layers are built up by lamellae formed by almost parallel microfibrils between which lignin and hemicellulose are located. (Figure 1.1.)

Lignin is chemically bound to the cellulose fibers of wood and it greatly influences the mechanical properties of wood. In papermaking the first step is the pulping, that is to recover a fibril structure. In chemical pulping this basically means the removal of the lignin, which acts as a glue between the fibers (see above). In

early papermaking, this step presented a considerable technical challenge.

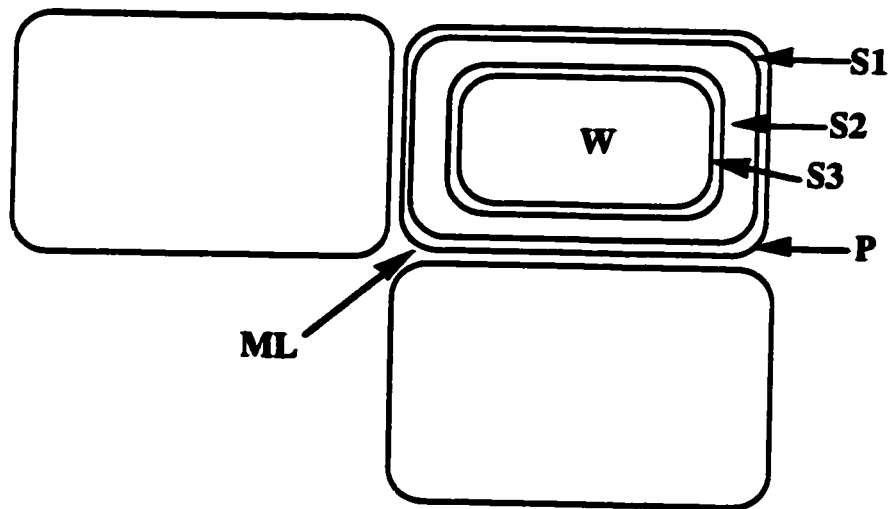


Figure 1.1.

Schematic representation of the structure of wood cells. ML: middle lamella, P: primary wall, S1,S2,S3: outer, middle and inner layer of the secondary wall, W: warty part.

Today pulping is done either by using different chemicals or with the help of mechanical and thermal energy. In chemical pulping there are sulfite pulping, the soda process or the sulfate (Kraft) process. Sulfite pulping, which is the oldest of the three, uses an aqueous solution of calcium hydrogen sulfite and sulfur dioxide in a pressurized system. The soda process uses sodium hydroxide at high temperature and pressure. However, this process is becoming less and less popular. Instead, a mixture of sodium hydroxide and sodium sulfide can be used, and this pulping is called Kraft pulping. During chemical pulping most of the lignin (a representative structure for lignin is shown later in Figure 1.7.) is removed from the wood by

hydrolyzing the ether bonds of the polymer (thus decreasing molecular weight and increasing solubility) and by addition of hydrophilic sulfite groups on lignin (in the case of sulfite pulping). However, in both cases cellulose and hemicellulose also undergo some degradation; thus the pulp yield of chemical pulping can never exceed 50-60%. Lignin can also be removed with the use of bleaching chemicals such as chlorine and chlorine based chemicals and with oxygen, but these methods are expensive and often produce large amounts of chemical waste.

In mechanical pulping lignin stays in the paper, therefore it is more sensitive towards photodegradation, but the yield can approach 95% (it is also called high-yield pulp). The potential uses of the paper are determined by (1) starting material and (2) difference in manufacturing. An improved performance for lignin-containing papers would be expected to create new markets for these products.

1.2.1. Structure of lignin³

The determination of the structural built-up of lignin has been a constant challenge for more than a hundred years. One of the main difficulties is the lack of adequate lignin isolation methods without having the lignin undergoing secondary reactions. According to the method of extraction, lignin can be named protolignin (as it exists in plant), Klason lignin, acid lignin, alkali lignin, methanol lignin, milled wood lignin, etc. These different types of extracted lignins differ in their chemical properties from each other, and from the original lignin.

In 1897, Peter Klason, a Swedish chemist, proposed that lignin is built up from coniferyl alcohol units⁴. This was the first appearance of the idea that no matter how complicated the structure of lignin is, it is built up in some kind of order, from continuously repeating building blocks. Later, in 1928, Freudenberg showed⁴ that the building blocks of lignin would probably contain a phenyl propane skeleton of various structures (Figure 1.2.). By the mid 1930's he introduced the concept of oxidative degradation of lignin, and later proposed a way in which lignin may be formed in nature from its cinnamic acid precursors. These precursors are in E-configuration *in vivo*. Light can induce EZ-isomerisation. However, in the case of formation of lignin in trees, this does not seem to be relevant regarding the fact that the lignin precursors are not exposed to light.

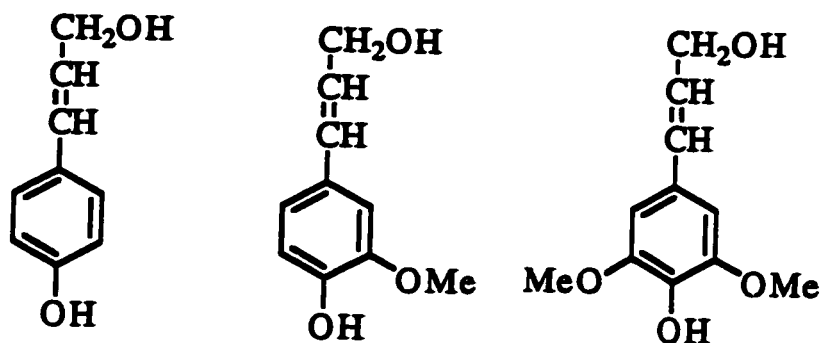


Figure 1.2.

Phenylpropanols which participate in lignin formation (coniferyl alcohol, syringyl alcohol, synapyl alcohol)

Although the importance of the phenylpropanoic units was discovered relatively early, it was impossible to give any

constitutional formula for lignin. It was apparent that in lignin two units are rarely alike. Also, there was no known method of degradation which yielded unaltered constituents of the polymer. Finally, the growth of lignin type molecules from coniferyl alcohol was examined⁵. After years of research, the first encouraging result was the isolation of a crystalline dimer, from the dehydrogenation product of coniferyl alcohol⁵. *In vivo* this process is catalyzed by enzymes, however, their identity is still not clear⁶. Later, this was followed by a series of compounds, called monolignols, dilignols, oligolignols and polyignols, according to the number of building units they contained.

Removal of a hydrogen atom from coniferyl alcohol yields a radical which has several resonance structures. The most important resonance structures for the biosynthesis of lignin are shown on Figure 1.3. The radical lifetime is about 45 sec in solution³.

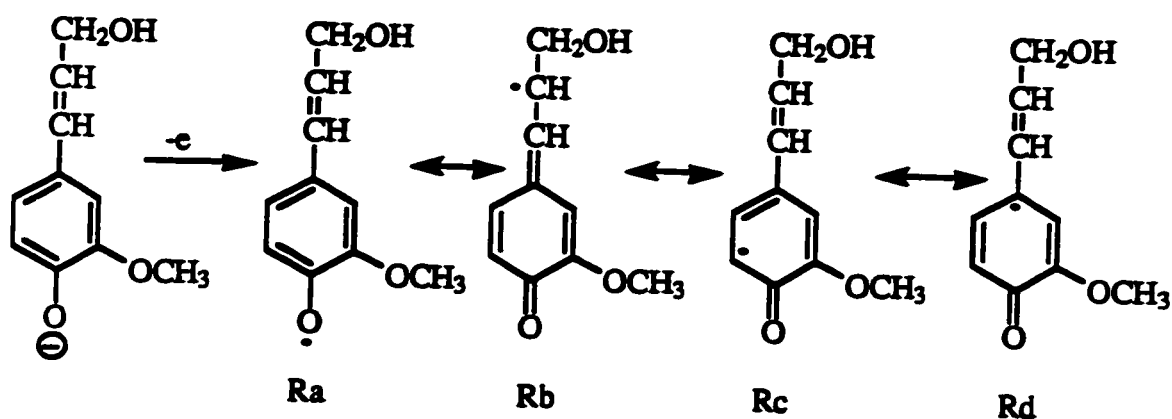


Figure 1.3.

Some resonance structures of coniferyl alcohol radicals

This radical can undergo further reactions, forming different dilignols. For example, from the combination of two radicals in Rb and Rc resonance forms, dehydroconiferyl alcohol can form, which, via oxidization, can form the corresponding aldehyde. (Figure 1.4)

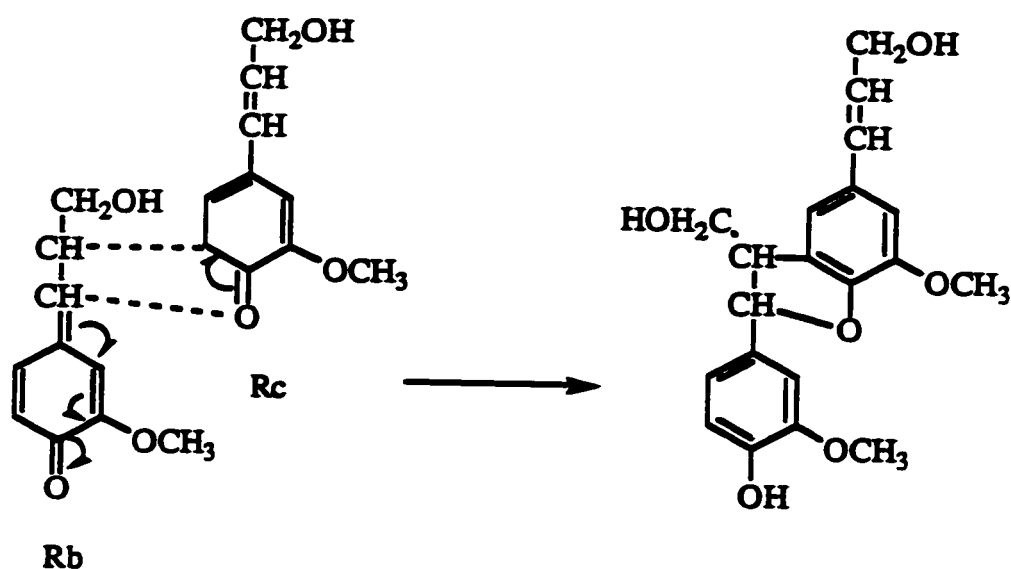


Figure 1.4.

Reaction of two coniferyl alcohol radicals with resonance structure Rb and Rc to form dehydroconiferyl alcohol

Table 1.1. lists the main dilignols and the resonance structures to which their formation is attributed. The actual dilignols are shown in Figure 1.5.

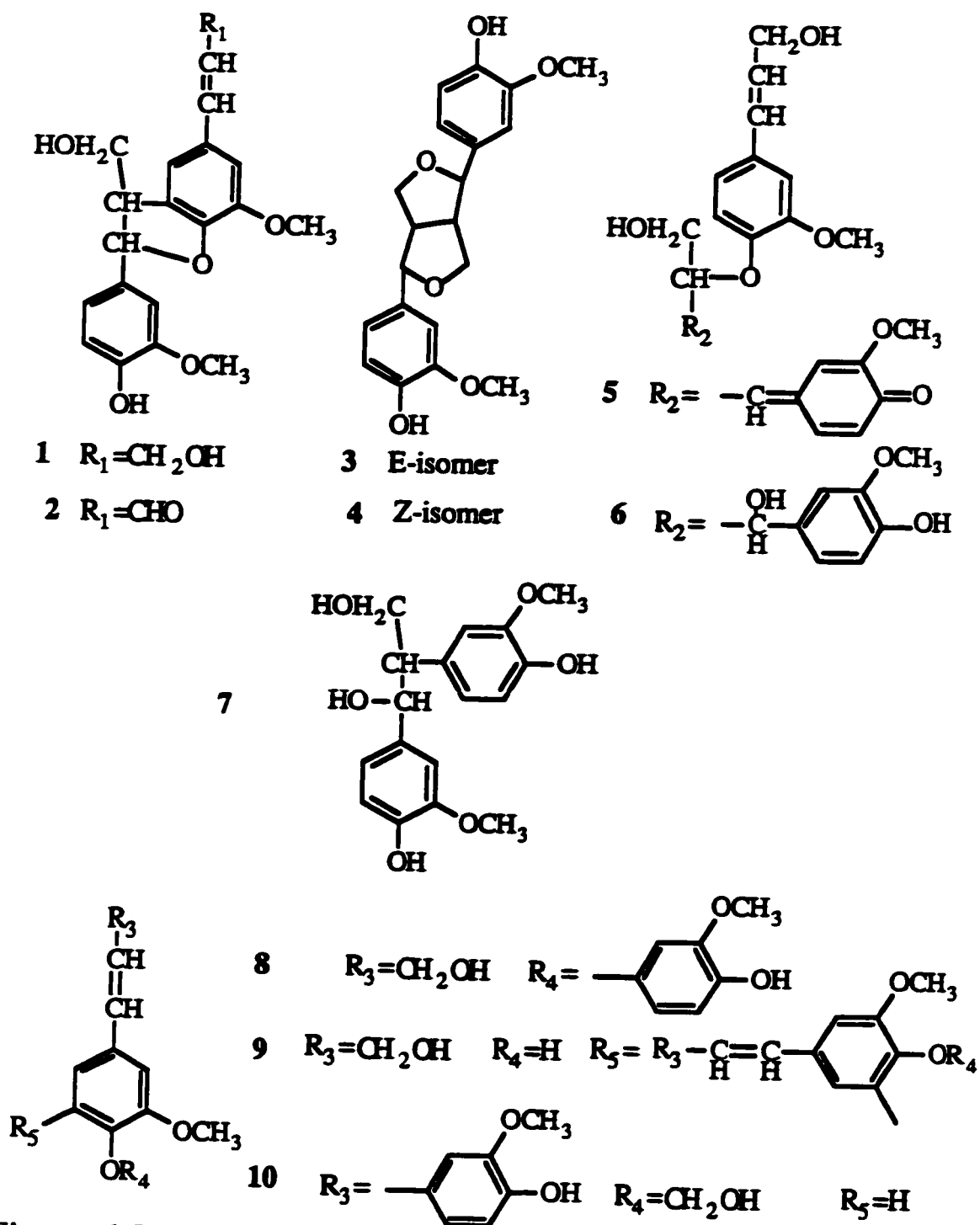


Figure 1.5.

Dilignols which can form via the reaction of two coniferyl alcohol radicals

resonance structure A	resonance structure B	dilignol	further derivatives
Rb	Rc	Dehydroconiferyl alcohol (1)	Dehydroconiferyl aldehyde (2)
Rb	Rb	Pinoresinol (3)	Epipinoresinol (4)
Rb	Ra	Quinine methide (5)	Guaiacylglycerol- β -coniferyl ether (6)
Rb	Rd	1,3-diguaiacyl propane-1,3 diol (7)	4,4'-dihydroxy-3,3'-dimethoxy stilbene (10)
Ra	Rd	Coniferyl alcohol guaiacyl ether (8)	
Rc	Rc	Dehydrobis-coniferyl alcohol (9)	

Table 1.1.

Dilignols which can be built up with the reaction between two coniferyl alcohol radicals of dominant resonance structures A and B

Dilignols which form in the highest yields are the guaiacylglycerol- β -coniferyl ether (6) and dehydroconiferyl alcohol (1). Quinone methides (5) play a key role in molecular growth during lignification, since they are able to add not only water but also to phenols (to form benzyl-aryl ethers) and carbohydrates; as such, they serve as the main linkage between the wood cellulose structure and lignin in wood (Figure 1.6.). Quinone methides can also polymerize, providing another mechanism for molecular growth.

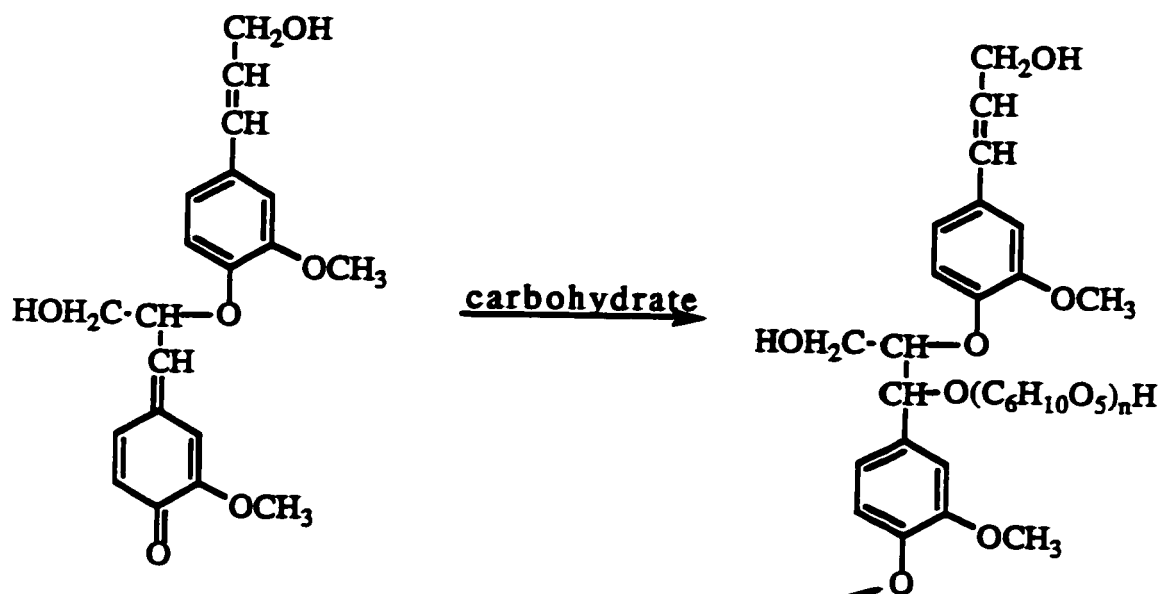


Figure 1.6.
Addition of carbohydrate chain to thequinone methide structure.

From dilignols, in a fashion similar to that shown above, one can deduce the various trilignols and polyignols. From these small and medium size aggregates, larger entities can form through the intermediacy of a radical of the Rb resonance structure. Any structural scheme of lignin is a more or less arbitrary mixture of these individual building elements. One of these is shown in Figure 1.7. This structure is built up from 18 C₉ units, and expresses quite well a number of the structural features of spruce lignin. The "goodness" of any model is judged according to the percentage of structural units which undergoes certain known reactions. For example³, this model expresses well the overall molecular formula, the oxygen distribution, and the number and type of carbonyl groups. The fastest rate of hydrolysis occurred when benzyl-aryl

ethers were hydrolyzed; in this model their number is underestimated.

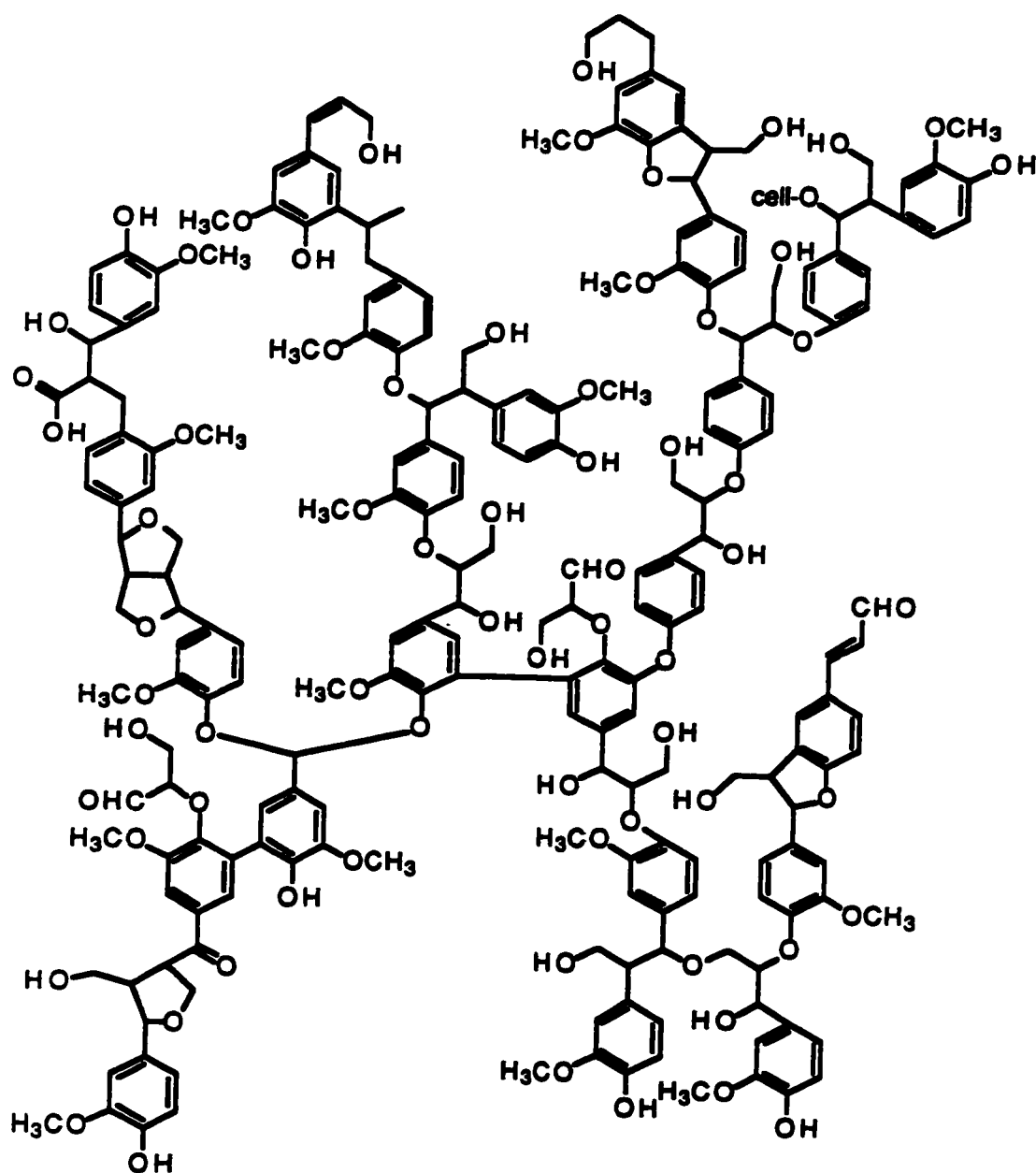


Figure 1.7.

A structural scheme of spruce lignin as proposed by Freudenberg³

The model of Figure 1.7. expresses quite well the number of units that undergo thioglycolic acid reaction and those which participate in the different stages of lignosulfonic acid formation. It also gives reasonable agreement when the methanol uptake is estimated (methanol uptake is measured during extraction of lignin with methanol from wood).

Only spruce lignin was investigated in sufficient detail to establish a reasonable model. The lignin content of various tree species are close, typically showing lignin content between 25 and 29%. The chromophore composition differs depending not only on the species of tree, but also on its origin. However, some general conclusions can be drawn from the results. The specific ratios of the three p-hydroxycinnamyl alcohols (coumaryl, coniferyl and synapyl) differs from species to species. For example beech wood has a ratio 5:49:46 while the ratio in spruce wood is 14:80:6³.

1.3. Photochemistry of lignin and lignocellulosic materials

The photochemistry of lignin and lignocellulosic materials (pulp) has been widely investigated. In the middle of the nineteenth century it became evident that paper containing mechanically processed, or groundwood pulp, yellowed at a much greater rate than paper containing chemically processed pulp, while the paper containing rag pulp had hardly yellowed at all, even after centuries¹. Soon, it also became evident that this sensitivity was due to a light-initiated attack on the lignin present in the mechanically processed pulp³. The photochemical investigation, however, is made more

difficult by the fact that the structure of lignin is not accurately described, and it has variations depending on the species and the natural environment of the tree. Further, depending on the procedure used to isolate lignin from cellulose, the structure of the lignin changes, and thus extracted lignin can only be used for research with some limitations⁷.

1.3.1. Establishing the mechanism for the photodegradation of lignin

In 1968 Leary⁸ using UV-visible diffuse reflectance spectroscopy, proved that significant yellowing occurs only in the presence of oxygen. He also examined the effects of different treatments, namely borohydride reduction, alkylation and esterification. Only methylation, acetylation and p-toluenesulfonylation were found to be efficient in retarding the yellowing. The loss of methoxy-groups during irradiation was also investigated. The author concluded that there is a limit to photodemethoxylation (in this case 30%) which leads to yellowing. This amount corresponds to the amount of free phenolic groups present in the lignin, and it refers to a phenoxy radical initiated photodemethoxylation. Therefore, the phenoxy radical was suggested to play a key role in yellowing (Figure 1.8.). Phenoxy radicals could be produced from phenols directly, or by hydrogen abstraction with the intermediacy of some excited state molecule. Later he suggested⁹ that the final products of the yellowing are quinoid structures.

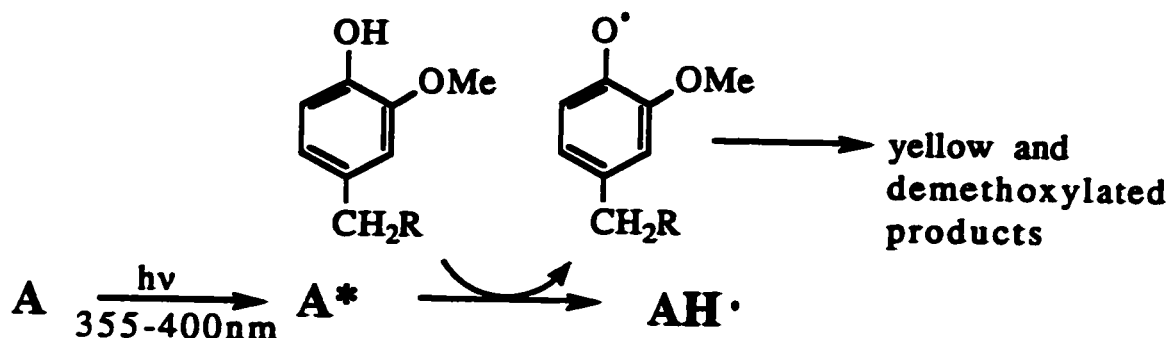


Figure 1.8.

Role of phenoxy radicals in photoyellowing as proposed by Leary⁸; A is a chromophore capable of hydrogen abstraction following excitation

In 1970 Lin et al.¹⁰ were the first to examine the photodegradation of different lignin model compounds and to compare these processes to those in lignin. The model compounds were built-up from a guaiacyl center and different side chains characteristic of lignin (Figure 1.9.). Compounds with saturated side chains or unconjugated double bonds had no absorption in this region (>300 nm); therefore, they did not decompose upon irradiation. α -Carbonyl, biphenyl and ring conjugated double bond structures responded to irradiation and yielded colored chromophores. From the similarity between the absorption curves of milled-wood lignin and α -carbonyl compounds they concluded that these chromophores assume the major role in the yellowing process.

Lin and coworkers were also the first to propose the participation of α -aryloxy acetophenone in the photodecomposition of lignin^{10,11} via the cleavage of the phenacyl aryl ether linkage (Figure 1.10.). This decomposition pathway later (1991)¹² was proven

to be the major source of yellowing, but when originally proposed it was largely overlooked.

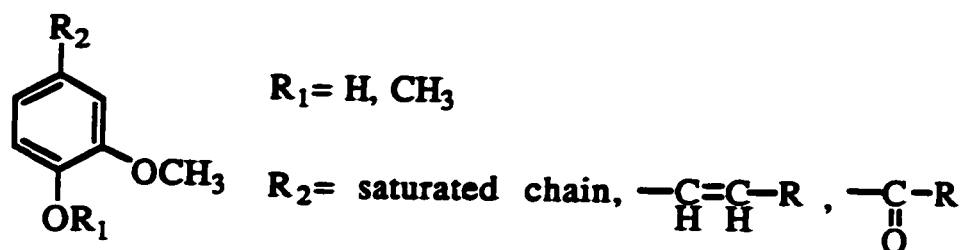


Figure 1.9.

Lignin model compounds examined by Lin et al.^{10,11}

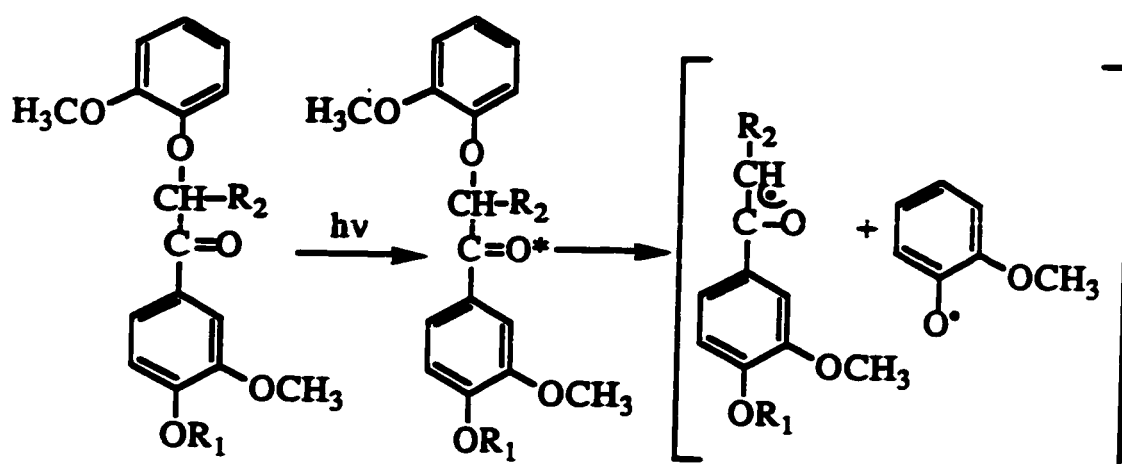


Figure 1.10.

Photodecomposition pathway of lignin proposed by Lin et al.¹⁰

These approaches, namely, (i) using model compounds, and, (ii) examining the effect of different treatments on yellowing, have been further employed in the late 1980's when the research on yellowing accelerated again. New techniques have been utilized for the analysis, such as ultrafast detection techniques to examine the

elementary processes of yellowing, as well as fluorescence, Raman, FTIR and NMR spectroscopies.

1.3.2. Utilization of model compounds

Castellan et al. used model compounds and incorporated them into different solid matrices¹³⁻¹⁵ such as bleached (Kraft) pulp and 2-hydroxypropylcellulose film. The molecules they studied contained different characteristic structural units of lignin such as (1) α -carbonyl structures¹⁶, (2) α -carbonyl free phenols, (3) phenolic stilbenes and phenolic phenyl coumaron structures and, (4) quinones and hydroquinones.

α -Carbonyl structures were shown to play a major role in the yellowing process^{11,12}. However, in solid matrices α -carbonyl compounds showed significant yellowing only if the molecule contained β -O-4 or β -1 structures. (Figure 1.11.)

In the case of α -carbonyl free structural units, significant difference was found between monomeric and dimeric structures. Phenols with a saturated side chain do not undergo significant discoloration. The same result was obtained in the presence of peroxides¹⁵. This was quite suprising, considering that in solution peroxides are known to abstract hydrogen from phenols¹⁷ and as such, phenoxy radicals could participate in further processes leading to yellowing. However, in this case both components are absorbed on a solid matrix, and therefore this result shows the importance of studies in the presence of the solid matrix. A solid matrix can restrict the movement of the reactants or promote interactions (for example,

hydrogen bonding) that can modify their reactivities. In contrast with monomers, dimeric phenols, especially the monomethylated compounds, showed photoyellowing; and they were more active in solid state than in solution¹³.

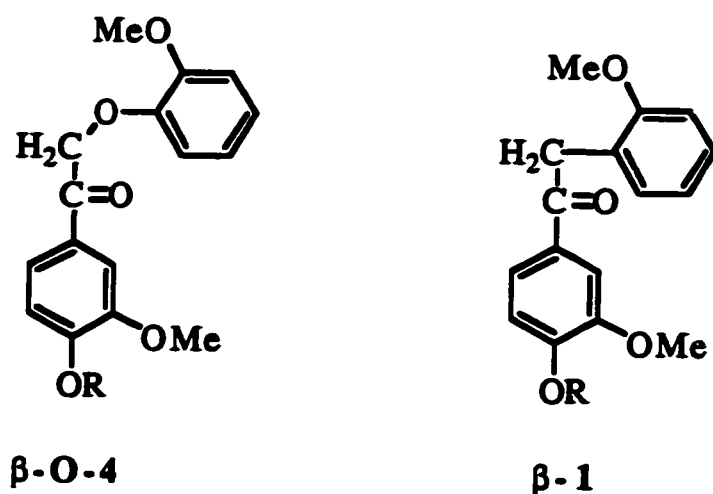


Figure 1.11.
Characteristic β -O-4 and β -1 structures in lignin

Diguaiacyl stilbenes were also easily photo-discolored. Quinones and hydroquinones are easily reducible and oxidizable¹⁴. In lignin they also participate in redox cycles, which ultimately involve the cellulose matrix, and leads to its destruction (Figure 1.12.). Presumably, mainly hemicellulose is involved in these reactions, since it is not crystalline and it is strongly linked to lignin. This process results in a permanently yellowed framework.

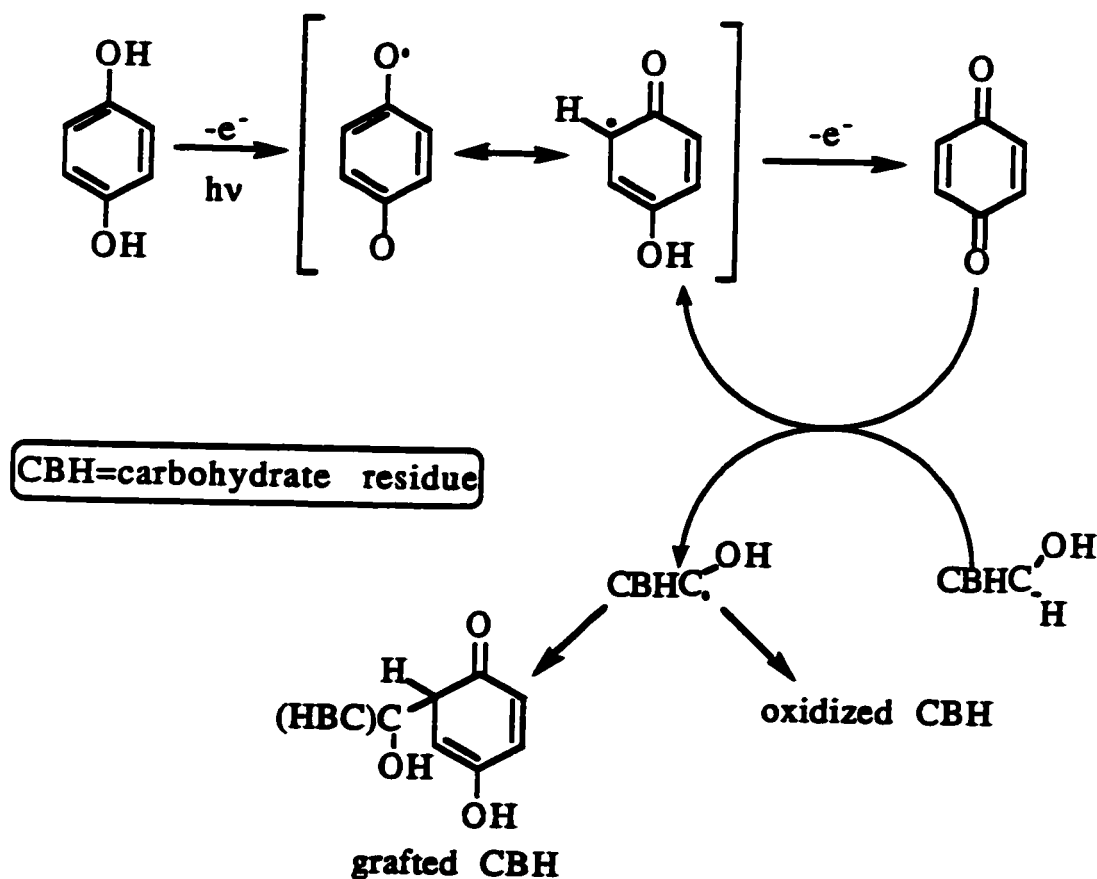


Figure 1.12.

Quinone-hydroquinone redox cycle, and its role in the irreversible yellowing of the carbohydrate (CBH) framework

Tylli and coworkers¹⁸ further examined the degradation of cellulose by using diffuse reflectance infrared spectroscopy. They found that some of the OH groups in cellulose disappeared, and carbonyl functions appeared upon irradiation. The process, once it has been initiated by light, continues for a long time as a dark reaction. They attributed this observation to the presence of free radicals.

Scaiano et al.¹² were the first to demonstrate that an important photo-degradation pathway is not the direct excitation of carbonyl groups, neither the direct excitation or free radical scavenging of the phenoxy radicals, but the formation of ketyl radicals, and the subsequent cleavage which results in the formation of ketones and phenoxy radicals¹².

The ketones formed as secondary chromophores can enter into the cycle again by absorbing a photon, and in the presence of oxygen phenoxy radicals can lead to the formation of strongly yellow quinones. These quinones also participate in a second cycle (which can be either photon initiated or redox), which may involve the polysaccharide framework and leads to irreversible damage. This decomposition mechanism is the latest and most accepted (Figure 1.13.).

This reaction pathway was also proven by Wan et al. using ESR techniques to detect the radicals¹⁹. Quantum yield studies on α -guaiacoxycetoveratrone (Figure 1.14) in solution in the presence of triplet quenchers showed²⁰ that the degradation originated from the singlet manifold. Johnston et al.²¹ included several substituted aryloxy acetophenones into different solid supports, such as silica, zeolite and cellulose. In cellulose and zeolites, the decomposition from the singlet manifold also plays an important role.

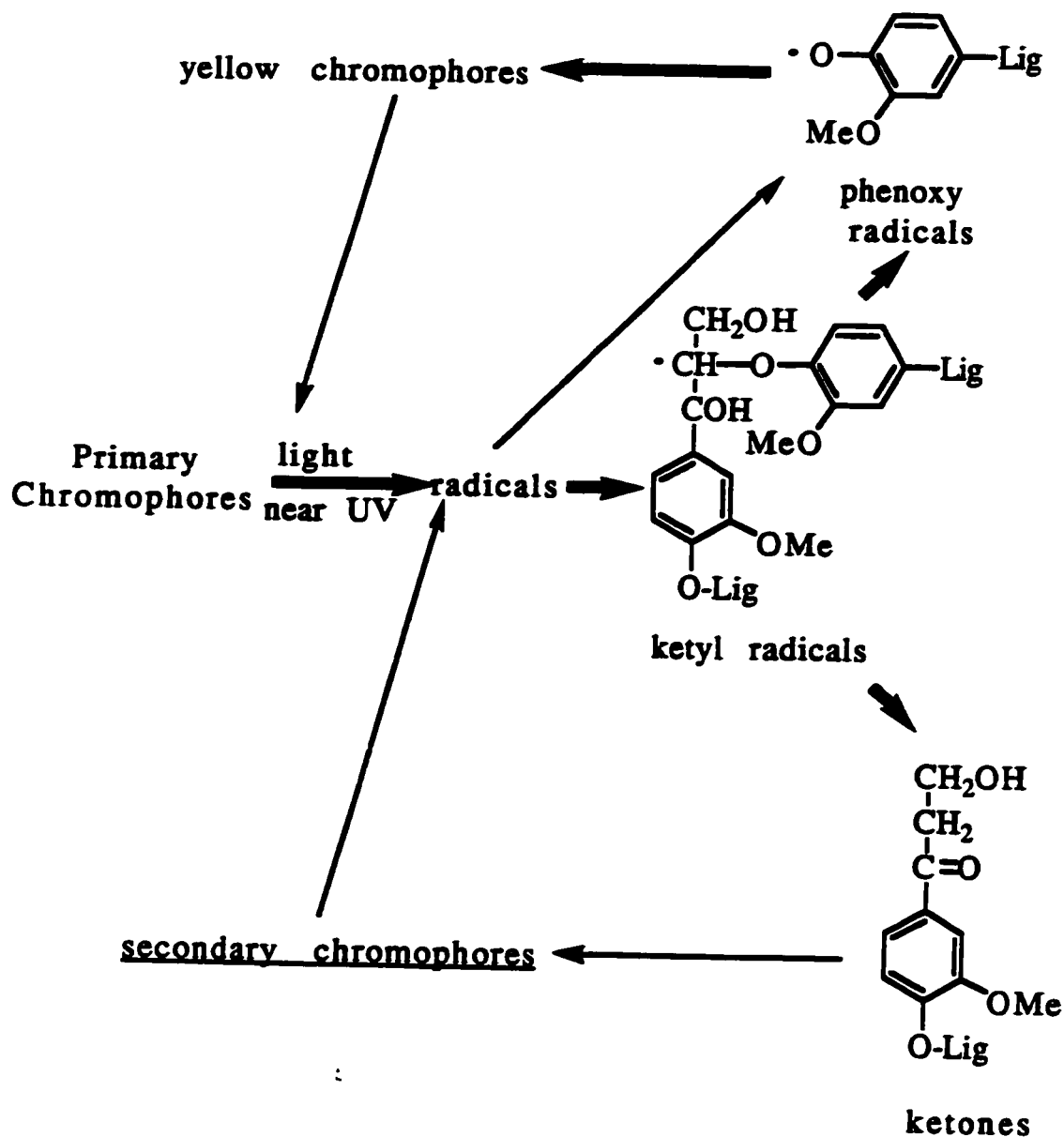


Figure 1.13.

Ketyl mediated degradation pathway of chromophores in lignin

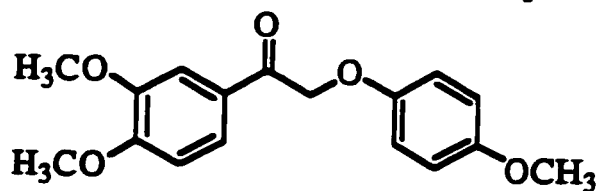


Figure 1.14.

α -Guaiacoxyacetoveratrone

1.3.3. Studies on pulp and paper

Studies on pulp are more scarce and frequently less informative due to the complexity and the non-uniformity of the media. One general approach is to determine the bulk changes that occur in the pulp upon irradiation. The other is to derivatize some structural units and as such either to protect them or to make them more amenable for certain types of experimental measurements.

Several studies were performed to determine the effect of irradiation on pulp. Forsskåhl et al.²² detected the changes in diffuse reflectance values upon irradiation by light of different wavelengths. They determined that color reversion is maximum upon irradiation at 310-320 nm. The already yellowed pulp was bleached upon irradiation at 420-430 nm. The authors assumed that the two bands are interrelated in some way, because upon photobleaching one, the intensity of the other increased and vice versa. This type of spectral cycling can be interpreted on the basis of several possible candidate-moieties in lignin, such as the already mentioned quinone-hydroquinone system, or cis-trans isomerism.

In other work²³ the effect of different metal ions and chelating agents was studied. Metal ions which have more than one stable oxidation state, such as Fe and Cu, accelerate yellowing, while those, which have only one oxidation state, have no effect. This observation is easily understandable in the context of Castellan's work¹⁴, i.e. the metal ions can participate in the redox cycle and accelerate yellowing. This participation of metal ions shows similarities with the

Fenton reaction. Chelating agents which can remove the metal ions are usually beneficial.

^1H and ^{13}C NMR spectroscopies as well as GC-MS analysis were used by Holmbom and coworkers²⁴ to determine the chemical changes in irradiated lignin. They generally confirmed the earlier observations relating to the cleavage of α and β -aryl bonds, the decrease of the number of methoxy groups, and the increase of the number of phenolic groups. Ortho-quinones were not found in substantial amounts; this is probably due to the instability of these compounds, especially in the presence of water²⁵.

Solid state ^{31}P -NMR spectroscopy was employed by Argyropoulos and Heitner to study different lignin chromophores²⁶. $\text{P}(\text{OMe})_3$ was used to derivatize quinones (this methodology will be described in Chapter 3) and α,β -unsaturated aldehydes and ketones present in lignin. Using these techniques they succeeded in establishing that quinones are present in pulp. In another work²⁷, this methodology was applied to develop a quantitative analytical method for ortho-quinones.

1.3.4. Usage of fluorescence spectroscopy to study lignocellulosic materials

Fluorescence spectroscopy has been widely used in the study of lignocellulosic materials. Several chromophores which are present in papers manufactured from high yield pulps fluoresce. If they undergo changes during the different processes of papermaking or during photoyellowing, these changes should be reflected in the

fluorescence spectra and lifetimes. However, the interpretation of fluorescence spectra of lignin and pulp are difficult. Cellulose itself fluoresces strongly, and as such it results in a strong background emission. Further, the emissions of chromophores often overlap, leading to broad peaks that cannot be assigned easily to particular chromophores. In addition, there has been considerable debate about the origin of the fluorescence emission.

Gray and coworkers interpreted their emission results attributing them mainly to cellulose²⁸. According to them, the apparent changes upon irradiation reflect only the changes of absorption of the lignin chromophores. These chromophores are absorbing the light emitted by the cellulose, and this causes an apparent change in the detectable fluorescence spectra. Later, they added that the role of the chromophores might not be only absorption, but possibly fluorescence quenching as well²⁹. After examining several different pulps they concluded that the decrease in fluorescent emission intensities corresponds to the new absorption bands appearing upon irradiation, as reported by Tilly et al.¹⁸.

Castellan and coworkers strongly opposed Gray's suggestion³⁰. In a series of studies, they examined the differences between stone-ground wood pulp and native wood³⁰⁻³². First they performed fluorescence emission and lifetime measurements on borohydride bleached and unbleached wood sections. They found that the bleached wood has an emission of higher intensity than the unbleached samples^{30,32}. This increase was attributed to the reduction of the carbonyl functions which are present in lignin and

behave as fluorescence quenchers. Furthermore, fluorescence lifetime measurements showed that the unbleached wood has a very short fluorescence lifetime, while bleached wood has longer half life which was deconvoluted using a double exponential decay treatment³¹. The double exponential can refer to either the presence of different chromophores or to different environments of one fluorescent species. Interpretation of these results led to the conclusion that the fluorescence does not originate from the cellulose or hemicellulose components. Later, these investigations were extended^{30,32} comparing the effects of different treatments on the fluorescence spectra. In addition, model compounds were adsorbed on filter paper, which is considered to be pure cellulose, and their dynamic and steady state fluorescent properties were identified. Castellan et al. attempted to assign certain compounds as the main sources of fluorescence, although with limited success³¹. Their final conclusion was again that the fluorescence cannot originate only from cellulose.

Another approach was also used by Gray et al. to use fluorescence as a mean of examining pulps³³. Chromophores, namely ortho-quinoid groups which are known to be not fluorescent, were derivatized by 1,2-phenylendiamine diamine, to form fluorescent phenazine. In this way the presence of ortho-quinones could be established using a very sensitive analytical technique. This approach proved useful in our own studies at the University of Ottawa. This is discussed in detail in Chapter 3.

1.4. Purpose of this thesis

The main interest of my research on the photoyellowing of paper products was centered around the ortho-quinone present in high yield pulp. In the first part of this thesis I describe a sensitive fluorescence method using derivatized pyrene compounds and other, more red-emitting fluorescent molecules to detect ortho-quinone structural moieties in high-yield pulp and paper. This method is selective, efficient, and by means of time resolved diffuse reflectance fluorescent spectroscopy I was able to examine the proximity of the ortho-quinoid groups formed. Furthermore, fluorescence microscopy made it possible to determine the morphological structures of the high yield pulp where the quinone formation occurs preferentially, and therefore where yellowing is most pronounced.

The second part of my thesis deals with ortho-quinone formation via multiphotonic processes from phenoxy radicals. This route of formation of ortho-quinones was previously not considered. To study multiphotonic processes, I have used the laser drop photolysis and two-laser two-color techniques.

Later, in the third part of the thesis, I applied the same methods to study other multiphotonic processes in solution, such as reactions of 1,3-dichloro-1,3-diphenylpropane.

Chapter 2

Laser Techniques and General Instrumentation

2.1. Introduction

The focus of this chapter will be the detailed description of the instruments and various laser techniques used during the course of the research described in this thesis. The more general experimental details (regarding for example the different synthetic techniques and the treatment of the pulp) will be described in the appropriate chapters.

In our laboratory there are a number of techniques for studying reactive intermediates. Besides conventional nanosecond laser flash photolysis, it is possible to study short lived intermediates by conventional flash photolysis³⁴, diffuse reflectance laser flash photolysis³⁵, time resolved conductance³⁶, singlet oxygen emission³⁷ and photoacoustic calorimetry³⁸. There is also a picosecond laser which is set up for pump-probe optical multichannel analyser (OMA) detection as well as a Hamamatsu picosecond fluorimeter. For the research described in this thesis, we also used laser-drop photolysis³⁹ and fluorescence microscopy equipped with a photographic camera⁴⁰.

2.2. Time-resolved fluorescence

Time-resolved fluorescence is used to gain information about the lifetime of the fluorescence as well as the nature of the fluorescence decay. These data can reveal details about the

interactions of the fluorophore with the environment. However, since fluorescence lifetimes usually are quite short, their measurement is difficult. There are generally two methods to measure fluorescence lifetimes⁴¹; the harmonic or phase-modulation method uses a sinusoidal modulated light source for excitation. Since the emission is a forced answer for the excitation, the emission will be modulated with the same sinusoidal frequency, but it will be delayed in phase and its relative amplitude will be smaller (Figure 2.1).

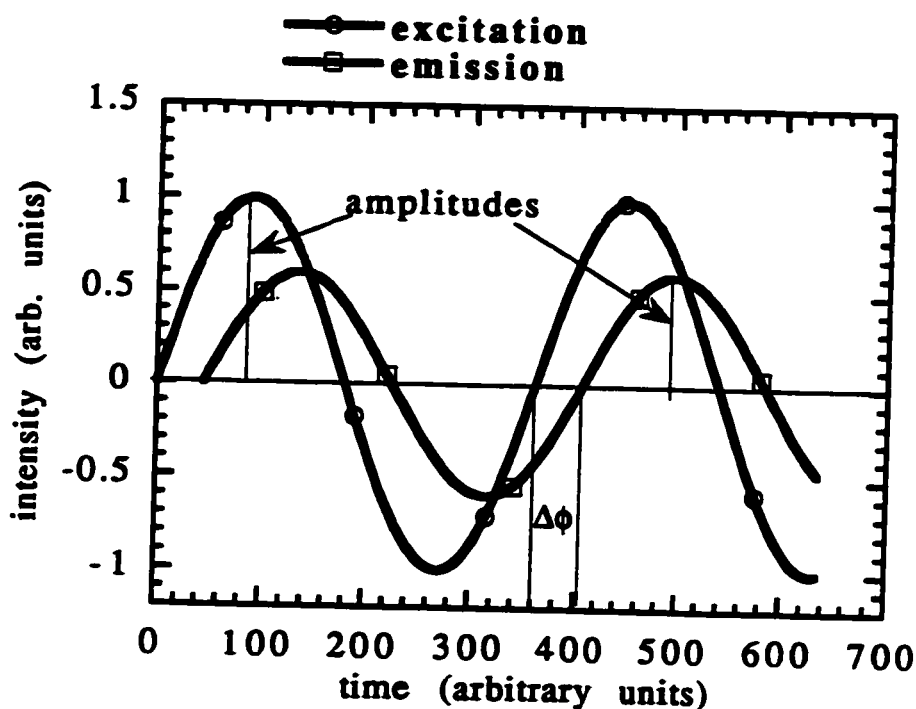


Figure 2.1.

Fluorescence emission intensity as a response to sinusoidal excitation

In the pulsed method, a short pulse is applied to excite the sample and the time dependent decay of fluorescence intensity is measured. Our system, at the University of Ottawa, uses this latter

method. As short duration excitation sources, nanosecond and picosecond lasers can be used. The pulse duration of the light source determines the shortest lifetime which can be measured and calculated by convolution. This time is generally half of the pulse duration, if the pulse shape is reproducible (Figure 2.2.).

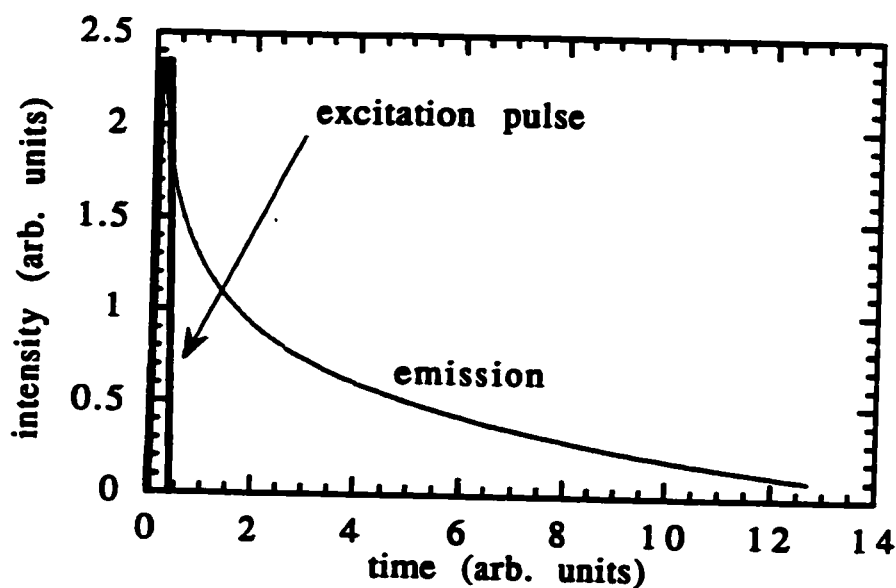


Figure 2.2.
Fluorescence emission upon pulsed excitation

All our experiments were carried out using the third harmonic of a Surelite Nd:YAG laser, which has a pulse duration of 6 ns and a wavelength of 355 nm (Figure 2.3.).

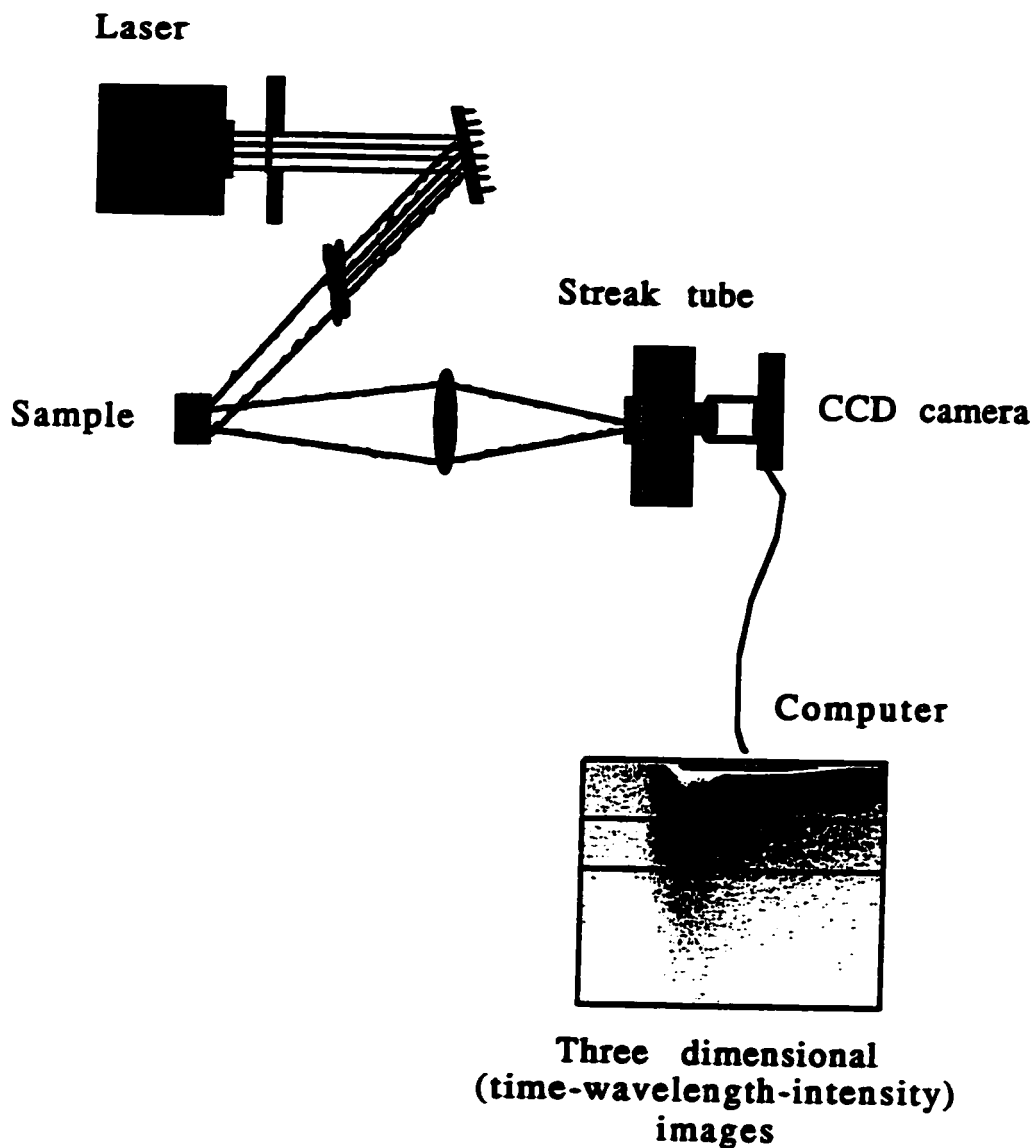


Figure 2.3.
Experimental set-up of the time-resolved fluorescence measurements

To obtain a fluorescence decay curve after pulsed excitation, two basic methods can be used. One can employ either the pulse-

sampling or the single-photon-counting method. In the pulse-sampling method, at a certain time after the excitation pulse the photomultiplier gain is pulsed on for a period of time which is short compared to the decay time.

After each excitation pulse the emission is sampled at different times, and in such way that a fluorescence decay curve is built up. In the single-photon-counting method, the time interval is measured between the lamp pulse and the arrival of a current pulse on the anode of the photomultiplier tube (PMT). The intensity is adjusted so that this current corresponds to the arrival of one photon. The amplitude of the signal corresponds to the time between the excitation pulse and the arrival of the photon. The detected pulses are recorded in a multichannel pulse height analyzer, where each channel corresponds to an amplitude of current that is a time interval between the lamp pulse and arrival of the current. From the number of times a particular voltage was generated a histogram can be constructed which represents the fluorescence decay.

In our system, a streak scope was used which can be regarded as a two-dimensional single-photon-counter. The incident light first reaches a photocathode where it is converted to an electron image. The electron image is passed through the deflection field which causes a sweep of electron image from top to bottom according to the time which elapsed between the light excitation and the arrival of the electrons into the deflection field (Figure 2.4.). Horizontally the photons are dispersed, according to their wavelengths, by means of a spectrograph. This two-dimensional image reaches a

phosphorescence screen where it is reconverted to light image. This streak image is read by a camera containing a charge coupled device (CCD) and its video signal is captured by a frame-grabber. The video signal is then transferred to a computer where it is stored as a three dimensional (time-wavelength-intensity) image. (Figure 2.3.)

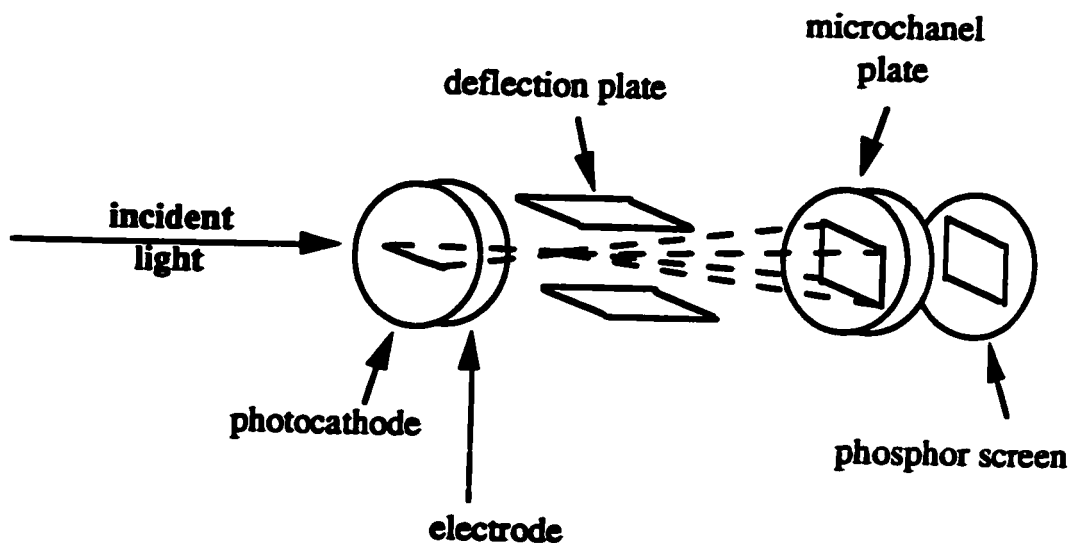


Figure 2.4.
Built-up of a streak tube

From this image a decay curve, characteristic of the selected wavelength region, or a fluorescence spectra, characteristic of a particular time region after excitation, can be extracted. The color of the streak image gives information about the number of photons which reached that particular section of the image. White-black-blue-green-yellow-red ranges towards increasing intensity (Figure 2.5.).

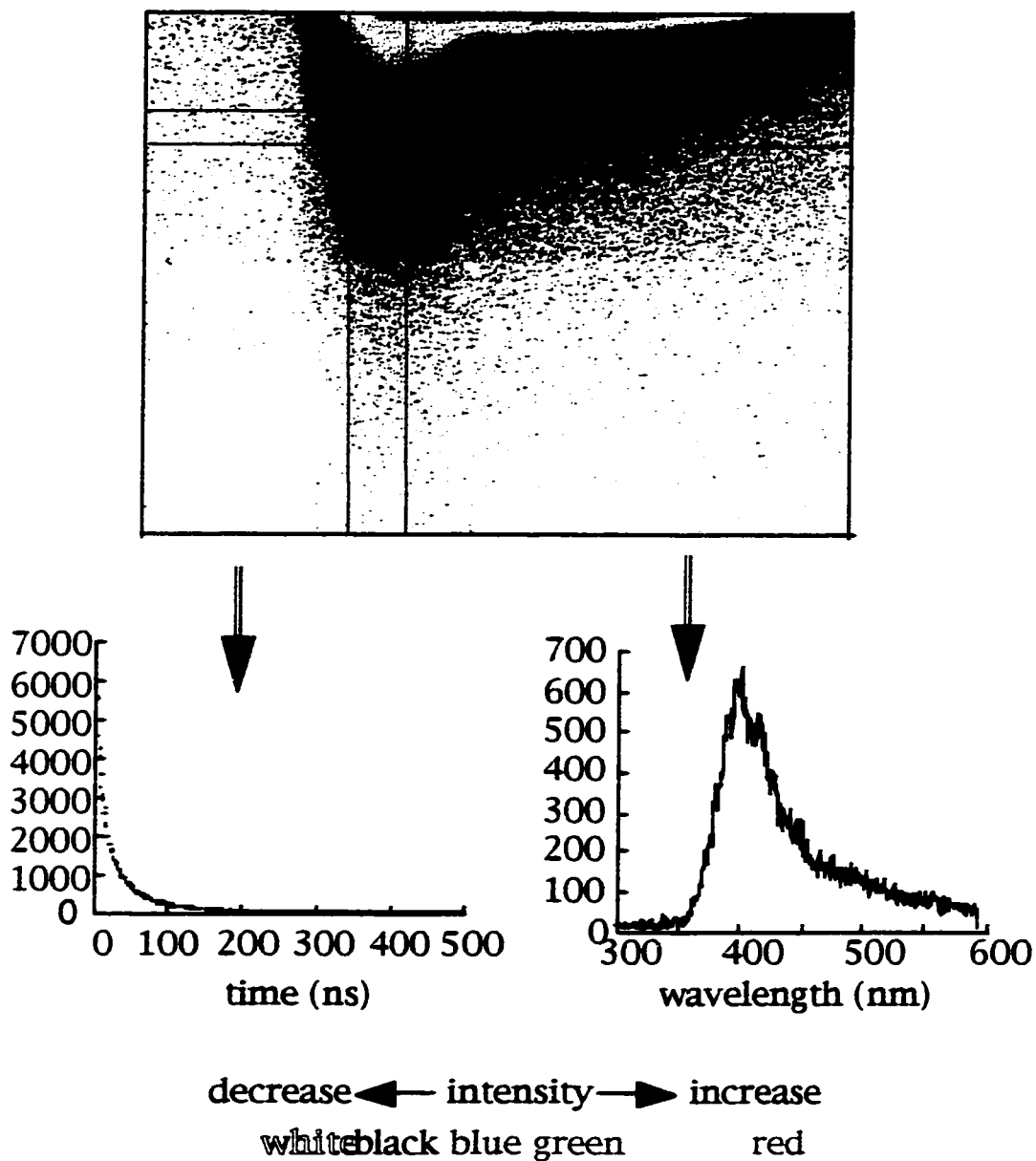


Figure 2.5.
Fluorescence decays and spectra as well as the original streak image. The decay corresponds to the vertical "cut" of the streak image, and the spectrum to the horizontal cut.

Solid samples were contained in 3 x 7 mm quartz cells. During the experiments the samples were regularly moved to avoid sample deterioration caused by the laser light.

2.3. Laser flash photolysis

The laser flash photolysis (LFP) system at the University of Ottawa has been described in detail⁴². Here, I will mention only the most important characteristics which were relevant to my work.

Laser flash photolysis was used to generate excited state species and investigate their kinetic behavior and spectral properties. The system consists of an excitation source and a fast spectrophotometer (Figure 2.6.). The fast excitation source is a laser; its wavelength and pulse duration determines which molecules and processes can be studied. The compound has to absorb the laser light producing a 10-50 μM concentration of transients. The half-life of the processes in which this transient participates must be longer than the pulse duration of the laser pulse. In our studies a number of different lasers were used (Table 2.1).

The fast spectrophotometer used in our studies consisted of a pulsed 150 Watt xenon lamp, a high intensity monochromator and a photomultiplier tube wired for fast response, with only six of the nine stages (dynodes) active. The signal created was captured by a Tektronix 2440 digital storage oscilloscope which was interfaced to a Macintosh computer. The software which we used to analyze the data was created within LabVIEW 3.1. environment. The solution data were expressed as change in absorbance (ΔOD).

laser	wavelength (nm)	energy (mJ/pulse)	duration (ns)
KrF excimer	248	<70	12
XeCl excimer	308	<100	8-10
Nd-YAG	266	<25	5-10
Nd-YAG	355	<50	5-10
Dye	depends on dye	<30 (depends on dye)	20

Table 2.1.

Lasers used to perform experiments described in this thesis

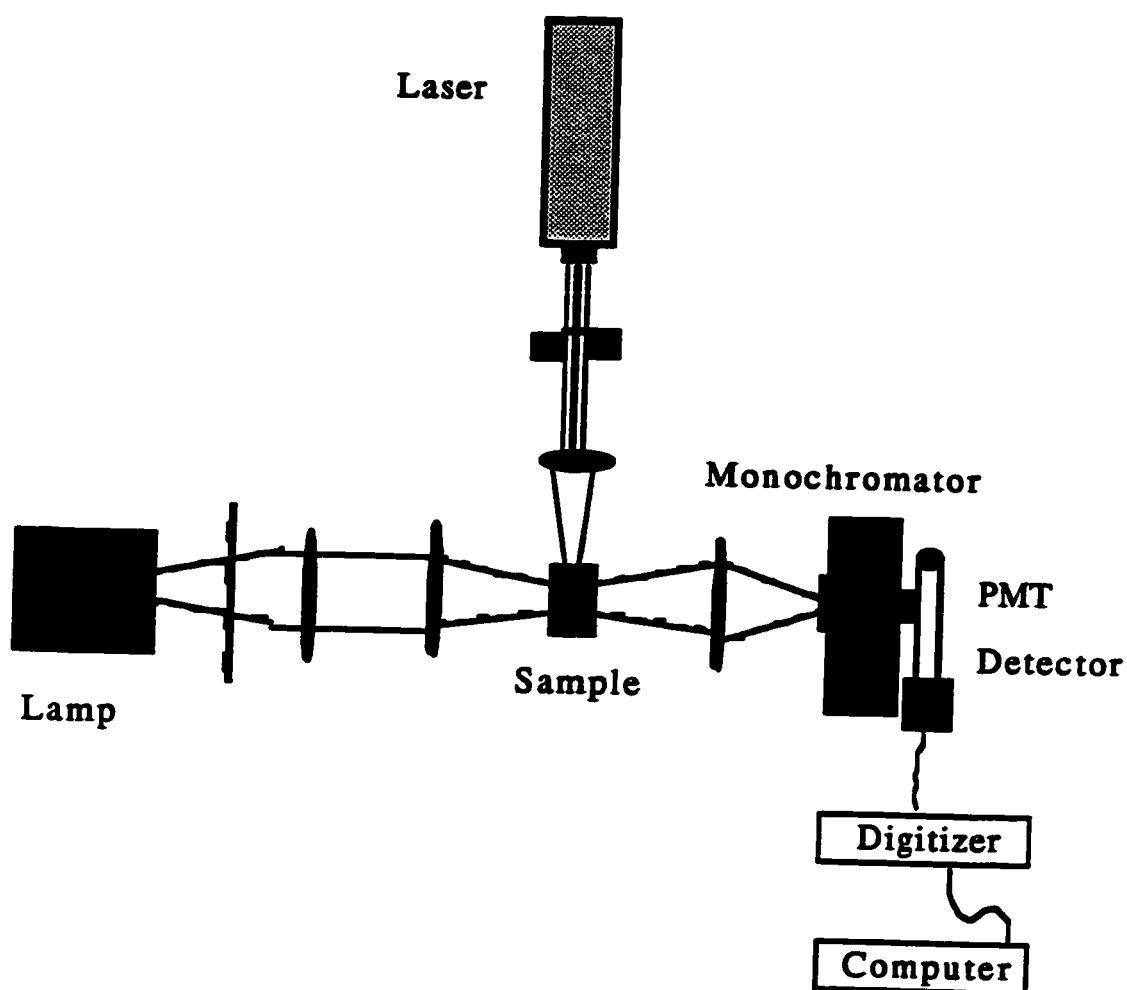


Figure 2.6.

Schematic representation of the laser system in transmission mode

Samples were prepared at a concentration such that the absorption at the laser wavelength was in the 0.2-0.6 range in a 7 x 7 mm Suprasil quartz cell. In some cases, to avoid product built up or sample depletion, they were flowed through a specially constructed sample cell. To examine the effect of inert (nitrogen) or oxygen-rich atmospheres, the solutions were saturated by bubbling with the desired gas for 15-30 minutes.

2.4. Two-laser-two-color laser flash photolysis

This technique is an extension of laser flash photolysis. It uses two lasers in succession. The first laser is the *synthesis laser* and it is used to produce the transient intermediate of interest. In a certain time after the first laser, a second laser is fired which excites the transients formed by the first laser. The second laser is called the *photolysis laser*. By utilizing two lasers, the timing, wavelength and energy of the two lasers can be independently controlled. While one can achieve two photon excitation by using one laser of sufficiently high energy, it is difficult to control the conditions enough to understand the kinetics and/or the mechanism of multiphoton processes under the conditions of a single pulse excitation.

There are some criteria that must be met in order to use two laser techniques. The wavelength of the synthesis laser is usually shorter than the wavelength of the photolysis laser. Given that the concentration of the transient species is usually very low compared to the concentration of the starting material, the wavelength of the photolysis laser should be chosen in a region where the main

absorbing species is the transient. Furthermore, the transient has to be sufficiently long-lived to have a suitable absorption when the second laser fires.

These experiments are similar to those described in the previous section. The difference is that before the first laser is fired, a signal is sent to a Stanford Research System Inc. Model DG535 4-channel Digital Delay/Pulse Generator. This delay generator then sends a signal to fire the first laser and after a set delay time, it sends another signal to fire the second laser. The beams of the two lasers overlap with each other and with the monitoring beam in the active volume of the reaction cell.

2.5. Laser-drop photolysis

Recently, a new preparative technique, laser-drop photolysis, has been developed in order to produce milligram quantities of multiphotonic products. This experimental setup consists of an excitation/optics system and a delivery/containment system. The excitation source is a pulsed laser. The laser must have a sufficiently high power, requiring at least 30 mJ in case of the excimer lasers, and 25 mJ in case of the Nd:YAG laser. The pulse frequency is 2-10 Hz. The laser light is passed through a quartz prism and a 200 mm focal length quartz lens. The focal point of the laser excites the drop of solution which is suspended from the tip of a 2 inch, 20 gauge needle in such a way that the beam does not touch the needle.

The absorbance of the photolysis solution is between 0.7-1.0 at the laser's wavelength in a 7 x 7 mm cell. This ensures that the

absorption of the drop which has a 1-2 mm diameter is around 0.1-0.3. This solution is delivered by a syringe through a syringe needle. The flow of the solution is controlled by a Sage Instruments Model 355 syringe pump.

The needle is placed into the laser-drop cell by inserting it through a rubber septum. The tip of the needle has to be slightly tipped from the horizontal. The rate of flow-in of the solution has to be adjusted depending on the pulse rate of the laser. The drop formed has to be only slightly larger than the cross section of the laser light. The size of the drop vs. time function is shown on Figure 2.7.

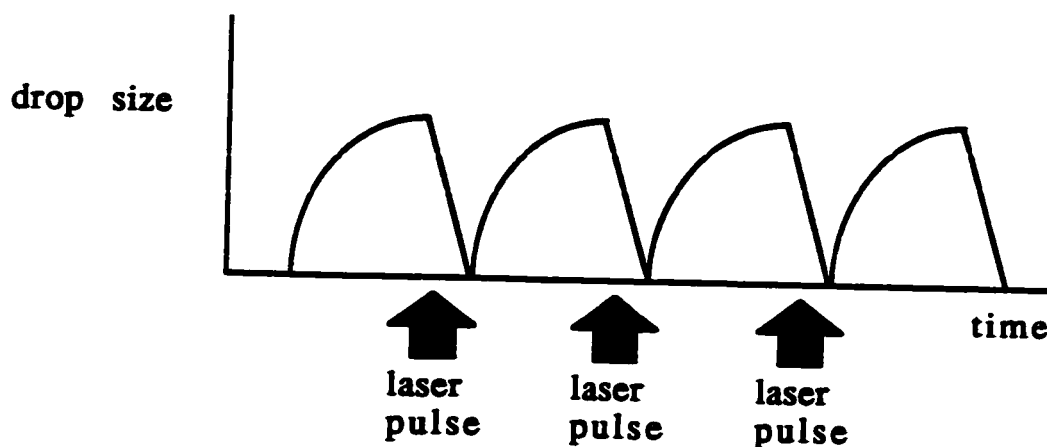


Figure 2.7.

Time-event representation of laser drop photolysis

The photolysis cell (Figure 2.8.) was constructed from an Ace Glass Ltd. photochemical cell. It was 300 mm in length and 50 mm in diameter with removable quartz windows at the ends. The cell was flushed by nitrogen before the irradiation was started in order to

avoid a possible explosion if the laser light hits the tip of the needle in the presence of oxygen.

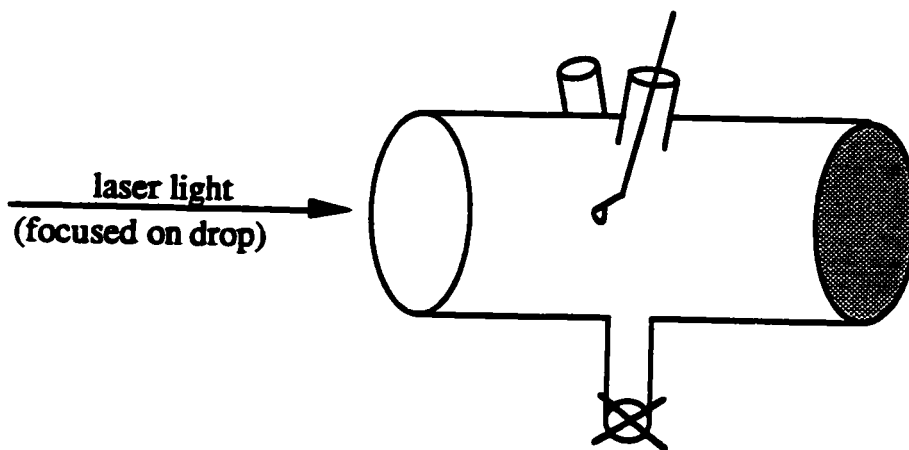


Figure 2.8.
Laser drop cell

2.6. Fluorescence microscopy

To obtain information on the exact position of the compounds used for fluorescence labeling, we used an Olympus BH3 Reflected Light Fluorescence microscope. The microscope could be operated in phase contrast or fluorescence mode. In both cases it used either a Planapo 10x lens with a Numerical Aperture (NA) 0.40 or a Planapo 20x lens with NA=0.70. For excitation a UV Excitation Cube BP405 was employed with an excitation cut-off of 405 nm. The emission was cut off at 420 nm. For sample mounting a 10% glycerol solution was used.

The system was set up with an Olympus PM-10ADS photomodule. For slide pictures Ektachrome 160T films were used, for the other photographs 400 ASA negative color-films and black

and white films were used. The timing of the photographs could be controlled in automatic or manual mode. The final picture magnification was objective x 1.25 x 3.3 x Enlargement.

2.7. Steady-state fluorescence spectroscopy

A Perkin-Elmer Model LS-50 Luminescence Spectrometer was used to record fluorescence emission and excitation spectra. The excitation source was a Xenon discharge lamp which had an equivalent to 20 kW for an 8 μ s pulse duration. Pulse width at half-peak height was <10 μ s. The detector was a gated photomultiplier. Excitation and emission slits were generally 5 nm. The scanning speed was 240 nm/min. When the intensity was too high, a built-in 1% emission attenuator was applied.

For liquid samples a 10 x 10 mm Pyrex fluorescence cell was used. For solid samples a special solid sample holder was used. Instrumental parameters were controlled by the Fluorescence Data Manager software. The processor was an Epson PC AX2. The spectra collected were transferred as ASCII files to a Macintosh computer, and Kaleidagraph 3.0 software was used to plot the data.

2.8. Steady-state irradiation

These were carried out in a homemade reactor with three separate irradiation chambers. Each irradiation chamber was equipped with either nine RPR-2540, RPR-3000 or RPR-3500 lamps which corresponded to wavelength maxima at 254, ~300 and ~350

nm respectively. The temperature in the irradiation chamber was in the 30-35°C range.

2.9. UV-visible spectra

All UV-Visible spectra of the liquid samples were recorded on a Hewlett-Packard Model 8451 diode array spectrophotometer. For solid samples a Varian Cary 1E spectrophotometer equipped with a diffuse reflectance accessory was used. The data collected was treated with the Kubelka-Munk treatment for strongly scattering samples, that is,

$$F(R) = K/S = [(1-R)^2]/2R$$

where R is the reflectance, S is the scattering coefficient and $K = 2 \epsilon c$ (ϵ is the extinction coefficient, c is the concentration).

Chapter 3

Development and Application of Fluorescence Techniques for Monitoring Photodegradation of Lignin-Rich Products

3.1. Introduction

As already indicated in Chapter 1 fluorescence spectroscopy has been a powerful tool for the study of photodegradation processes. Fluorescence analysis has some advantages over other spectroscopic techniques. In fluorescence analysis there are two variables (excitation and emission wavelengths), as opposed to only one in the case of absorption and diffuse reflectance, thus making fluorescence a better diagnostic method. Further, fluorescence measures emitted light, while absorption measures a change in light intensity, therefore the sensitivity of fluorescence measurements is usually higher. Generally, fluorescence has a linear range of about six orders of magnitude; that of absorption, however, is only 2-3 orders of magnitude⁴³.

3.1.1. Effects of molecular structure on fluorescence

Figure 3.1. shows the photophysical processes in which a molecule can participate after the absorption of a photon (I) which promotes it to a higher electronic energy level. If the ground state is a singlet, this higher level is an excited singlet state. Since the lowest spin-allowed excited state is the emissive state in the case of

fluorescence, its absorptivity is crucial. Organic molecules which have a forbidden $S_0-S_1^*$ transition (such as n,π^*), usually are not intensely fluorescent even if its $S_0-S_2^*$ transition is strongly allowed (as opposed to a situation where the lowest energy transition is a π,π^* transition).

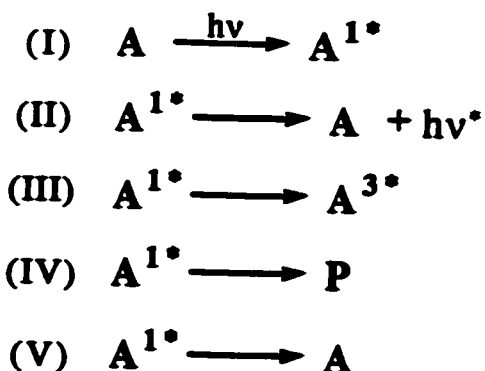


Figure 3.1.

Relevant photophysical processes after absorption of a photon

There are several ways for the excited state molecule to lose its excess energy (Reactions II-V). The excited molecule can undergo intersystem crossing (ISC), thus forming a triplet state molecule (III). To minimize process III, the molecule should not contain structural features or functional groups which enhance the probability of a nonradiative transition. For example, there are some substituents (e.g. a nitro-group or heavy atoms) which increase the rate of ISC, that is the probability of a singlet-triplet interconversion. The singlet state molecule can participate in a photoreaction (IV) leading to product P. To minimize the tendency for photodissociation, the energy of the S_0-S_1 transition should be relatively low. Also, the electron which is promoted to a higher energy level should occupy an

orbital which is not strongly involved in bonding (to avoid bond breakage). It can lose energy via a nonradiative transition (V). As one can see, there are a number of processes which compete with the fluorescence (II).

There are three possible ways to study fluorescence properties. The most common is the measurement of the emission intensity upon excitation with a monochromatic light. The spectrum that one obtains in this way is called an emission spectrum. Emission spectra give information about the characteristics of the excited states of a molecule as well as its interaction with the solvent. Measuring the dependence of emission intensity while changing the excitation wavelength produces the excitation spectrum. Excitation spectra should be identical to the absorption spectrum since both measure the S_0 - S_1 transition. However, due to instrumental artifacts they show some differences. If excitation and emission wavelengths change synchronously keeping a certain wavelength difference, a synchronous spectrum is obtained. Synchronous spectra can be used to obtain information about complex mixtures of fluorescent compounds. Details of this technique will be provided in the third part of this chapter.

I employed fluorescent compounds in order to develop a highly sensitive and selective technique to monitor ortho-quinones in pulp and paper. The basis of the reaction of the derivatization ortho-quinones with phosphorus(III) compounds. Phosphorus triphosphites participate in a cycloaddition with the ortho-quinones. As a result,

cyclic phosphite ethers are formed. This reaction has been developed by Ramirez⁴⁴, and applied to pulp by Argyropoulos²⁶ (Figure 3.2.).

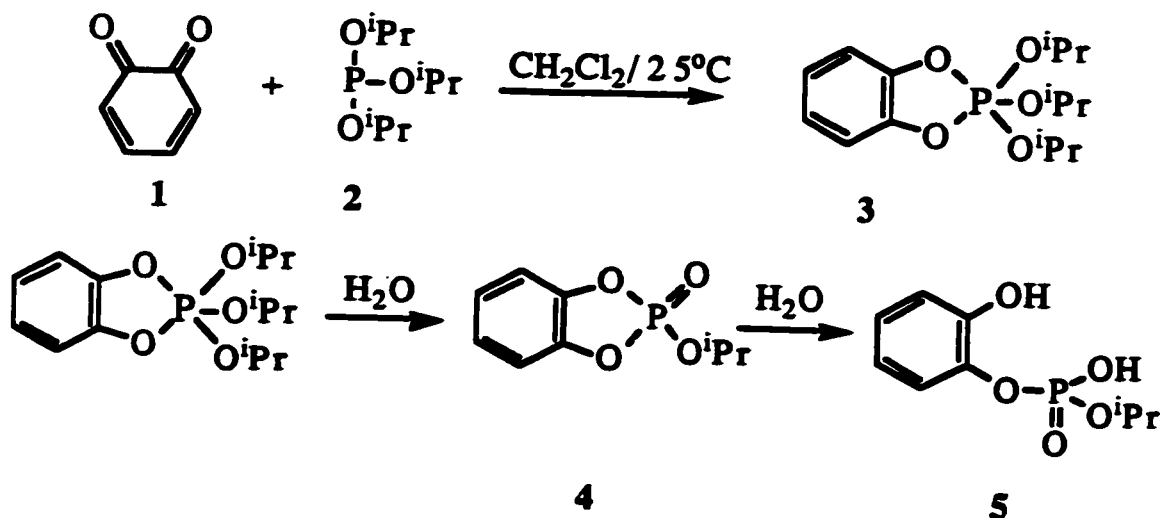


Figure 3.2.

Cycloaddition of ortho-quinone and trialkyl phosphite⁴⁴ and hydrolysis of cyclic phosphite esters²⁶

In the presence of available protons, the cyclic compound hydrolyzes. In the first hydrolytic step one iso-propyl unit hydrolyzes, and the bonds around the phosphorus rearrange to a more favorable trigonal pyramidal structure (leading to the loss of a second isopropyl). The phosphorus compound formed has a structure analogous to trialkyl phosphates, which are fairly stable molecules. In a reaction with a second proton the phosphate ether ring opens up. In the case of pulp the first step occurs spontaneously due to the fact that some water is always present²⁶.

Ortho-quinones are hard to detect in pulp. Besides the fact that the amount of ortho-quinones present in pulp is small, they also lack

a very characteristic, easily measurable property. For example, ortho-quinones are not fluorescent, their infra-red or absorption spectra overlap with those of the other chromophores of the pulp, and their characteristic ^{13}C -NMR signal is rather weak. The two reactions shown above provide a simple way to introduce fluorescent groups in ortho-quinone sites when a fluorescent probe with acidic protons is applied to hydrolyze the cyclic phosphate ester 4. In this way a fluorescent group can be introduced to ortho-quinone sites and their detection, even in small amounts, is possible with highly sensitive fluorescence spectroscopy.

There are a number of conditions a fluorescent probe has to fulfill to be useful as a probe, and specifically to monitor ortho-quinones in pulp and paper: (1) it has to be fluorescent with a high fluorescence quantum yield in order to allow the detection of small amounts of ortho-quinone present in irradiated pulp; (2) the probe should participate in reaction 3.2. That is, it needs a terminal acidic carboxylic function, and preferably, an alkyl chain sufficiently long to minimize steric hindrance; (3) in addition, the probe should be inert towards other structural units in the pulp. This last condition is very restricting given the variety of functional groups present in high-yield pulp and their reactivity.

3.2. Application of pyrene-containing fluorescent probes

Fluorescence is a very useful and sensitive analytical technique. However, only about 10% of all compounds fluoresce⁴³.

One of the most studied compounds is pyrene (Figure 3.3.) and substituted pyrene compounds.

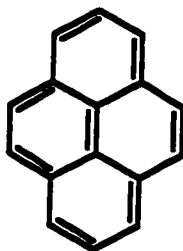


Figure 3.3.
Pyrene

The relevant photophysical properties of pyrene (Py) are absorption of light (VI), fluorescence emission (VII), excimer formation (VIII) and excimer emission (IX) (Figure 3.4.)⁴⁵.

Both the absorption and fluorescence spectra of pyrene show characteristic band structures. The five principal bands of the fluorescence spectrum are numbered I-V. Their positions at 4K are listed in Table 3.1.⁴⁶.

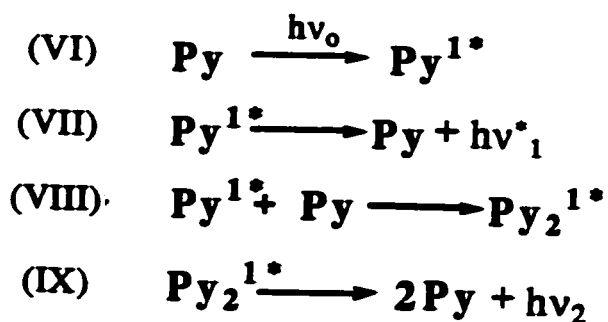


Figure 3.4.
Relevant photophysical properties of pyrene

Relative intensities of the bands strongly depend on the environment. Band I corresponds to the 0-0 transition which in

apolar solvents and in gas phase is a forbidden transition, which therefore has a very low intensity. A more polar environment breaks the local symmetry and in this way increases the oscillator-strength of the symmetry-forbidden transition. Therefore, the intensity of the 0-0 transition relative to the other bands changes. This is called the "Ham" effect⁴⁵.

number	position (nm)
I	372.51
II	378.95
III	383.03
IV	388.55
V	393.09

Table 3.1.

Principal fluorescence bands of pyrene at 4 K⁴⁶

Other symmetry-breaking effects, such as substituents on the pyrene structure have a similar effect. In the case of pyrene the ratio of band I/band III (the latter is the least sensitive to the solvent environment) is used as a sensor of solvent polarity^{45,46} (Table 3. 2.). This is normally referred to as the "Py scale".

Besides the above mentioned Py polarity scale, the lifetime of pyrene emission also gives information about its environment. The lifetime of the fluorescence emission of unsubstituted pyrene is 450 ns in cyclohexane, and shorter in more polar solvents⁴⁶.

Solvent	I_1/I_3
Vapor	0.41
Hexane	0.58
Benzene	1.05
Ethanol	1.18
Ethyl acetate	1.37
Acetone	1.64
Water	1.87

Table 3.2.

Representative relative intensities of the band I and band III of pyrene fluorescence emission⁴⁵

Substituents on pyrene can alter the lifetime of the emission and the characteristic band-structure of the pyrene fluorescence via symmetry-breaking effects. Therefore, substituted pyrenes are grouped according to the nature of their substituents. Groups that do not perturb much the electronic structure of pyrene (such as alkyl groups) do not alter significantly the characteristic band structure of the fluorescence spectrum, and the lifetime, though shortened, is still in the hundred-nanosecond region (Table 3.3.)⁴⁶. Other, more polar substituents, result in band broadening, red-shifting, and lifetime shortening⁴⁶.

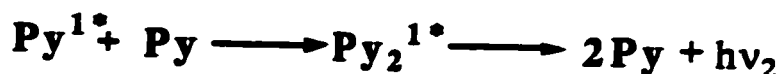
The decay of the fluorescence is generally monoexponential. However, when different pyrene molecules are in different environments their fluorescence shows bi- or multiexponential decay. In this way, one can obtain information about the uniformity of the environment around pyrene.

Solvent	pyrene	1 - Methylpyrene	1-Pyrene carboxylaldehyde
Cyclohexane	0.6 (450 ns)	0.48 (235 ns)	< 0.01
Dioxane	0.44 (295 ns)	0.46 (195 ns)	0.004 (<2 ns)
Water	0.27 (200 ns)	0.34 (145 ns)	0.42 (5.1 ns)

Table 3.3.

Fluorescence quantum yield (Φ) and singlet lifetime (τ , in brackets) for various substituted pyrenes in various solvents

The other important property of pyrene is its ability to form excimers. Excimers (for excited dimer) are formed by an excited state and a ground state molecule. On the energy surface, the excimer is situated in an energy well below that of the excited state monomeric pyrene.



Equation 3.1.

Excimer formation and emission

The excimer exhibits different fluorescent characteristics from those of monomeric pyrene. To form excimers in solution the concentration of pyrene must be high enough that an excited state pyrene can encounter a ground state pyrene before deactivation. In solid systems and organized media where the position of pyrene is more or less fixed, two pyrenes must be close enough to each other and their spatial orientation must be appropriate in order to form the excimer⁴⁷. Two possible orientations are depicted in Figure 3.5.

On the left the two pyrenes are in a face-to-face conformation. This case is the most common for excimers. However, the two pyrenes can be slightly shifted, and still there is a possibility of energetic stabilization, i.e. excimer formation. This type of excimer has slightly different fluorescent characteristics.

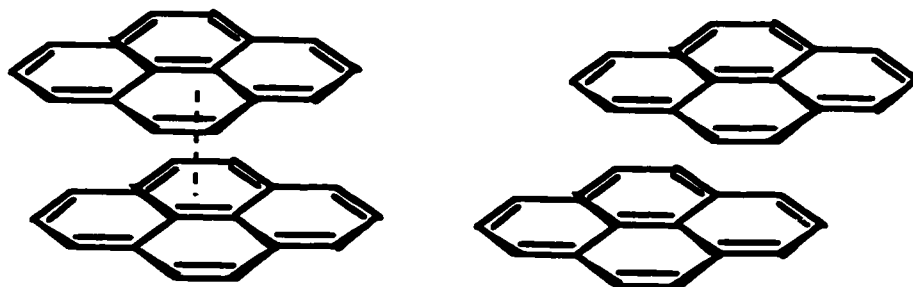


Figure 3.5.
Two possible pyrene excimers

Excimer fluorescence appears as a broad emission band between 400-550 nm. The exact position and lifetime of this band is also solvent and substituent dependent, being red shifted in the case of polar solvents or polar substituents⁴⁶.

Pyrene has been frequently employed as a fluorescent probe in organized media such as biological systems, micelles⁴⁸ and polymers⁴⁹. In all cases, one can obtain the greatest degree of information about the microenvironment when the fluorescence probe has a strong and selective affinity for the environmental site of interest. This goal can be reached by either one of the two ways: (1) The probe, due to its polar properties, prefers a particular environment; (2) the pyrene moiety is an integral part of the

structure, as in the case of covalent bonding. Pyrene itself is usually employed because of the large amount of information that can be extracted. For example, the position of the bands and their relative intensities give information on the polarity of the environment. Measuring fluorescence decay, we can determine the mobility of the probe, the uniformity of the environments around the pyrene, etc. The study of excimer fluorescence helps probe the proximity and the diffusion of the probes.

Pyrene has a high fluorescence quantum yield. Therefore, even small amounts of ortho-quinones can be detected by measuring probe fluorescence. Pyrene is available with different substituents. This enables us to use it in a reaction which is specific to ortho-quinones; and therefore to avoid its reaction with other functional groups. Our original project was to use pyrene as a probe which enables the determination of the proximity between the ortho-quinone groups due to the possibility of excimer formation. Furthermore, we assumed that if we can detect excimer emission, we could show that formation of ortho-quinones are not uniform throughout the sample, that is, some starting "grain" for the yellowing process exists. Since the pulp also has a strong fluorescence emission in this region, the long lifetime of the pyrene emission can help to discriminate between the fluorescence of the pulp and the pyrene probe. In other words, while they overlap spatially, they can be easily separated in time.

An alternate approach to the incorporation of fluorescent probes has been developed by Gray and co-workers, who have

reacted *ortho*-quinones with *o*-phenylenediamine to generate fluorescent phenazines³³. A similar technique has been employed by us in the study of multiphoton processes (See Chapter 4).

As already noted, two methods were employed. In the first one the fluorescent moiety is incorporated as part of the phosphite. While this method initially appeared to offer the simplest approach to probe incorporation, it eventually proved to be the least specific of the two, and the one requiring more synthetic effort.

3.2.1. Method I: pyrene-derivatized phosphites

The probe molecule in this case was 4-pyrenylbutyldimethyl phosphite (6), prepared by the reaction of dimethylchlorophosphite with pyrene butanol (Figure 3.6.).

In this case derivatization of *ortho*-quinones should yield the corresponding cyclic derivative, e.g.:

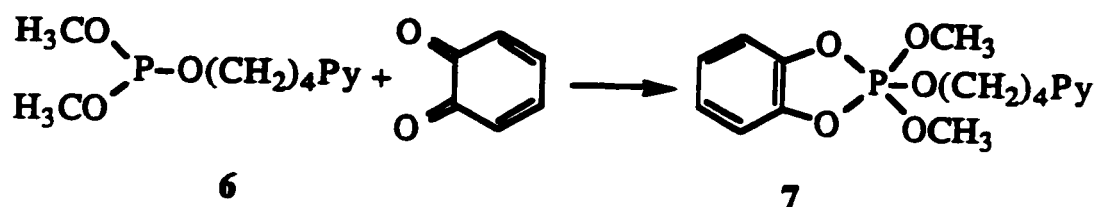


Figure 3.6.

Derivatization of *ortho*-quinones with 4-pyrenebutyldimethyl phosphite

where 'Py' represents the pyrene moiety attached at 1-position. However, during the first hydrolytic step (as in Figure 3.2.), the side product is either methanol or pyrene-butanol, i.e. there is a

possibility that some of the pyrene butanol group will be eliminated. Based on statistics, even this case leads to retention of approximately two thirds of the pyrene moieties.

Figure 3.7. shows the results of an experiment performed on paper from thermomechanical pulp TMP under two different combinations of irradiated, and treated with 6 (phosphite with fluorescence moiety) or treated with 2 (phosphite without fluorescence moiety). The same is shown for non-irradiated samples in Figure 3.8.

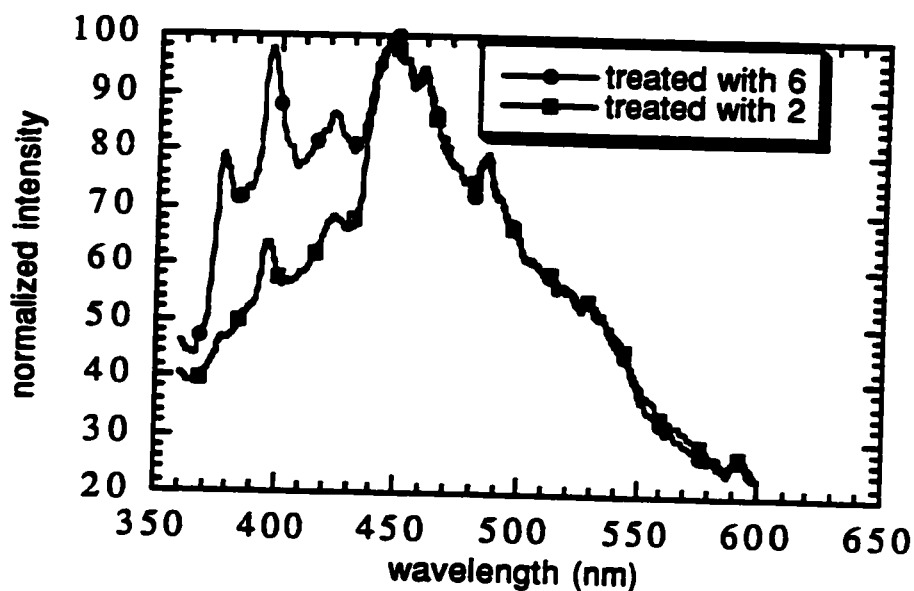


Figure 3.7.
Fluorescence spectra of irradiated TMP paper with 2 and 6.
Excitation wavelength 330 nm

Dry methylene chloride proved to be the best solvent for the reaction between ortho-quinone and trialkylphosphite. We have

tested several solvents in order to determine if the reaction occurs under our experimental conditions. These solvents were benzene, acetonitrile, chloroform and ethanol. According to ^{13}C -NMR studies, there was no other solvent found in which the reaction between ortho-quinone and triisopropyl phosphite occurs more efficiently under our conditions.

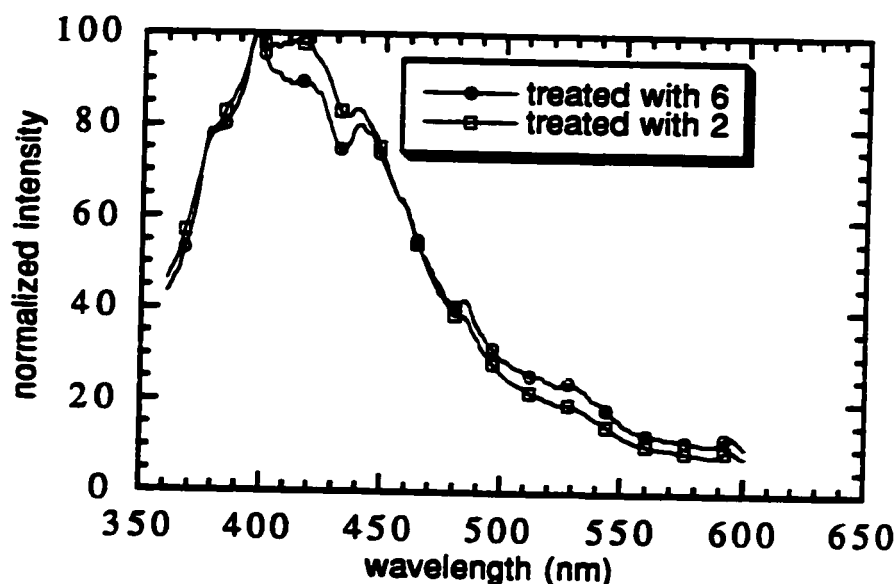


Figure 3.8.
Fluorescence spectra of non-irradiated TMP paper with 2 and 6.
Excitation wavelength 330 nm

Figure 3.9. also shows a difference spectrum, where the non-irradiated/treated spectrum has been subtracted from that for the irradiated/treated sample.

The emission spectrum is clearly that of the pyrene monomer. It has maxima at 375, 394 nm and around 415 nm. These values are

red-shifted compared to those at 4 K (See Table 3.1.), which is due to the fact that the pyrene is in a different environment, and that it is substituted. In the case of the non-irradiated pulp in addition to the 375 and 394 nm pyrene peaks, a small bleaching is observed between 400 and 450 nm.

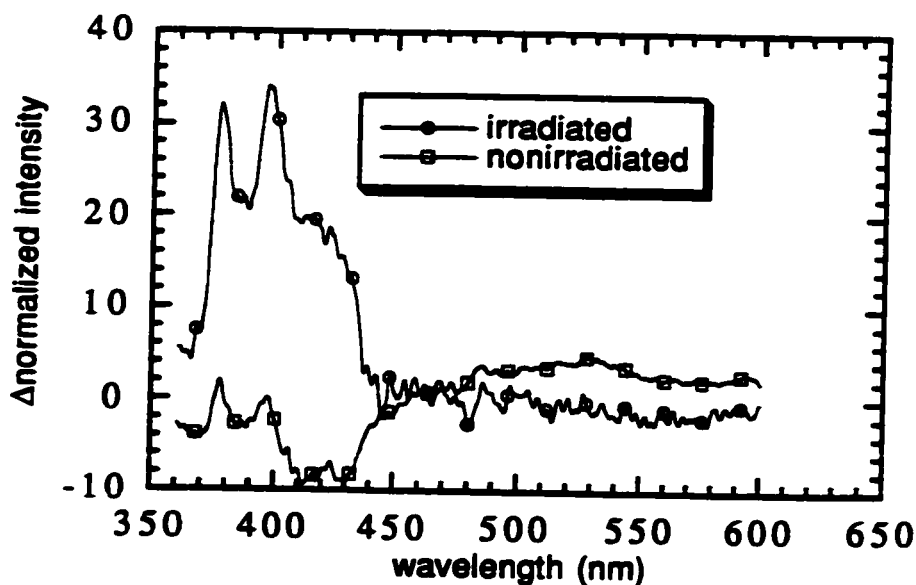


Figure 3.9.

Difference fluorescence spectrum of irradiated and non-irradiated TMP paper treated with 6 and 2

Pyrene incorporation in the unirradiated sample is probably due to the presence of some ortho-quinoid structures which formed either in a thermal reaction during the storage, or during the manufacturing of the paper. The result shows that quinone generation by UV photolysis of the paper leads to enhanced incorporation of pyrene moieties. Under these conditions we did not detect any evidence for excimer emission. It is also evident from

Figure 3.9. that there is considerable interference from the luminescence from paper.

The origin of the reduction in fluorescence intensity of the irradiated and derivatized TMP paper between 400 and 450 nm is not known. According to the more popular model³⁰⁻³², it shows the disappearance of chromophores which fluoresce at this wavelength. However, according to Gray and coworkers, who recently characterized emission of TMP in considerable detail, this would mean the formation of chromophores which absorb the fluorescence of the carbohydrate framework in this wavelength region^{28,50}. Our opinion will be given in section 3.4, where our results regarding the origin of fluorescence of the high-yield pulp will be presented. Experiments with thermomechanical pulp (TMP) led to similar conclusions (Figure 3.10.). The amount of incorporated pyrene, however, is obviously different.

As already mentioned, the emission from the pulp interferes with the emission from the pyrene. Due to this problem, excimer emission cannot be observed at all under steady state conditions, and the study of monomer fluorescence is also hindered to a certain degree. Therefore, several excitation wavelengths (from 316 to 360 nm) were employed in an attempt to optimize the emission spectra (Figure 3.11.). In general, longer excitation wavelengths lead to improved spectra, largely as a result of better discrimination in favor of the excitation of the pyrene, rather than lignin.

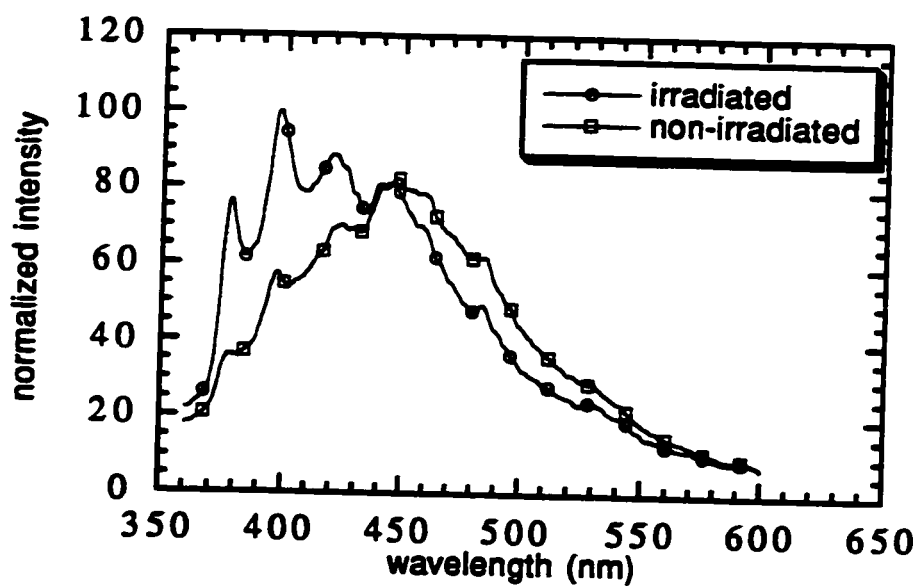


Figure 3.10.

Difference spectrum between irradiated and non-irradiated TMP treated with 6 and 2

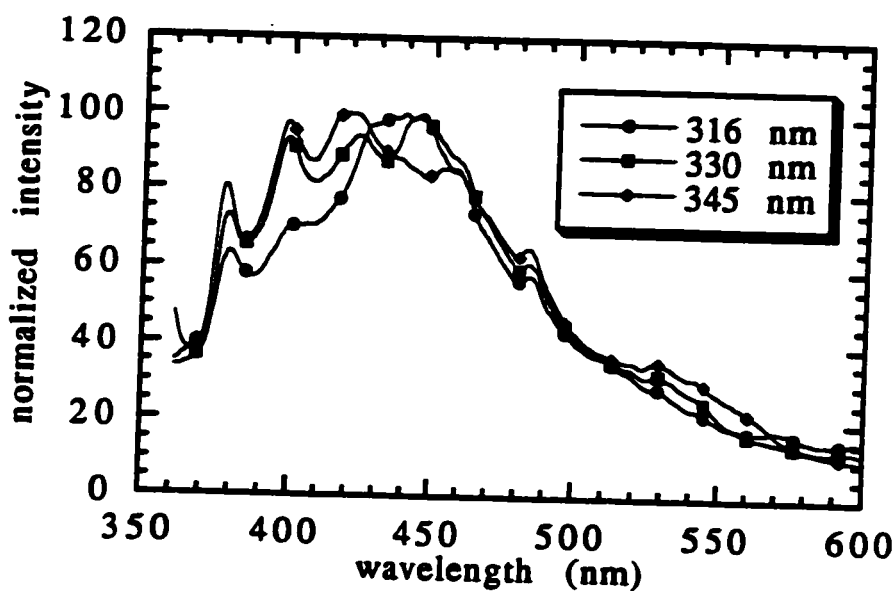


Figure 3.11.

Effect of different excitation wavelengths on the fluorescence of thermomechanical pulp after treatment with 6

One of the main problems encountered is that the reaction of 5 is not specific to *ortho*-quinones. Some other carbonyl compounds (see Table 3.4) which are present or formed in irradiated pulps react readily⁴⁴. Some of them (acids, acid-anhydride) can be removed or neutralized. The others, however, are present in high yield pulp and paper to a similar or greater extent than the *ortho*-quinones. When we looked at these structures, we realized that most of them probably do not undergo hydrolysis in the same way (see Figure 3.2.) as the cyclic phosphite ester formed from *ortho*-quinones (for example the cyclic compound formed from β -enone).

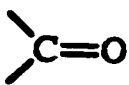
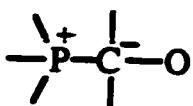
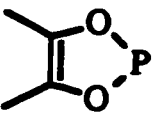
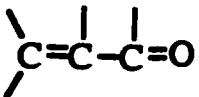
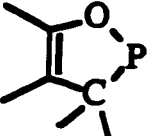
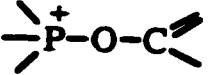
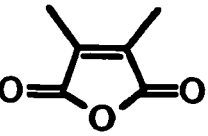
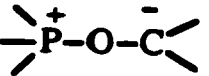
carbonyl compound	product
	
	
	
	
	

Table 3.4.

Reactions of different functional groups (present in TMP) with trialkyl phosphites

Aliphatic alcohol groups which are present in lignin can participate in transesterification reaction with lignin. However, since these groups do not participate in the photoyellowing process, their contribution does not change, therefore emission originated from this source can be regarded as a constant "background" emission.

In the other cases, if the acid used for hydrolysis contains the fluorescent probe, instead of the phosphite, the probe would be covalently bound to the hydrolyzed phosphite, rather than to the lignin framework (these assumptions, however, were verified by ^{13}C -NMR studies, see below). This led us to try our second approach, described below, that proved to be more specific and easier to implement.

3.2.2. Method II: hydrolysis of cyclic phosphorous compounds

This approach is based on the acid hydrolysis of cyclic phosphorous compounds of the type 4. The molecule used as a probe is pyrenebutyric acid, 8.

Probe molecule 8 (Figure 3.12.) is used to perform the second hydrolytic step of method II in Figure 3.2.

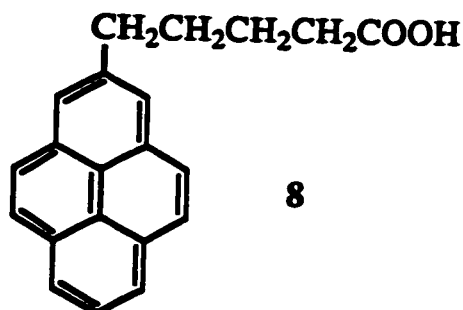


Figure 3.12.
Pyrenebutyric acid

3.2.2.1. NMR reactivity studies

In order to better establish the mechanism of method II and the selectivity of this reaction, it was examined by ^{13}C NMR using $\text{CH}_3^{13}\text{COOH}$ as a model reactant. Pyrenebutyric acid could not be used since it cannot be dissolved to the extent required for ^{13}C NMR experiments. Therefore, we felt that acetic acid which has similar chemical functionalities should be a good model for the hydrolysis reaction. Three model compounds, 9-11, all of them structurally relevant to lignin chemistry and all able to participate in reactions with phosphorus(III) compounds were examined.

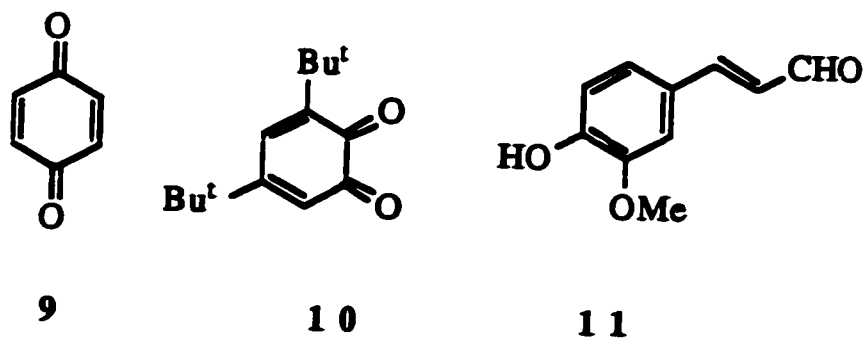


Figure 3.13.

Model compounds used in ^{13}C -NMR experiments. p-Benzoquinone (9), 4,6-di-*tert*-butyl-orthoquinone (10) and conyferaldehyde (11)

p-Benzoquinone (9) was expected to participate in a reaction with triisopropyl phosphite, but not in the hydrolytic step. Coniferaldehyde (11) was also expected to participate in a reaction with triisopropyl phosphite, but the result of hydrolysis needed to be tested. In the case of 4,6-di-*tert*-butyl ortho-quinone (10), we wanted to demonstrate that it does participate in both reactions. We

used 10 as a model *ortho*-quinone since it is a commercially available stable *ortho*-quinone.

Other structural components, such as organic acids or anhydrides may also react with phosphite, but they would be destroyed by base washing during the pre-treatment of the pulp. Our experiments were aimed at establishing if, under our experimental conditions, *ortho*-quinones incorporated selectively the fluorescent probe.

Under our experimental conditions, coniferaldehyde (11) was not reactive. The same applied to β -ionone, another α,β -unsaturated aldehyde briefly tested. In the case of *p*-benzoquinone (9) reaction with triisopropyl phosphite occurred readily, as shown in Table 3.4.; however, addition of $\text{CH}_3^{13}\text{COOH}$ caused no change in the spectrum of the adduct, suggesting that the acid hydrolysis step does not work in this case, as expected (Table 3.5, Figure 3.14).

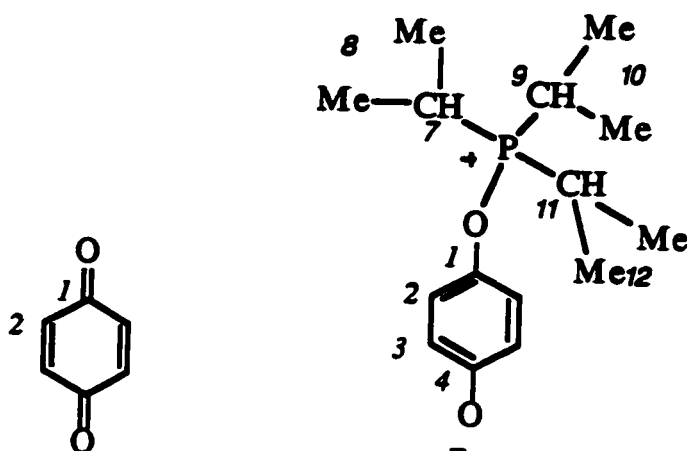


Figure 3.14.

Assignment of ^{13}C -NMR results presented in Table 3.4.

9		9+2		9+2+acid	
C-1	188 (187.0*)	C-1	158	C-1	158
C-2	137 (136.4*)	C-2	124	C-2	124
		C-6		C-6	
		C-3	119	C-3	119
		C-5		C-5	
		C-4	147	C-4	147
		C-7	68-76	C-7	68-76
		C-9		C-9	
		C-11		C-11	
		C-8	24-28	C-8	24-28
		C-10		C-10	
		C-12		C-12	
				COOH	176
				CH ₃	25(?)

* from reference⁵¹

Table 3.5.

¹³C-NMR results in ppm, see text

In the case of *ortho*-quinone 10, reaction with P(OPri)₃ occurs readily (see Figure 3.15.b.) leading to the corresponding cyclic compound (see Figure 3.2.). Addition of CH₃¹³COOH gave unequivocal evidence for reaction with the cyclic phosphorous product, as illustrated in Figure 3.15.c.

The spectra (see Figure 3.15.c.) are somewhat complicated by the obvious formation of more than one product, as expected from the two possible modes of ring opening in this asymmetric system (Figure 3.16.). ³¹P NMR (not shown) also showed more doublet peaks, in the -2 to -4 ppm region (relative to 85% H₃PO₄), in

agreement with the reported solid state spectrum for the open phosphite ester²⁷.

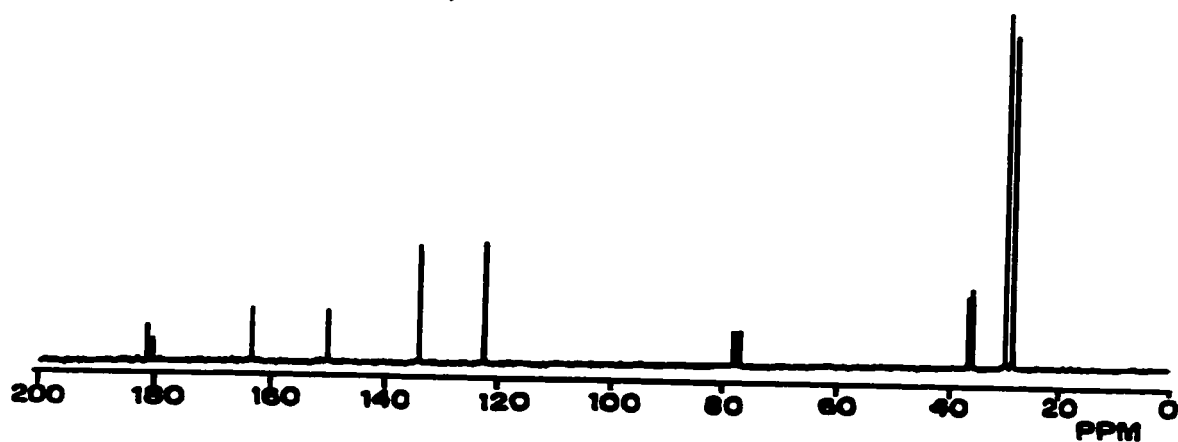


Figure 3.15.a.
¹³C-NMR spectrum of 10 in CDCl₃

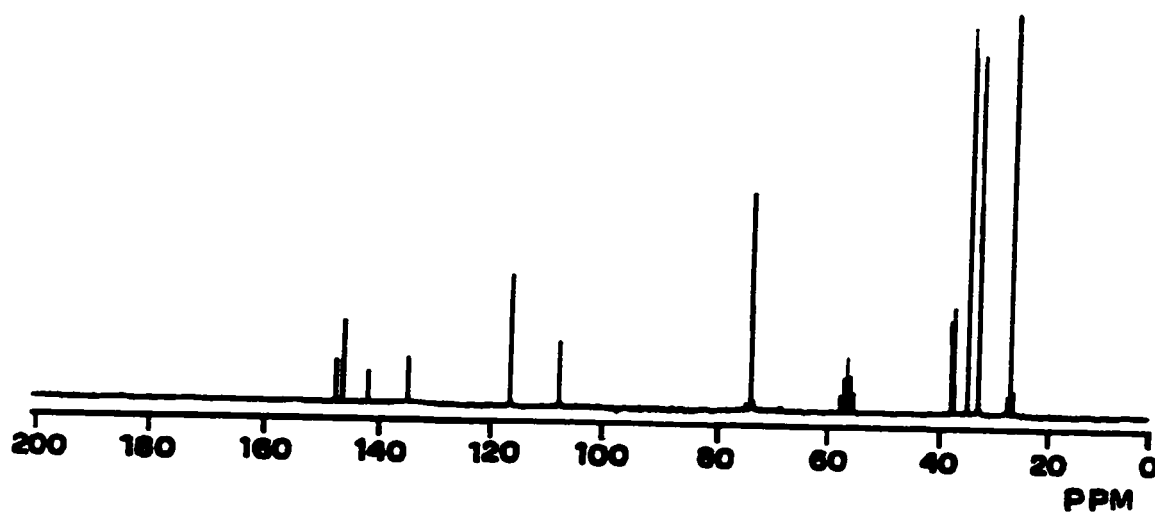


Figure 3.15.b.
¹³C-NMR spectrum of cyclic phosphite ester of 10 in CD₂Cl₂

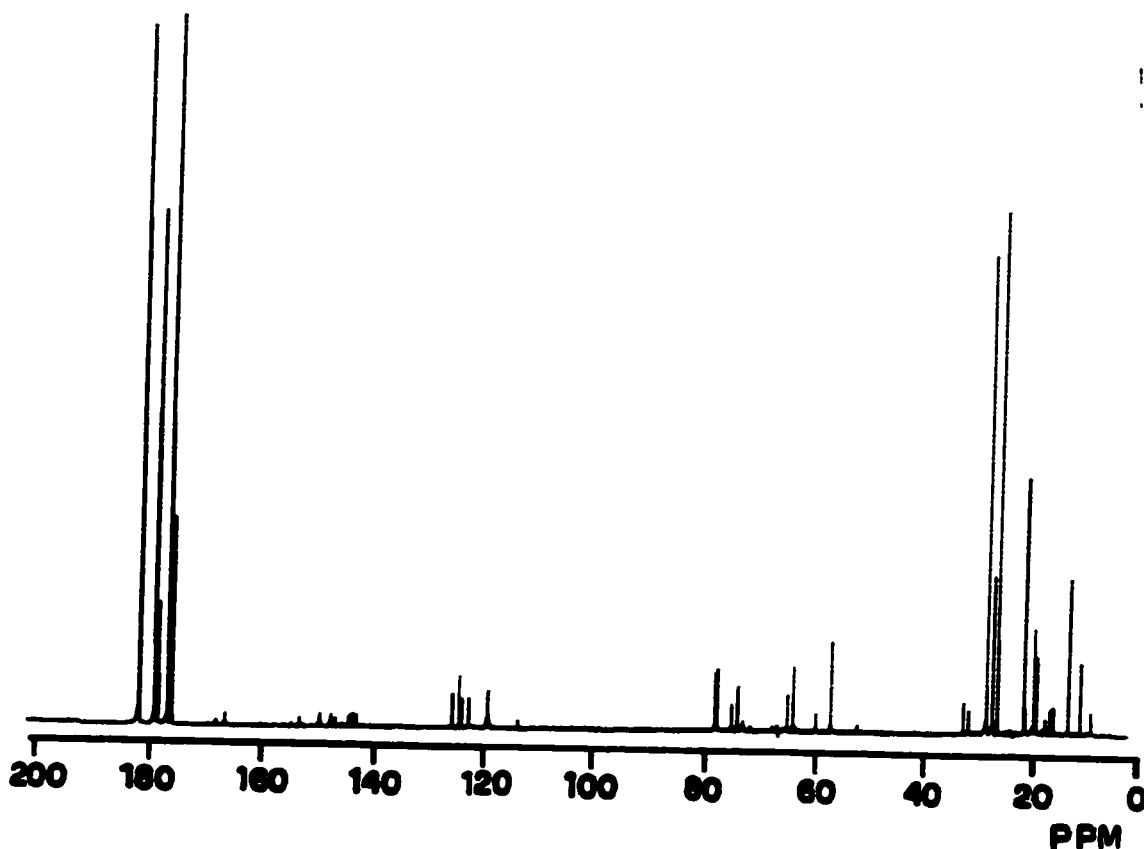


Figure 3.15.c.
Cyclic phosphite ester of 10 after reaction with $\text{CH}_3^{13}\text{COOH}$

Further analysis of ^{13}C NMR results of the region 178-179 ppm (acid carbon region) are neither easy, nor essential to establish that acid hydrolysis occurs efficiently only in the case of 10. However, in the region of the aromatic carbons (110-125 ppm), the spectrum shows more doublet peaks which correspond to the different products of ring opening.

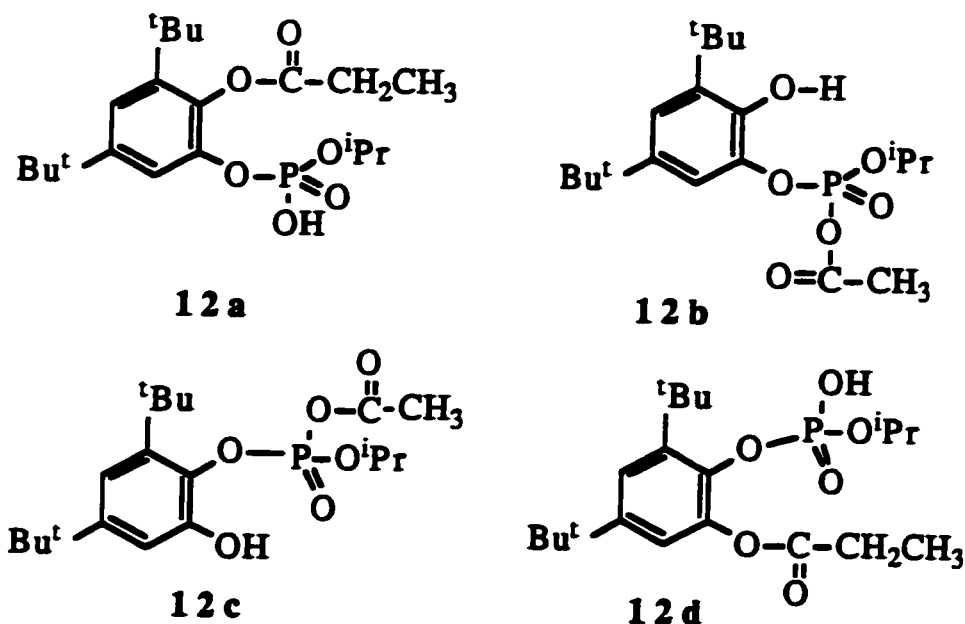


Figure 3.16.

Four ring opening possibilities for cyclic phosphite ether of 10 upon hydrolysis with $\text{CH}_3^{13}\text{COOH}$

3.2.2.2. Steady state fluorescence spectroscopy

Experiments employing method II involved the same type of controls already described for method I. Figure 3.17. illustrates a series of experiments performed on unbleached TMP. The spectra reveal quite clearly the incorporation of pyrene centers resulting from UV irradiation of the pulp. All other emission spectra presented from this point on have been corrected in a similar manner, and only the difference spectra will be given.

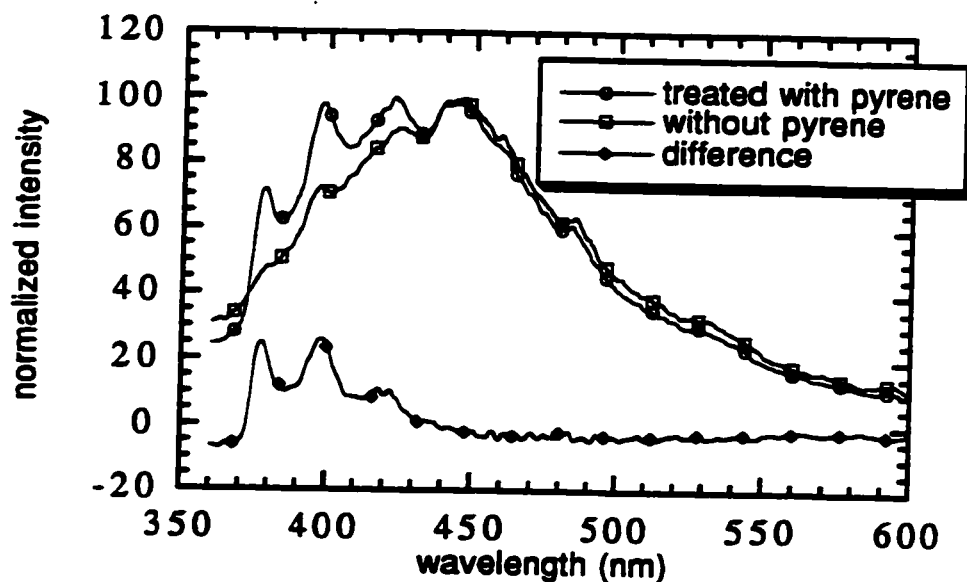


Figure 3.17.

Fluorescence spectra (excitation wavelength 330 nm) of irradiated TMP with and without pyrene as well as the difference spectrum

Figure 3.18. illustrates the difference spectrum obtained from TMP paper, along with the diffuse reflectance spectra of samples treated and untreated with pyrene. The latter show that the amount of pyrene incorporated is in fact small enough, not to make a significant difference in the absorption (reflectance) spectrum of the sample. However, the fluorescence spectrum clearly shows the presence of pyrene. This experiment also demonstrates the advantage of using fluorescence spectroscopy as a very sensitive detection technique. The fluorescence spectrum on paper is quite comparable with that from pulp, with characteristic pyrene bands at 375 and 397 nm. No evidence for excimer emission was obtained in

these studies, although time resolved work tells a more complete story (*vide infra*).

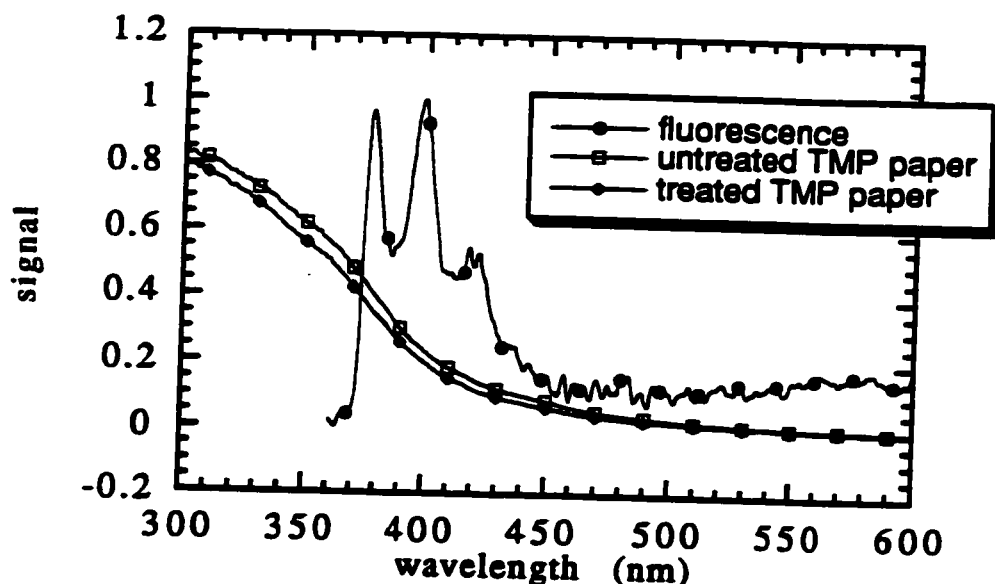


Figure 3.18.

Fluorescence difference spectrum (excitation wavelength 330 nm) and diffuse reflectance spectra of treated TMP paper, and diffuse reflectance spectrum of untreated TMP paper

The effect of changing the irradiation wavelength was also examined (Figure 3.19). We found that there was no significant difference between samples irradiated at 300 and 350 nm. According to previous studies, however, the irradiation wavelength plays an important role controlling which chromophore would decompose²². Our results show, that the chromophore which led to quinone formation must be absorbing at both wavelengths. In natural light both 300 and 350 nm are present, though part of the 300 nm irradiation is filtered, and its intensity is therefore lower.

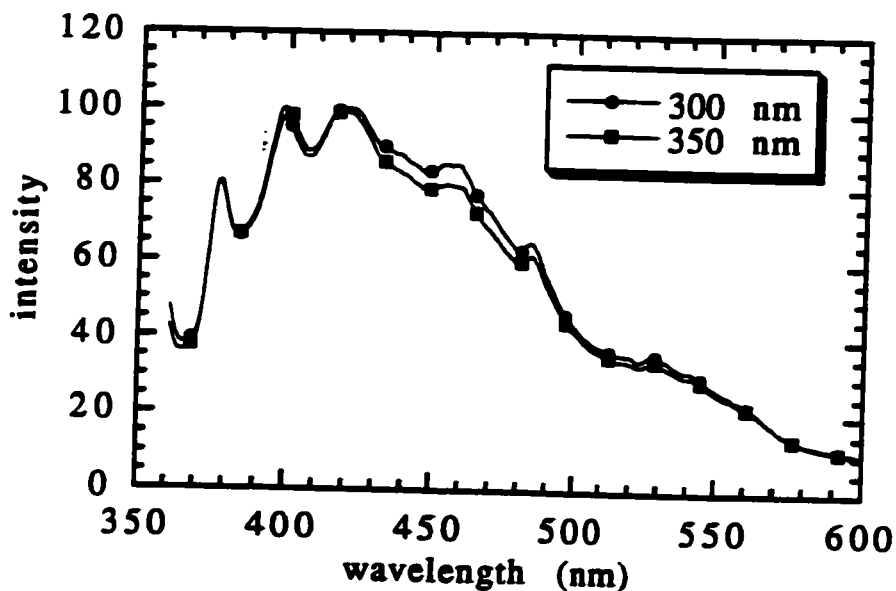


Figure 3.19.
Effect of irradiation wavelength on the fluorescence of irradiated and treated TMP (excitation wavelength 330 nm)

The amount of pyrene that can be incorporated on the pulp depends on the surface area undergoing irradiation. The light used for irradiation can cause photodegradation only in the upper surface layer. The amount of lignin in this layer therefore determines the amount of quinoneunits formed in the process of photodegradation.

Besides the chemical reaction with ortho quinones, there is a possibility of pyrene adsorption on the solid surface of the pulp. To determine if this effect is important or not, we irradiated pulp samples of different thickness, and after the usual treatments, an increasing amount of fluorescent probe was incorporated. If there had been only physical adsorption, the amount of probe which can be incorporated would have only depended on the amount of pulp

present in the reaction mixture, which was the same in all cases. In this case the maximum intensity of pyrene fluorescence would have been the same in all cases. However, since the pyrene was selectively bound to the ortho-quinone as a product of the photodegradation, the maximum intensity of the pyrene emission reached a plateau (when all the available ortho-quinone is derivatized).

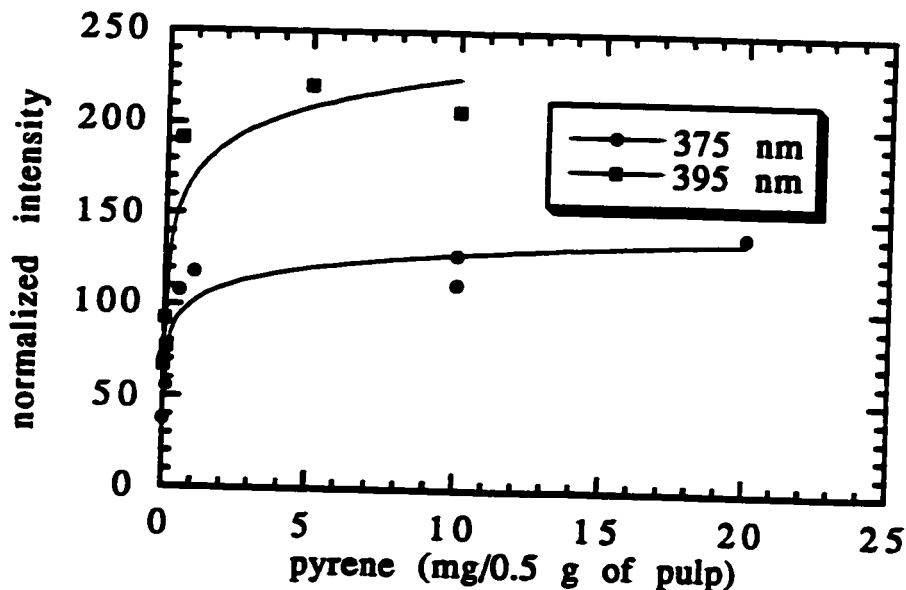


Figure 3.20.
Normalized intensity of pyrene fluorescence upon treatment of TMP with different amounts of pyrene

If we assume that photodegradation occurs only in the upper layer to a certain thickness, then when irradiating pulp of different thickness, the relative amount of pulp undergoing photodegradation would be inversely proportional to the thickness of the pulp. Thus, the fluorescence intensity (after normalization as described in the experimental section) was plotted. In all cases the intensity reached

a plateau (see for example Figure 3.20.). This plateau was inversely proportional to the thickness of the original pulp sheets, and thus proportional to the relative amount of pulp subjected to the irradiation (Figure 3.21.). Therefore, the main source of pyrene fluorescence is shown to be the chemically bound pyrene.

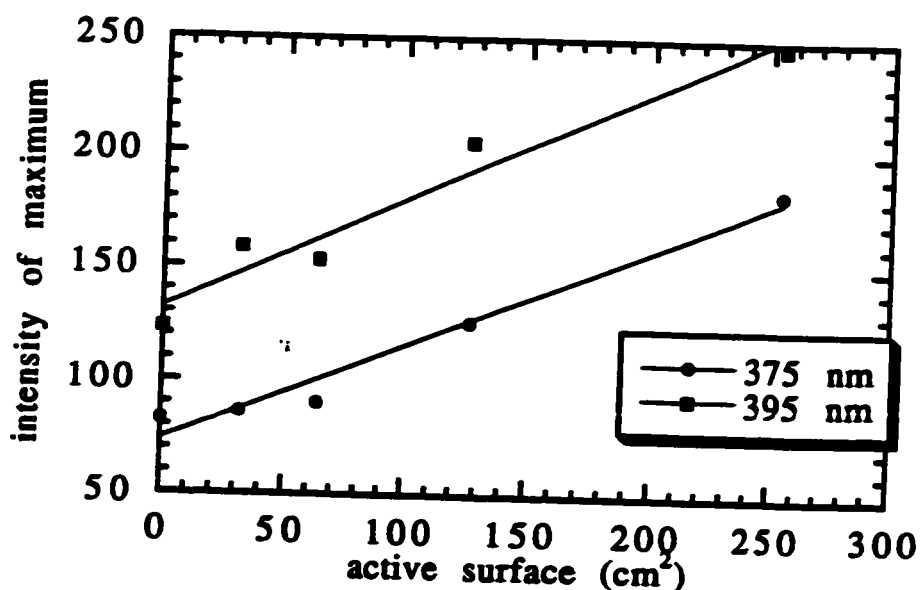


Figure 3.21.
Maximum intensity of pyrene fluorescence (plateau at maximum pyrene incorporation for samples subjected to irradiation)

As mentioned in Chapter 1, bleaching is an important step in paper manufacturing. Therefore, we examined the photodecomposition of unbleached pulp as well as two differently bleached pulps.

Figure 3.22. shows the difference in pyrene incorporation following irradiation, for samples bleached with hydrogen peroxide or with sulfite (see the experimental section for details of the

experiments). Quite clearly, bleaching promotes the subsequent incorporation of pyrene following irradiation.

The same observation was made when we used bleached TMP handsheets as opposed to the unbleached pulp. While both reductive and oxidative bleaching processes induce this effect, it is apparent that peroxide treatment is most effective in causing enhanced degradation. We attribute the enhanced yellowing to the formation of quinone precursors during peroxide bleaching via the partial oxidative breakdown of the lignin. Since we have shown that in method II pyrene incorporation is a highly selective indicator of the formation of *ortho*-quinones, we conclude that bleaching enhances the tendency toward lignin photodegradation in this manner.

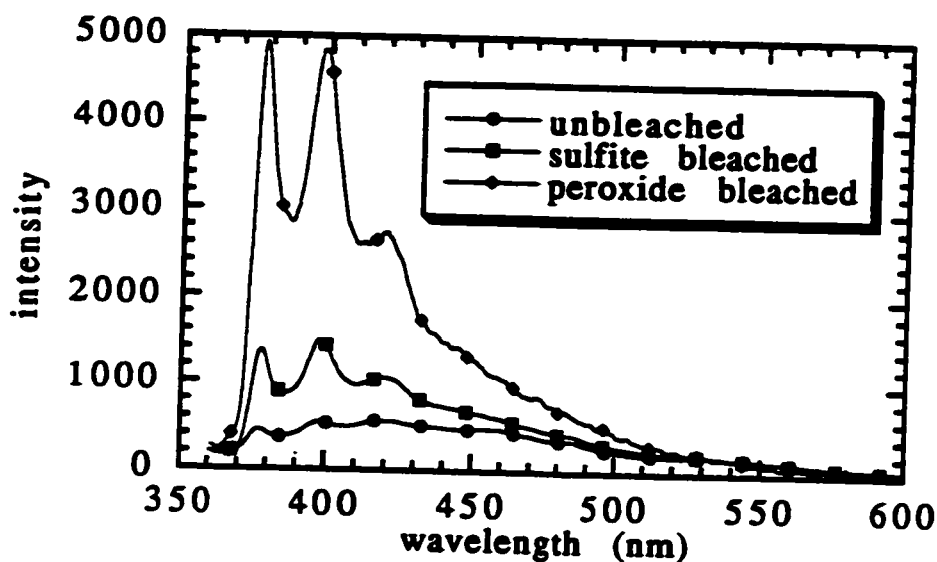


Figure 3.22.
Effect of bleaching on pyrene incorporation (excitation wavelength 345 nm)

Under extended irradiation (≥ 24 hours) the amount of incorporated pyrene decreased. This supports the observation made by others⁵², that reaching the maximum, upon further irradiation, the quinone itself undergoes photodegradation.

3.2.2.3. Time resolved fluorescence spectroscopy

We have noted earlier that the luminescence from pulp tends to interfere with pyrene emission, specially in the case of the pyrene excimer. In spite of detailed spectroscopic work, no measurements of the emission lifetimes have been reported. The pulp emission, centered around 480 nm, was much shorter than the 355 nm pulse (~ 6 ns) from our nanosecond Nd/Yag laser. Given that pyrene emissions tend to be longer lived, this allows for the straightforward differentiation of pulp and probe luminescence, by appropriate gating of the detection system. Figure 3.23. shows spectra of treated and untreated pulps. Note that untreated pulp shows no emission in the 53-115 ns window.

Pyrene incorporation experiments following irradiation were carried out for two different levels of pyrene incorporation. They are referred as "low" and "high" pyrene, and full details of the incorporation are provided in the experimental section.

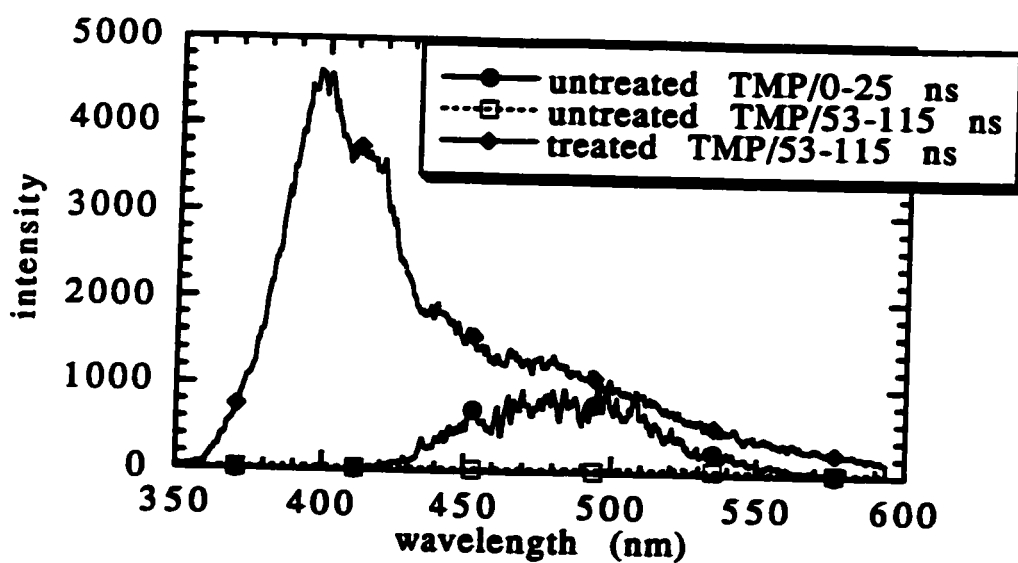


Figure 3.23.
Gated spectra of treated and untreated TMP in different time windows

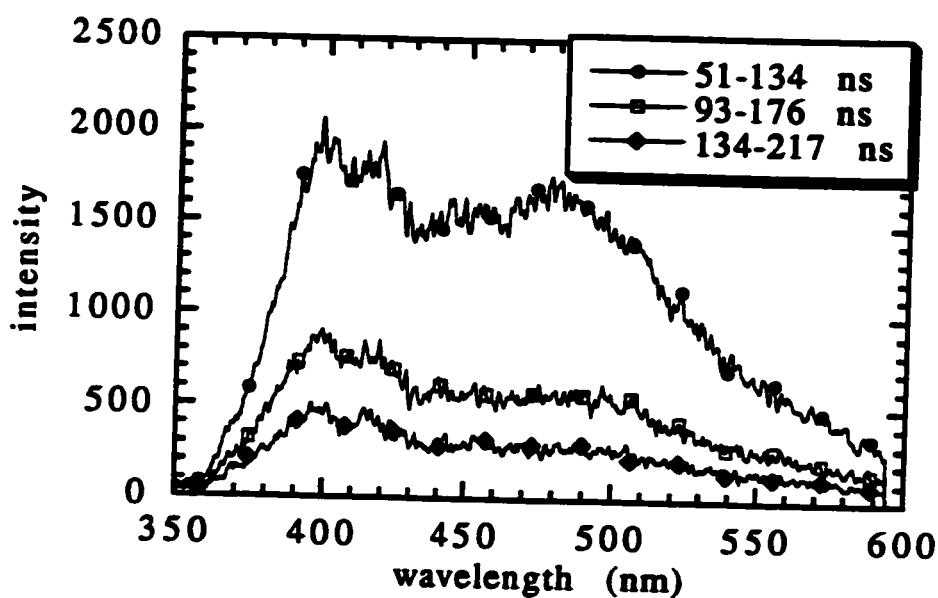


Figure 3.24.
Time-resolved fluorescence spectra of irradiated TMP treated at high pyrenebutyric acid concentration

Figure 3.23. shows the spectra recorded for the low pyrene sample under nitrogen. No change in spectra was recorded in a time window from 53 to 115 ns following the 6 ns, 355 nm laser pulse. The small shoulder in the 450-500 nm region is indicative of some excimer emission. Note also that the pyrene-free sample shows no detectable emission in the excimer region in the 53-115 ns window, indicating excellent temporal discrimination between pyrene and pulp emission. Kinetic studies show that the decay is essentially insensitive to saturation with air. Biexponential analysis (starting 30 ns after the laser pulse) provides a reasonable fit to the data with lifetimes of ~16 ns and 57 ns.

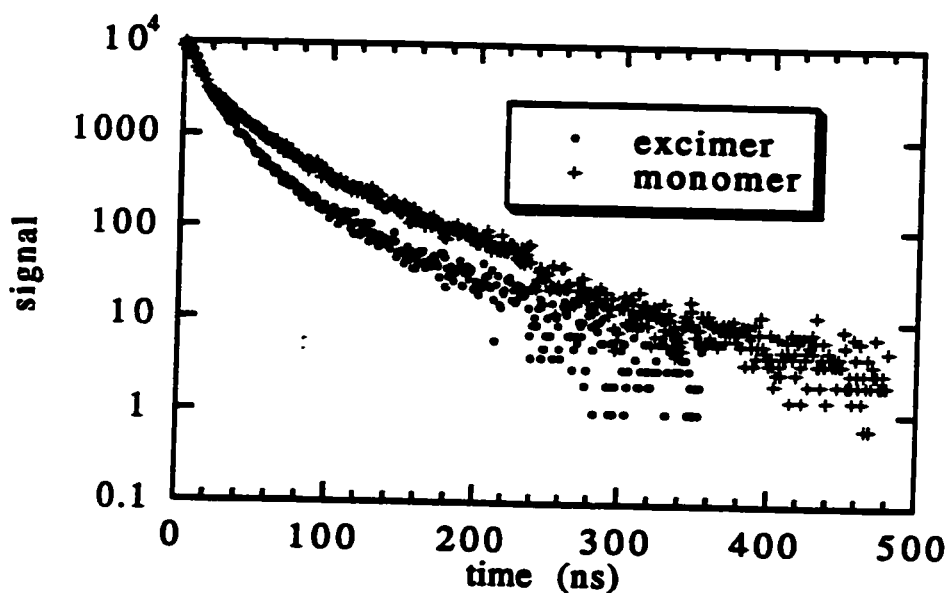


Figure 3.25.

Decay kinetics of monomer and excimer emission of "high" pyrene sample. Detection system was delayed by 30 ns

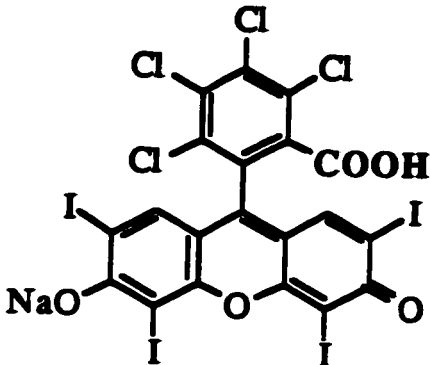
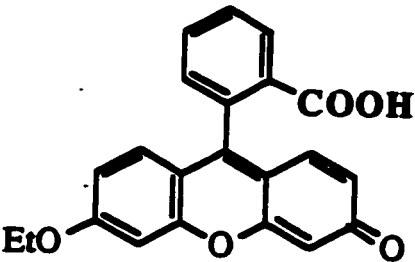
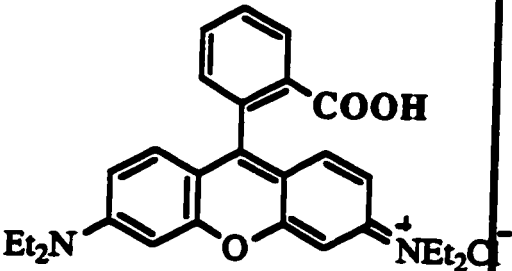
The decay of the pyrene emission in high load pulps is also comparable under nitrogen and under air, where a biexponential analysis led to lifetimes of 15 ns and 65 ns. In the excimer region, the lifetimes were about 13 ns and 80 ns. The spectra recorded at different times following laser excitation are shown in Figure 3.24., while Figure 3.25 illustrates the fluorescence decay traces.

3.3. Application of more red-emitting fluorescent probes

Pyrene-containing fluorescent probes are useful to map ortho-quinone distribution and to probe their environment. However, there was one major disadvantage of these probes. Their possible excitation wavelength spans only up to ~370 nm, and their emission occurs at wavelengths less than 450 nm. This region strongly overlaps with the fluorescence excitation and emission spectra of pulp. Therefore, selective excitation is not possible and it is hard to distinguish between the two sources of fluorescence. Indeed, distinction is only possible in time resolved experiments due to the significantly different lifetime of the two emissions. In these experiments a time window can be chosen where pyrene emission is high while the pulp emission has already decayed. This approach, however, could not be used in fluorescence microscopy, since it was not possible to "gate" the emissions. For this reasons it was desirable to develop a probe with red emission (>450 nm).

As mentioned in the introduction of this chapter, only fluorescent molecules with a -COOH function and red emission could be used. We examined a number of molecules which could be

grouped according to their fluorescent moieties. Table 3.6. shows all the molecules examined, along with their fluorescent excitation and emission maxima. From the table it is obvious that all of these probes only partly fulfill the requirements mentioned in the introduction.

name	molecular formula	excitation maximum	emission max.
Rose Bengal (13)		460	548
Fluorescein (14)		495	515
Rhodamine B (15)		545	565

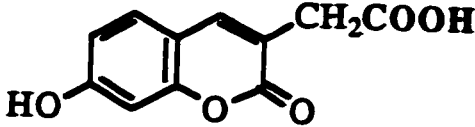
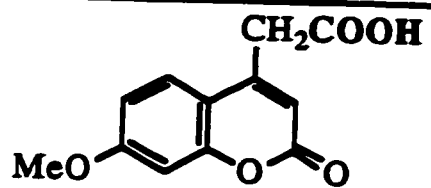
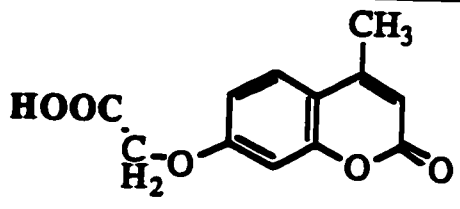
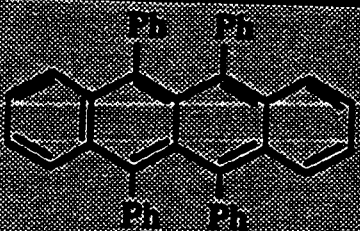
7-Hydroxy-coumarin-4-acetic acid (16)		405	460
7-Methoxy-coumarin-4-acetic acid (17)		400	460
7 - (Carboxymethoxy)- 4-methyl coumarin (18)		395	460
*Rubrene (19)		530	560
*Fluoranthene (20)		360	465

Table 3.6.

Red emitting fluorescent compounds used for fluorescent derivatization of ortho-quinones

* These compounds were not available with appropriate substituent. Therefore we attempted to derivatize them (see Section 3.3.3.)

3.3.1. Application of Rose Bengal, Fluorescein and Rhodamine B

All of the above compounds are well known fluorescent probes. Their emission maxima are at longer wavelengths than the emission of pyrene, as well as the emission maximum of pulp.

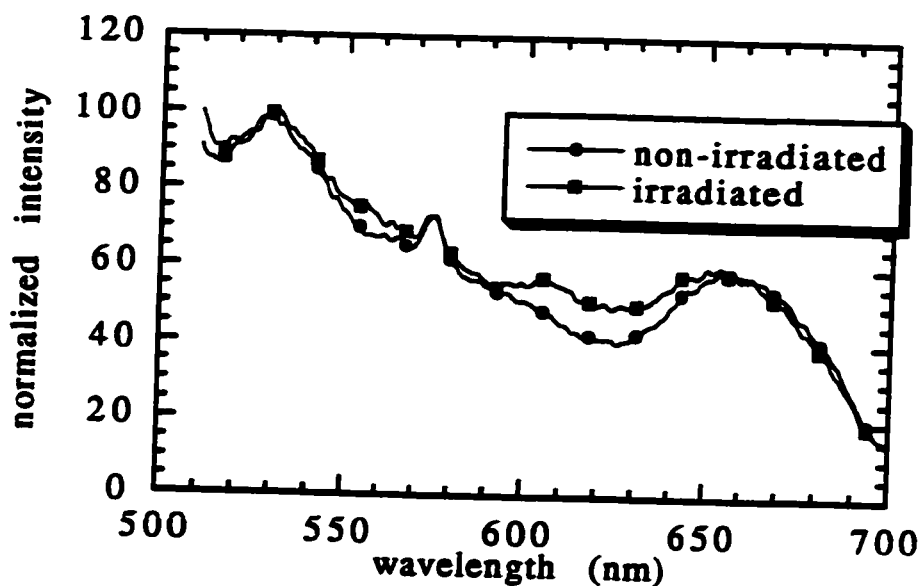


Figure 3.26.

Fluorescence spectra after treatment of irradiated and non-irradiated pulp with (13) (excitation: 490 nm)

Figure 3.26. shows the results obtained with Rose Bengal. There is no significant difference in fluorescence intensity of the irradiated and the non-irradiated pulp after treatment with the fluorescence probe. The fluorescence of irradiated pulp is slightly higher around the expected emission wavelength of Rose Bengal (548 nm), but there is obviously a major contribution from another source of fluorescence.

Figure 3.27. shows results obtained treating high-yield pulp with Rhodamine B. Normalization of the spectra are also difficult given that there is no reference point where the two spectra would be expected to be of equal in their intensities. Using an arbitrary reference point the red end-point of the spectra, the irradiated pulp fluoresces less than the non-irradiated sample.

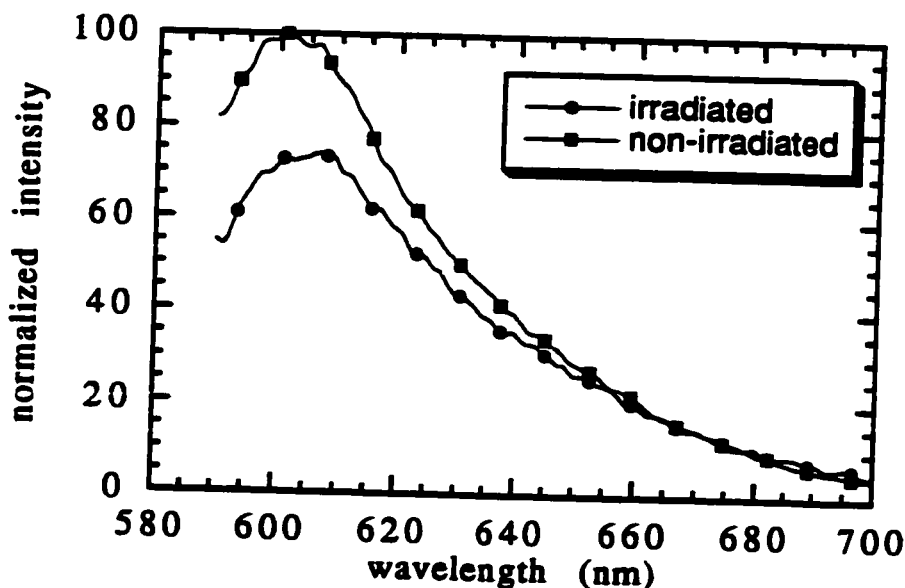


Figure 3.27.

Fluorescence spectra after treatment of irradiated and non-irradiated pulp with 15 (excitation: 490 nm)

The fluorescence maxima are also significantly red shifted which can be due to two reasons: (1) Environmental changes around the fluorescent probe. This is highly unlikely given the results obtained with pyrene probes where the microenvironment around the probe was shown to be polar; i.e. comparable with the solvent normally used to obtain the fluorescence maximum for Rhodamine B

(methanol); and (2) a chemical reaction which significantly changes the electronic structure of the probe as well as its fluorescent properties. Obviously, if this is the case, a reaction must exist in which Rhodamine B participates. This reaction must be preferred over the hydrolysis step of the derivatized cyclic phosphite ester (see section 3.2.).

Figure 3.28. shows fluorescence spectra of irradiated and non-irradiated TMP pulp after treatment with fluorescein. Using this probe there is a significant increase in the fluorescence intensity.

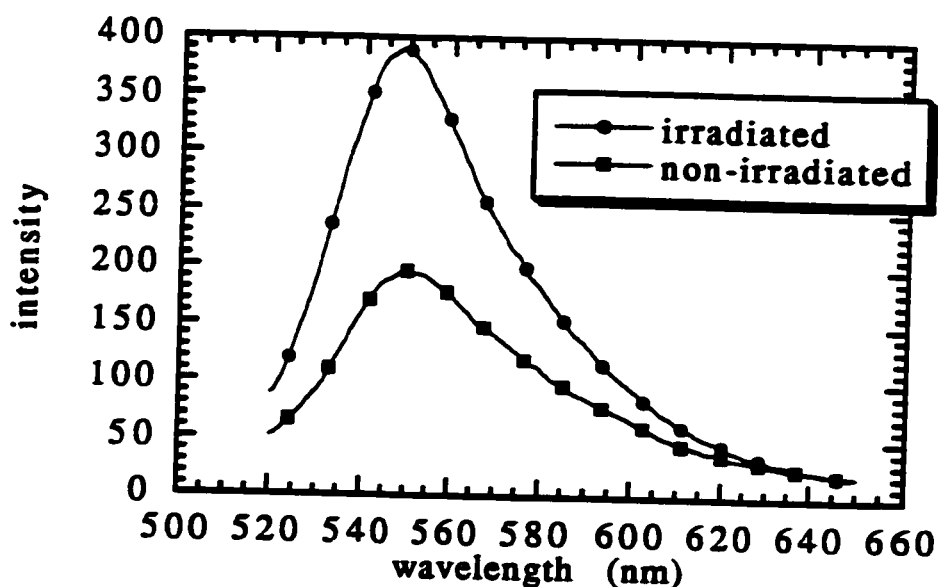


Figure 3.28. Fluorescence spectra after treatment of irradiated and non-irradiated pulp with 14 (excitation: 500 nm)

The maximum of fluorescence emission is also red shifted which suggests an additional chemical reaction with some other structural unit of the high-yield pulp. In the case of fluorescein,

however, this reaction is not dominant but rather competitive with the hydrolytic step of the cyclic phosphite ester.

3.3.2. Application of coumarines

Our next choices for fluorescent labeling of ortho-quinone units in high-yield pulp were different substituted coumarines. All selected coumarines had a $\text{CH}_2\text{-COOH}$ side chain. This feature may favor the hydrolytic reaction over any other reactions by eliminating a possible slowdown of the hydrolysis because of steric hindrance.

All of the selected coumarines are well-known laser dyes with high fluorescence quantum yields. Unfortunately, their fluorescence maxima are closer to that of the pulp than the previous group. Also, they have a lactone ring which can be quite sensitive to ring opening under various chemical conditions (such as acid or basic hydrolysis).

The main difficulty, however, was not any of the above mentioned, but the fact that these coumarines are insoluble in methylene chloride which was the only solvent of the cyclization reaction between ortho-quinones and trialkylphosphite. Therefore, an extended reaction time was applied to allow (in case of extreme low solubility) the slow dissolution and reaction of the coumarines with the cyclic phosphite esters.

The results, presented in Figures 3.29.-31. demonstrate that application of these probes were not successful.

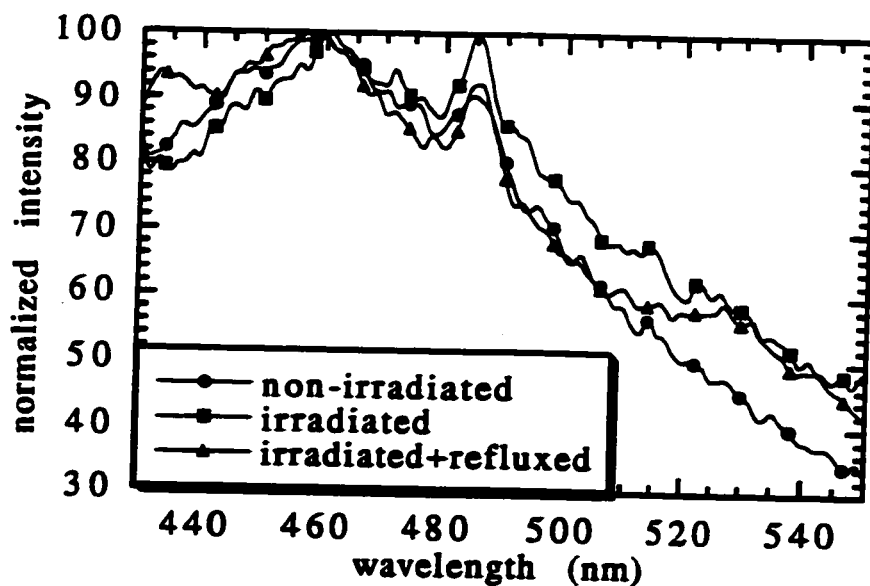


Figure 3.29.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 16 (excitation wavelength: 400 nm)

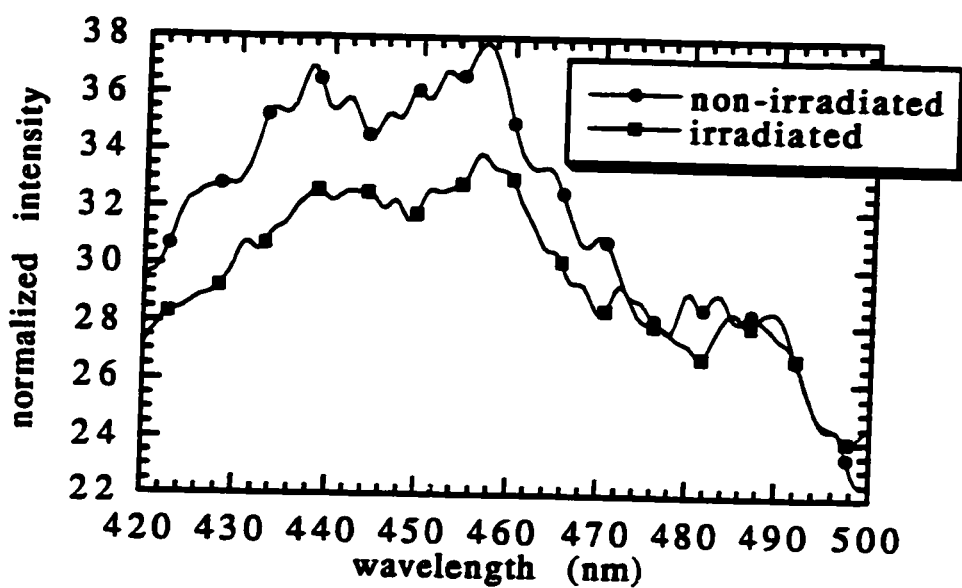


Figure 3.30.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 18 (excitation wavelength: 400 nm)

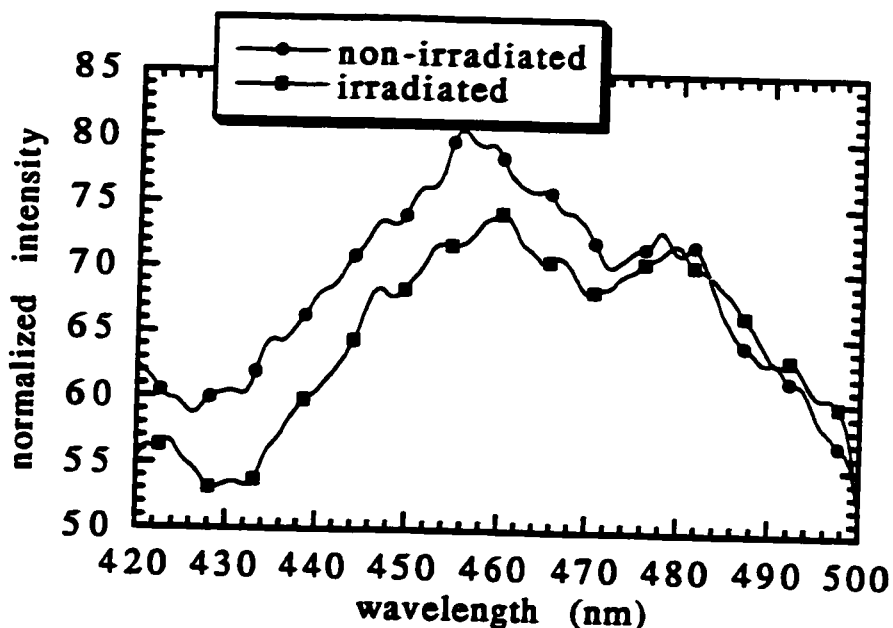


Figure 3.31.

Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 17 (excitation wavelength: 400 nm)

These fluorescence spectra showed no incorporation at all (16), even upon heating the reaction mixture to facilitate the dissolution of the dye (see: irradiated and refluxed). In the other two cases incorporation of the probe in the non-irradiated pulp was slightly higher. This could be due to the uncertainties in the normalization of the spectra (i.e. to normalize we had to find a region where fluorescence intensity does not change upon irradiation or derivatization with the fluorescent probe).

3.3.3. Application of polycyclic aromatic compounds

In section 3.2. I described the application of pyrene butyric acid as a fluorescent probe. The main advantages and disadvantages were also discussed. Polycyclic aromatic compounds usually have high fluorescence quantum yields, and as such, they can be useful as fluorescent probes. Among these compounds there are some with emission well over 450 nm, such as rubrene and fluoranthene. However, these molecules are generally not available in substituted form, and for us the application of these molecules represented a synthetic challenge. Due to the closed aromatic structure of these molecules they are relatively inert.

3.3.3.1. Derivatization of fluoranthene

Figure 3.32 shows synthesis of 3-fluoranthenol³.

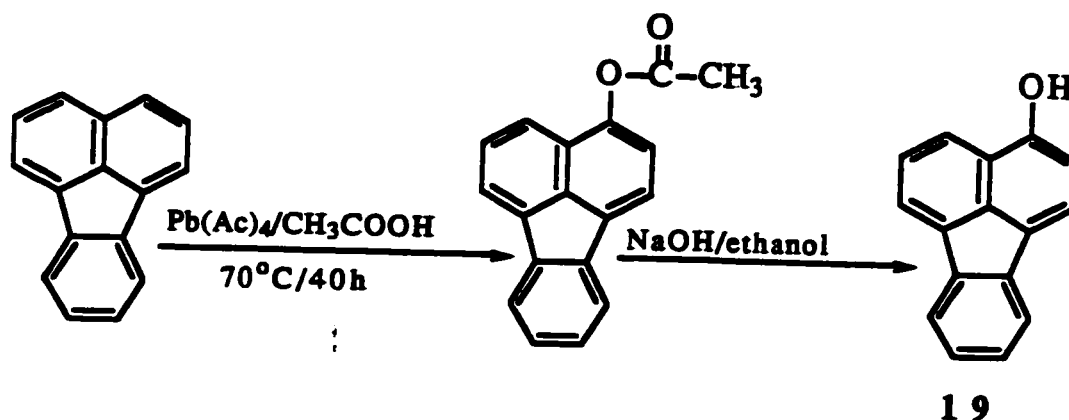


Figure 3.32.

Synthesis of 3-fluoranthenol (19)⁵³

To 3-fluoranthanol a long carbon chain with an ester unit in the end was connected from which a corresponding carboxylic acid could be obtained via hydrolysis. (Figure 3.33.)

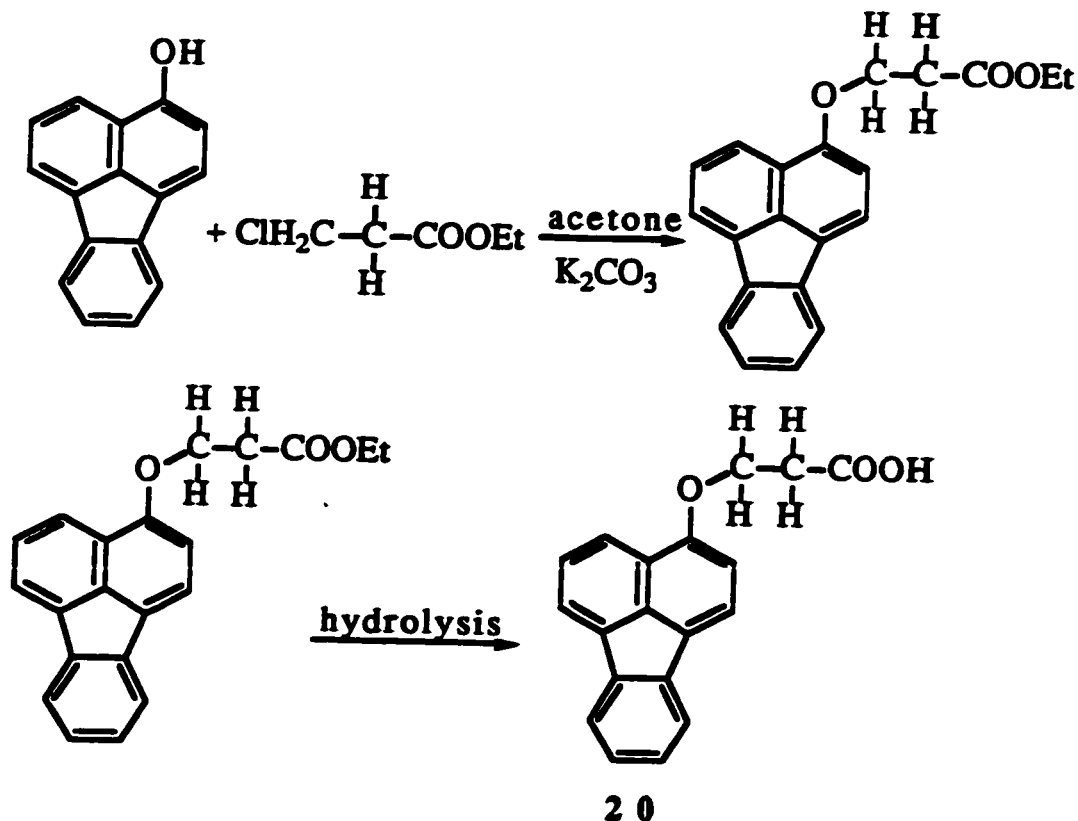


Figure 3.33.
Synthesis of the 3-fluoranthanol derivative (20)

When we employed this derivative 20 of fluoranthene on pulp and paper, we saw a difference between the irradiated and non-irradiated paper (Figure 3.34. and Figure 3.35.).

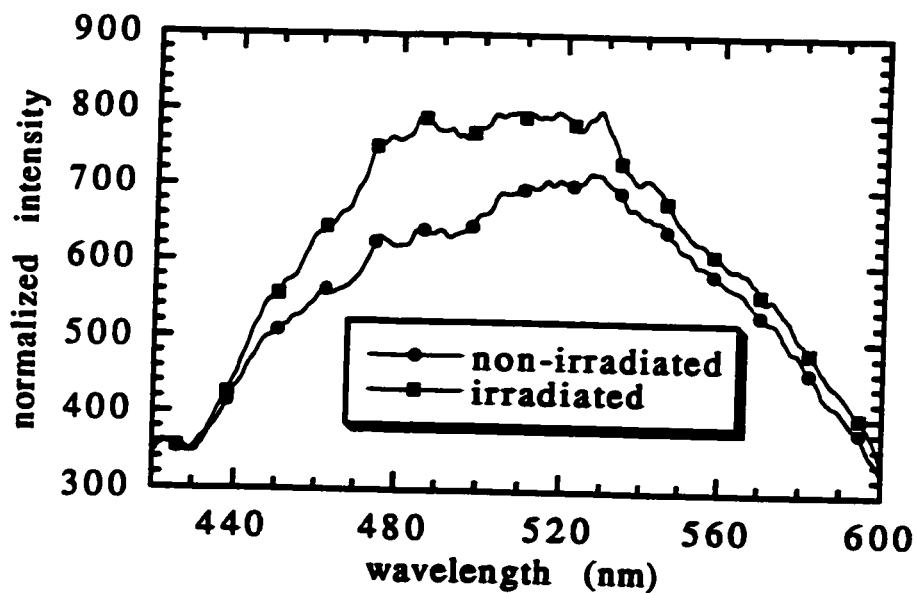


Figure 3.34.
Fluorescence spectra of irradiated and non-irradiated pulp after treatment with 20. Excitation wavelength: 395 nm

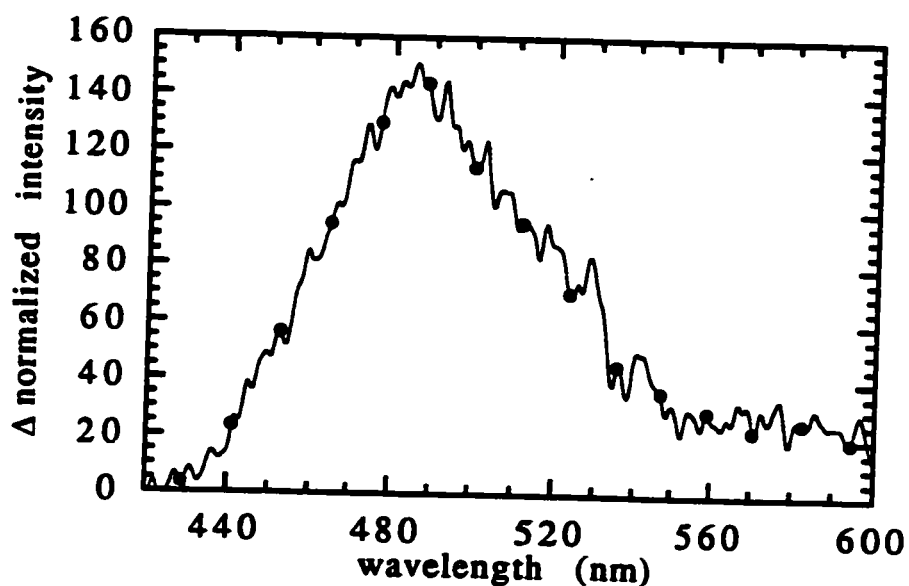


Figure 3.35.
Difference spectrum of irradiated and non-irradiated pulp after treatment with 20

The difference of the emission intensity is not as significant as it is with some other probes (such as fluorescein). However, in this case, there is a better way to normalize the emission of different samples to obtain a more correct picture of the actual probe incorporation. (i.e., normalization in the 560-600 nm region of the spectra). Figure 3.35. also supports this, since the difference spectra of the irradiated and not-irradiated pulp has a maximum at 480 nm. This corresponds to the wavelength maximum measured in dichloromethane solution of 20.

3.3.3.2. Derivatization of rubrene

Friedel-Crafts alkylation and acylation¹⁰ were used for the derivatization of rubrene. Figure 3.36. shows the reactions performed.

The alkylation resulted in a cyclic structure and decreased the extent of the aromatic delocalization. This is consistent with the change in color which was observed (orange to yellow). With acylation an appropriate structure was obtained which was used as a probe on TMP pulp (Figure 3.37.).

From Figure 3.37. it is obvious that the fluorescence spectra is considerably blue-shifted compared to that of the parent compound. In addition, the band structure of the fluorescence of the rubrene disappeared. This might be due to the fact that there is a considerable steric hindrance between the phenyl groups of the rubrene, and any changes in their structure can change this delicate equilibrium. It is also clear that there is no difference between the

amount of **21** incorporated into the irradiated and non-irradiated pulp.

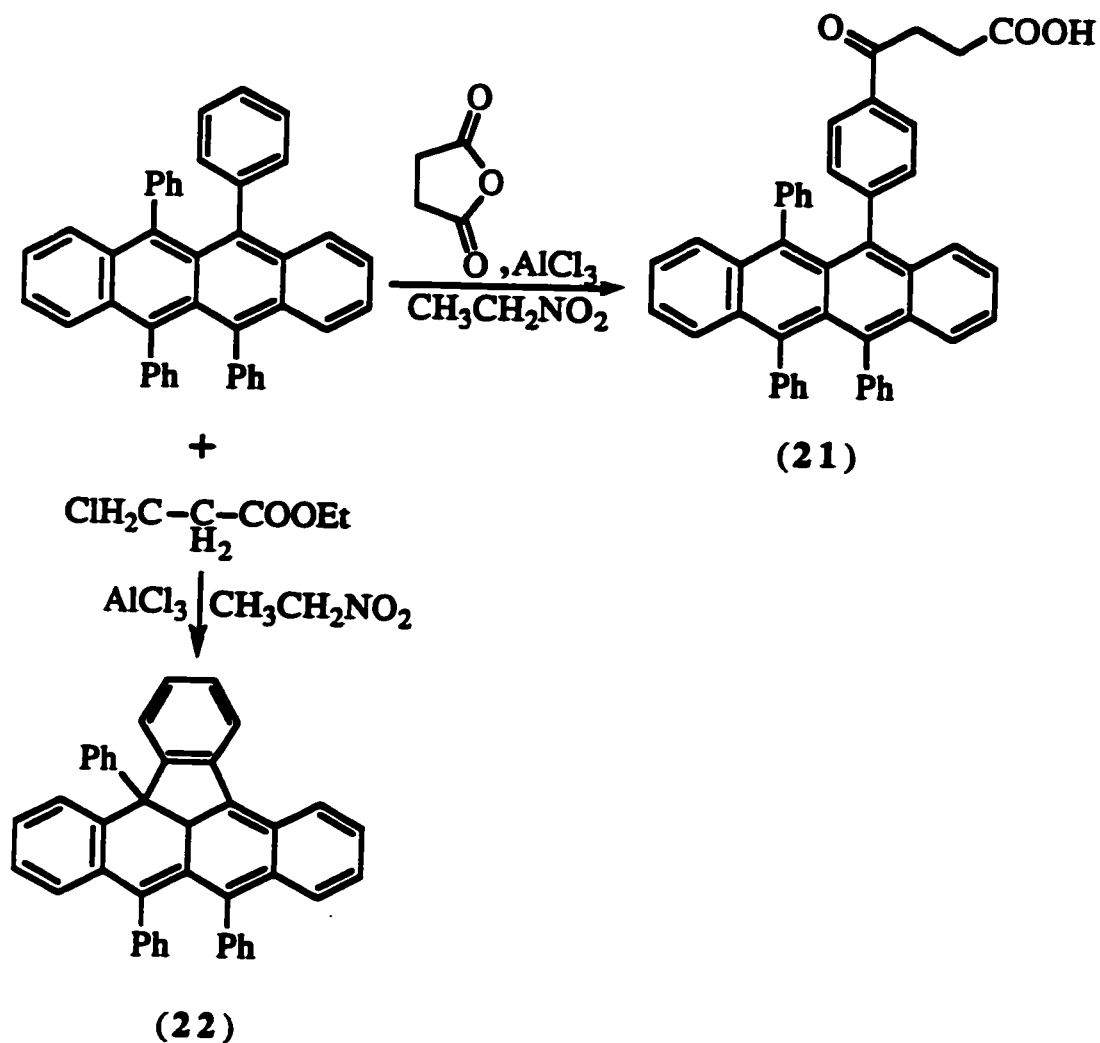


Figure 3.36.
Friedel-Crafts acylation and alkylation of rubrene

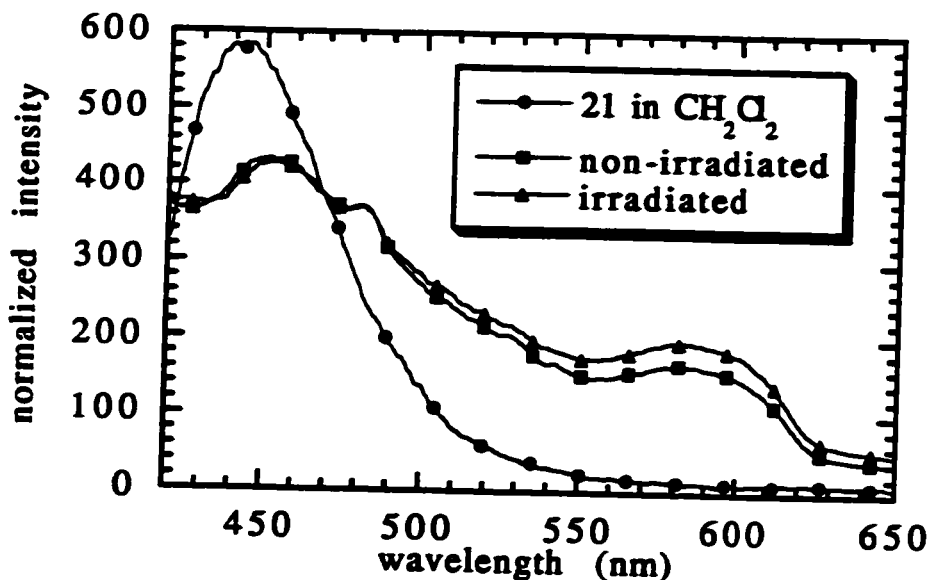


Figure 3.37.

Fluorescence spectra of irradiated and non-irradiated pulp treated with 21, as well as the fluorescence spectrum of 21 in dichloromethane. (Excitation: 400 nm)

3.4. Fluorescence microscopy

These experiments were carried out in order to map the formation of quinone centers, in the hope of establishing whether degradation occurred in specific regions of the fibers. We used only the pulp which has been treated with pyrene since our results were the most clear in this case. These measurements were difficult because of the interference from pulp fluorescence. Unfortunately, these experiments do not have any temporal resolution and the type of discrimination shown in Figure 3.23. cannot be achieved in the microscopy experiments. Figure 3.38. illustrates the fluorescence and phase contrast photographs from an irradiated and treated

(method II) sample. While the luminescence is evident, we found that it was difficult to draw any conclusions from examination of a small number of photographs. An examination of large number of photographs leads to the conclusion that pyrene incorporation (and thus quinone formation) is enhanced in fines (Figure 3.39) Fragmented fibers also appear to be more prompt to photoyellowing (See in Figure 3.40 that end of the large fiber exhibits more fluorescence than the rest of the fiber), while large intact fibers appear to be somewhat more resistant to degradation. On Figure 3.41. another example is shown where the most fluorescent regions are the broken parts of the fibers, as well as the agglomerations of small fines.



Figure 3.38
Fluorescence and phase-contrast micriscopic photographs of fibers
treated with pyrenebutyric acid accordig to method II
(Magnification 3000)



Figure 3.39.

The fluorescence of a very thin fine is particularly intense (Magnification: 8000)



Figure 3.40.

Fluorescence is more intense in damaged fibers (Magnification 4000)



Figure 3.41.

Fluorescence microscopy photograph of one part of the pulp which shows the higher fluorescence of the fine agglomerations and that of the damaged fibers (Magnification is 4000)

3.5. Study of pulp fluorescence applying synchronous technique

In our studies of the incorporation of fluorescence probes to detect ortho-quinone in high -yield pulp, we faced numerous difficulties. Namely, during irradiation and during probe incorporation, the fluorescence of pulp sometimes changed radically. The region between 390 and 490 was especially subjected to major change during irradiation. In addition, given the nature of the experimental technique (front-face fluorescence spectroscopy), the spectral intensity recorded greatly depends on the scattering nature

of the surface⁵⁴. Unfortunately, the inhomogeneity of the surface using high-yield pulp is high. Therefore, all spectra had to be normalized. It was difficult to find a region in the fluorescence spectra where the assumption that fluorescence of pulp upon irradiation and during the different treatments did not change. In the case of pyrene, where the fine structure of the probe fluorescence facilitated establishing which peaks originate from the probe and which from pulp, this arbitrary normalization seemed valid. However, in other cases, it was more problematic. Therefore, we decided to study the fluorescence of the pulp, and examine how it changes during irradiation. Furthermore, we would have liked to assign different chromophores to different regions in the fluorescence spectra, which in return would have clarified some complex cases in connection with the fluorescence probes.

As already mentioned in Chapter 1, fluorescence studies on pulp have been conducted mainly by two groups, and there is a basic difference in the interpretation of the results. Castellan and coworkers interpreted the fluorescence as the superposition of individual fluorescence emissions³⁰⁻³². Therefore, the changes directly reflect the changes in abundance of fluorescent molecules. According to Gray and coworkers, the main source of the fluorescence is the emission from cellulose⁵⁰. This emission is modified via some type of an inner filter by the chromophores present in pulp. Therefore, all change in fluorescence simply reflects the change of the absorption properties of the chromophores in the pulp.

We found that traditional fluorescence techniques are not able to solve the problem. Therefore, we decided to use a special fluorescence technique which is not very well known but which has been successfully applied to analyze complex mixtures^{55,56}. This technique is synchronous fluorescence spectroscopy. In synchronous spectroscopy the excitation and emission are simultaneously scanned with a fixed $\Delta\lambda$ difference between them. Therefore, there is a third variable which can be changed to obtain information ($\Delta\lambda$).

Some of the reported advantages of synchronously scanning a spectra are narrowing of the spectral band, simplification of the emission spectra and reduction of the spectral range⁵⁵.

We examined a number of model compounds. However, given the complex nature of lignin as a chromophore, or as a possible source of fluorescence, it was highly improbable that these model compounds could cover the whole spectra of fluorophores found in lignin. Therefore, our first approach was highly qualitative. Figure 3.42 shows the model compounds studied. Some of them were highly fluorescent, such as the stilbene-type 23. Others are more characteristic of the lignin, but their fluorescence is weaker, such as 24 and 25.

Comparing the synchronous spectra of pure cellulose recorded with different $\Delta\lambda$ and that of these chromophores absorbed on the filter paper as a solid matrix (Figure 3.43), we have not seen any significant difference in the cases of 24 and 25 (Figure 3.45). In the case of 23, there is a significant difference (Figure 3.44.).

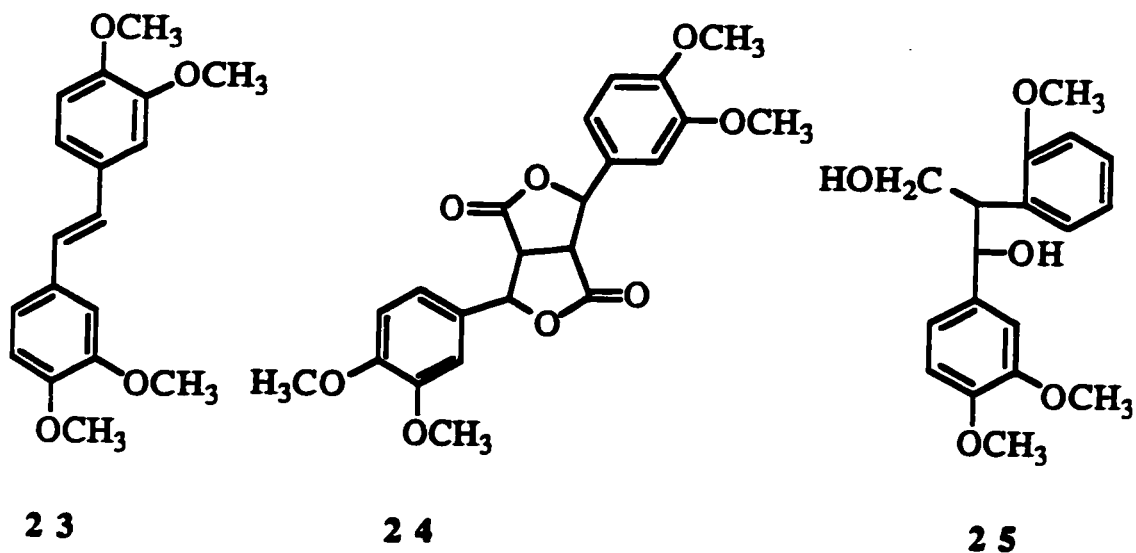


Figure 3.42.

Model compounds used for synchronous measurements

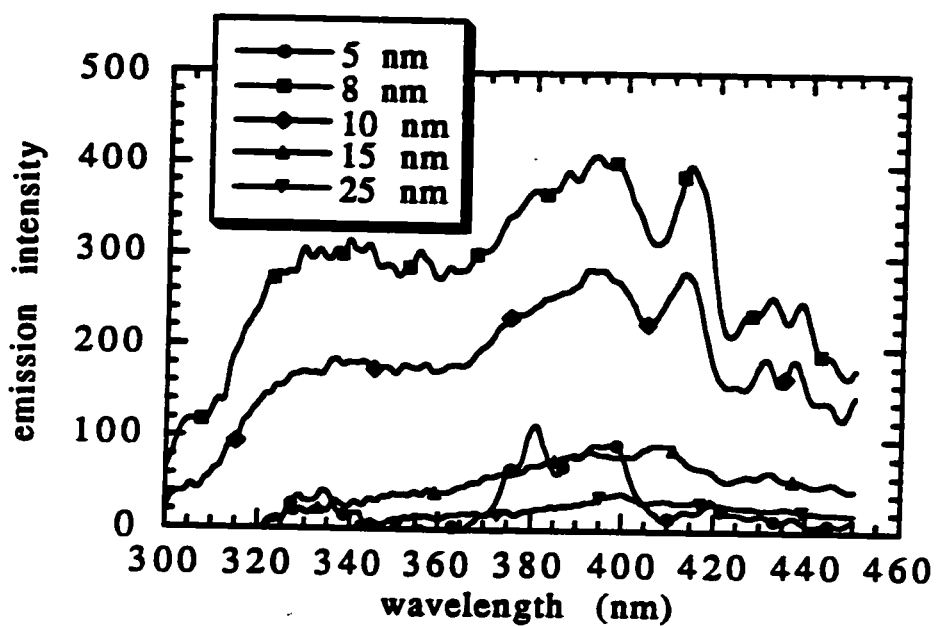


Figure 3.43.

Synchronous spectra of Whatman filter paper

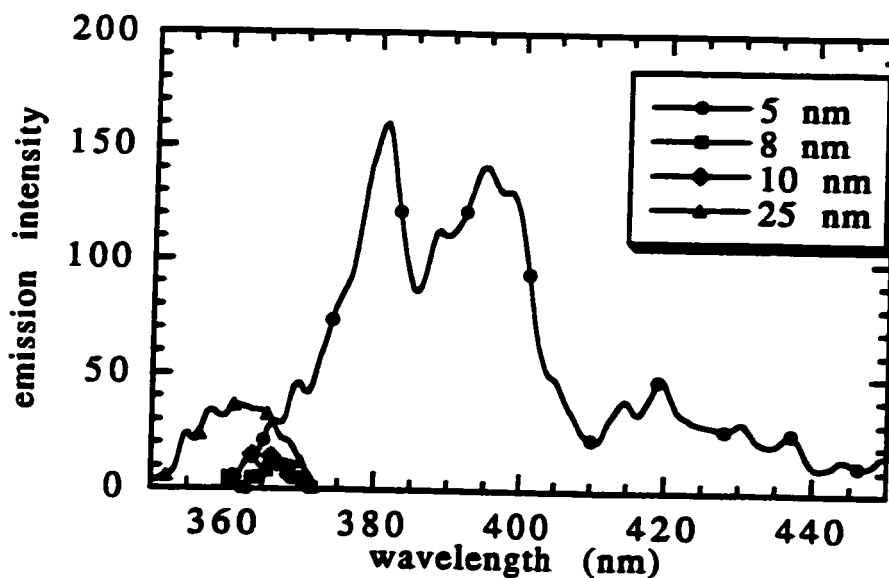


Figure 3.44.

Synchronous spectra of 23 absorbed on Whatman filter paper

Only in the case of 23 we could see differences in the synchronous spectra. However, even in this case, application of the most characteristic $\Delta\lambda$ resulted in the same spectral shape. Further, the spectral simplification using filter paper did not occur to the required extent. All of these support the hypotheses that the actual fluorescence seen in the fluorescence spectra is mainly due to the carbohydrate framework and that the changes seen are the result of changes in the absorbing characteristics of the chromophores upon irradiation.

3.6. Discussion

The results presented in this chapter demonstrate that it is possible to employ fluorescence spectroscopy as a tool to study the photodegradation of pulp and paper. However, as our results using synchronous fluorescence spectroscopy show, it is not possible to use fluorescence spectroscopy directly, since the recorded fluorescence spectra are basically that of the cellulose with a very small contribution from the actual fluorescence of the lignin. Therefore, it is necessary to use fluorescent probes which have high characteristic fluorescence quantum yield to be detectable in the presence of the background fluorescence. In this way, a particular structural group of the lignin or its photodegradation product can be probed, and as such more useful information can be gained.

Pyrene probes, particularly when incorporated by method II are highly specific for the detection of *ortho*-quinones. There are advantages and disadvantages related to the specific use of pyrene derivatives as probes. Pyrene has the advantage that its long fluorescence lifetime (even if considerably reduced in pulp) allows temporal discrimination from pulp emission. Further, excimer emission can provide a probe for chromophore proximity and distribution.

The vibrational structure of pyrene is well known to be sensitive to the environment, and detailed studies of solvent effects are frequently used as a *yardstick* to determine local polarity. This sensitivity is due to the Ham effect⁴⁵, which unfortunately is strongly symmetry dependent and therefore reported calibrations are not

directly applicable to substituted pyrenes. However, examination of the emission intensity ratio for the III/I vibrational bands suggests a relatively polar environment. This is consistent with the presence of phenols, alcohols and water in the lignin-rich regions of the pulp.

Diffuse reflectance studies (see Figure 3.11.) indicate that the actual amount of pyrene incorporated is very small. In spite of this, our time resolved work indicate some excimer emission, even in the case of low pyrene loading. At the same time, we failed to resolve any time resolved growth component in the long wavelength excimer emission. This observation suggests that those pyrene moieties responsible for excimer emission are already in close proximity at the time of excitation, and that excimer formation requires none, or minimal diffusion. This, combined with the low pyrene loading implies that quinone formation is not a random process, but rather, that chromophores are formed within *domains* or *islands* in the pulp. Whether this is due to the inhomogeneous nature of the distribution of quinone precursors, or the result of a cooperative effect, cannot be established from our experiments. A cooperative effect could result from increased accessibility of environmental oxygen to regions that have already undergone some degradation. The result is consistent with fluorescence microscopy data that suggest enhanced degradation in fines and fragmented fibers.

Time resolved studies lead to pyrene emission lifetimes significantly shorter than those usually obtained in a homogeneous solution, even when the pulp samples are saturated with a nitrogen atmosphere. This can be attributed to either one of two factors or

more likely, to a combination of both. First, pyrene singlets usually have relatively shorter lifetimes in hydroxylic media, especially in water⁵⁷. Even "dry" pulp probably contains enough moisture to influence the singlet lifetimes. Second, it is possible that some of the functionalities in pulp act as quenchers for pyrene singlets. Such groups may include substituted stilbenes. Pyrene is prone to electron transfer interactions and may interact with some of the abundant electron-rich moieties in pulp.

It has been found difficult to find other appropriate fluorescence probes to derivatize ortho-quinone. This is mainly due to the chemical reactions which can occur between different functional groups in the pulp and the probe molecules. For example, many red-emitting probes are excluded due to the presence of amine groups which are known to react with the chromophores in high yield pulp. Finally, we have tried 8 different molecules (molecules 13-18, 20, 21) which according to their structures can be organized in three different groups.

Group 1: (Molecules 13-15) These molecules, besides having relatively inert structures, are well known fluorescence probes. Unfortunately, the carboxylic acid function is directly connected to the aromatic structure. This acid function participates in the hydrolysis step of the cyclic phosphite ester to form the open phosphite ester structure which contains the fluorophore. This hydrolytic step is probably most sterically hindered in the case of Rose Bengal. The fact that the irradiated and non-irradiated pulp fluoresces in the same region with the same intensity before and

after treatment with Rose Bengal shows two things: beside steric effects in the hydrolysis, it is possible that the heavy atoms which are present in the molecule (I, Br) can also participate in some reactions involving pulp. If this reaction involves a structural unit which is not affected by the irradiation, the amount of included rose bengal would be the same, therefore no difference would be manifested in the fluorescence spectra.

As already mentioned in section 3.3., the fluorescence spectra of rhodamine B clearly shows dominance of a chemical reaction over the hydrolysis step. We can also state that probably some of the chromophores which participate in this competing process reacted during irradiation. In the case of the structurally similar fluorescein, there are still at least two reactions in which the probe can participate, but the hydrolysis of the cyclic phosphite ester is preferred.

Group 2: (Molecules 16-18) These coumarin-type molecules did not participate in the hydrolytic step. One reason is the insolubility of these molecules in the solvent normally used for this work. Another possibility is that these lactone structures are quite sensitive to acids and bases, and, as such, they might react with some of the basic groups present (acidic groups were eliminated during the pre-treatment of the pulp).

Group 3: (Molecules 20, 21) Given their chemical inertness, the polycyclic aromatic molecules which are members in this group, present a synthetic challenge. At the same time their inertness prevents undesirable side reactions to occur. Therefore the

fluoranthene-derivative was capable of monitoring quinones. The rubrene-derivative, probably as a result of the bulkiness of the molecule, did not differentiate between the irradiated and non-irradiated pulp.

Finally, in the context of yellowing inhibition, our results suggest that given the non-homogeneous distribution of the photodegradation process, it would be desirable to target those domains where degradation occurs with the development of inhibitors capable of seeking these regions. While this clearly poses a major scientific and technical challenge, it is also evident that such targeting would reduce the loading of inhibitor required, something that would obviously be economically desirable. The development of such domain-specific inhibitors would require further studies aimed at fully establishing the nature, polarity and accessibility of the degradation-prone regions of the fibers.

3.7. Experimental section

Materials. Triisopropyl phosphite, 1,6-benzoquinone, 3,5-di-tert-butyl-1,2-benzoquinone (98%), conyferaldehyde, rubrene, fluoranthene, rose bengal, fluorescein, rhodamine B, 7-hydroxy-coumarin-4-acetic acid, 7-methoxy-coumarin-4-acetic acid, 7-(carbomethoxy)-4-methyl coumarin, 3-chloro-propionic acid, lead(IV)acetate, aluminium(III) chloride, succinic anhydride and deuterated solvents were obtained from Aldrich (the purity was the purest which was available in each particular case), ^{13}C -labeled

acetic acid was obtained from Cambridge Isotopes, pyrenebutyric acid was purchased from Fluorescent Probes Inc., and the solvents were purchased from BDH. Molecules 23-25 were kindly supplied by Prof. N. Weir (Lakehead University).

Synthesys of dialkylpyrene phosphite: 4.5 ml (50 mmol) dimethylphosphite was added to a vigorously stirred and cooled dispersion of 10 g (48 mmol) phosphorus pentachloride in 100 ml chloroform. After all the phosphorus pentachloride reacted, the reaction mixture was distilled first at atmospheric pressure to remove the solvent at 75°C, then under reduced pressure (20 mm Hg/65°C). NMR of the starting material in CDCl_3 : 6.2 ppm (dd), 7.25 (d). $J^1(\text{P-H})=60\text{Hz}$, $J^2(\text{P-H})=12\text{ Hz}$, $J(\text{H-H})=0.76\text{ Hz}$. NMR of the product in CDCl_3 : 5.38 (d), 5.3(d). To 5 ml chloroform solution of 0.1 ml dimethylchlorophosphite 5 ml solution of 100 mg pyrenebutanol was added dropwise. The mixture was stirred and refluxed for 3 hours followed by washing with two portions of water, and drying over MgSO_4 . After this, the solution was concentrated and chromatographed on a silica gel column with a chloroform-hexane mixture. Product purity was checked by GC (>99%), and its pyrene content was verified by UV-visible absorption spectroscopy and ^1H -NMR in CDCl_3 : 8.2-7.5 ppm (br, 9H), 3.0 ppm (dt, 6H), 1.8-0.5 ppm (br, 8 H)..

Synthesis of 3-fluoranthanol:(19)⁵³ A mixture of 25 g fluoranthene, 85 g lead(IV) acetate and 800 ml glacial acetic acid are stirred for 40 h at 70°C. After cooling, the unchanged lead(IV) acetate is filtered off and the filtrate is poured into 1.5 l water. The precipitated solid is

filtered off, dried and extracted with ether. After removing the ether, the residue (fluoranthene and fluoranthenyl acetate) is refluxed with 300 ml 10% ethanolic NaOH for 4h. After cooling, the mixture is poured into 1 l of icy water and the precipitated fluoranthene is filtered off. After removing ethanol, the solution is acidified using 5% HCl and the precipitated fluoranthanol is filtered off. It was used without further purification. $^1\text{H-NMR}$ (CDCl_3): 8.1-7.6 ppm (br, 7H), 7.4-7.2 (br, 2H), 1.7 ppm (br, 1H)

Synthesis of 3-(3-fluorantheno)-propionic acid (20): 1 g (5 mmol) fluoranthanol and 0.67 ml (~5 mmol) ethyl chloropropionate was refluxed in 20 ml of acetone in the presence of 1.7 g K_2CO_3 . The reaction was followed by TLC (eluent: dichloromethane). After 8 h the reaction mixture was filtered and acetone was removed in vacuo. The residue was dissolved in ether and extracted with 2M NaOH solution and water. The organic layer was dried (Na_2SO_4) and the ether removed in vacuo. To the residue 2g of NaOH was added in 8 ml of water. After 10 min. of reflux, the mixture was cooled, poured into water and acidified. The precipitate was filtered. $\text{Mp.} > 315^\circ\text{C}$. $^1\text{H-NMR}$: 7.6-7.2 ppm (multiplet), 2.6 ppm (dd), 2.4 ppm (t)

*Synthesis of (21)*⁵⁸: 100 mg of rubrene (0.19 mmol) and 160 mg of succinic anhydride was mixed in 6 ml nitroethane and cooled to 10°C . Anhydrous AlCl_3 (480 mg) was added slowly. The reaction mixture was stirred overnight, and then poured on ice. Concentrated HCl was added. The solution was extracted by ether, washed and dried (MgSO_4). Upon concentration a yellow material formed. $^1\text{H-NMR}$ shows a 1:1 substituent:rubrene ratio. $^1\text{H-NMR}$: 8.8 ppm (d, 1H), 8.5

ppm (d, 1H), 8.1 ppm (m, 3H), 8.8-7.3 ppm (m, 10H), 7.1 ppm (d, 1H), 6.8-6.5 ppm (m, 8H), 6.4 ppm (d, 2H), 5.2 ppm (s, 1H), 3.4 ppm (t, 2H), 2.8 ppm (t, 2H).

Friedel-Crafts alkylation of rubrene: 54 mg of rubrene and 60 μ l chloropropionic acid-ethyl ester was mixed in 6 ml nitroethane, and 0.3 mg of AlCl_3 was added slowly. After 1.5 h of stirring the work-up procedure of (20) was followed. Upon cooling, orange crystals of (22) were obtained. The crystals were examined by X-ray single crystal diffractometry, which confirmed their structure (Figure 3.45.).

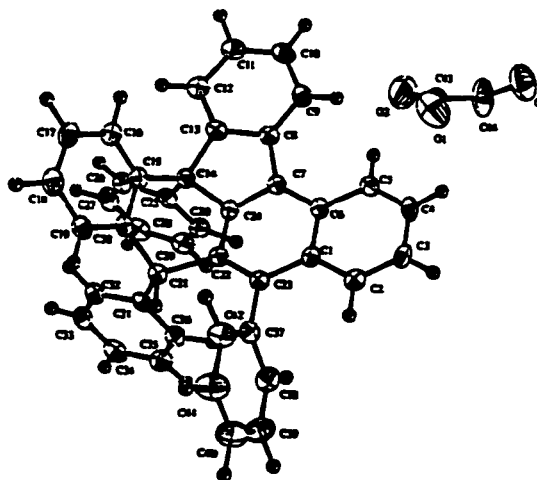


Figure 3.45.
ORTEP diagram of 22

Pulp origin and pre-treatment. Pulp used in all these experiments was made of softwood (spruce) in Abitibi-Price via thermomechanical pulping. The geographical origin of the spruce is not known. A measured amount of the dried pulp was stirred for two-three hours to separate the fibers. After this, a thin sheet with a smooth surface was prepared, dried, and irradiated at 350 nm.

Alkaline peroxide bleaching and hydrogen sulfite bleaching were performed before making the handsheets. The bleaching of the pulp followed exactly the method described in the literature²⁶.

The irradiation of the pulp was carried out at either 300 nm or 350 nm for 4 h employing a home built photochemical reactor fitted with 8 Rayonet lamps.

Pulp post-irradiation treatment. The first step in this treatment is the neutralization of the carboxylic acid groups in the pulp. The pulp sample was dispersed in 0.1 M NaCl solution and the pH was adjusted to 10 by 0.1 M NaOH. The pulp was stirred for two hours, followed by filtration, washing with water, ethanol and acetone.

Oxyphosphorylation of the pulp. The pulp was dried in an oven at 80°C, and then cooled down in vacuum to remove as much of the adsorbed water as possible. The dry sample (generally 0.5 g) was reacted overnight in dry methylene dichloride with 1 ml triisopropyl phosphite. After the reaction was complete, the sample was washed with several portions of the solvent, and reacted with pyrenebutyric acid overnight (Method II). After several washings, the sample was dried under a nitrogen flow, and the fluorescence spectra were taken. In some experiments, 4-pyrenebutyldimethyl phosphite (VI) was used directly instead of triisopropylphosphite. In this case the second step was not necessary.

Preparation of the samples for time resolved experiments. For these experiments 2 x 4 cm² rectangles of the TMP handsheets were used (~0.2 g). After performing the treatment mentioned above, they were

reacted with 5 mg pyrenebutyric acid in the case of low pyrene load, and with 30 mg in the case of high pyrene load.

Chapter 4

High Intensity Laser Generation of *ortho*-Quinones from 2-Methoxyphenols

4.1. Introduction

Photodegradation of high-yield pulp and paper leads to yellow chromophores. In Chapter 1, in Figure 1.13. the main photodegradation pathways of the lignin chromophores were presented^{59,60}. According to this mechanism, a very important role is played by the carbonyl chromophores which, after the absorption of light, form ketyl radicals. When these carbonyl groups are a part of a β -O-4 structure (these are characteristic building blocks in lignin, see chapter 1) there is a possibility of bond cleavage. This cleavage leads to the formation of another ketone, originally in its enol form, and a phenoxy radical. The ketone part can participate in absorption of further photons, thus inducing further photodecomposition. On the other hand, phenoxy radicals can participate in reactions which lead to formation of yellow compounds, and ultimately to the characteristic yellowing of paper.

The properties of phenoxy radicals have been thoroughly investigated, mainly because of their role in the chemistry of antioxidants⁶¹. In the laboratory these radicals are frequently generated via hydrogen abstraction by a tert-butoxy radical⁶¹ from phenol. The transient spectra of several phenoxy radicals are well known^{62,63}. The unsubstituted phenoxy radical has absorption bands at 315 nm near 400 nm (which in most cases is used for their

identification)⁶⁴, and a weak and diffuse band in the 600 nm region. In the case of the substituted phenols, the position and relative intensities of these bands can vary. These absorptions correspond to a π - π^* transition in all cases⁶³.

The process of yellowing was shown to involve oxidation of phenoxy radicals, since in an oxygen free atmosphere, the yellowing was considerably slower, or completely suppressed^{8,9}. However, the final products of this reaction were not known. Leary proposed ortho-quinones (which are known to be highly colored products), as potential reaction products as early as 1968⁹, but proof of their existence in high-yield paper was only obtained in the 1990's. Later, the mechanism of a possible oxidation was thoroughly described^{65,66}. Ortho-quinones can be detected by infrared spectroscopy. In lignin, however, numerous carbonyl groups are found in much higher amount, thus spectral overlap makes detection of quinones difficult⁶⁷.

Solid state NMR spectroscopy has been used to prove the presence of quinones as photoproducts. Holmbom and coworkers, using ^1H and ^{13}C -NMR were not able to detect the presence of ortho-quinones²⁴. An upper limit of 1.5 ortho-quinone/100 aromatic units was given. They attributed this low concentration of quinones to the fact that quinones are sensitive to a hydrolytic environment, and thus can easily decompose. However, since ^{13}C -NMR itself is quite insensitive due to the low abundance of ^{13}C in the nature, and it is especially insensitive in the case of quinone-carbons (since they are quaternary carbons), it is not surprising that it was difficult to detect

them using this technique in the presence of many other aromatic compounds.

Recently, several research groups have shown that quinones are present in high-yield pulp^{27,33}. In our laboratory we have also shown that the quinone is present and that its amount increases upon irradiation until a certain time, and then, upon prolonged irradiation, decreases⁶⁸ (see also chapter 3).

Argyropoulos and coworkers used ^{31}P -NMR spectroscopy¹⁷ to establish the presence of quinones, following derivatization with P(III) compounds. ^{31}P -NMR is more sensitive than ^{13}C -NMR due to the 100% abundance of ^{31}P in nature. At the same time, the peaks are much broader and spectral identification is more difficult. In chapter 3 we were using similar chemistry to that developed by Argyropoulos., when a group of compounds was selectively derivatized. The resulting NMR spectra was greatly simplified, and it allowed not only the detection of the ortho-quinone units, but also their quantification, as well as the detection of some other structural moieties present in lignin. We later developed a method based on fluorescence studies (chapter 3, method I).

We wanted to determine if quinones could be formed directly from phenols or phenoxyl radicals. Formation of substituted 1,2- and 1,4-benzoquinones from phenols is possible via the sequential absorption of two photons (Figure 4.1.). It was thus of interest to examine whether the two-photon process of reaction 4.1. was possible. In solution the short lifetime of phenoxyl radicals limits the participation in further photochemical processes. However, in a solid

matrix such as the pulp itself, phenoxyl radicals are probably sufficiently long lived⁶⁹ (hours, or even days) to undergo photoinduced processes. Further, the absorption spectra of phenoxyl radicals generally overlaps with the solar spectrum; thus, it seemed feasible that a multiphotonic process may be responsible for part of the yellowing of high-yield pulps.

Some of the laser techniques developed in our laboratory (for example, two-laser-two-color laser flash photolysis, laser-drop photolysis) offer a unique opportunity to explore this question.

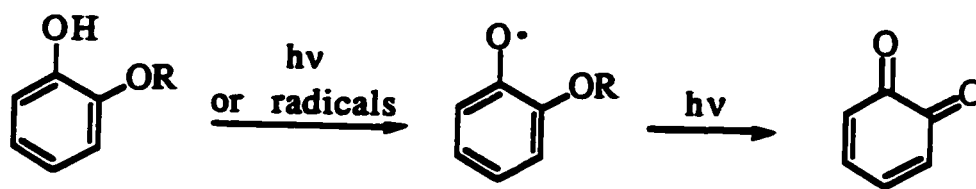


Figure 4.1.

Formation of ortho-quinones from phenols via multiphotonic pathways

4.2. Results

4.2.1. Derivatization of ortho-quinones

Given the difficulties with the direct detection of ortho-quinones, we utilized a derivatization technique that greatly enhances the detection sensitivity. 1,2-Benzoquinones can participate in cycloaddition reactions with several compounds (e.g.: trialkyl phosphites⁴⁴, 1,2-phenylenediamine⁷⁰ or diphenylethylene); the resulting compounds are frequently stable and can be readily characterized (Figure 4.2.).

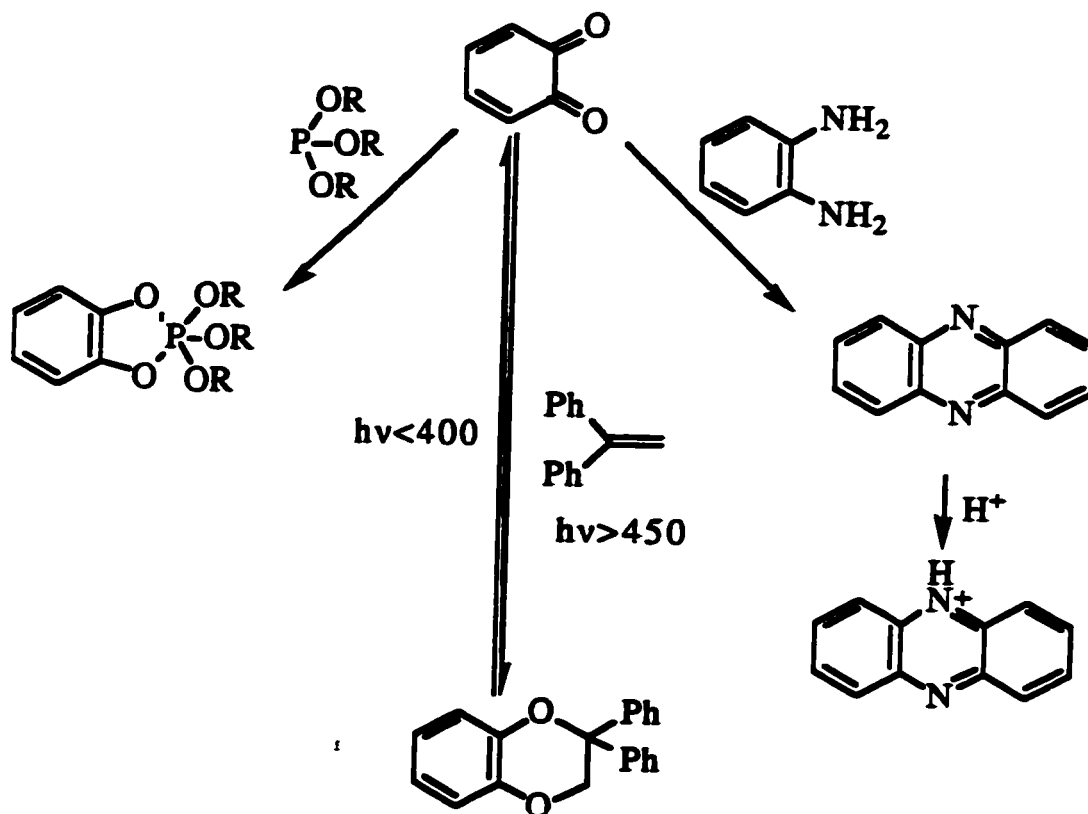


Figure 4.2.

Some cycloaddition reactions of ortho-quinones^{27,33,44,70}

For example, the cycloaddition product with trialkyl phosphite was used in experiments described in Chapter 3 to attach fluorescent probes to ortho-quinones. The reaction between ortho-quinone and diphenylethylene upon irradiation (>400 nm) results in a cyclic product, while a higher energy irradiation will regenerate the starting materials. Reaction of ortho-benzoquinone and 1,2-phenylenediamine readily forms phenazine. Given the low-stability of the ortho-quinones, especially the unsubstituted 1,2-benzoquinone, and the expected relatively low quantum yield, we decided to apply 1,2-phenylenediamine for derivatization. The

protonated form of the phenazine has a characteristic fluorescence band with a maximum at 520 nm. Another advantage of using phenazine is that it absorbs at relatively long wavelengths, where the starting material and the other products present do not; hence, selective phenazine fluorescence excitation is possible even in the presence of relatively large amounts of starting materials or other products. However, it was necessary to examine the reliability of this method. Unfortunately, in the presence of oxygen the starting material 1,2-phenylenediamine decomposes after protonation and forms highly colored decomposition products.

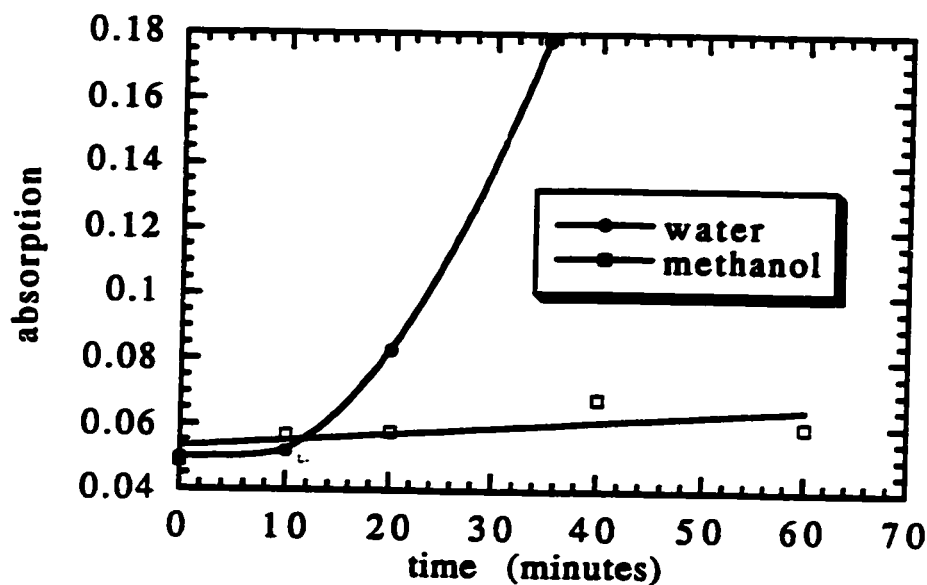


Figure 4.3.

Thermal decomposition of phenylenediamine in water and in ethanol in the presence of oxygen (monitored at 395 nm)

Since in our experiments the 1,2-phenylenediamine/ortho-quinone ratio was expected to be high, a small amount of the

decomposition product of phenylenediamine which absorbs the excitation light during fluorescence measurements can significantly alter the results. Therefore, we tested several solvents and also acids that could protonate the phenazine formed to determine the optimum conditions. Application of methanol (Figure 4.3.) and acetic acid (Figure 4.4.) did not cause significant interference in the fluorescence spectra over the period of sample preparation and analysis. Furthermore, the fluorescence intensities were more intense in the presence of acetic acid.

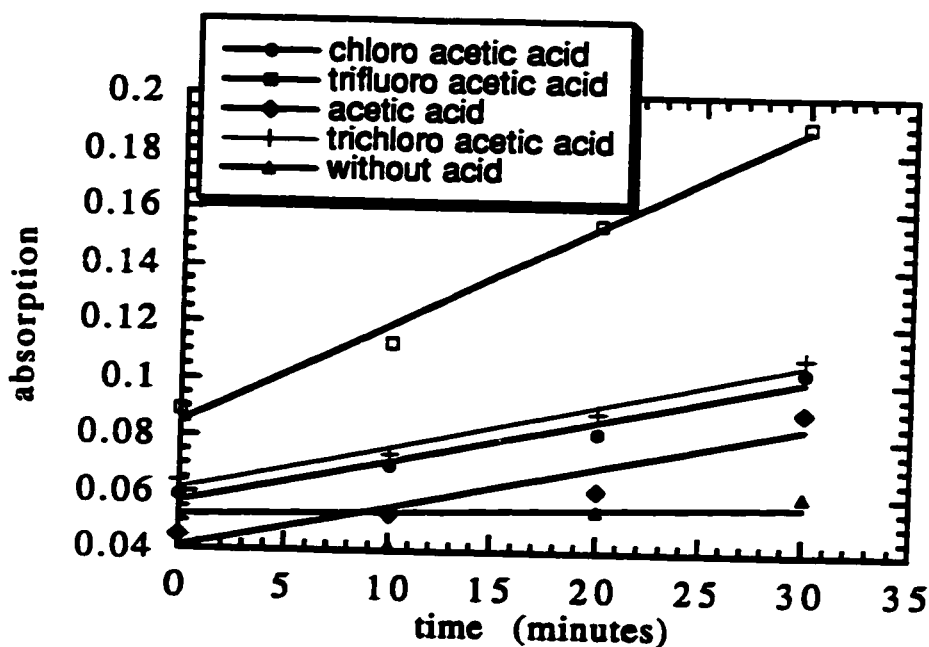


Figure 4.4.

Decomposition of 1,2-phenylenediamine in the presence of different acids in methanol under air (Monitored at 395 nm)

In this way, the phenazine formed was fluorescent and stable during a reasonable period of time for different analytical techniques to be employed. Mainly two techniques were used to do the analysis.

The fluorescence measurements were sensitive to even an extremely small amount of phenazine. In addition, the chemical identification of the product formed was achieved by GC-MS.

Since 1,2-phenylenediamine is heat sensitive (see above), we tested different ratios of ortho-quinone to 1,2-phenylenediamine. We have seen that the amine decomposition significantly interferes in cases where the ratio is smaller than 1:1000.

Some attempts were made to remove the amine by selective protonation by taking advantage of the different basicities of the amine and phenazine. While this procedure worked well with the model experiments, it failed when we used the same method with the reaction mixture, probably because of the large difference in the amount and ratio of compounds present; thus, it was not possible to remove the amine using this technique.

4.2.2. Choice of starting materials

As already mentioned in the introduction, one of the cleanest methods to produce phenoxy radicals in a chemical reaction is the irradiation of the corresponding phenols in the presence of tert-butyl peroxide³. (Figure 4.5.). It is also possible to directly irradiate phenols, and upon breaking the O-H bond, phenoxy radicals form. However, the quantum yield of this reaction is very low.

A third possibility is the irradiation of lignin-type β -phenoxyacetophenones (for example α -guaiacoxyacetoveratrone, a frequent choice as a lignin model, see structure in chapter 1.), which,

after bond breakage, produces phenoxy radicals^{20,71-74}. This reaction has a high quantum yield.

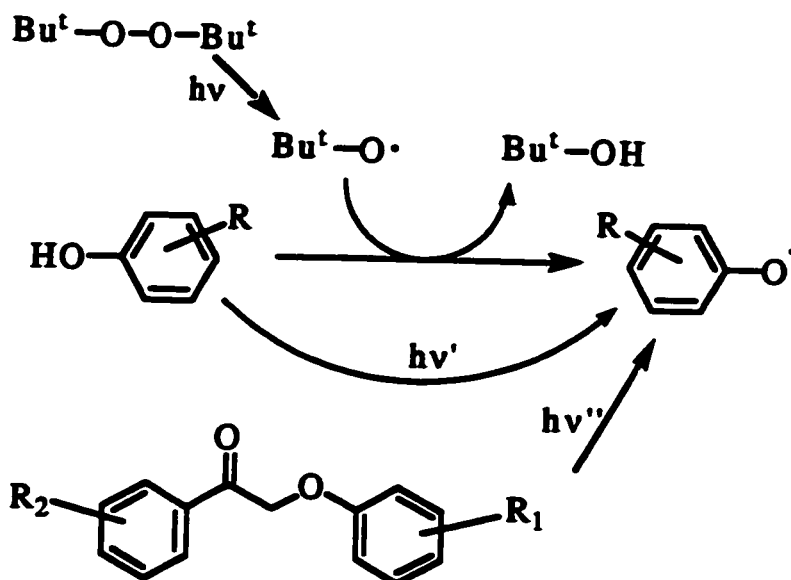


Figure 4.5.
Different mechanisms to generate phenoxy radicals

In all cases radical reactions are involved; these radicals can participate in many other reactions, which, as a result, can greatly complicate the product mixture.

4.2.3. Low-intensity irradiation

With low intensity irradiation only monophotonic products can form due to the low photon-flux. Therefore, these experiments were used as a control to differentiate between mono and multiphotonic products. All possible starting mixtures were irradiated. Here, however, only results obtained with 2-methoxyphenols in cyclohexane will be presented due to the fact that this mixture was

the only one which produced the desired multiphotonic product upon high intensity irradiation (see Section 4.2.4.2.). Results of low-intensity irradiation of α -guaiacoxyacetoveratrone will be presented in Figures 4.9. and 4.10.

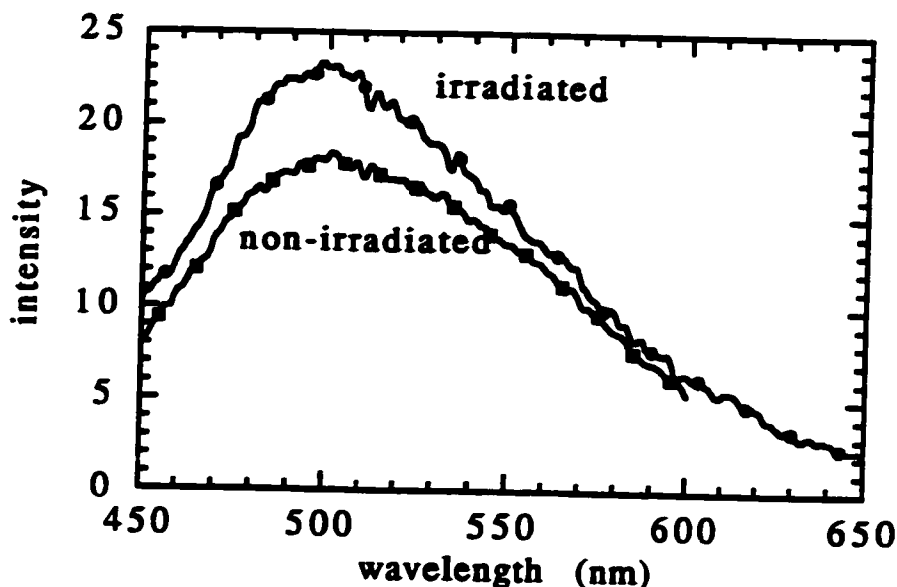


Figure 4.6.

Comparison of the fluorescence of non-irradiated and irradiated (low intensity, 254 nm light) of 2-methoxyphenol in hexane (following treatment with 1,2-phenylenediamine) (excitation: 420 nm)

Figure 4.6. shows the fluorescence results of the low-intensity irradiation in the case of 2-methoxyphenol in cyclohexane compared to the non-irradiated solution which was subjected to the same treatment with 1,2-diphenylenediamine. The small emission enhancement observed is probably due to either a slight decomposition of 1,2-phenylenediamine during the attempted

quinone derivatization, or to traces of quinone present in the starting phenol. The latter possibility may be due to the decomposition of the starting material, which in the presence of oxygen can form quinones²⁵.

Pure 1,2-phenylenediamine does not absorb in this wavelength region (≥ 375 nm); hence, it should not luminesce, although it is light and heat sensitive, and the oxidation products are fluorescent in the same region. Ortho-quinone formation was not observed using any of the starting materials (1-5) under conditions of low light intensity excitation.

4.2.4. High-intensity experiments

4.2.4.1. Experiments with α -Guaiacoxyacetoveratrone

α -Guaiacoxyacetoveratrone was used first to evaluate the occurrence of multiphotonic processes of phenoxyl radicals using two-laser-two-color laser flash photolysis since this reaction produces phenoxy radicals in high yield (Figure 4.7.).

In this technique, the first laser (*synthesis laser*) is used to generate the phenoxyl radicals, and the second laser (*photolysis laser*) is used to supply the second photon which is necessary for the excitation of the phenoxyl radical and the eventual formation of quinone. Using a 308 nm laser as the synthesis laser, we were not able to see any bleaching of the guaiacoxy radical using 355 nm excitation for the *photolysis laser*.

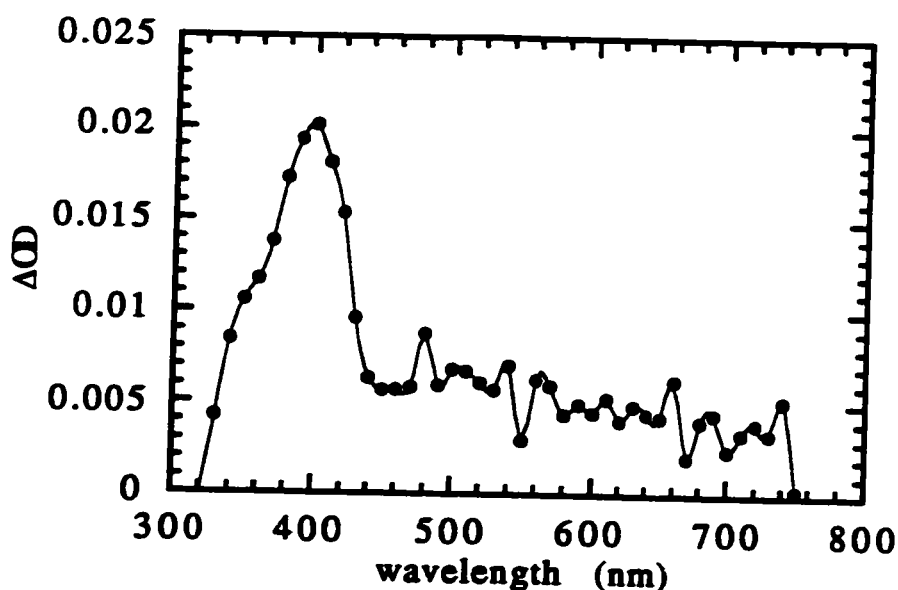


Figure 4.7.

Phenoxy radicals formed from α -guaiacoxyacetoveratrone, using the attenuated (45%) pulses from a 308 nm laser

The 308 nm laser drop photolysis (LDP) of α -guaiacoxyacetoveratrone produced a very complex mixture of products. Fluorescence analysis of some of the different possible products (Figure 4.8.) after the usual treatment with 1,2-phenylenediamine all showed fluorescence around 520 nm upon excitation at 395 nm, though the maximum of the emission occurred at a somewhat lower wavelength (Figure 4.8.).

In order to be able to analyze the spectra obtained (knowing that the ortho-quinone is probably a minor product of the photolysis) the following assumptions were made: given that the quantum yield of quinone formation was assumed to be very low, the main process

is the cleavage of the starting material. Therefore the two main anticipated products of the reaction are acetoveratrone and 2-methoxyphenol (guaiacol). This assumption represents a very rough approximation, since it is well known that there are other radical products which form during photolysis (such as, for example, products formed via ortho, meta and para substitution of the phenol). However, we assumed that those other products would not absorb significantly at the excitation wavelength used, and therefore that they would not fluoresce under our experimental conditions. After taking into account these assumptions, we had some indication that the formation of ortho-quinone is more favourable in apolar solvent (comparing benzene to acetonitrile, Figure 4.9. and Figure 4.10.).

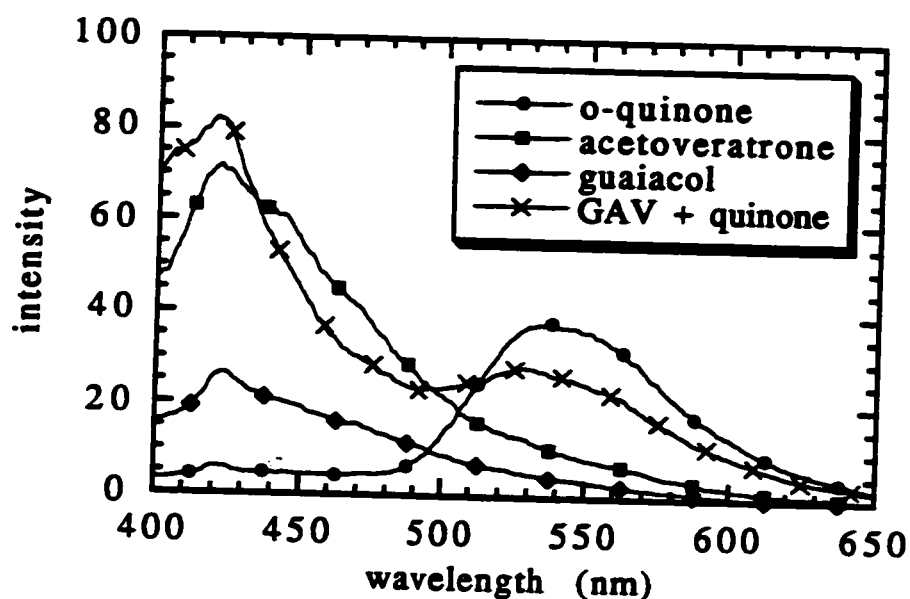


Figure 4.8.

Fluorescence of possible products and the starting materials for the photolysis of α -guaiacoxyacetoveratrone after treatment with 1,2-phenylenediamine

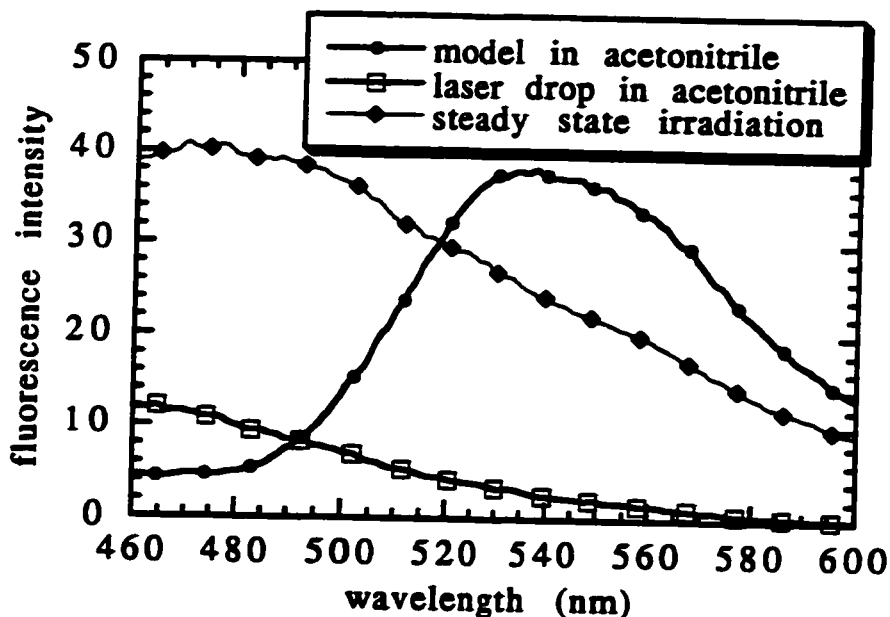


Figure 4.9

Fluorescence spectra of 3-methoxy-1,2-orthoquinone and α -GAV after steady state and laser drop irradiation in acetonitrile and treatment with 1,2-phenylenediamine

However, we decided that due to the questionable assumptions we would chose another starting materials which produces a cleaner reaction. This led us to the use of phenols as radical precursors.

4.2.4.2. Experiments with substituted 2-methoxy phenols

We have studied the multiphoton chemistry of 2-methoxyphenol (1), 2,6-dimethoxyphenol (2), 2-methoxy-6-fluorophenol (3), 2-methoxy-4-allylphenol (4) and 2-isopropoxyphenol (5) (see Figure 4.11.).

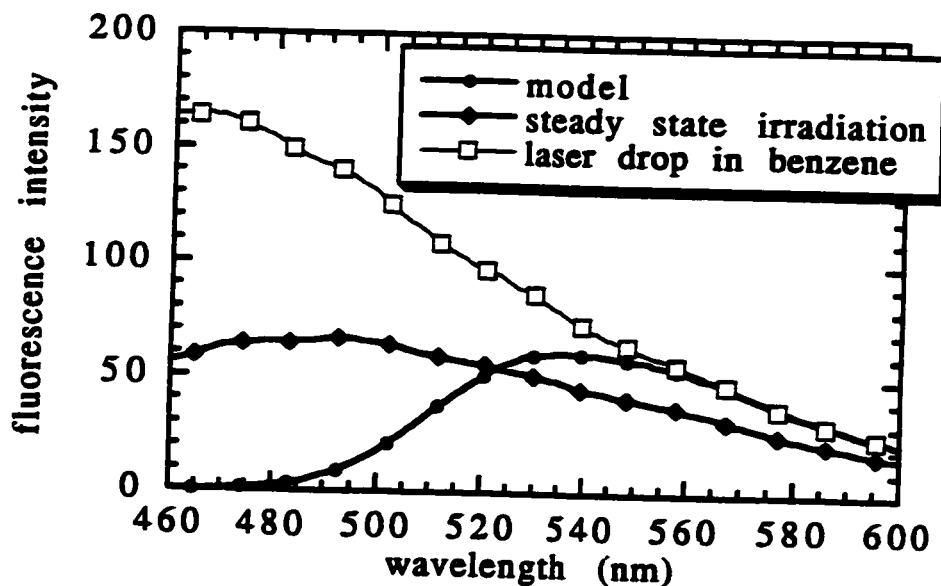
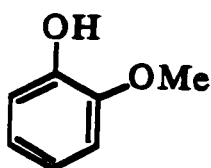
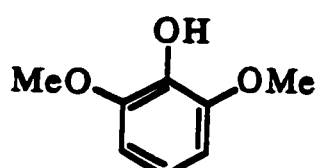


Figure 4.10

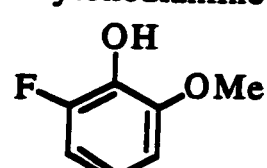
Fluorescence spectra of model quinone (3-methoxy-1,2-orthoquinone), and α -GAV after steady state and laser drop irradiation in benzene and treatment with 1,2-phenylenediamine



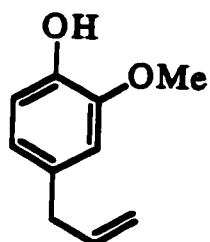
1



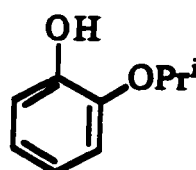
2



3



4



5

Figure 4.11.
Model phenols

These compounds were chosen as model compounds because of the following reasons: 2-methoxyphenol (guaiacol) is the simplest of the compounds which have the necessary structural features to participate in multiphotonic processes and produce ortho-quinones. By comparison of 2-methoxyphenol (1) to the molecule with an additional methoxy group (2) or an additional allyl group (4), we were able to explore the importance of electron donating groups in the ortho or para position on the formation of phenoxyl radicals. Further, electron-donating groups stabilize the ortho-quinone formed as final product. Irradiation of 6-fluoro-2-methoxy-phenol (3) could show the effect of an electron withdrawing group.

The second step of the hypothetical pathway of quinone formation is the breakage of a carbon-oxygen bond in the radical and the release of a methyl radical. Comparing the results from 1 and 5, one could explore the role of different leaving groups, and as such, one may be able to evaluate the importance of the second step in the reaction mechanism.

When generating phenoxy radicals from 2-methoxyphenol by *tert*-butyl-peroxide, the same result was obtained as when the phenoxyl radicals were generated directly via absorption of the light. This suggests that the quantum yield of reaction must be low (*vide infra*), although we note that this wavelength is not ideal (355 nm) and may lead to some signal compensation due to weak absorption by the precursors in this spectral region. We have also used the LDP technique (308 nm) with solutions of 2-methoxyphenol and *tert*-butyl peroxide. These solutions did not lead to any detectable

formation of ortho-benzoquinone from 2-methoxyphenols after LDP irradiation.

When in a two-laser-two-color experiment, the 248 nm excimer laser was used as the synthesis laser, and in the presence of 2-methoxyphenol, the yield of phenoxyl radicals was very small. In LDP experiments using the same laser, however, we were able to detect ortho-quinone formation. It is possible that under these conditions absorption of a second photon by the radical itself is favored.

Figures 4.12. and 4.13. show the emission and excitation fluorescence spectra of the irradiated and unirradiated samples of 2,6-dimethoxyphenol in hexane. Clearly, phenazine is not the only product of the irradiation and subsequent derivatization of the products. One of the other products, according to the GC-MS, is 9-fluorenone, which also fluoresces at slightly longer wavelengths. The origin of this compound remains unclear, most probably due to some impurity since its formation from 2-mthoxyphenols can not be explained otherwise in this solvent. Unreacted 1,2-phenylenediamine is also present as well as the other products of the reaction. To achieve better analytical discrimination, we changed the excitation wavelength (see Figure 4.14.) in order to optimize the conditions of the analysis.

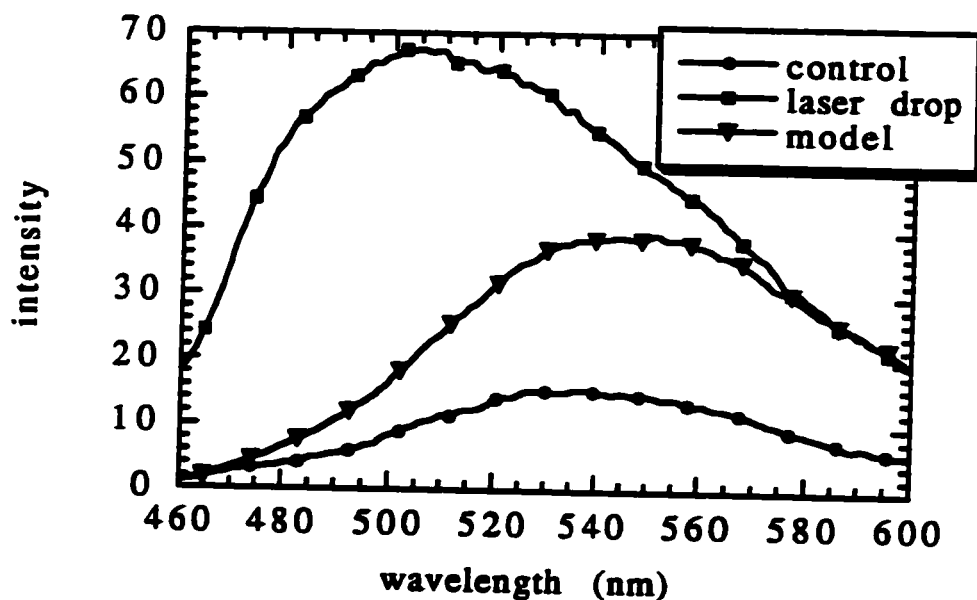


Figure 4.12.

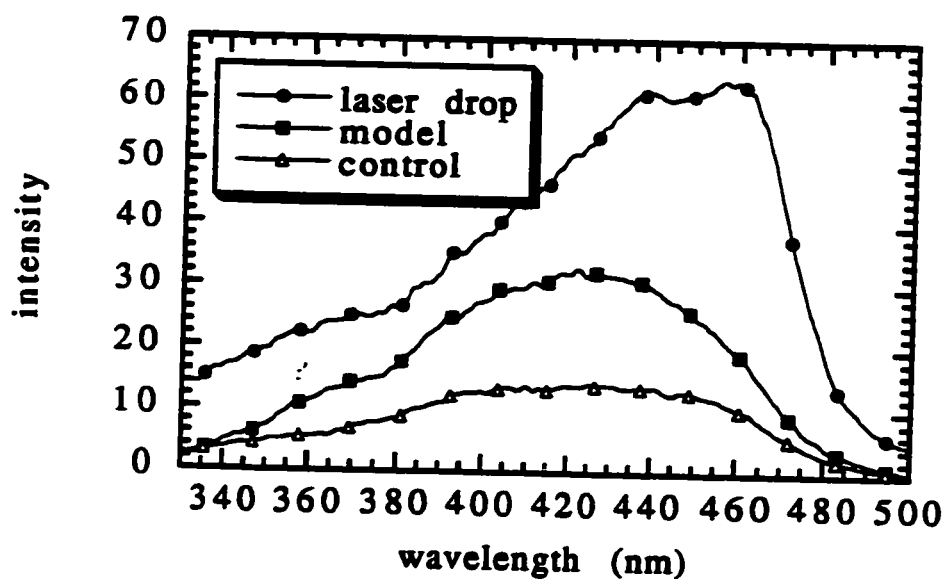


Figure 4.13.

Fluorescence emission spectra (Figure 4.12) (420 nm excitation) and excitation spectra (Figure 4.13), (monitored at 520 nm) of 3-methoxyquinone, 2,6-dimethoxy phenol (3) before and after LDP in hexane and treatment with 1,2-phenylenediamine. Fluorescence monitored at 520 nm

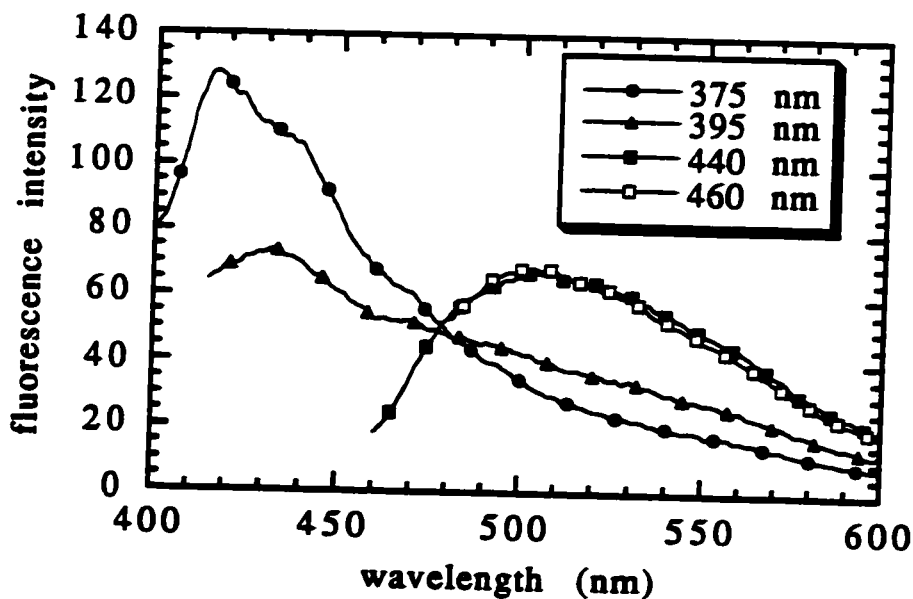


Figure 4.14.

Effect of excitation wavelength on the fluorescence emission of **2** after LDP and treatment with 1,2-phenylenediamine

Increasing the excitation wavelength helps to separate the signals, since at the longer wavelengths the other products and the starting material are transparent. Similar experiments were repeated in acetonitrile (see Figure 4.15.); no fluorescent product formation was observed under this solvent.

Figure 4.16. shows the fluorescence spectra of the different substituted 2-methoxyphenols, after LDP and 1,2-phenylenediamine derivatization. In each case we observed the formation of the corresponding 1,2-benzoquinone.

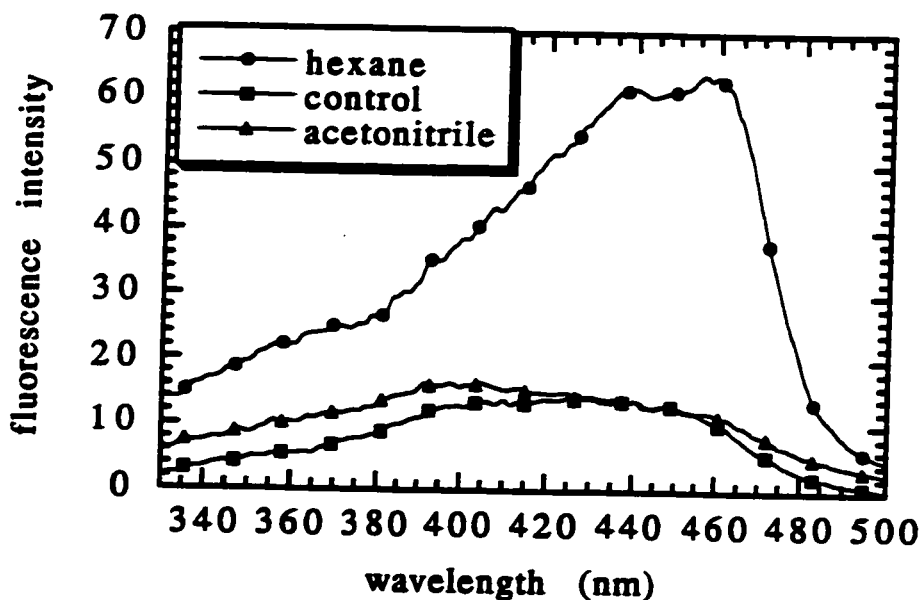


Figure 4.15.

Comparison of the results of laser drop photolysis of 2-methoxyphenol in hexane and in acetonitrile to the unphotolyzed starting material in hexane after the usual treatment with 1,2-phenylenediamine (fluorescence monitored at 520 nm)

The excitation and emission spectra (Figure 4.16 and Figure 4.17., respectively) show that electron donating substituents decrease the yield of the two-photon product, and that this effect is especially pronounced in the allyl substituted case (4). Electron withdrawing groups showed a small increase in the fluorescence yield (and the product yield as well). A possible explanation may be that the electron withdrawing groups weaken the C-O bond, which helps the product formation, but destabilizes the final product. The electron donating group would have the opposite effect.

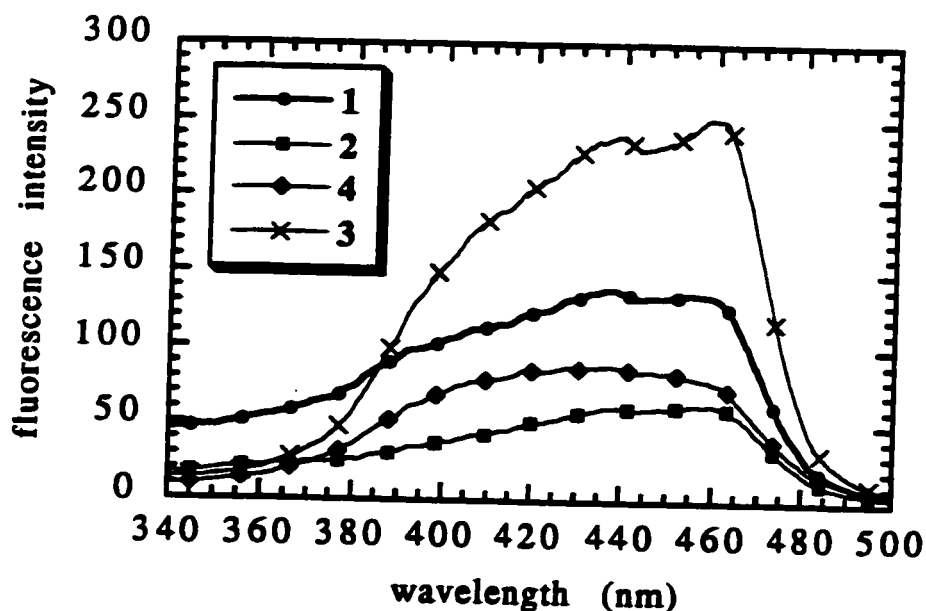


Figure 4.16.

Excitation spectra of different substituted 2-methoxyphenols after laser drop irradiation and treatment with 1,2-phenylenediamine (fluorescence monitored at 520 nm)

We have measured the relative fluorescence quantum yields, taking the unsubstituted compound as a reference (see Table 4.1) to gain information about the relative amounts of substituted ortho-quinones formed.

The emission quantum yield is especially high in the case of the allyl compound (4). When 2-isopropoxyphenol (5) was used instead of 2-methoxyphenol (1), we observed some increase in the product fluorescence (see Figure 4.18.).

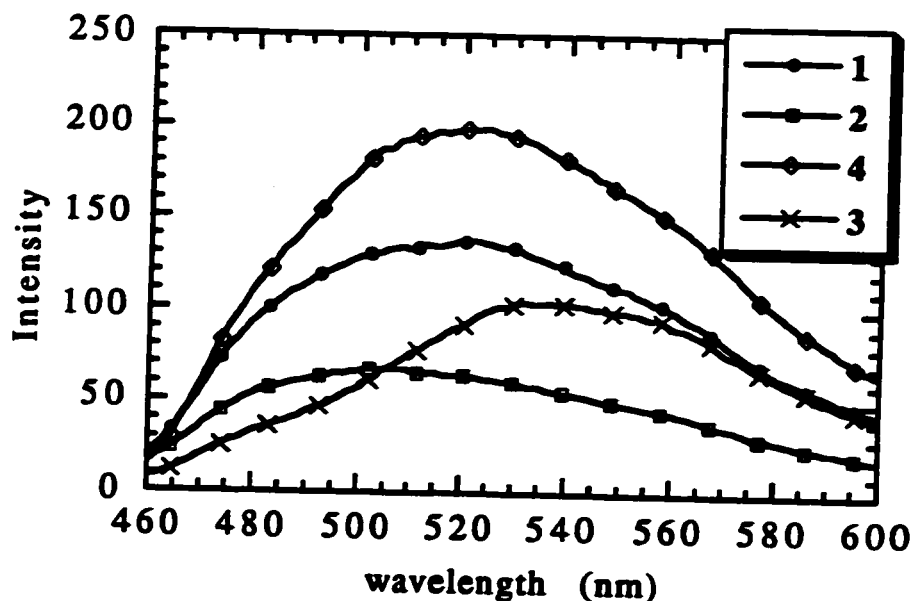


Figure 4.17.

Emission spectra of different substituted 2-methoxy phenols after laser drop irradiation and treatment with 1,2-phenylenediamine (excitation: 420 nm)

compound	relative quantum yield of fluorescence
1,2-benzoquinone	1
3-methoxy-1,2-benzoquinone	2.52
3-fluoro-1,2-benzoquinone	2.03
4-allyl-1,2-benzoquinone	47.0

Table 4.1.

Relative fluorescence quantum yield for substituted phenazines formed by reaction of 1,2-phenylenediamine with various model quinones. (excitation wavelength 420 nm)

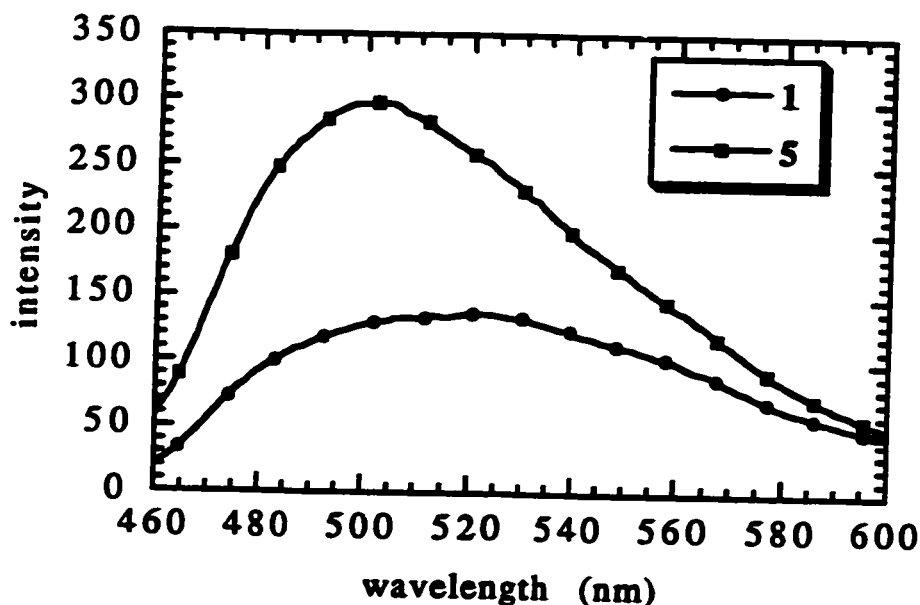


Figure 4.18.

Effect of the leaving group. Fluorescence spectra following laser drop irradiation of 2-methoxyphenol and 2-isopropoxyphenol in hexane followed by treatment with 1,2-phenylenediamine (excitation wavelength 420 nm)

In two cases (1 and 2) we monitored the formation of the corresponding phenazine by GC-MS analysis. The mass spectra confirm the formation of the fluorescent sensor; however, the yields are very small. The relatively high 1,2-phenylenediamine–ortho-quinone ratio used during derivatization caused serious problems in the GC-MS analysis, since the amine itself can decompose, thereby making the observation of phenazine difficult.

4.3. Discussion

In all our experiments the extreme instability of the 1,2-benzoquinones represented a major problem. The parent compound is known to decompose at 40°C²⁶. In addition, ortho-quinones are known to be light sensitive. Most likely, this problem tends to effectively reduce the apparent yields of quinone due to *in-situ* photodecomposition. Methoxy substituents increase the stability of the quinone, and this may be the way in which quinones achieve additional stabilization within the lignin structure.

The results of our work show that ortho-methoxyphenols can lead to ortho-quinones via a two-photon process. The first step in this sequence is the formation of the corresponding phenoxyl radical, which can occur by absorption of the first photon, or by hydrogen abstraction from the corresponding phenol¹⁹. This is followed by absorption of a second photon by the phenoxyl radical, breaking the methoxy carbon-oxygen bond and forming the corresponding 1,2-benzoquinone with low quantum yields. In solution this process occurs only under high intensity irradiation, although one can anticipate that the same result can be obtained at low intensities if the phenoxyl radical lifetime is extremely long⁶⁹. In a solid matrix such as pulp or paper phenoxyl radicals may indeed be sufficiently long lived to absorb other photons⁶⁹, even if the irradiation is not high-intensity, such as ambient light or sunlight. This process is possible since the absorption spectra of many phenoxyl radicals have a band in the 370-410 nm region, well within the spectral region to which papers are exposed under normal use. Clearly, this is not

expected to be the *only* source of ortho-quinones; most of the ortho-quinones are probably formed from the reaction phenoxyl radicals and other radicals which are present in the oxidative environment of the pulp.

It is interesting to note that the current work links several complementary pieces of information to add another pathway to the known routes for quinone formation in pulp and paper. Specifically, Wan and coworkers have shown that phenoxyl radicals are very long lived on paper (some hours to days) ⁶⁹, thus making them excellent candidates for further photolysis. Weir and coworkers⁷⁵ have shown that deep-UV photolysis of lignin leads to the formation of methane, consistent with the formation of methyl radicals in reaction 4.1. ($R = CH_3$). Gray et al. showed³³ that 1,2-phenylenediamine reacts with ortho-quinones to yield phenazines as excellent fluorescent reporters for quinone formation. Combined these tools provided the basis to make our analysis of multiphoton processes possible.

4.4. Experimental section

2-Methoxyphenol, 2-isopropoxyphenol, 2,6-dimethoxyphenol, eugenol, 6-fluoro-2-methoxyphenol, 1,2-phenylenediamine and sodium periodate were from Aldrich. 1,2-Phenylenediamine, 2-methoxyphenol, 2,6-dimethoxyphenol, were sublimed under reduced pressure before utilization. *Tert*-butyl peroxide was from Aldrich, and it was purified by passing through an alumina column prior to utilization. α -Guaiacoxycetoveratrone (α -GAV) was supplied by A. Berinstein. Solvents were all spectroscopic grade from BDH.

Synthesis of quinone model-compounds

Several quinones had to be prepared in order to provide for suitable reference materials for the fluorescence work; these included 1,2-benzoquinone (6), 3-methoxy-1,2-benzoquinone (7), 3-fluoro-1,2-benzoquinone (8), 4-allyl-1,2-benzoquinone (9). In all the synthesis we used the corresponding methoxy-phenols (0.02 mol in 150 ml of solution), which were stirred in cold water with one equivalent of NaIO_4 dissolved in cold water ²⁵. After a short period of mixing, the solution was extracted with CH_2Cl_2 , dried over Na_2SO_4 and filtered. After concentrating the solution to 20 ml, hexanes were added, and the precipitate was filtered. In the case of eugenol (4) and 6-fluoro-2-methoxyphenol (3), the solvent was totally evaporated and the oil obtained was used for the experiments. The compounds obtained were not pure (50%), but all further attempts at the purification failed. We determined the major contaminants which were the starting material and the corresponding ortho-diphenol, and since these compounds do not interfere in our fluorescence experiments, we used the mixtures as is.

Fluorescence relative quantum yield measurements

Given the problems in purifying these unstable ortho-quinones, we were only able to determine relative quantum yields of emission. 1,2-Benzoquinones were reacted with 1,2-phenylenediamine (see reaction 4.2.); 20 μl acetic acid was added and the sample absorbances were matched at the excitation wavelength; and the fluorescence was then recorded and integrated.

Photolysis and sample treatment

For laser drop photolysis the starting material was dissolved in the appropriate solvent so that the solution formed had an absorption around 1 at the laser wavelength. When tert-butyl peroxide was used and the starting material had no absorption at 308 nm, the absorption of the sample was not higher than 0.3. In cases where the sample absorbed at 308 nm, the absorption of the solution was adjusted to 0.2 with the phenol, and then to 0.5-0.7 by adding tert-butyl peroxide. All absorptions were measured in a 7 x 7 mm quartz cell.

For low-intensity irradiation and time-resolved laser experiments the absorptions of the sample were adjusted to be between 0.3 and 0.6.

For all photolysis (LDP as well as low intensity and laser flash photolysis), the samples were deaerated using nitrogen. After photolysis, the sample absorption was measured, then 2 ml 1,2-phenylenediamine of 1 mg/mL in methanol was added, solvent was evaporated to ~0.3 ml under reduced pressure. It was then kept at 70°C for 2 minutes. For the GC-MS analysis, this sample was used. For fluorescence analysis, the sample was diluted using methanol, and 20 μ L 5% acetic acid solution was added.

The different methods of photolysis are described in the experimental section of this thesis (Chapter 2).

Chapter 5

Multiphoton Chemistry of 1,3-Dichloro-1,3-diphenyl Propane

5.1. Introduction

As it was demonstrated in Chapter 4 laser drop photolysis is a useful tool to study multiphotonic processes. In this chapter I describe another application of this technique, the multiphoton chemistry of 1,3-dichloro-1,3-diphenyl propane. Beside LDP, other methods, such as LFP were employed to examine the kinetics of these processes.

5.1.1. Photochemistry of bichromophoric systems

Photochemical investigation of bichromophoric systems started in 1960's. These systems generally consist of two different chromophores, such as, for example, naphthalene and benzophenone. After excitation of one of the chromophores, studies on energy and/or electron transfer were performed. These works ultimately led to, for example, the observation of long range electron transfer (in cases when chromophores were spatially separated) and to the verification of the existence of the Marcus inverted region^{76,77}.

Systems containing two identical chromophores were first studied by Butcher and coworkers in mid 1980's when they examined the photochemistry of *bis*-dibenzylketones⁷⁸⁽¹⁾. This system contains two carbonyl chromophores which are separated by a long carbon chain, therefore the two chromophores behave

with high intensity light⁷⁹. Products are formed from (a) a monophotonic process; (b) simultaneous biphotonic absorption; and, (c) sequential excitation of the starting material (Figure 5.2.).

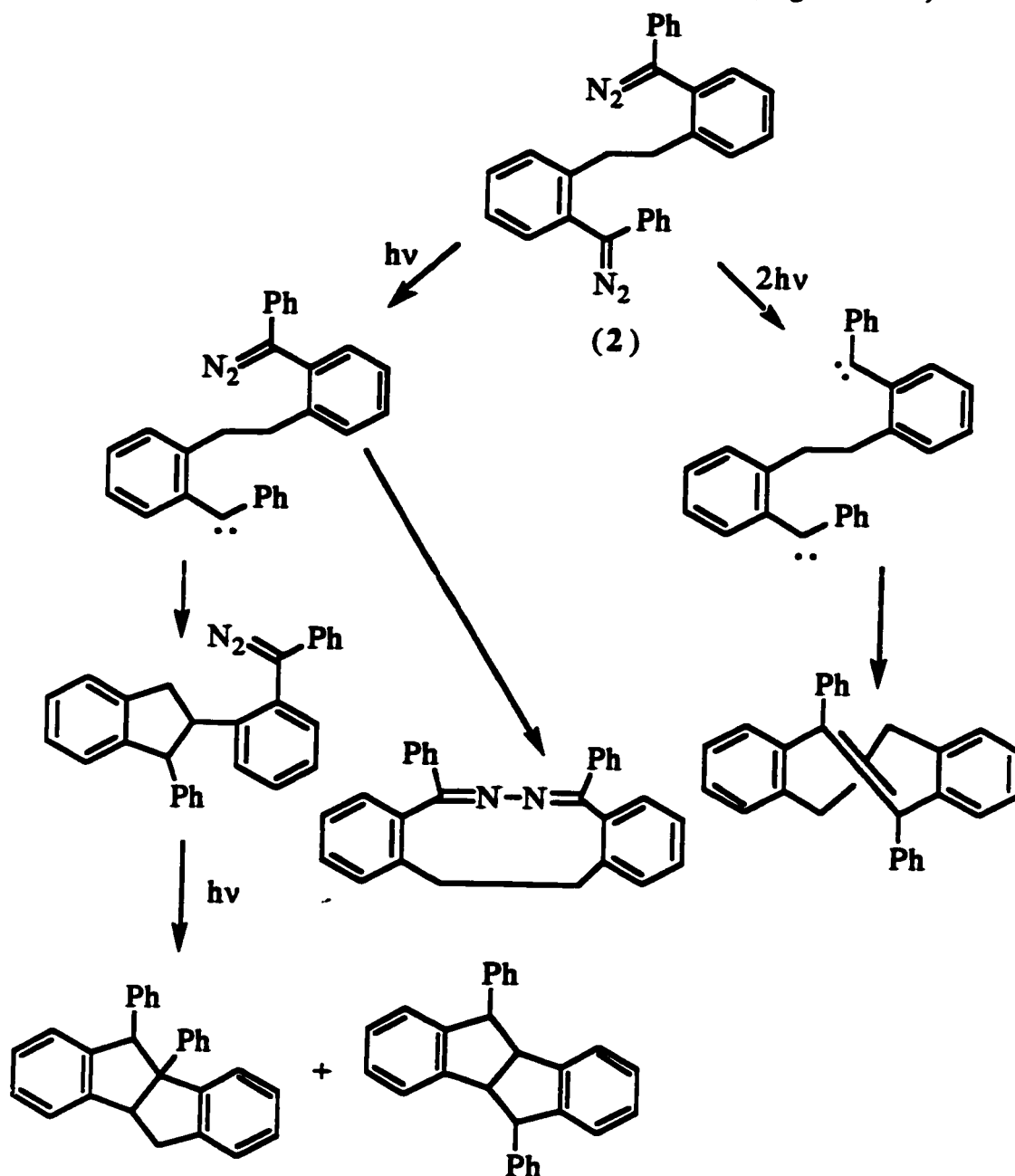


Figure 5.2.
Multiphoton chemistry of bis(diazomethane)⁷⁹.

Although halides are less photoreactive than either benzyl ketones or diazo compounds, they are more easily accessible, therefore studies of dihalides have also been of interest recently.

5.1.2. Photochemistry of the carbon-halogen bond⁸⁰

Irradiation of alkyl halides in solution affords a mixture of ionic and radical products. In an apolar solvent the first step is a homolysis, leading to the formation of two radicals. In a polar solvent heterolysis can also occur, in addition to the homolytic processes, with formation of ionic products. The ratio of radical and ionic products is influenced mainly by the nature of the halide and the solvent in which the reaction takes place (Figure 5.3).

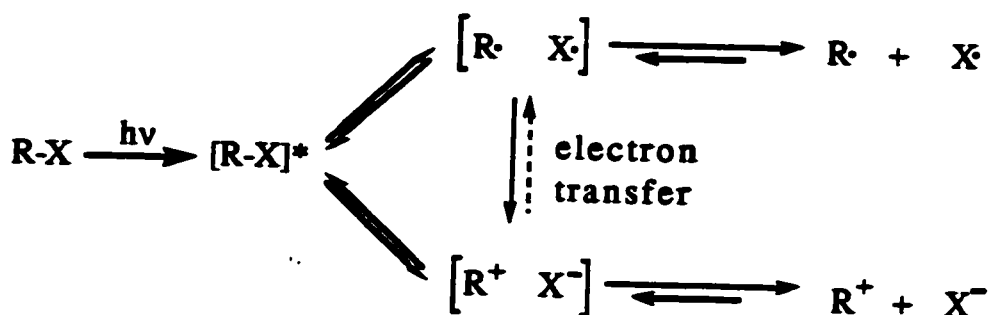


Figure 5.3.
Photochemistry of the carbon-halogen bond

The behavior of geminal dihalo compounds (3) resembles that of the monohalides (Figure 5.4.)⁸¹. After the initial homolytic cleavage (I) of the carbon-halogen bond to form a radical pair, reduction (IV) and elimination (V) products are formed. Also, hydrogen abstraction from the solvent (II) can occur. In polar media

deprotonation or electron transfer (III) can follow the initial homolysis.

Vicinal dibromides (4) undergo photodecomposition to yield bromine atoms⁸². (Figure 5.5.) Most simple dibromides undergo rapid photoinduced C-Br bond cleavage. In non-stabilized systems, the β -bromo substituted radical formed undergoes rapid cleavage to yield a second bromine atom and the corresponding alkene. The cleavage is frequently followed by hydrogen abstraction from the solvent to yield HBr.

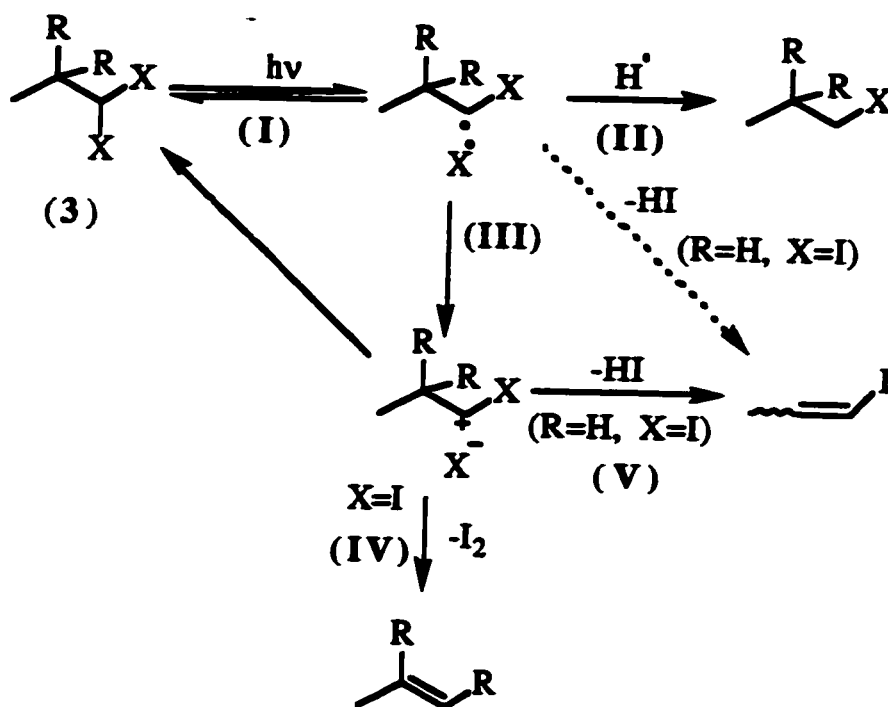


Figure 5.4.

Photochemistry of geminal alkyl dihalides⁸¹

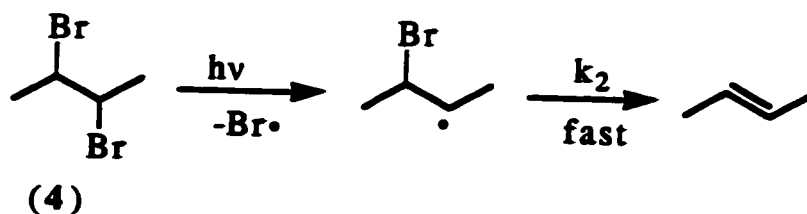


Figure 5.5.

Photochemistry of acyclic vicinal dibromides⁸²

In the above cases of geminal or vicinal dihalides, the two halogen atoms obviously influence the behavior of the other halogen. A system, in which the position of halogen atoms is neither vicinal nor geminal, was studied by Ouchi and coworkers^{83,84}. It contains the carbon-halogen groups connected through a single naphthyl group (1,8-bis(halomethyl)naphthalene) (5). Ouchi and coworkers studied the mono and multiphotonic processes of 5. Excitation of this molecule with high intensity laser light leads to double-activation. The resulting biradical (6) can undergo recombination at the carbon-halogen bond or radical coupling leading to acenaphthene (7) (Figure 5.6.). However, the yield of 7 is very small, and the two C-X bonds cannot be regarded as fully independent chromophores.

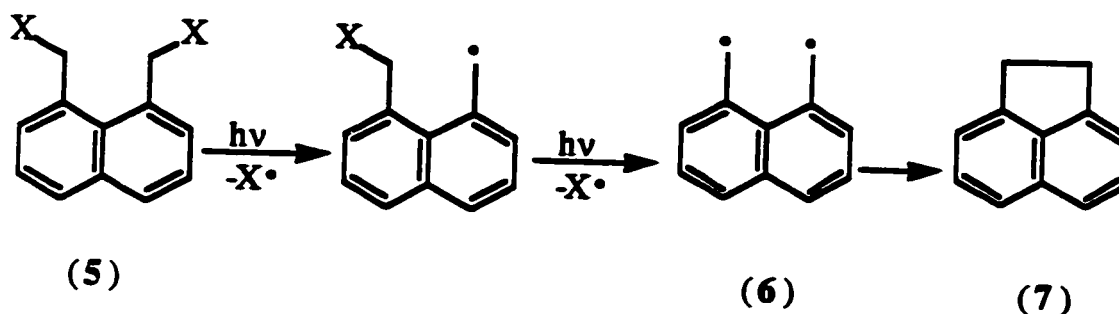


Figure 5.6.

Photochemistry of 1,8-bis(halomethyl)naphthalene^{83,84}

5.1.3. Photochemistry of (α,ω)-dihalo-(α,ω)-diphenyl alkanes

A number of (α,ω)-dihalo-(α,ω)-diphenyl alkanes have been investigated in our laboratory (Figure 5.7.). In the systems studied by us, the two carbon-halogen bonds are separated by a saturated hydrocarbon chain, and as such the two chromophores can be regarded as being independent.

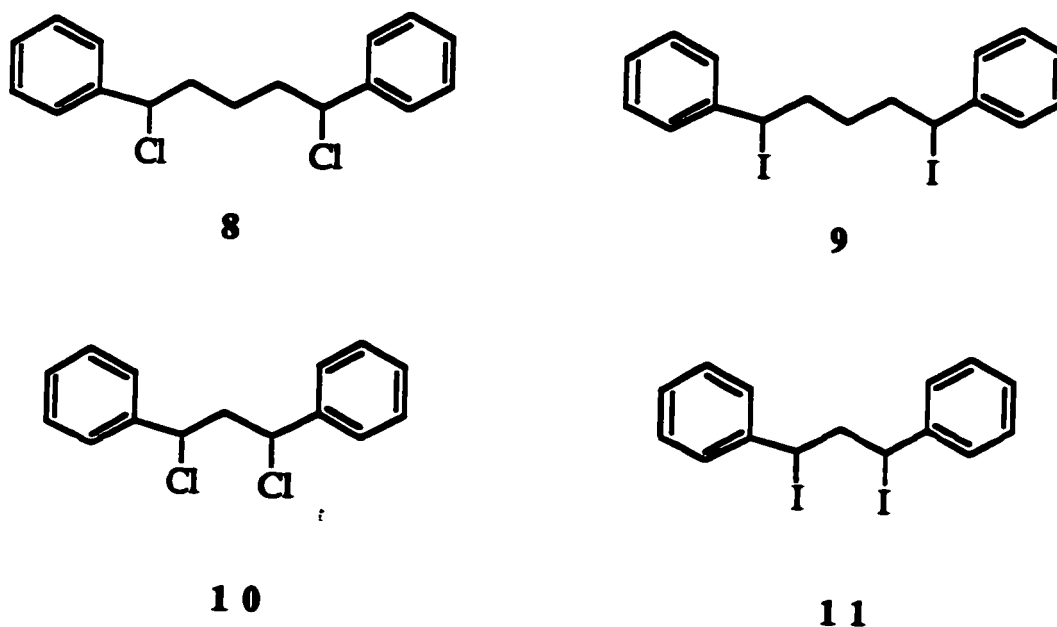


Figure 5.7.

(α,ω)-dihalo-(α,ω)-diphenyl alkanes studied in our laboratory

For these studies, conventional lamp irradiation, laser flash photolysis, two-laser-two-color laser flash photolysis and laser drop photolysis were used. While using conventional lamp irradiation, only monophotonic products can form. Application of high-intensity laser light can promote biphotonic as well as other monophotonic processes. Using two-color-two-laser experiments sequential absorption of two photons is possible; further, another technique

developed in our laboratory, laser drop photolysis, is very efficient promoting bi- and multiphotonic processes³⁹.

The low intensity photolysis of both 8 and 9 can be understood using considerations similar to those of the monohalo compounds. Upon irradiation the primary cleavage occurs at one carbon-halogen bond, and the second chromophore is not involved in this step. However, there is a significant difference in the fate of the two monohalo-benzyl radicals (12)⁸⁵ and (14)⁸⁶.

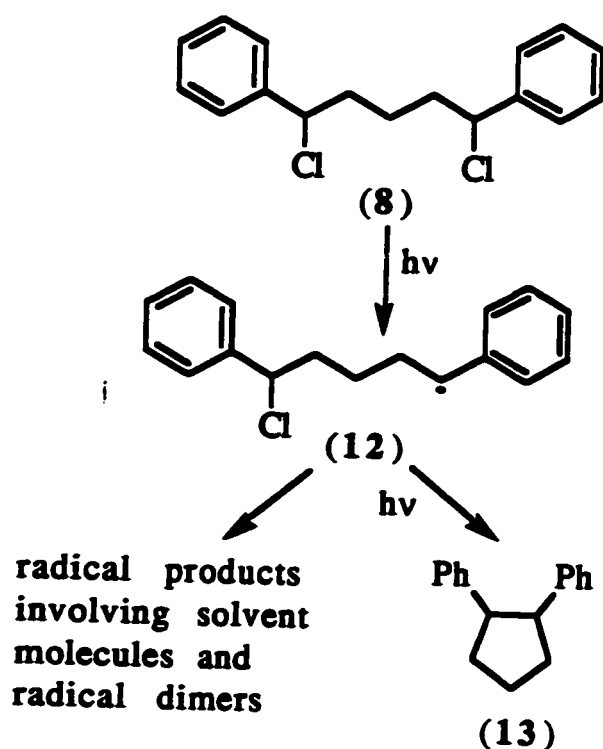


Figure 5.8.
Photochemistry of 1,5-dichloro-1,5-diphenylpentane in cyclohexane⁸⁵

While 1,5-dichloro-1,5-diphenylpentane gives the expected radical recombination products involving radical dimers as well as

radical products with the solvent (Figure 5.8.), the product mixture formed from 1,5-diiodo-1,5-diphenyl pentane is quite simple (Figure 5.9). For example, no radical dimers are present. Also, the transient spectrum of **8** is identical to that of the benzyl radical (with λ_{max} around 320 nm, lifetime $> 2 \mu\text{s}$, quenched by oxygen), which proves the involvement of **12**.

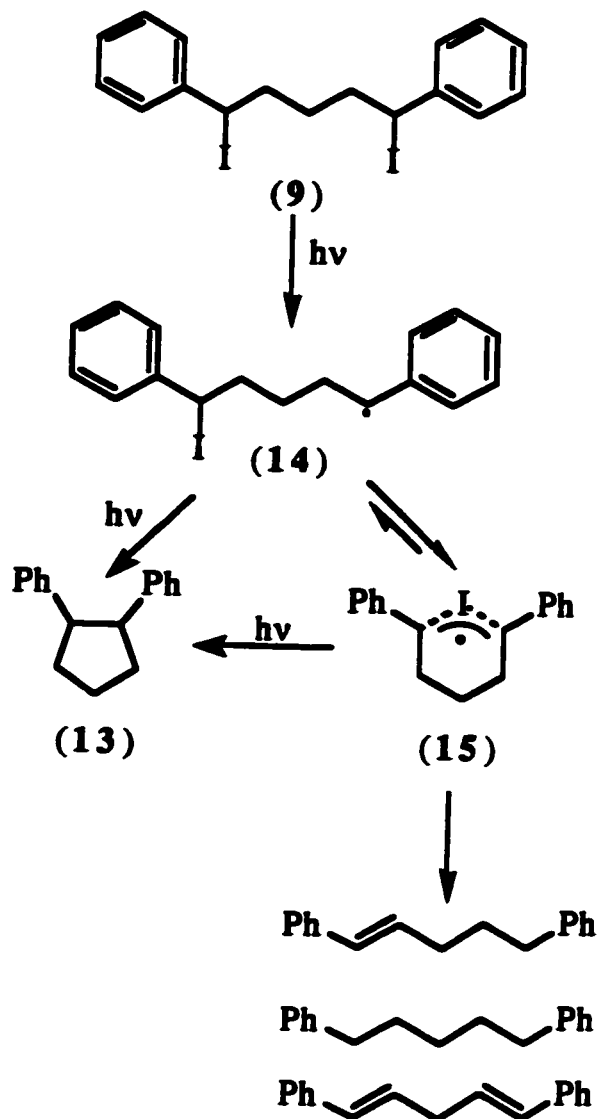


Figure 5.9.

Photochemistry of 1,5-diiodo-1,5-diphenylpentane in cyclohexane⁸⁶

However, transient spectrum of **9** shows a broad absorption which is totally unaffected by oxygen. Also, the relatively simple product distribution after photolysis does not correspond to the involvement of a benzylic radical. To explain these observations hypervalent iodine radical **15** has been proposed as an intermediate.

This hypervalent iodo-radical appears to be quite stable, lacking the tendency to react with other radicals. Rather, it either absorbs a second photon, or eliminates HI, generating different alkenes. Support for the existence of the hypervalent iodine radical was provided by Tanner⁸⁷, but it had never been observed directly. Chateaufneuf and coworkers proposed a hypervalent iodine radical⁸⁸ in the TEMPO-methyliodide system, however, there was no direct proof, that the observed transient is really a divalent iodine radical. Among other hypervalent halogen radicals, bromo radicals are known to participate in bromine elimination reaction forming a bridged intermediate⁸⁹. Formation of hypervalent chlorine radicals is less favorable, due to its reduced tendency for bridging.

High-intensity laser irradiation in the cases of **8** and **9** lead to the formation of 1,2-diphenylcyclopentane via a biradical intermediate (Figures 5.8. and 5.9.).

In the following parts I describe studies on 1,3-dichloro-1,3-diphenylpropane (**10**).

5.2. Results

As mentioned earlier, different behaviors were observed in polar and apolar solvents. To examine this difference we used

cyclohexane and 2,2,2-trifluoroethanol or in some cases acetonitrile and freon-1,1,3 as solvents (for the numbering of the compounds, see Figure 5.10., which will be discussed later).

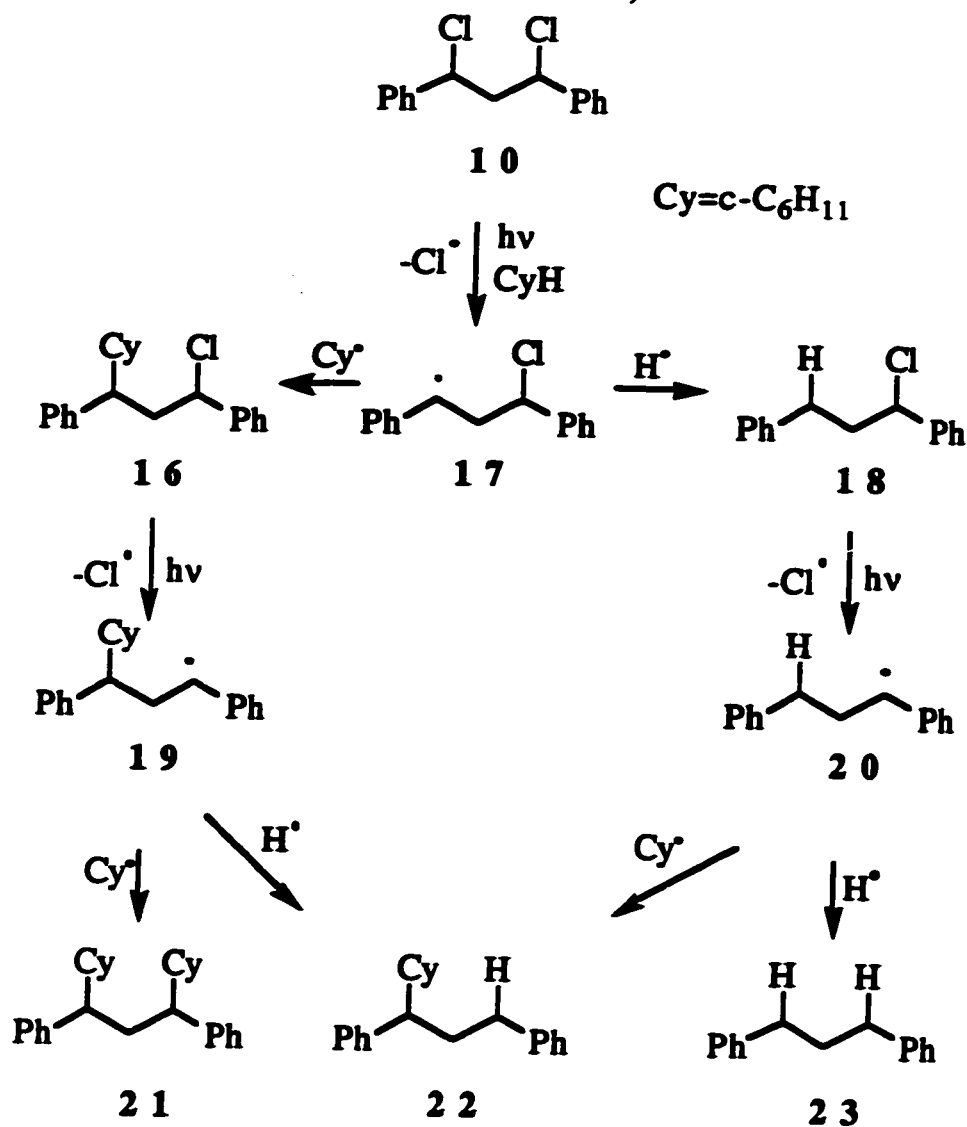


Figure 5.10.

Low intensity irradiation of 1,3-dichloro-1,3-diphenylpropane in cyclohexane⁸⁵

5.2.1. Studies in apolar solvents

5.2.1.1. Laser Flash Photolysis studies

Laser flash photolysis of deaerated solutions of **10** at 266 nm yielded a narrow spectrum, with maxima at 320 (weak), 340 (weak) and 360 nm (strong), see Figure 5.11. The decay of the 340 and 360 nm peaks follows approximately the same kinetics throughout this region of the spectrum with halflives around 10 μ s under our experimental conditions (Figure 5.12.). in contrast, the kinetics of the 320 nm peaks has a half life of 2-3 μ s (Figure 5.13.). Oxygen saturated solutions of **10** in cyclohexane led to a reduced half life of 0.6 μ s at 360 nm (Figure 5.15).

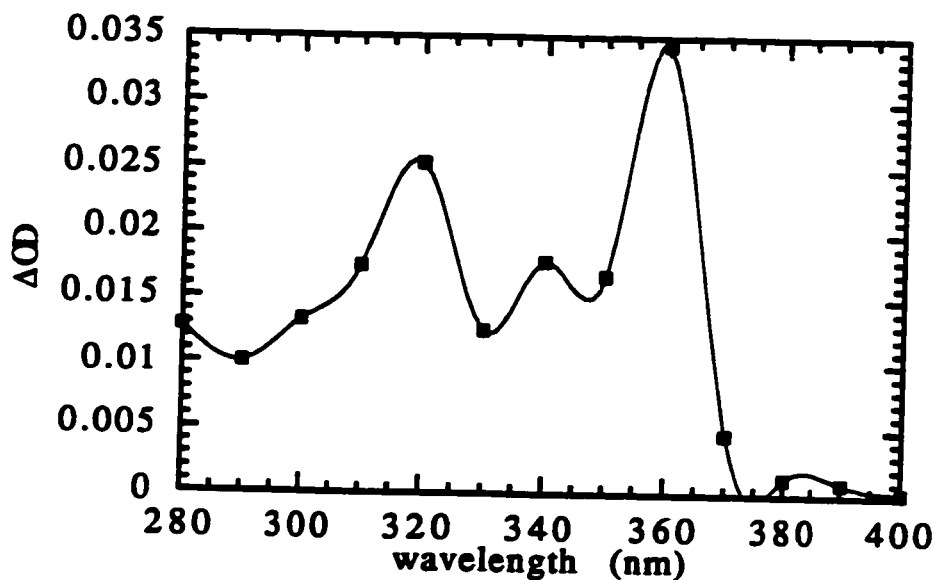


Figure 5.11.

Transient absorption spectra obtained by irradiation of 1,3-dichloro-1,3-diphenyl propane in cyclohexane. (Excitation wavelength 266 nm, recorded 770 ns after the laser pulse)

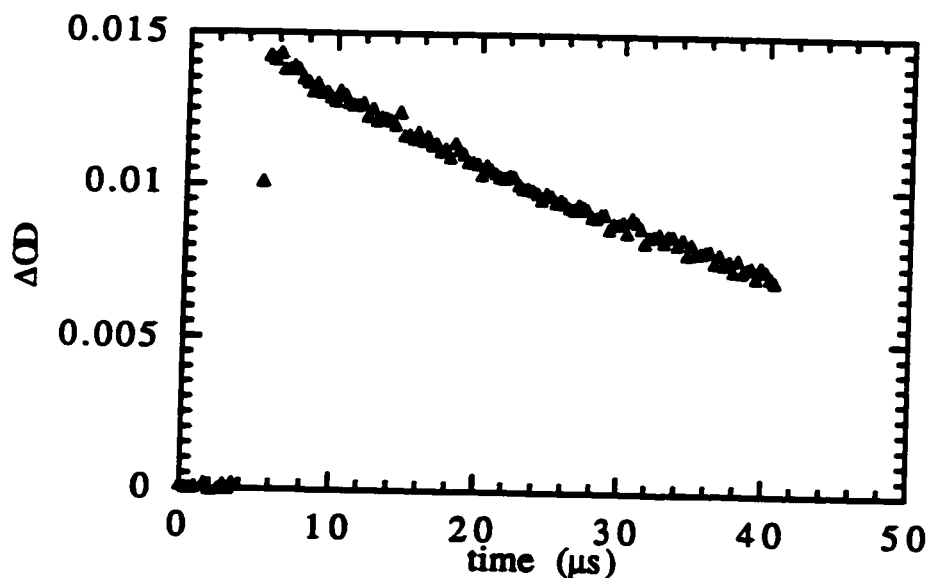


Figure 5.12.

Decay at 360 nm of 1,3-dichloro-1,3-diphenyl propane in cyclohexane after excitation with 266 nm light.

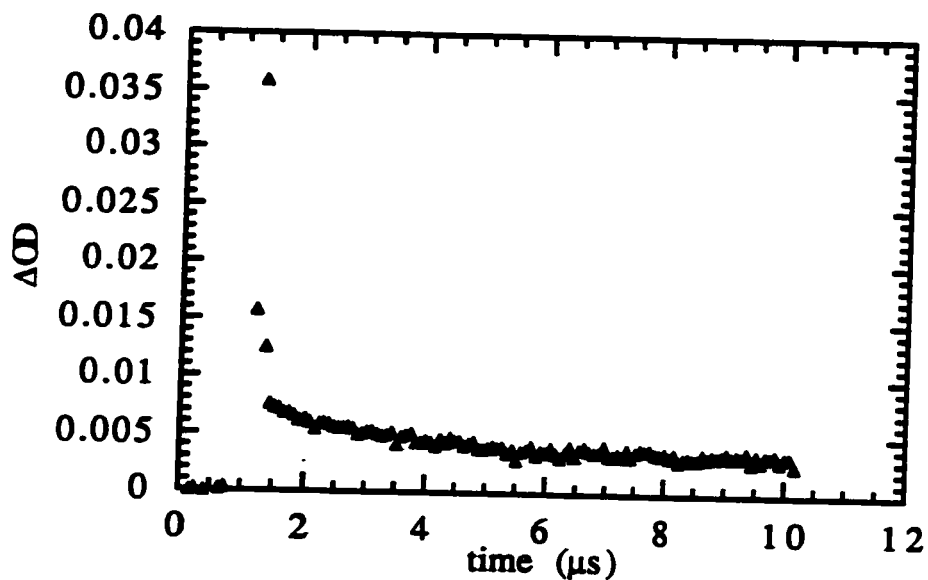


Figure 5.13.

Decay at 320 nm of 1,3-dichloro-1,3-diphenylpropane in cyclohexane after excitation with 266 nm light.

As this long-lived intermediate could not be the 3-chloro-1,3-diphenylpropyl radical (17) (which would be expected to absorb at ~ 320 nm²⁹) we checked the possibility that 17 could lose hydrogen chloride to give the allyl radical 24, Figure 5.14. Thus, experiments were carried out with 3-chloro-1,3-diphenylpropene⁹⁰ (25) in an attempt to establish the nature of the transient. Laser flash photolysis of a 0.5 mM solution of 25 in cyclohexane gave rise to a transient whose absorption matched that described above (Figure 5.16.). Theoretical calculations on the allyl radical 24 predict an absorption maximum at close to the observed values⁹¹. Oxygen quenched this transient (i.e. shortened its lifetime), but increased its yield of production (Figure 5.17.); fluorescence measurements under a nitrogen, air or oxygen atmosphere showed that the fluorescence of 3-chloro-1,3-diphenylpropene is quenched by oxygen. We tentatively suggest that oxygen promotes intersystem crossing and enhances triplet formation.

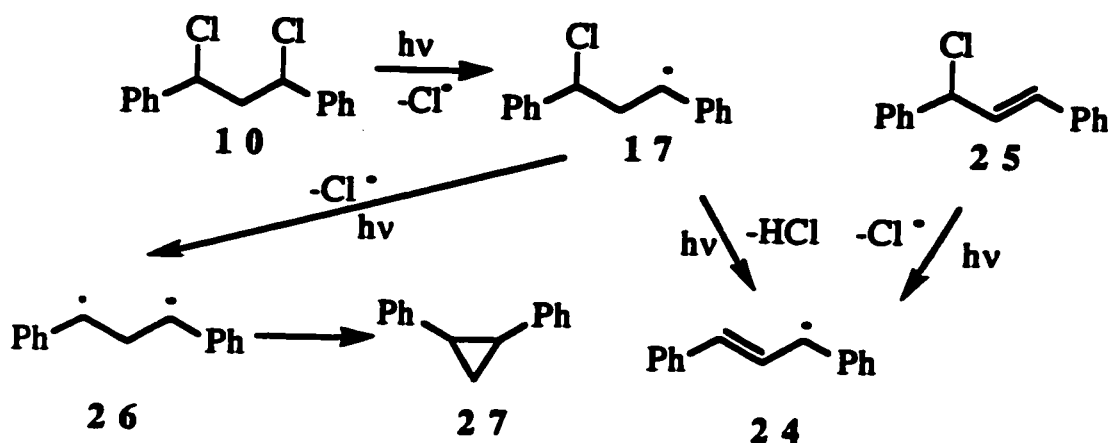


Figure 5.14.

Multiphoton chemistry of 1,3-dichloro-1,3-diphenylpropane and 3-chloro-1,3-diphenylpropene in cyclohexane

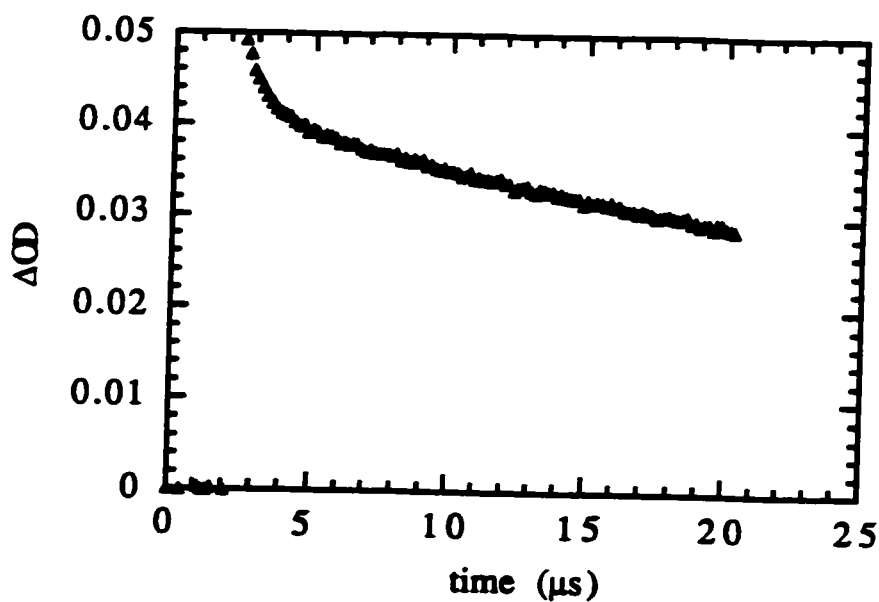


Figure 5.15.
Transient decay at 360 nm of 1,3-dichloro-1,3-diphenylpropane in cyclohexane under air after excitation with 266 nm light

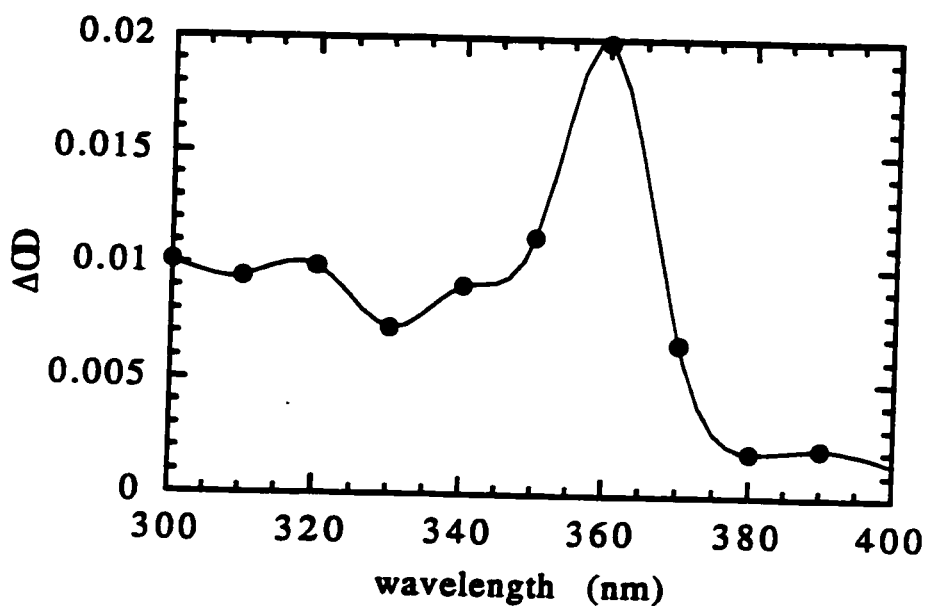


Figure 5.16.
Transient spectra recorded for 3-chloro-1,3-diphenylpropene in cyclohexane following excitation at 266 nm.

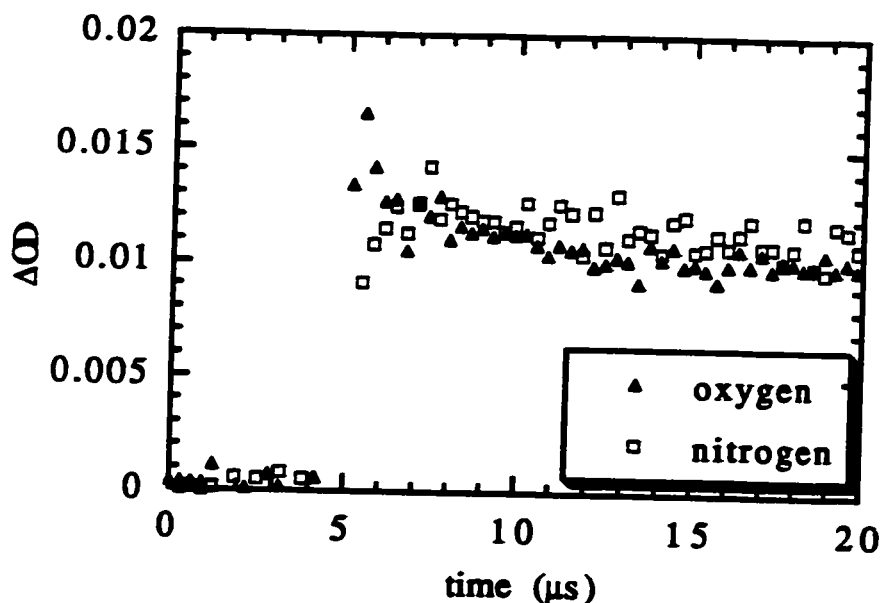


Figure 5.17.

Decay monitored at 360 nm of 3-chloro-1,3-diphenylpropane in cyclohexane following excitation at 266 nm.

Oxygen leads to a complex mixture of products, characteristic of radical processes. The reaction mixture obtained under oxygenated condition was analyzed by Julia Pérez-Prieto and it showed that 1,3-diphenylpropene oxide (31), the two isomeric chalcones (28 and 29) and some dibenzyl ketone (30) are among the products (Figure 5.18.)

Attempts to detect singlet oxygen luminescence were unsuccessful, suggesting that the triplet state of 25 is very short lived. This result is consistent with the involvement of radicals rather than a long lived excited state. Thus, 24 may originate from a short lived triplet state.

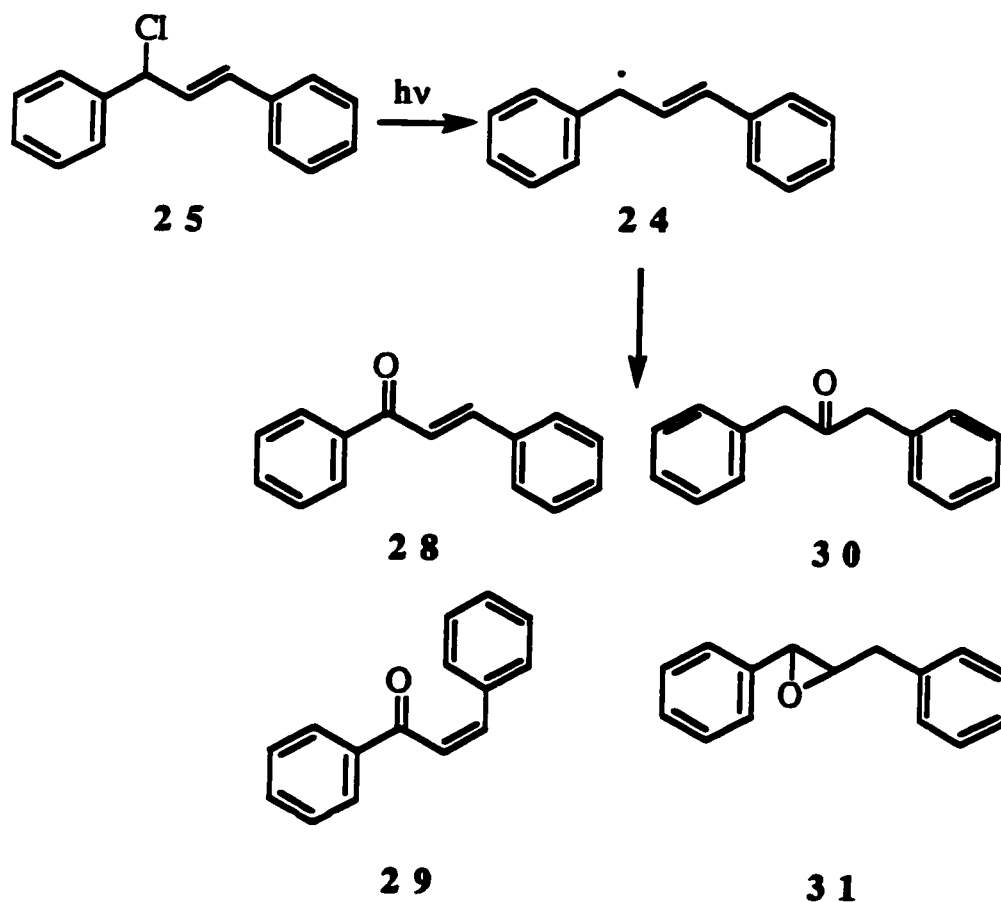


Figure 5.18.

Products of irradiation of 3-chloro-1,3-diphenylpropane under oxygen in cyclohexane

Radical 24 was also obtained when a 50/50 di-*tert*-butyl peroxide/benzene solution was irradiated (355 nm, Nd:YAG) in the presence of 1,3-diphenylpropene (Figure 5.19.). Here, allylic hydrogen abstraction by *tert*-butoxy radicals should provide a clean source of 26⁹² (Figure 5.20.).

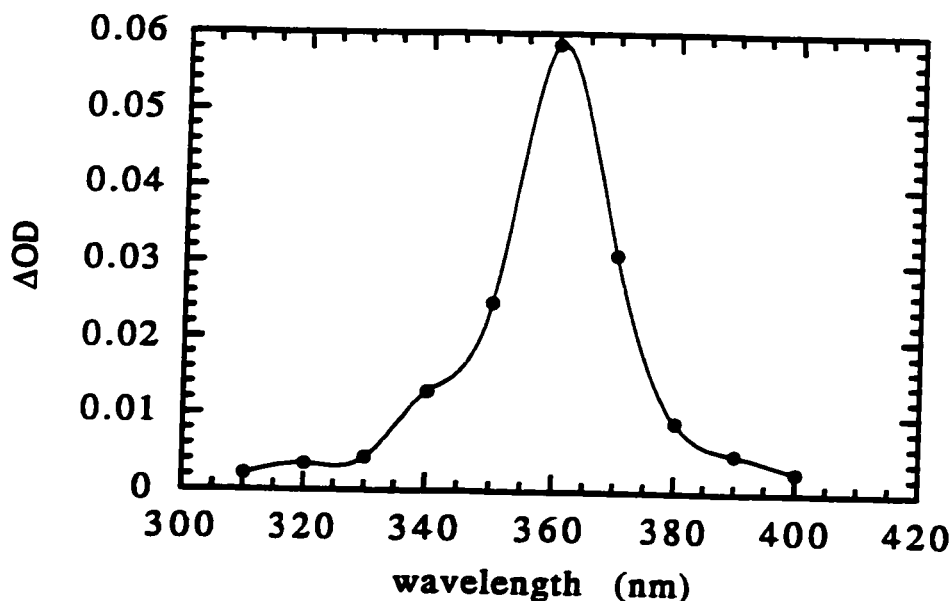


Figure 5.19.

Transient spectra obtained upon irradiation of 1,3-diphenylpropene in 50/50 di-*tert*-butyl peroxide/ benzene at 355 nm

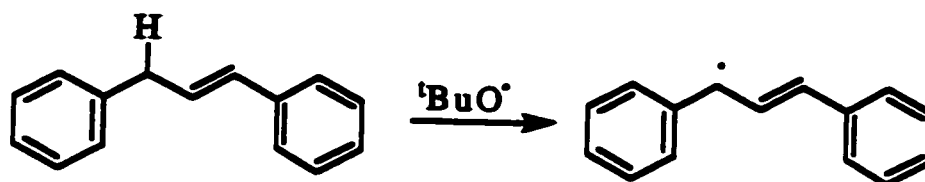


Figure 5.20.

Hydrogen abstraction by *tert*-butoxyl radical

The formation of the allyl radical **24** from 1,3-dichloro-1,3-diphenylpropane under laser irradiation was not consistent with the monophotonic products obtained by lamp irradiation, thus suggesting that a two-photon process was also taking place under laser excitation. In order to minimize multiphoton processes in the laser flash experiments, we placed a beam diffuser (made with a *frosted*

quartz plate) in front of the sample. This avoids high intensity regions in the beam and promotes monophotonic behavior. The spectrum obtained under these conditions showed a stronger band at 320 nm, compared to the 360 nm band (see Figure 5.21.). The 320 nm band had a lifetime of ca. 2-3 μ s and was readily quenched by oxygen (Figure 5.22.).

These data allowed us to assign with confidence the 320 nm transient to the benzyl radical 17^{92} .

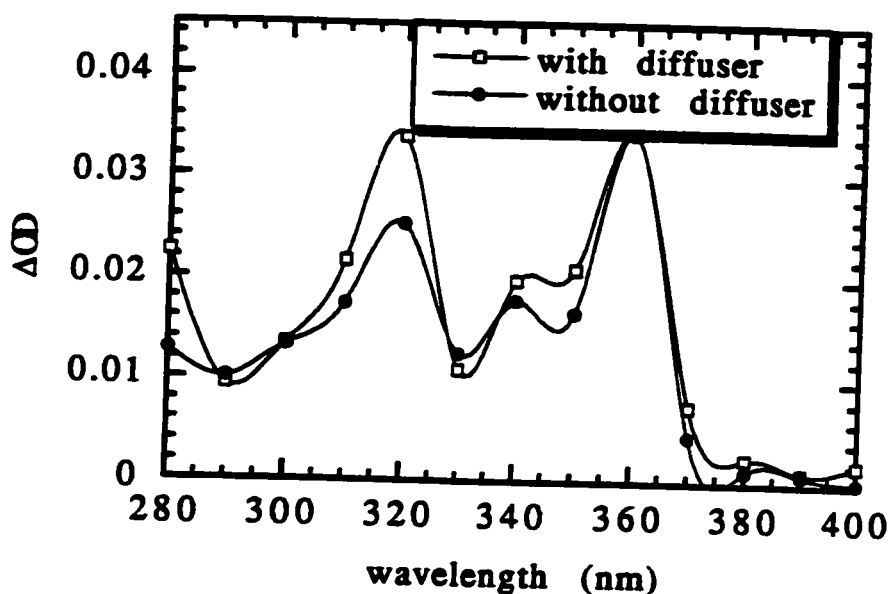


Figure 5.21.

Transient absorption spectra of 1,3-dichloro-1,3-diphenylpropane recorded with and without a diffuser in cyclohexane, under nitrogen. Excitation at 266 nm

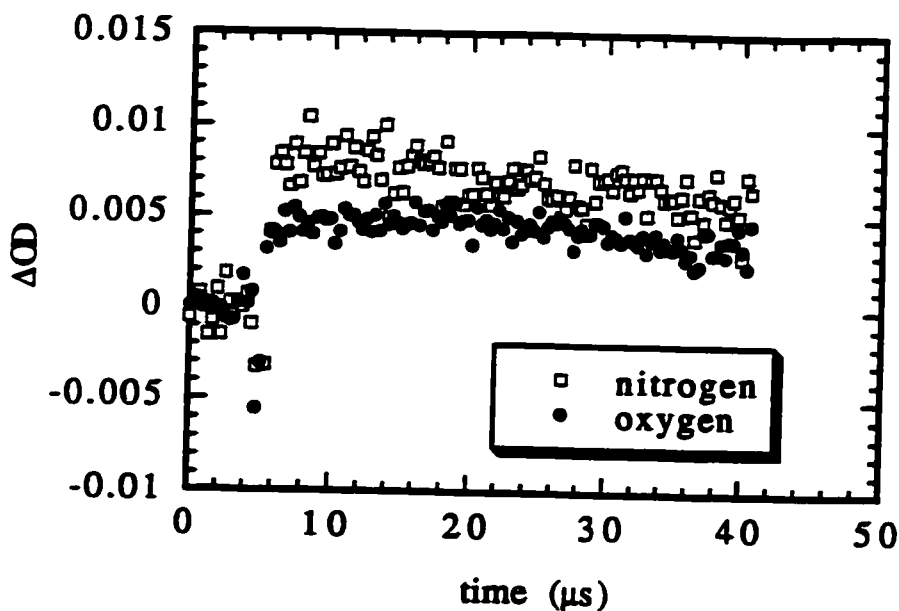


Figure 5.22.

Effect of oxygen on 320 nm band in the absorption spectra of 1,3-chloro-1,3-diphenylpropane upon excitation with 266 nm light in cyclohexane in the presence of a beam diffuser

An investigation of the effects of light intensity on the magnitude of the signals at 320 and 360 nm was carried out by attenuating the laser beam with a set of calibrated neutral density filters. At 360 nm the dependence of the signal intensity with laser dose was characteristic of two-photon processes. Interestingly, the formation of allyl radical is consistent with the elimination of hydrogen chloride from radical 17.

5.2.1.2. High intensity product studies

Laser flash photolysis studies using 266 nm excitation show that a two-photon process is responsible for the formation of 1,3-

diphenylpropenyl radicals as one of the transients under high intensity conditions. This radical had been prepared earlier from the 1,3-diphenylallyl anion by electron transfer⁹³, but neither lifetime nor absorption spectra had been obtained. Further, product studies under low and high intensity conditions show that *cis*- and *trans*-1,2-diphenylcyclopropanes are exclusively formed by a two photon route.

Laser irradiation was conducted in 0.01 M solutions of **10** in cyclohexane using 248 or 266 nm laser excitation with the sample in a spectrometer cell. The mixture was analyzed using GC-MS spectroscopy by Julia Pérez-Prieto. Compounds **16**, **18** and **21-23** were again obtained, but in this case significant amounts of cyclopropanes **27** were also formed. Any role of 1,3-diphenylpropenyl radical in the formation of the cyclopropane derivatives is highly unlikely, since these compounds were also obtained when an oxygenated solution of **10** was photolyzed (Nd:YAG, 266 nm), conditions under which **24** is scavenged by oxygen.

In contrast, the short lifetime of the biradical **26** ($\tau \approx 15$ ns) could preclude its quenching by oxygen^{94,95}. No dimerization products derived from the allyl radical were observed, probably as a consequence of the low substrate concentration, and the dominance of reactions with other more reactive radicals, such as those derived from the solvent.

5.2.1.3. Laser-Drop Photolysis studies

We also employed the laser-drop technique since it provides a way of performing high intensity photolysis while minimizing the amounts of secondary products. When drops of deaerated solutions of **10** in cyclohexane were irradiated by the focused output from a 266 nm laser (1 cycle) the product distribution changed dramatically. The efficiency of transformation was very low (<10 %) but the major products were *cis*- and *trans*-diphenylcyclopropanes; minor amounts of 1,3-diphenylpropenes and products containing the cyclohexyl moiety were also observed. The formation of the cyclopropane derivatives implies that both chlorine atoms are extruded during the laser pulse, presumably to produce the 1,3-diphenylpropanediyl biradical.

5.2.2. Studies of polar solvents

5.2.2.1. Laser Flash Photolysis studies

Laser flash photolysis of a 1 mM deaerated solution of **3** in 2,2,2,-trifluoroethanol (TFE) at 266 nm led to instantaneous (<20 ns) formation of a broad absorption centered at 490 nm (Figure 5.23.).

Since most of the transient is formed through a relatively slow process over the next 40 μ s (Figure 5.24.), the fraction which was produced instantaneously (within 20 ns) was originally attributed to a biphotonic process. The power dependence of this component was examined by plotting the ratio of instantaneous-to-total signal against the laser pulse energy (Figure 5.25.). This plot did not show any dependence on the laser power. Further, dependence of the

instantaneous signal against the laser pulse energy (Figure 5.25.), the plot did not show any dependence on the laser power. Further, plotting the dependence of the instantaneous signal vs. laser power showed linear relationship signaling the monophotonic origin of the instantaneous signal (Figure 5.26.).

Therefore, we concluded that the main path to the allyl cation is monophotonic and it must originate from two different intermediates.

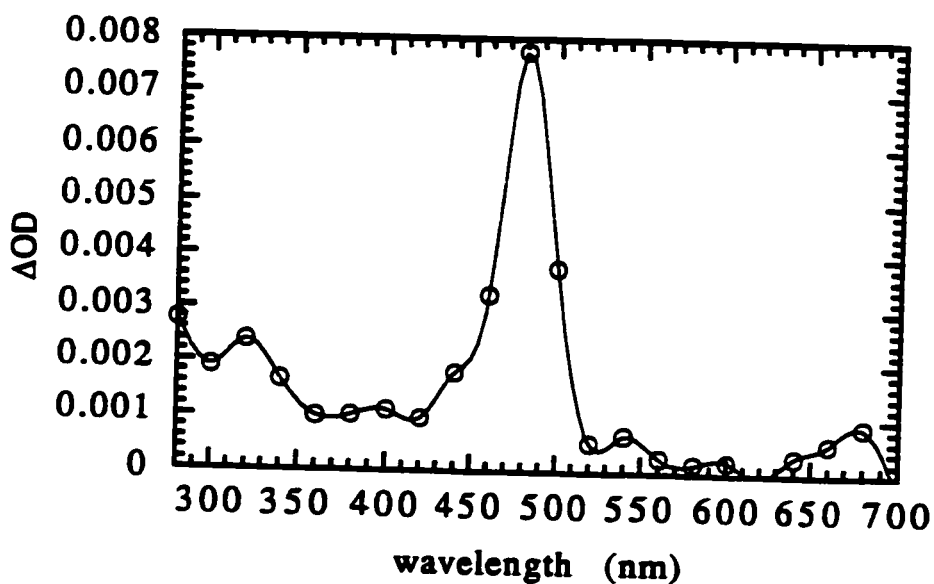


Figure 5.23.

Transient absorption spectra from 10 in TFE following 266 nm laser excitation; spectrum recorded 850 ns after the laser pulse

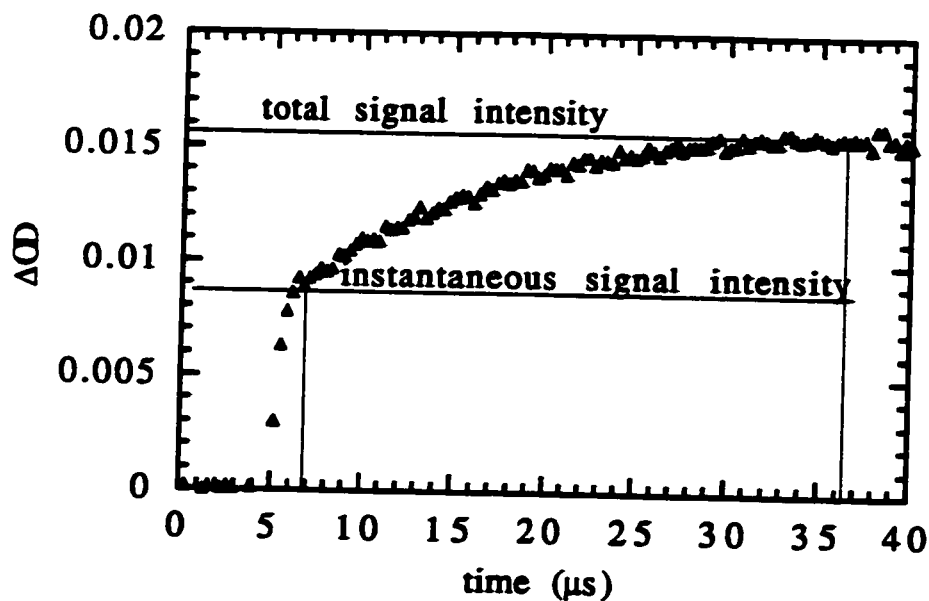


Figure 5.24.
Kinetic trace at 490 nm of 10 in TFE following 266 nm laser excitation, showing instantaneous and total signal intensities

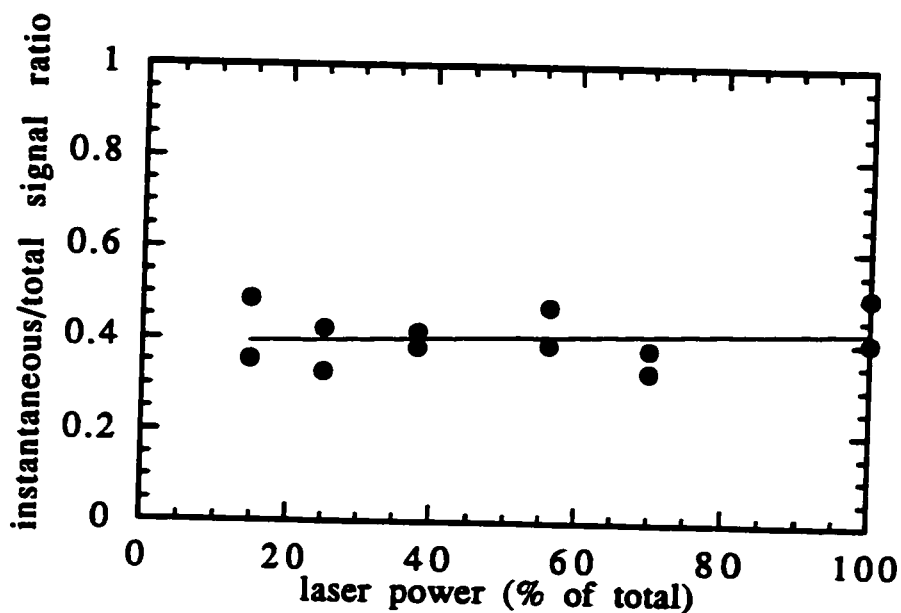


Figure 5.25.
Instantaneous/total signal intensity of 1,3-dichloro-1,3-diphenyl propane after irradiation with 266 nm laser light in TFE

The absorption at 490 nm decays with first order kinetics and has the same lifetime across the spectrum ($\tau=120 \mu\text{s}$, $k=8 \times 10^3 \text{ s}^{-1}$ at 25°C). This strong signal matched well that obtained for allyl cation in CH_2Cl_2 solution^{96,97} and in an acidic, zeolite matrix⁹⁸. This absorption was not quenched by oxygen which is consistent with its assignment to a carbocation (*vide infra*).

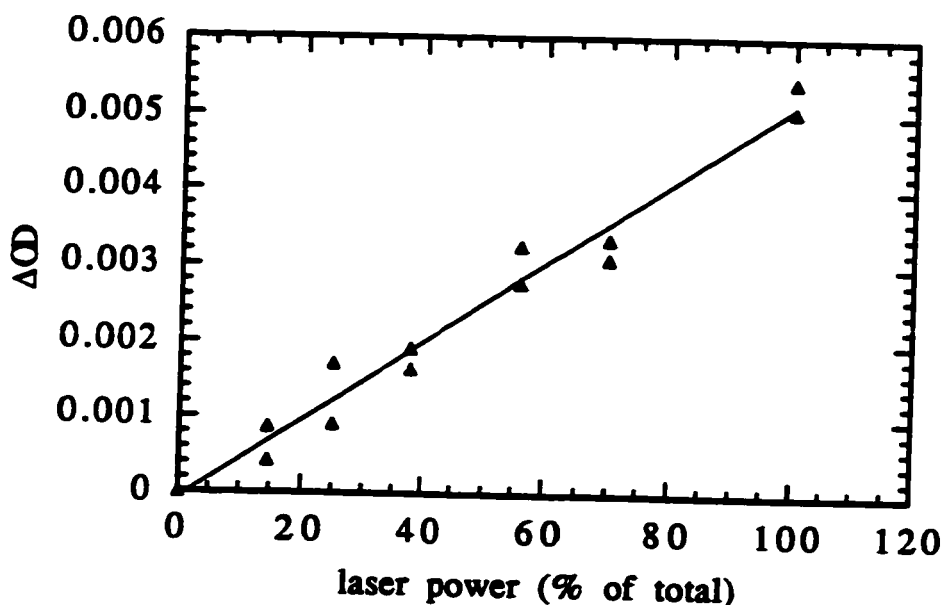


Figure 5.26.

Laser power dependence of the initial jump at 490 nm after irradiation of 1,3-dichloro-1,3-diphenylpropane in TFE by 266 nm laser light

The absorption spectrum and transient lifetime shows close resemblance with Kirmse's work who generated the carbocation via protonation of carbenes from methanol in TFE^{99,100}. However, the long lifetime could not be explained by the low nucleophilicity of TFE,

since related phenethyl cation has a lifetime of 2 μs in this solvent. Even more stabilized cations, such as the 4-methoxyphenethyl and 4-methylcumyl cations were shorter lived than 10 μs ^{101,102}.

We have also photolyzed 1,3-dichloro-1,3-diphenyl propane in acetonitrile. In this case, the allyl radical (λ_{max} 360 nm) along with the 490 nm carbocation signal was observed⁸⁵ (Figure 5.27.). The allyl radical probably arises from a competing photohomolysis. The kinetics of allyl cation formation were significantly different in acetonitrile compared to those in 2,2,2-trifluoroethanol. No resolved initial jump in absorbance was seen, and the growth of the signal occurred with a lifetime of 200 ns, which is a bit shorter than the lifetime reported in this solvent (Figure 5.28.)^{103,104}.

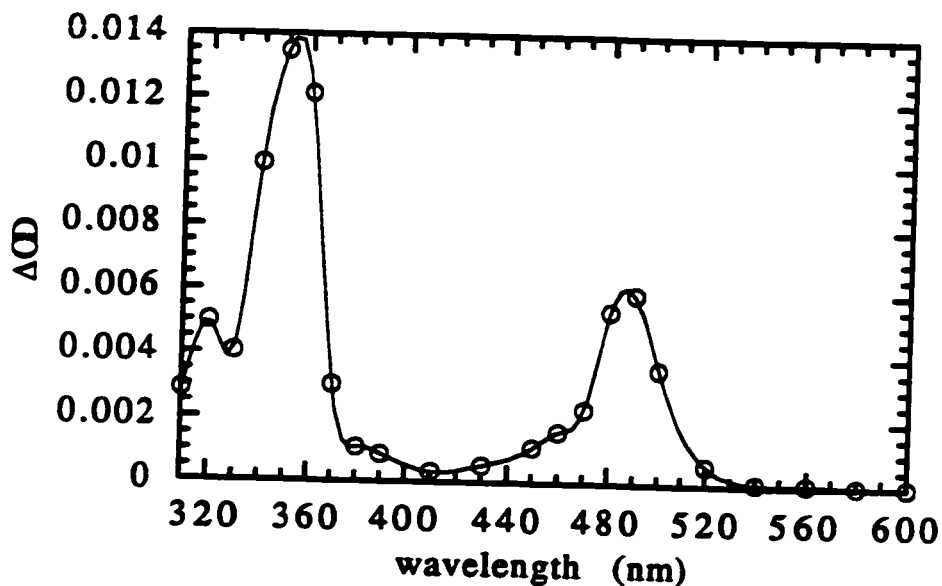


Figure 5.27.

Transient absorption spectra of 10 in acetonitrile following 266 nm laser excitation. Recorded 1.2 μs after the laser pulse

As an alternate source of the cation, a 0.5 mM deaerated solution of 3-chloro-1,3-diphenylpropene in TFE was prepared and irradiated at 266 nm. As expected, an instantaneous broad absorption at 490 nm appeared showing the formation of the allyl cation. Figure 5.29. shows a decay trace monitored at 490 nm.

Thus the following mechanism was suggested. Photolysis of 1,3-dichloro-1,3-diphenyl propane leads to the formation of 28a which may be in equilibrium with a hypervalent cation 28b (Figure 5.30.).

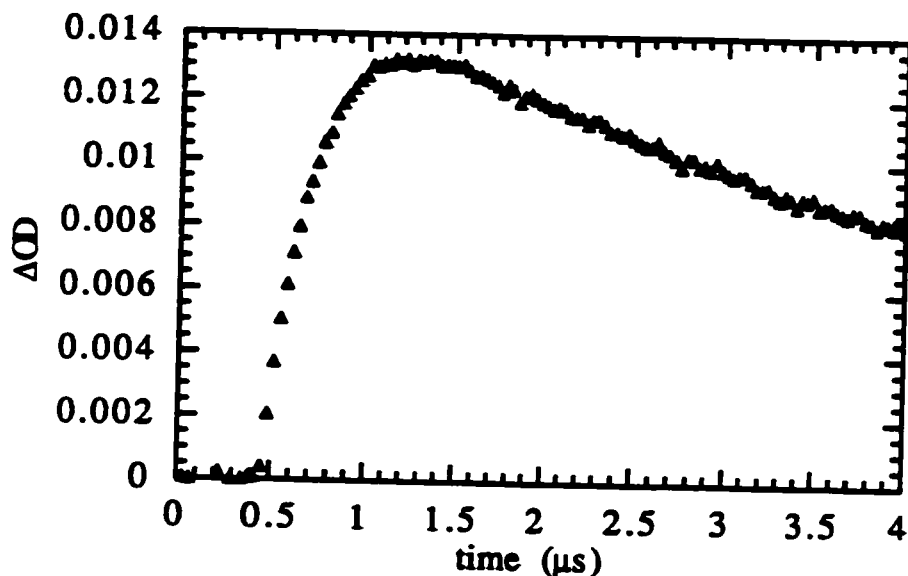


Figure 5.28.

Kinetic trace at 490 nm of 1,3-dichloro-1,3-diphenylpropane in acetonitrile after irradiation with 266 nm laser light

The vacant orbital of the cation **28a** may interact with a lone electron pair of the chlorine atom, causing it to bridge to the cation site. Three-, five- and six-membered halonium ions have been shown to be in equilibrium with open haloalkylcarbocations^{105,106}. ¹³C-NMR has been used to evaluate the equilibrium constant for several system¹⁰⁶, and MINDO/3 calculations have been used to predict halonium ion stabilities¹⁰⁵. At higher temperature the open carbonium ion becomes the dominant species. At the same time the presence of methyl substituents has also a considerable effect on the equilibrium constant, substantially stabilizing the cyclic halonium cations.

We conclude that the HCl loss probably occurs from the open carbonium ion, turning **28a** into **30**. This process corresponds to the instantaneous signal intensity. Depleting **28a** will cause a shift in equilibrium, and a slow transformation of **28b** to **28a** becomes the rate determining step for the slow growth of the 490 nm signal.

To better establish the character of **30** and **28** we examined their reactions with various molecules and ions. The bimolecular rate constant (k_{expt}) can be measured from the slope of plots of the experimental pseudo first order rate constants as a function of the quencher concentration. (Equation 5.1.)

$$k_{\text{expt}} = k_0 + k_q [Q]$$

Equation 5.1.

In this equation k_0 is the rate of the growth/decay in the absence of quencher and k_q is the rate constant for the reaction of the given molecule or ion for reaction with either 28 or 30.

The quenching rate constants are consistent with the assignment of the 490 nm transient and its precursor to carbenium ions. As expected, they show a large range of rate constant for reactions with azides, halides, sulfur, amines and alcohols. Azide, which is a well known cation quencher, reacts with 28 and 30 at a rate close to the diffusion controlled limit (*vide infra*).

Nucleophile	k_q (28) ($M^{-1}s^{-1}$)	k_q (30) ($M^{-1}s^{-1}$)
N_3^-	$4.8 \cdot 10^9$	$6.4 \cdot 10^9$
Cl^-	see text	$2.2 \cdot 10^8$
I^-	see text	$6.7 \cdot 10^9$
MeOH	$6.6 \cdot 10^5$	$1.3 \cdot 10^5$
EtOH	$1.7 \cdot 10^5$	
$iPrOH$		$1.0 \cdot 10^5$
Pr_2S	$5.6 \cdot 10^9$	$5.5 \cdot 10^8$
CySH	$5.6 \cdot 10^9$	$6.8 \cdot 10^7$
CyNH ₂	$9.7 \cdot 10^7$	$6.8 \cdot 10^7$
Piperidine		$7.8 \cdot 10^7$
$(C_6H_{13})_3N$	$3.38 \cdot 10^8$	$1.2 \cdot 10^8$

Table 5.1.

Rate constant of quenching of 28 and 30 with different nucleophiles. Monitored at 490 nm, after excitation of 10 with 266 nm light in TFE.

The reaction of 30 is very fast with other anions also. In these cases, we observed the common ion rate depression. This phenomena

is a good evidence for the formation of free chloride ions, since increasing the concentration of halide ion in the solution favours a recombination process between the two ions formed in the initial photoheterolysis.

Reaction of 28 with halogen ions leads to a complex kinetic behavior (Figure 5.32.). The intensity of the initial jump does not change by addition of increasing amounts of halogen ions. Therefore, we assume that 28a (which is the less stabilized of the two 28 intermediates) undergoes a fast HCl loss, i.e., at least faster than the quenching rate would be, and forms 30 (Figure 5.32.). The other isomer 28b, however, can form 31. Similarly, a three-member transition state is well known in organic chemistry in halogen elimination reactions.

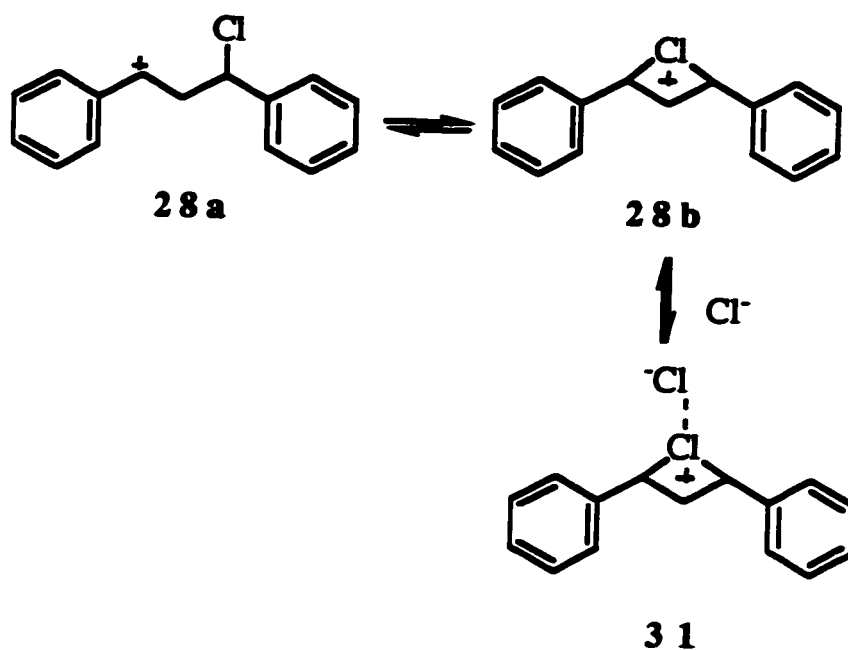


Figure 5.31.

Quenching of 28 by chloride ion

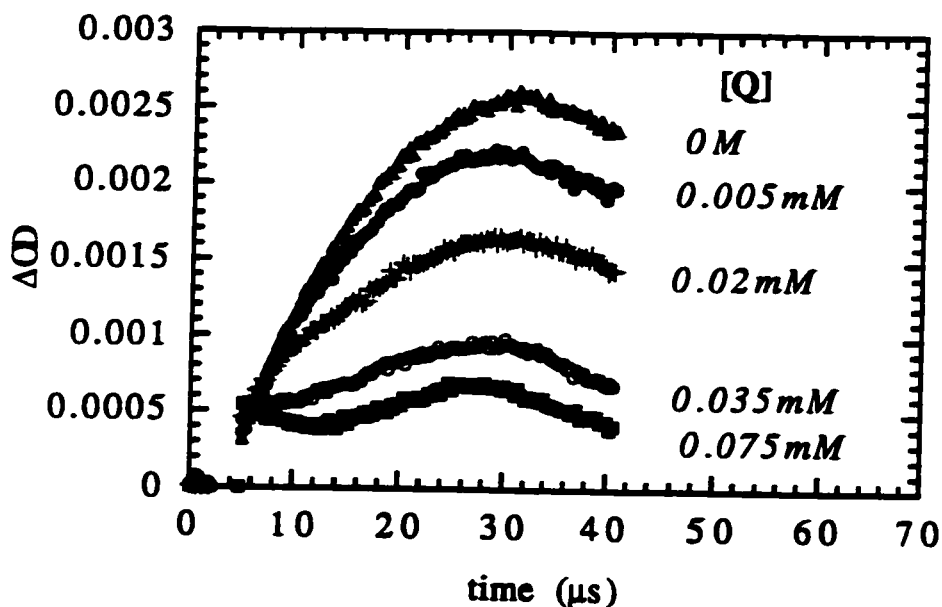


Figure 5.32.

Transient of 1,3-dichloro-1,3-diphenyl propane after irradiation (266 nm) monitored at 490 nm and its quenching with bromide

The quenching plots for the reaction of cation 30 with alcohols, though not linear, lead to rate constants in the range of $0.3\text{--}1.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ at low alcohol concentration, which are of the same order of magnitude as those reported for the Ph_2CH^+ cation by Kirmse and coworkers⁹⁹. The non linearity of these cases is due to the alcohol self-association in 2,2,2-trifluoroethanol. Similar effects are well established in the quenching of carbenes by alcohols¹⁰⁷. Along the alcohol series, methanol, 2-propanol, and 2-methyl-2-propanol, k_q is the highest for methanol, due to the fact that the availability of the lone pair in the nucleophile, while augmented by increasing methyl substitution, is counterbalanced by a parallel steric effect. The

extensive charge delocalization between C_1 and C_3 for this system could account for its lower reactivity compared to that of diarylmethyl.

Quenching of cation **28** with various alcohols also results in nonlinear quenching plots. The values of quenching are of the same order of magnitude as those for **30**. Since for the open form of **28** there is no significant charge delocalization, the smaller values (compared to those of diarylmethyl) could refer to the presence of the four-membered chloronium-cation, which effectively decreases the amount of free carbocation present and thus the rate of the reaction. The quenching constants for other nucleophile are between the value of diarylmethyl cation¹⁰⁷ and 1-methyl-1,3-diphenylpropenyl cation which suggests that the actual charge delocalization is somewhere between these two examples.

5.2.2.2. Effect of the second laser on the allyl cation

Cation **30** has two different possible stereoisomers with slightly different absorption maxima.

We examined the possibility of cation photoisomerization using two-color-two-laser experiment. After photolysis of **10** under air in TFE, a second laser was used to excite the cation at 490 nm, and a new absorption at 510 nm appeared (Figure 5.33.). The formation of this new species was more pronounced under air than under nitrogen. Further, in the UV region, the two spectra showed peaks at 320 nm under oxygen, and around 360 under nitrogen.

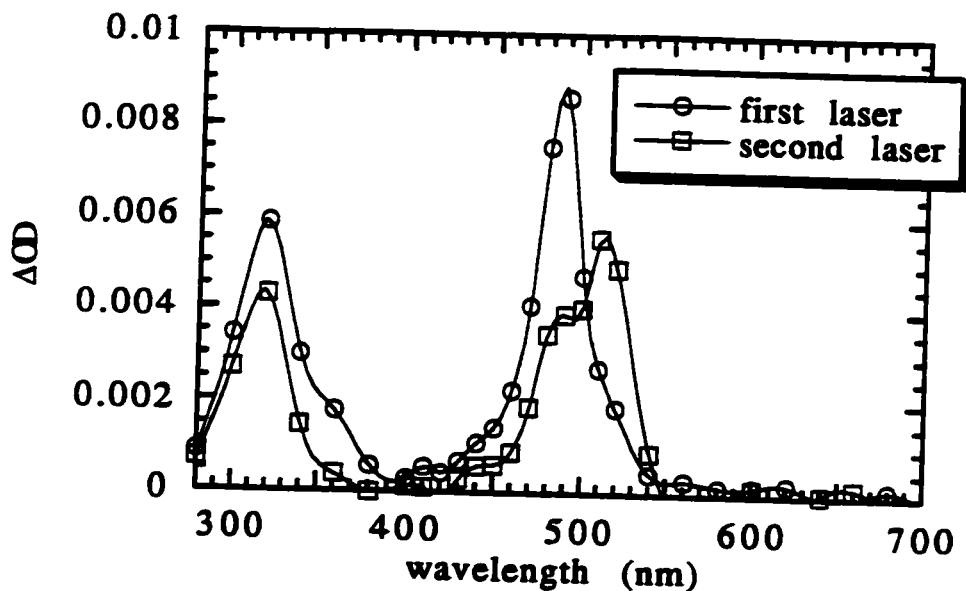


Figure 5.33.

Effect of second laser on transient spectrum of allyl cation 30. Irradiation of 10 with 266 nm laser and 490 nm dye laser in TFE

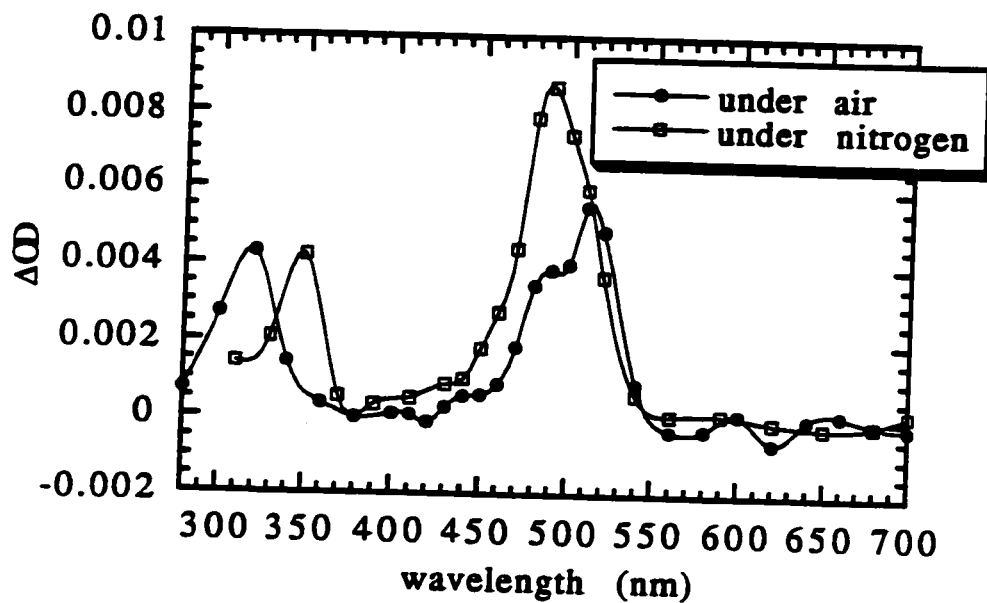


Figure 5.34.

Transient spectra in TFE following production 30 by 266 nm excitation and its photolysis with 490 nm pulses from a dye laser

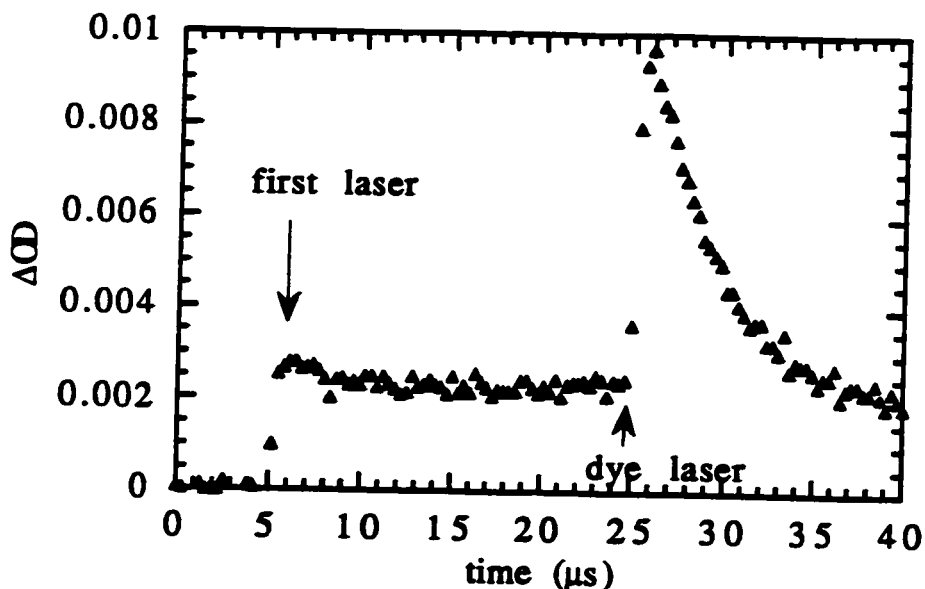


Figure 5.35.

Transient absorption at 510 nm following two laser excitation (266 nm and 490 nm) of **10** in TFE under air

Figure 5.35. shows the kinetic trace recorded at 510 nm. The transient formed upon irradiation with the second laser has a shorter half life than the allyl cation at 490 nm. The identity of this species is not firmly established, although it is tentatively assigned as a stereoisomer of **30**⁹⁹.

5.3. Discussion

The photochemistry of 1,3-dichloro-1,3-diphenylpropane has been studied in cyclohexane and in 2,2,2-trifluoroethanol. Excitation in these two solvents leads to two very different photochemical reaction pathways.

The products of the low-intensity irradiation were characterized in cyclohexane, and they showed the expected radical-derived products. The radical formed via homolytic cleavage of the C-Cl bond in 1,3-dichloro-1,3-diphenylpropane can participate in hydrogen abstraction from the solvent, or in a radical recombination with cyclohexyl radicals derived from the solvent (see Figure 5.9.). Cyclohexyl radicals form efficiently from the reaction between chlorine atoms and cyclohexane. The primary products (16,18) can further participate in the absorption of a second photon. The absorption of the second photon results in the cleavage of the second C-Cl bond, followed by hydrogen abstraction or radical recombination. The final products of the photolysis are the different radical derived products; some examples are 21, 22, 23.

Laser flash photolysis was used to study the kinetics of the photochemical reactions of 10. Using LFP, the transient spectra show the presence of the expected benzyl radical (320 nm) as well as allyl radical (360 nm). The identity of the 360 nm peak was confirmed by independent experiments using different starting materials. This allyl radical can be formed by (a) the cleavage of the two C-Cl bonds via two photon excitation or (b) by HCl elimination from the benzylic radical. Power dependance studies showed the dominance of the two photon pathway. Allylic radical 24 has a high stability due to resonance stabilization which involves the two phenyl rings as well. This stabilization results in a relatively long radical lifetime (10 μ s). The benzyl radical (320 nm) has a typical lifetime of 2-3 μ s.

Laser flash photolysis of 1 mM 1,3-dichloro-1,3-diphenyl propane in TFE gives rise initially to the 3-chloro-1,3-diphenylpropyl cation. Formation of this cation confirms that in TFE heterolytic cleavage of the C-Cl bond is favoured. Beside the benzylic cation, the allyl cation (which has an absorption at 490 nm) was also formed. However, as opposed to cyclohexane, the formation of the allyl radical occurs via thermal HCl elimination from the benzylic cation formed in the first step. Further, in the formation of the allyl cation, we can distinguish between a fast (instantaneous <20 ns) and a slow process, both of them monophotonic. The rise time (~ 20 μ s) of the slow process is longer than the lifetime of the benzylic cation, which suggests that there is an additional species involved in the formation of the allyl radical. We suggest that the benzyl cation is in equilibrium with a four membered cyclic hypervalent chloronium cation. The participation of this cyclic chloronium cation can explain the lack of biphotonic products in a fashion similar to the case of a recently reported hypervalent iodide radical⁹.

To further characterize the allylic cation and its precursor, we employed quenching experiments. However, since the benzylic precursor was not detected spectroscopically, we detected the changes in the lifetime of the growth of the allyl cation upon addition of the quencher. In a similar manner the effect of quencher on the decay is characteristic of the reactivity of the allyl cation itself. For the quenching studies several anions and nucleophiles were employed. Generally, quenching rate constants are comparable or slightly higher in the case of 28. Quenching rate constants reflect that the two

species are stabilized compared to a "pure" cation such as Ph_2CH^+ . This observation also proves that the precursor of 30 cannot be a typical benzylic cation.

Quenching rates increase by increasing the nucleophilicity of the heteroatom in the order $\text{O} < \text{N} < \text{S}$. However, in the alcohol series the increasing nucleophilicity is counterbalanced by the decreasing steric availability of the lone pair. With the azide anion, a diagnostic carbocation quencher, both cations are quenched at close to the diffusion controlled limit. Different halide ions were also used as quenchers. In the case of 30, using Cl^- , common ion repression was observed. Cation 28 showed complex chemical behaviour which may be explained by invoking the equilibrium between 28a and 28b. While 28a undergoes a fast quenching reaction, 28b is stabilized by increasing amounts of quencher anion. This stabilization acts as a kinetic barrier in reestablishing the equilibrium (after the disappearance of 28a), and results in retarded quenching.

High intensity irradiation was investigated in cyclohexane, and leads to the formation 1,3-diphenylallyl radical as well as the 1,3-biradical. Formation of this biradical was especially pronounced using laser drop photolysis, which is an efficient method to promote multiphotonic processes. This biradical has a short lifetime and therefore it is not quenched by oxygen. It leads to a different set of products, compared to the characteristic monophotonic decomposition, including diphenylcyclopropane.

We did not observe any multiphotonic processes in TFE. Irradiation of the allylic cation 30b with a second laser leads to the

formation of an intermediate with an absorption maximum at 510 nm. Similar transients was observed by Kirmse et al.²⁶, and it was tentatively attributed to the Z-isomer of the cation.

The results above reveal an unexpectedly complex behaviour of the 1,3-dichloro-1,3-diphenylpropane compared to the 1,5-dichloro analogue. Other members of this family of compounds are currently being investigated; they include 1,3-diiodo-1,3-diphenylpropane and 1,4-dihalo-1,4-diphenylbutanes.

5.3. Experimental section

2,2,2-Trifluoroethanol, ethanol, sodium azide, tricyclohexylamine, piperidine, cyclohexyl mercaptan, dipropylsulfide, cyclohexylamine and tetrabutyl ammonium chloride and bromide were from Aldrich. Solvents were spectral grade from BDH. 1,3-dichloro-1,3-diphenylpropane, 1-chloro-1,3-diphenylpropane, 1,3-diphenyl propene were supplied by Julia Perez-Prieto.

Detailed descriptions of the experimental techniques are given in Chapter 2.

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References

- (1) Badger, R. G. *The Romance of Paper*; The Gornham Press: Boston, 1933, p 88.
- (2) Sjöström, E. *Wood Chemistry, Fundamentals and Applications*; Academic Press Inc.: New York, 1981, p 223.
- (3) Freudenberg, K.; Neish, A. C. *Constitution and Biosynthesis of Lignin*; Springer-Verlag New York Inc.: 1968; Vol. 2, p 129.
- (4) Adler, E. In *150th meeting of the American Chemical Society*; American Chemical Society, Washington D.C.: Atlantic City, 1965; p vii.
- (5) Freudenberg, K. *Science* **1965**, *148*, 595.
- (6) Daubress, N.; Chupeau, Y.; Francesch, C.; Lapierre, C.; Pollet, B.; Rolando, C. *J. Chem. Soc. Chem. Com.* **1997**, 1489.
- (7) Lai, Y. Z.; Sarkanen, K. V. In *Lignins. Occurrence, formation, structure and reactions*; K. V. Sarkanen and C. H. Ludwig, Eds.; Wiley-Interscience: New York, .
- (8) Leary, G. J. *Tappi* **1968**, *51*, 257.
- (9) Leary, G. J. *Nature* **1968**, *217*, 672.
- (10) Lin, S. Y.; Kringstad, K. P. *Tappi* **1970**, *53*, 658.
- (11) Gierer, J.; Lin, S. Y. *Svensk Papperstidning* **1972**, *75*, 233.
- (12) Scaiano, J. C.; Netto-Ferreira, J. C.; Wintgens, V. J. *Photochem. Photobiol. A.: Chem.* **1991**, *59*, 265.
- (13) Castellan, A.; Girard, P.; Vanucci, C. J. *Wood Chem. Techn.* **1988**, *8*, 73.
- (14) Castellan, A.; Nourmamode, A.; Jaeger, C.; Forsskåhl *Nordic Pulp and Paper Research Journal* **1993**, 239.

- (15) Castellan, A.; Noumamode, A.; Colombo, N.; Jaeger, C.; Noutary, C.; Zhu, J. H. In *6th Int. Symp. Wood. Pulp. Chem.*; TAPPI Press: Melbourn, Australia, 1991; p 151.
- (16) The name "a-carbonyl" and "b-O-4" refer to the usual nomenclature used in lignin-chemistry referring to the phenyl ring as reference point.
- (17) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162.
- (18) Tylli, H.; Forsskühl, I.; Olkkonen, C. *J. Photochem. Photobiol. A.: Chem.* **1993**, *76*, 143.
- (19) Shkrob, I. A.; Depew, M. C.; Wan, J. K. S. *Chemical Intermediated* **1992**, *17*, 271.
- (20) Schmidt, J. A.; Berinstain, A. B.; de Rege, F.; Heitner, C.; Johnston, L. J.; Scaiano, J. C. *Can. J. Chem.* **1991**, *69*, 104.
- (21) Hurrell, L.; Johnston, L. J.; Mathivanan, N.; Vong, D. *Can. J. Chem.* **1993**, *71*, 1340.
- (22) Forsskühl, I.; Janson, J. In *6th Int. Symp. Wood Pulp chem.*; TAPPI Press: Melbourn, Australia, 1991; p 255-262.
- (23) Janson, J.; Forsskühl, I. *Nord. Pulp Pap. Res. J.* **1989**, *3*, 197.
- (24) Holmbom, B.; Sjöholm, R.; Åkerback, N. In *6th Int. Symp. Wood Pulp Chem.*; Melbourn, Australia, 1991; p 443.
- (25) Alder, E.; Magnusson, R. *Acta Chem. Scand.* **1959**, *13*, 505.
- (26) Argyropoulos, D. S.; Heitner, C.; Morin, F. G. *Holzforschung* **1992**, *46*, 211.
- (27) Argyropoulos, D. S.; Heitner, C. "31P NMR spectroscopy in wood chemistry. Part IV. Solid state 31P NMR of trimethyl phosphite

- derivatives of chromophores and carboxylic acids present in mechanical pulps: a method for quantitative determination of ortho-quinones," Pulp and Paper Research Institute of Canada, 1992.
- (28) Olmstead, J. A.; Gray, D. G. *J. Photochem. Photobiol. A: Chem.* **1993**, *73*, 59.
- (29) Olmstead, J. A.; Zhu, J. H.; Gray, D. G. *Can. J. Chem.* **1995**, *73*, 1955.
- (30) Castellan, A.; Choudhury, H.; Davidson, R. S.; Grelier, S. J. *Photochem. Photobiol. A: Chem.* **1994**, *81*, 117.
- (31) Castellan, A.; Davidson, R. S. *J. Photochem. Photobiol. A: Chem.* **1994**, *78*, 275.
- (32) Castellan, A.; Choudhury, H.; Davidson, R. S.; Grelier, S. J. *Photochem. Photobiol. A: Chem.* **1994**, *81*, 123.
- (33) Zhu, J. H.; Olmstead, J. A.; Gray, D. G. *J. Wood Chem. Technol.* **1995**, submitted.
- (34) Scaiano, J. C.; Chen, C.; McGarry, P. F. *J. Photochem. Photobiol. A: Chem* **1991**, *62*, 75.
- (35) Wilkinson, F.; Willsher, C. J.; Casal, H. L.; Johnston, L. J.; Scaiano, J. C. *Can. J. Chem.* **1986**, *64*, 539.
- (36) Asmus, K. D.; Janata, E. In *Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*; J. Basendale and F. Busi, Eds.; Reidel Publishing: 1982; p 91.
- (37) Arnason, J. T.; Guérin, B.; Kraml, M. M.; Mehta, B.; Redmond, R. W.; Scaiano, J. C. *Photochem. Photobiol.* **1992**, *55*, 35.
- (38) Belt, S. T.; Scaiano, J. C.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1993**, *115*, 1921.

- (39) Banks, J. T.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 6409.
- (40) Konya, K.; Scaiano, J. C. *Chem. Mat.* **1994**, *6*, 2369.
- (41) Lakowitz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983, p 496.
- (42) Berenstein, A. Ph. D. Thesis, University of Ottawa, 1996.
- (43) *Practical Fluorescence*; 2nd, Revised and Expanded ed.; Guilbault, G. G., Ed.; Marcel Dekker, Inc.: New York, 1990, p 812.
- (44) Ramirez, F. *Pure Appl. Chem.* **1964**, *9*, 337.
- (45) Dong, D. C.; Winnik, M. A. *Can. J. Chem.* **1984**, *62*, 2560.
- (46) Kalyanasundaram, K.; Thomas, J. K. *JACS* **1977**, *99*, 2039.
- (47) Winnik, F. M.; Tamai, N.; Yonezawa, J.; Nishimura, Y.; Yamazaki, I. *J. Phys. Chem.* **1992**, *96*, 1967.
- (48) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 675.
- (49) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.
- (50) Zhu, J. H.; Gray, D. G. *J. Photochem. Photobiol. A: Chem.* **1993**, *73*, 67.
- (51) Breitmaier, E.; Voelter, W. *Carbon-13 NMR spectroscopy*; third, completely revised ed.; VCH: Weinheim, 1989, p 515.
- (52) Argyropoulos, D. S.; Heitner, C.; Schmidt, J. A. "Observation of Quinonoid Groups During the Light-Induced Yellowing of Softwood Mechanical Pulp," Pulp and Paper Research Institute of Canada, 1994.
- (53) Shenbor, M. I.; Cheban, G. A. *Zh. Org. Kim.* **1969**, *5*, 143.
- (54) Kortüm, G.; Braun, W.; Herzog, G. *Ang. Chem. internat. Edit.* **1963**, *2*, 333.
- (55) Vo-Dinh, T. *Anal. Chem.* **1978**, *50*, 396.

- (56) Lloyd, J. F. B.; Evett, I. W. *Anal. Chem.* **1977**, *49*, 1710.
- (57) Lianos, P.; Lux, B.; Gerard, D. *J. Chim. Phys.* **1980**, *77*, 908.
- (58) Eisenbraun, E. J.; Hinman, C. W.; Springer, J. M.; Burnham, J. W.; Chou, T. S.; Flanagan, P. W.; Hamming, M. C. *J. Org. Chem.* **1971**, *36*, 2480.
- (59) Heitner, C.; Scaiano, J. C.; Editors *Photochemistry of Lignocellulosic Materials*; American Chemical Society: Washington, 1993; Vol. 531.
- (60) Leary, G. J. *J. Pulp Paper Sci.* **1994**, *20*, J154.
- (61) Foti, M.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 9440.
- (62) Land, E. J.; Porter, G.; Strachan, E. *Trans. Far. Soc.* **1960**, *57*, 1885.
- (63) Johnston, L. J.; Mathivanan, N.; Negri, F.; Siebrand, W.; Zerbetto, F. *Can. J. Chem.* **1993**, *71*, 1655.
- (64) Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 563.
- (65) Neumann, M. G.; Machado, A. E. H. *J. Photochem. Photobiol.* **1989**, *3*, 473.
- (66) Jovanovic, S. V.; Konya, K.; Scaiano, J. C. *Can. J. Chem.* **1995**, *73*, 1803.
- (67) Kimura, F.; Kimura, T.; Gray, D. G. *Holzforshung* **1992**, *46*, 529.
- (68) Kónya, K. G.; Scaiano, J. C. *Chem. Mater.* **1994**, *6*, 2369.
- (69) Wan, J. K. S.; Depew, M. C. *Res. Chem. Intermed.* **1996**, *22*, 241.
- (70) Vecera, M.; Gasparic, J. *Detection and identification of organic compounds*; Plenum Press: New York, 1971.

- (71) Berinstain, A. B.; Whittlesey, M. K.; Scaiano, J. C. In *Photochemistry of Lignocellulosic Materials*; C. Heitner and J. C. Scaiano, Eds.; American Chemical Society: Washington, 1993; Vol. ACS Symp. Ser. no. 531; p 111.
- (72) Vanucci, C.; Fournier de Violet, P.; Bouas-Laurent, H.; Castellan, A. *J. Photochem. Photobiol., A: Chem.* **1988**, *41*, 251.
- (73) Schmidt, J. A.; Goldsmidt, E.; Heitner, C.; Scaiano, J. C.; Berinstain, A. B.; Johnston, L. J. In *Photochemistry of Lignocellulosic Materials*; C. Heitner and J. C. Scaiano, Eds.; American Chemical Society: Washington, 1993; Vol. ACS Symp. Ser. no. 531; p 122.
- (74) Scaiano, J. C.; Berinstain, A. B.; Whittlesey, M. K.; Malenfant, P. R. L.; Bensimon, C. *Chem. Mater.* **1993**, *5*, 700.
- (75) Weir, N. A., personal communication.
- (76) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670.
- (77) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18.
- (78) Butcher, J. A.; Hinz, H. R.; Tsou, N.; Shah, S. *Tetrahedron Lett.* **1984**, *25*, 5483.
- (79) Hannemann, K.; Wirz, J. *Angew. Chem. Int. Ed. Eng.* **1988**, *27*, 853.
- (80) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177.
- (81) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084.
- (82) Weldon, D.; Barra, M.; Sinta, R.; Scaiano, J. C. *J. Org. Chem.* **1995**, *60*, 3921.
- (83) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* **1992**, *33*, 5359.
- (84) Adam, W.; Ouchi, A. *Tetrahedron Lett.* **1992**, *33*, 1875.

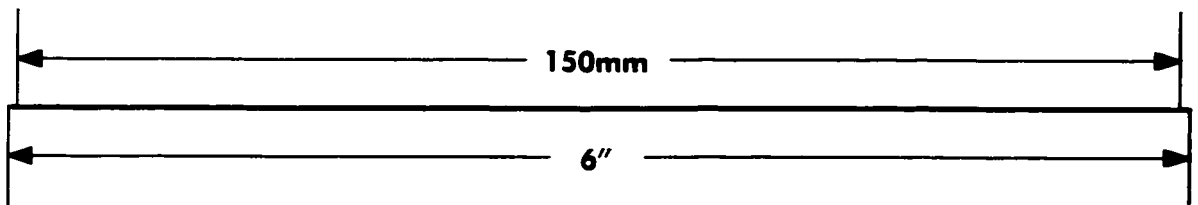
- (85) Pérez-Prieto, J.; Miranda, M. A.; Garcia, H.; Konya, K.; Scaiano, J. *C. J. Org. Chem.* **1996**, *61*, 3773.
- (86) Banks, J. T.; Garcia, H.; Miranda, M. A.; Perez-Prieto, J.; Scaiano, J. *C. J. Am. Chem. Soc.* **1995**, *117*, 5049.
- (87) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917.
- (88) Chateaufneuf, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1437.
- (89) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.
- (90) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.
- (91) Carsky, P.; Zahradnik, R. J. *J. Phys. Chem.* **1970**, *74*, 1249.
- (92) Chatgililoglu, C. In *Handbook of Organic Photochemistry*; J. C. Scaiano, Ed.; CRC Press: Boca Raton, Florida, 1989; Vol. II; pp 3.
- (93) Boche, G.; Schneider, D. R. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 869.
- (94) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549.
- (95) Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797.
- (96) Olah, G. A.; Spear, R. J.; McClelland, R. A.; Novak, M. J. *J. Am. Chem. Soc.* **1994**, *97*, 1539.
- (97) Sonderrmann, J.; Kuhn, H. *Chem. Ber.* **1966**, *99*, 2491.
- (98) Cano, M. L.; Fornes, V.; Garcia, H.; Miranda, M. A.; Pérez-Prieto, J.,

- (99) Kirmse, W.; Strehlke, I. K.; Steenken, S. *J. Am. Chem. Soc.* **1995**, *117*, 7007.
- (100) Kirmse, W.; Krzossa, B.; Steenken, S. *Tet. Lett.* **1996**, *37*, 1197.
- (101) McClelland, R. A.; Chan, C.; Cozens, F. L.; Modro, A.; Steenken, S. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1337.
- (102) McClelland, R. A.; Cozens, F. L.; Steenken, S.; Amyes, T. L.; Richard, J. P. *J. Chem. Soc. Perkin Trans.* **1993**, *2*, 1717.
- (103) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1991**, *112*, 6918.
- (104) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918.
- (105) Beatty, S. D.; Worley, S. D.; McManus, S. P. *J. Am. Chem. Soc.* **1978**, *100*, 4254.
- (106) Henrichs, P. M.; Peterson, P. E. *J. Am. Chem. Soc.* **1973**, *95*, 7449.
- (107) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 1913.

Claims to Original Research

1. *Development of fluorescence probes to detect ortho-quinone as a product of the photodegradation of high-yield pulp.* By utilization of pyrene as a fluorescent probe, it is possible to detect ortho-quinones as a product of the photodegradation of lignin. Our study shows that photodegradation occurs mainly in fines and broken fibers. Examination of excimer fluorescence shows that the photodegradation occurs in domains, with quinone moieties produced in close proximity.
2. *Observation of multiphoton processes leading to formation of ortho-quinones from phenols.* This is the first time that ortho-quinones were detected forming upon high-intensity irradiation of 2-methoxyphenols. Our detection technique enables us to detect fluorescence of derivatized ortho-quinones as well as to determine the relative amount product formed. We found that this multiphoton process has very low quantum yield. A similar process may account for quinone formation in pulp and paper, where the long lifetime of the phenoxy radicals would make high intensity unnecessary.
3. *Description of photochemistry of 1,3-dichloro-1,3-diphenylpropane.* In apolar solvents high intensity irradiation leads to the formation of the 1,3-diphenylallyl radical, and a characteristic set of products resulting from the excitation of the two carbon-halogen bonds. In polar solvents only monophotonic processes were observed. This is the first time that the corresponding allyl cation, which forms by spontaneous dehydrochlorination of the benzyl

radical, is described and characterized using different quenchers in solution.



A collection of various optical illusion patterns, including numbers and letters that appear to be 3D or distorted when viewed from different angles.