

THE UNIVERSITY OF LEICESTER

DEPARTMENT OF CHEMISTRY

***Some Photoinitiated
Polymerisations and
Related Reactions***

BY

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A thesis submitted for the degree of Doctor of Philosophy
in the Faculty of Science of the University of Leicester.

(1981)

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ACKNOWLEDGEMENTS

I would like to record my gratitude to my Supervisor, Professor R S Davidson for his tuition, encouragement and enthusiasm at all stages of the Project. I am indebted to Dr G Kemp for many illuminating comments and the proof reading of the script. I am grateful to Dr R Holman and Dr E Cawkill for helpful discussions. I thank my colleagues and the technical staff of the laboratories in which I have worked - in particular Mr J Abrahams and Mr C Whitehead for technical assistance. I would like to thank Ms M Pollock for the typing and Mr R J Pooley for the diagrams contained in this Thesis. I am indebted to SRC and Fishburn Printing Ink Co for the provision of a grant.

TO MY PARENTS

STATEMENT

The experiment work in this Thesis has been carried out by the author in the laboratories of the Chemistry Department of the University of Leicester, between October 1977 and September 1979; the Department of Chemistry of the City University between October 1979 and September 1980 and the Research Laboratory of Fishburn Printing Ink Co Ltd., Watford. This work has not been presented and is not being presented for any other degree.

JW Good

8.4.81.

University of Leicester.

Some of this work has been previously published, as follows:

Photoinduced homolysis of aryl halides - Tetrahedron Letters
2911, (1980).

Mechanistic aspects of the triethylamine assisted photo-induced
dehalogenation of halogeno-aromatic compounds. 163 (1981) *Ibid.*

ABSTRACT

A description of the absorption of light by organic molecules and the ways by which the energy gained can be lost by the excited compounds has been presented. The Stern-Volmer equation has also been described.

Free radical photoinitiation of polymerisation has been reviewed. An investigation has been carried out of ketone / amine photoinitiation of polymerisation of thin film and bulk polymerisations of acrylate esters. The photoreduction and photooxygenation of the amines used in the polymerisations, α - ω -dimorpholinoalkanes α - ω -N,N,N,N-tetraethyldiaminoalkanes and others have been carried out in an attempt to rationalise the observations made in the polymerisation experiments.

The dehalogenation of aryl halides has been described. The photolysis of ω -(4-halophenoxy)alkyl bromides and ω -phenoxyalkyl halides has been carried out and evidence presented for the nature of the excited state responsible for reaction. Criteria for the intervention of radical ions in the photoreactions of aromatic halides with triethylamine have been given and where appropriate evidence for the intermediacy of such species has been presented. The photo-Claisen rearrangement has been studied and the effect of hydrogen bromide on the reaction investigated.

The photoinitiation of cationic polymerisation by sulphonium and iodonium salts has been reviewed and a study carried out of thin film polymerisations in printing inks. The photochemistry of triaryl-sulphonium, thioxanthylum and diaryliodonium salts in methanol have been examined and a mechanism proposed for the decomposition. The photosensitization of photoinitiated cationic polymerisation has been investigated and Stern-Volmer plots recorded of the quenching of their fluorescence by cationic photoinitiators carried out.

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Chapter 1.

Introduction

GENERAL INTRODUCTION

For most organic molecules there are four types of electronic excitation $\sigma \rightarrow \sigma^*$; $n \rightarrow \sigma^*$; $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The different excitations require different amounts of energy. In general a $\sigma \rightarrow \sigma^*$ transition needs more energy than a $n \rightarrow \pi^*$ excitation and thus light of a shorter wavelength. The photochemistry of organic compounds is normally associated with the excitation from $\pi \rightarrow \pi^*$ and from $n \rightarrow \pi^*$. Since carbonyl compounds have a molecular orbital description $(\sigma_{co})^2 (\pi_{co})^2 (n_o \uparrow \downarrow)^2$ they exhibit the two forms of excitation, $\pi \rightarrow \pi^*$ and at longer wavelength $n \rightarrow \pi^*$. This can be seen in the ultra-violet absorption spectrum of diarylketones, there is a $\pi \rightarrow \pi^*$ excitation involving the aromatic π system and an $n \rightarrow \pi^*$ excitation involving the non-bonding electrons on oxygen. The participation of non-bonding electrons in electronic excitations of carbonyl compounds was first proposed by Mulliken¹. The absorption process and resultant electronic transitions have been previously reviewed².

Promotion of a molecule to an excited state occurs when a molecule absorbs a quantum of light in accordance with the Franck-Condon principle. The transition of the electron results in an excited singlet state containing an excess of vibrational energy.

In the liquid phase the excess of vibrational energy is rapidly transferred to the environment, leaving an excited singlet state in the lowest vibrational level. Most promotions are to the first excited singlet state (S_1) but promotions to the second and higher excited singlet states can occur, these however usually drop very rapidly (about 10^{-12} seconds) to the S_1 state. The loss of energy from this state can occur in many ways.

Internal Conversion

A radiationless transition to the ground state is possible. This effect, called internal conversion, can lead to ground states of sufficient vibrational energy to undergo chemical reaction³. This internal conversion process, because of its comparative slowness, is not of major importance in most molecules⁴.

Fluorescence

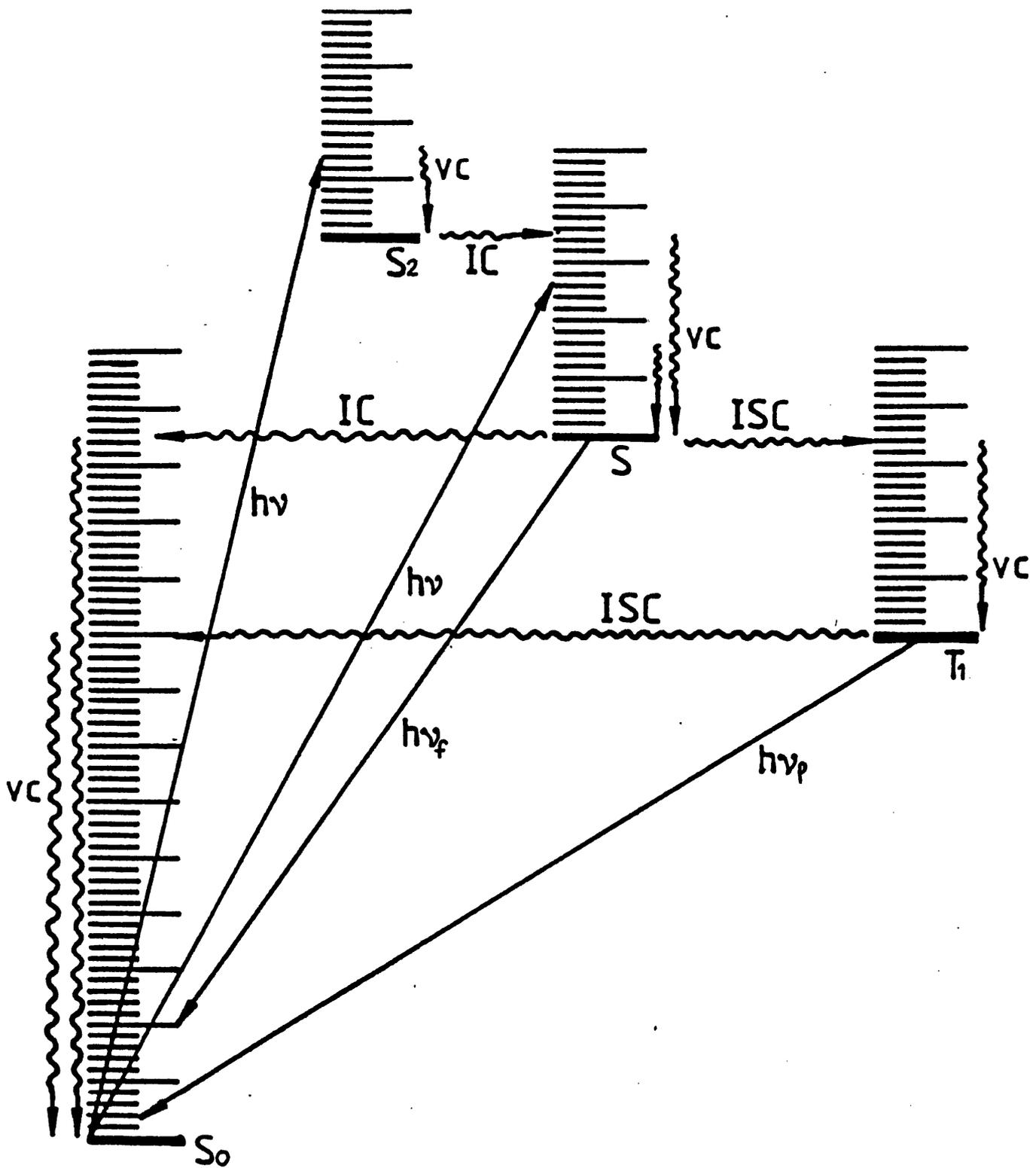
The excited singlet state can lose energy in dropping to a low vibrational ground state by the emission of light. This emission, and that between states of like multiplicity is called fluorescence. Examination of the fluorescence spectrum can provide information about the energy and the lifetime of the first excited singlet state⁵. Fluorescence has also been observed from the second excited singlet state to the ground state⁶.

Intersystem Crossing

Another process which the excited singlet state can undergo is the 'forbidden' spin inversion of an unpaired electron to give the first excited triplet state, this is known as intersystem crossing. Measurement of the quantum yield of intersystem crossing has been developed by Lamola & Hammond⁷. In an analogous manner to the excited singlet state, the triplet state is vibrationally excited and can lose its excess of energy and return to the ground state by a radiative or non-radiative process. A molecule in the first triplet state (T_1) may return to the ground state (S_0) by giving up light, this is termed phosphorescence.

The process is slow ($\sim 10^{-3} - 10^1$ seconds) because the transition is spin forbidden. As a consequence of the greater lifetime of the triplet state compared with the singlet state the former is more likely to undergo chemical reactions when there is a high quantum yield of intersystem crossing. The triplet state has been studied by several methods⁸, and has been the subject of a number of reviews^{9, 10}.

These processes can be illustrated by a Jablonski diagram (scheme 1). Radiative processes are shown by straight lines and internal conversion processes or non-radiative processes by wavy lines.



Key:-

I.C. = internal conversion; I.S.C. = intersystem crossing

vc = vibrational cascade; $h\nu_f$ = fluorescence;

$h\nu_p$ = phosphorescence.

QUENCHING PROCESSES

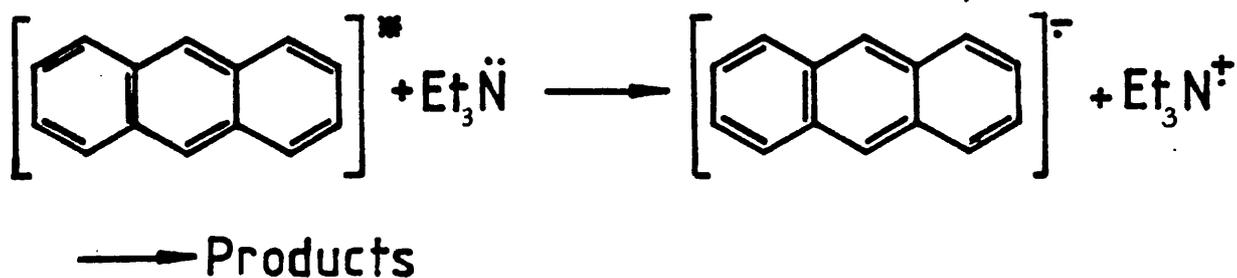
When a substance accelerates the decay of an electronic excited state to the ground state, or an excited state of lower electronic energy, the process is described as quenching. This phenomenon can be observed as a reduction of the quantum yield of light emission.

There are several mechanisms by which quenching can occur, these can be induced by many different compounds. Quenching processes seem to be collisional in most cases and as such are subject to the spin - conservation rules. The entity in which the quenching occurs is an encounter complex or an excimer/exciplex, the difference between these being the distance separating the components. An encounter complex tends to have more random relative orientations and the elements are separated by more than $\sim 7\text{\AA}$, a significant overlap of the orbitals being the only requirement. Excimers are formed by the association of both ground and excited states of the same species. Exciplexes are produced by the association of two different species, one ground state, the other in an excited state. These excited species occupy energy minima in the excited state and, therefore, possess definite geometries.

Quenching by a different chemical species can occur by three different paths, by electron transfer, by heavy atom effects and by energy transfer.

Electron transfer quenching can be observed in an exciplex formed between an aromatic hydrocarbon and an amine causing a shift to the red and a diminution in intensity of the emission spectrum becoming zero in solvents of high dielectric constant¹¹. Flash photolysis

experiments show the generation of an amine radical cation and a hydrocarbon radical anion as a transient suggesting total electron transfer from the amine to the hydrocarbon. An example of this is in the irradiation of anthracene with triethylamine in acetonitrile¹². (Scheme 2).



The products being 9, 10 dihydroanthracene, tetrahydroanthracene and aminated anthracene. The results indicate that electron transfer is a primary process, the simplest hypothesis is that in polar solvents the exciplex dissociates into solvated ions.



Strong evidence for electron transfer quenching is found in the quenching of aromatic hydrocarbons by quadricyclane, it has been shown that the quenching cannot be attributed to energy transfer or chemical quenching¹³.

Heavy Atom Effect

Fluorescence can be quenched by compounds containing heavy atoms. This appears to occur by formation of a singlet exciplex which undergoes enhanced intersystem crossing to the triplet exciplex due to the heavy atom effect, followed by dissociation to its

components. Evidence in support of the phenomenon has been provided by the quenching of aromatic hydrocarbons by xenon¹⁴.

The excited states of many organic molecules can be quenched by oxygen¹⁵. The process can occur from both triplet and singlet states and is diffusion-controlled. In the singlet state the process seems to depend on enhanced intersystem crossing, the triplet state could be quenched by a similar process to the ground state or by the generation of singlet oxygen via triplet energy transfer.

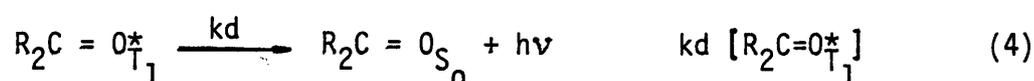
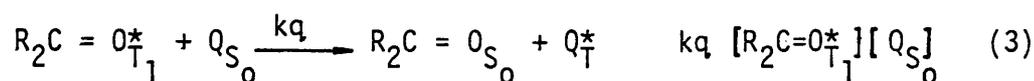
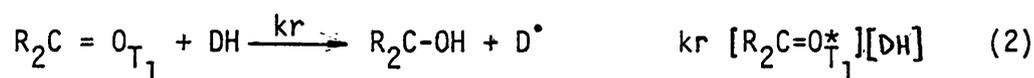
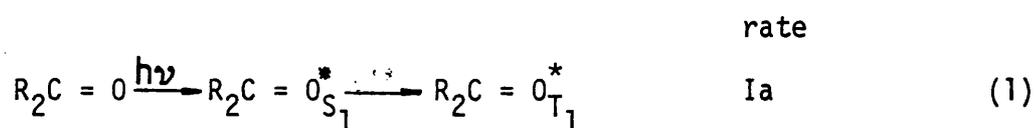
Sensitization

An important type of deactivation involves the direct transfer of electronic energy selectively to the acceptor. Whilst the excited donor molecule is collapsing to its ground state, the acceptor molecule is promoted to an excited state. A commonly cited example of this is the deactivation of benzophenone by naphthalene using flash photolysis¹⁶. The light flashed so that it was only absorbed by benzophenone resulted in an absorption spectrum characteristic of triplet naphthalene. Examination of the relative energy levels show that the transfer occurred between the triplet states since the excited singlet state of naphthalene is of higher energy than the benzophenone first excited singlet state. Transfer from singlet benzophenone to triplet naphthalene can be discounted as it is spin-forbidden.

Ketchum and Moore¹⁷ studied the variation in quantum yield of benzophenone disappearance when its reduction by benzhydrol was quenched by different concentrations of naphthalene. They obtained a value for the ratio of $\frac{k_q}{k_r}$ of 455 (k_q is the bimolecular quenching rate constant and k_r is the bimolecular hydrogen abstraction rate) and concluded that the quenching was diffusion controlled.

Stern-Volmer Equation

The effect of quenchers on fluorescence or reaction has been studied and the relationship between quantum yield and quencher concentration is given by the Stern-Volmer equation. This can be illustrated by considering the photoreduction of a ketone.



(1) is the excitation step using light intensity I. The yield of triplets is a.

(2) is the hydrogen abstraction step with a rate constant k_r .

(3) is deactivation of the triplet ketone by the quencher (Q).

(4) is deactivation of the triplet ketone by other routes, eg. phosphorescence.

The rate of disappearance of the triplet ketone can be expressed as:

$$\frac{-d [R_2C = O_{T_1}^*]}{dt} = I_a - (kr [DH] + kq [Q] + kd) [R_2C = O_{T_1}^*]$$

under steady state conditions this becomes:

$$I_a = (kr [DH] + kq [Q] + kd) [R_2C = O_{T_1}^*]$$

The quantum yield for the disappearance of the ketone is given by:

$$\phi = \frac{kr [R_2C = O_{T_1}^*] [DH]}{I}$$

therefore
$$\frac{1}{\phi} = \frac{1}{a} + \frac{kd}{akr [DH]} + \frac{kq [Q]}{akr [DH]}$$

A plot of $1/\phi$ against $1/[DH]$ will give a straight line with an intercept of $1/a$ and a slope of k_d/akr . If the value of $[DH]$ is kept constant and $[Q]$ is varied, a plot of $1/\phi$ against $[Q]$ will give a straight line of slope

$$\frac{kq}{akr [DH]}$$

Because diffusion dominates bimolecular quenching processes in solution it is important to have a reliable method of estimation.

The following equation is most commonly used¹⁸.

$$R \text{ diff} = \frac{8RT}{2000\eta} \quad (1 \text{ mole}^{-1}\text{S}^{-1})$$

R is the gas constant, T is the temperature and η is the viscosity (in poise). Wagner and Kochevar¹⁹ proposed that in more viscous solvents triplet energy transfer is diffusion controlled but at lower viscosities the rate of transfer is lower than that for diffusion of the donor and acceptor, together.

Chapter 2.

***Free Radical
Photoinitiation of
Polymerisation***

INTRODUCTION

The interaction of U.V. light with organic molecules to produce radical fragments is well known²⁰. When certain photosensitive compounds are fragmented by light in the presence of vinyl monomers, a radical chain polymerisation results.

The use of photoinitiator systems for polymerisations are a relatively modern concept, originating on the discovery in the 1940's. that uranyl nitrate would catalyse the polymerisation of vinyl chloride in sunlight. Since that time a considerable amount of attention has been given to photopolymerisable resins and photoinitiators²¹.

The application of ultra violet light for polymerisation has found extensive use in many areas, including dentistry, wood varnishing²² and, in particular, the printing industry - in dry offset and lithographic printing. The U.V. initiated polymerisations or U.V. curing inks have been used widely on account of their many advantages over conventional inks. A brief list of these is shown in Table 1.

Table 1

1. Immediately dry print at the end of the press.
2. Improved environmental conditions for printing (no solvent).
3. Printing presses are cleaner and require less maintenance.
4. Reduction in waste.
5. Faster production.
6. Good resistance to rub.
7. Low odour and taint level.
8. Can print on non-absorbant surfaces such as tin foil and plastic.

9. Relatively thick films can be used.
10. Less space requirements for storage of printed material.

Printing inks are a blend of pigment, resin (oligomer), diluent (monomer) photoinitiator and minor additives such as waxes, plasticisers and wetting agents. The scope within each area is fairly wide and thus there is some latitude for variation in the properties of each ink.

Of the various components of inks, the photoinitiator, the resin and certain types of pigment, can affect the rate of polymerisation.

The most commonly-used white pigments are the two forms of titanium dioxide, anatase and rutile titanium dioxide. These oxides, however, strongly absorb ultraviolet light in the same region as that of many photoinitiators, thus some difficulty in polymerising such inks would be expected. However, the titanium dioxide scatters the light efficiently as well as absorbing it so there is little deceleration in the rate of initiation²³.

Acrylic acid esters are widely used in the printing industry as the resin because their rate of polymerisation is greater than other types of resin.

Photoinitiators.

Photoinitiators are the single most important factor determining the speed of cure in printing inks. In assessing photoinitiators two criteria have to be satisfied:

- i. The efficient absorption of ultra-violet light and production of polymerisation initiating species,
- ii. Polymerisation does not occur in the absence of light, ie good thermal stability.

The photoinitiation of radical polymerisation involves three stages:

- population of the chemically reactive excited state
- formation of initiator radicals
- and
- initiation of polymerisation by interaction of initiator radicals with reactive monomers and oligomers.

The overall efficiency of photoinitiation is the product of the efficiencies of each stage of these processes. Thus it is the product of the quantum yield of initiator radicals and the fraction of these which initiate polymerisation. The major processes in competition with this, which reduce the efficiency, is quenching by oxygen of monomer and initiator radicals.

Photoinitiators for radical polymerisation fall into three main categories, these are:

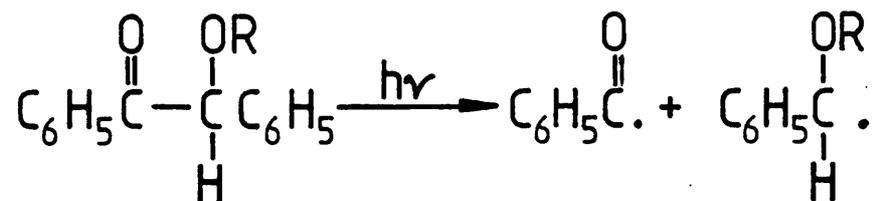
- a. Photoinitiation by homolytic fission from the excited state of the molecule.
- b. Photoinitiation by hydrogen abstraction from a donor molecule.
- c. Photoinitiation by electron transfer between the photoexcited initiator molecule and another component.

Photoinitiation by homolytic fission

Photoinitiation by homolytic fission is characteristic of several types of photoinitiators, the benzoin ethers, O-acylated α -oximino ketones, halogenated compounds and dialkoxyacetophenones.

Benzoin ethers were among the earliest patented initiators, they undergo a Norrish type I photocleavage to produce benzoyl and benzyl ether radicals²⁴

Scheme 3



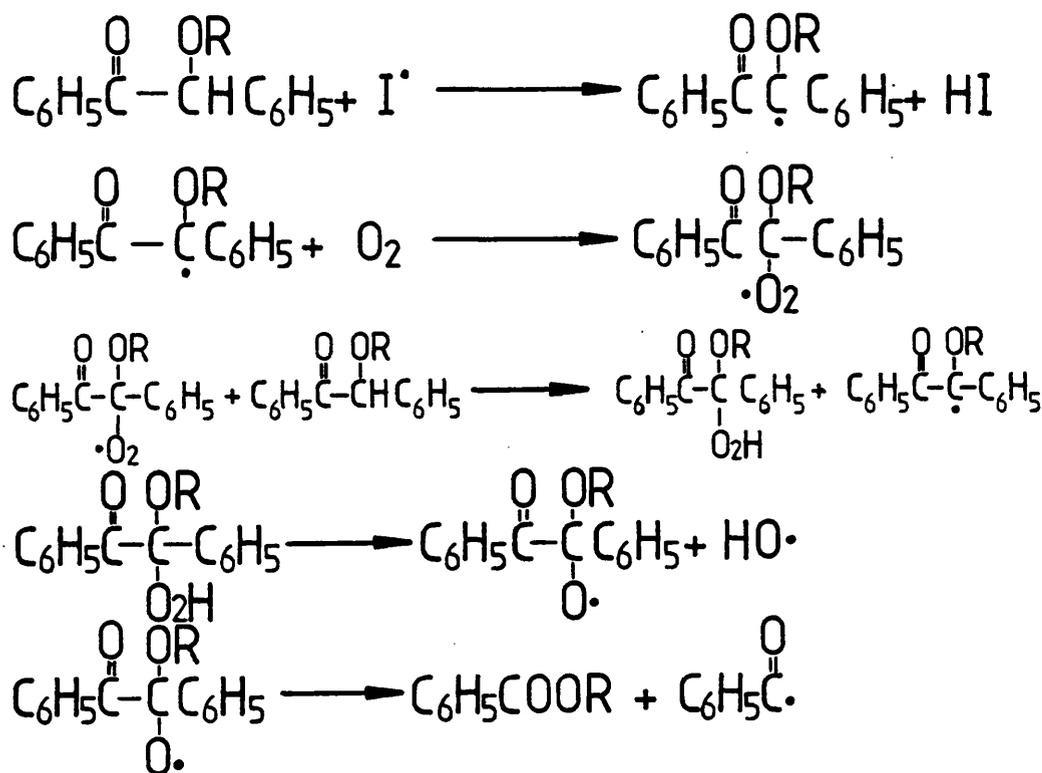
R=alkyl.

This mode of initiator radical production is supported by product identification and polymerisation studies²⁵ using C-14 labelled benzoin methyl ethers²⁶. The labelling study also showed that both radicals are equally effective in the polymerisation of acrylates and methacrylates. However, with styrene, there is evidence to suggest a greater reactivity for the benzoyl radical²⁷.

Experiments with triplet quenchers suggest that the reaction may occur from the excited singlet manifold²⁵, but other studies employing sensitization²⁴ suggest the triplet state is responsible. The energy needs of the system to allow bond dissociation is estimated to be $\sim 63 \text{ Kcal mole}^{-1}$, as the energy of the $n\pi^*$ triplet is about $73 \text{ Kcal mole}^{-1}$; this requirement is easily met.

A major advantage of benzoin ethers is the lack of quenching of photocleavage, this indicates a rate constant of greater than 10^{10} sec^{-1} along with a high quantum yield this leads to a relatively efficient initiator. The major disadvantage is the thermal instability of the systems benzoin itself decomposing in less than one day at 60°C ²⁷. A possible mechanism for this instability is radical initiated auto-oxidation²⁸ as shown in Scheme 4.

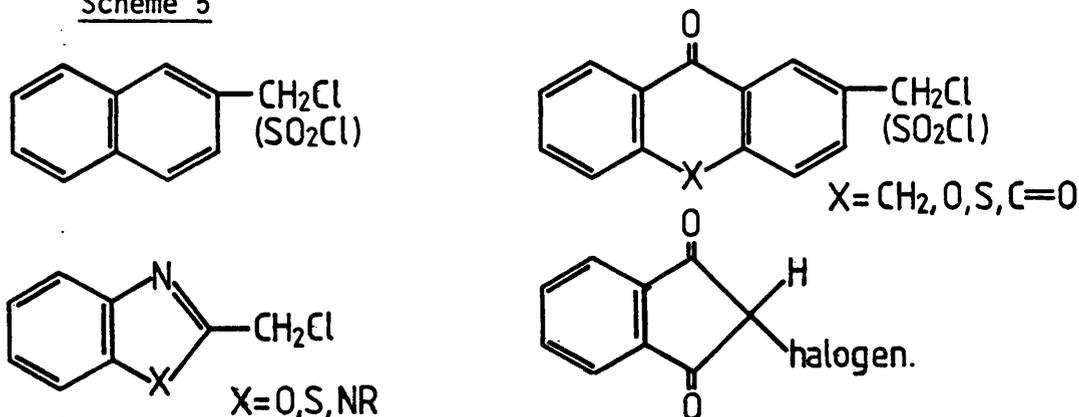
Scheme 4



Halogenated compounds

Various halogenated molecules have been reported to be photo-initiators for acrylate and styrene/unsaturated polyester coatings^{29,30,31}. Some examples are given below in Scheme 5.

Scheme 5

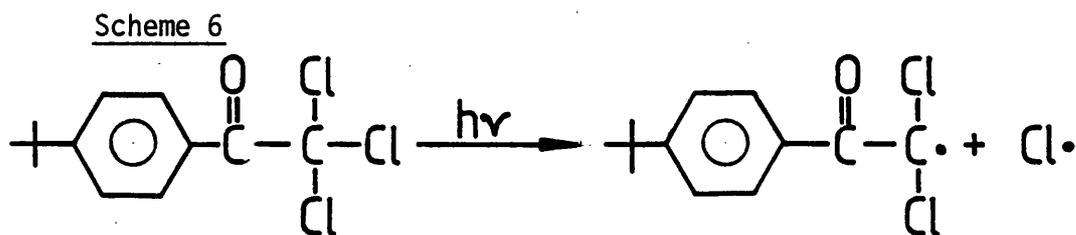


Modification of the aromatic groups leads to widely differing absorption spectra which can overcome absorption by pigments in the inks. The initiators enjoy the further advantage of ease of synthesis either by chloromethylation or chlorosulphonation of the parent ring system..

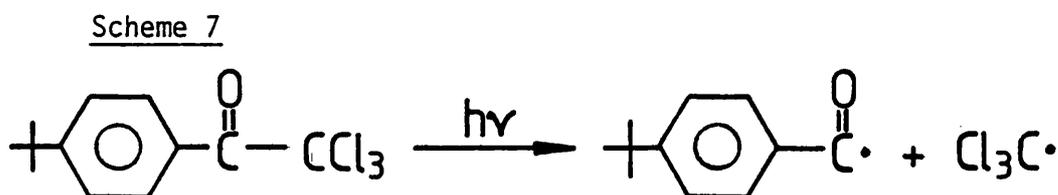
The probable mechanism for the formation of radicals is photocleavage of the C -Cl or S -Cl bond. (See Chapter 3).

The bond energies of the arylchloromethyl derivatives are about 60 - 70 kcal per mole, the values for bromomethyl and chlorosulphonyl groups about 10 kcal per mole lower³².

Trichloroacetophenones have also been used as initiators fragmenting on irradiation by β -cleavage as shown in Scheme 6.



Studies by chemically induced nuclear polarisation measurements showed an appreciable amount of cleavage by Norrish type I reactions as illustrated in Scheme 7.



The halogen initiators can also be sensitized using for example thioxanthone, this is especially useful for irradiations utilising light of wavelength $>360\text{nm}$.³³

The speed of cure can also be improved using amines²⁹. (See Chapter 3)

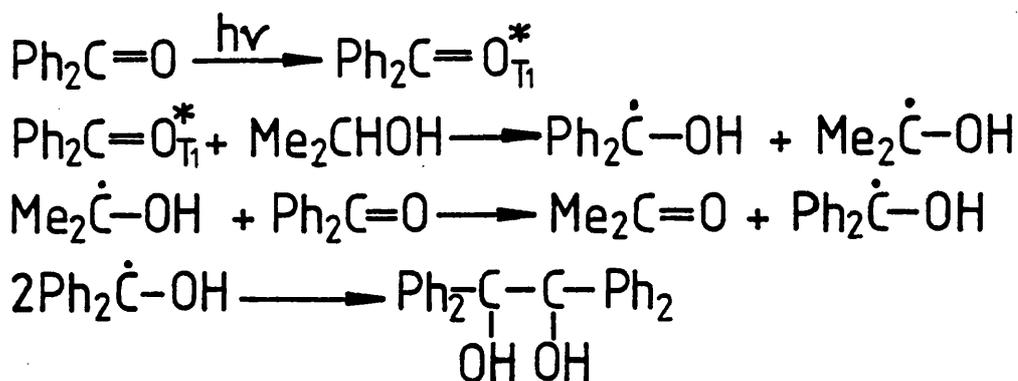
Photoinitiation by hydrogen abstraction

Benzophenone and its derivatives have found uses as initiators in vinyl polymerisations³⁴. The mechanism of the hydrogen abstraction

reactions has been extensively studied, much of the early work has been reviewed by Schonberg and Mustafa³⁵. It has been found that in addition to alcohols and amines, aliphatic and aromatic alkanes^{36,37,38}, ethers and thiols are efficient hydrogen donors to the excited carbonyl group.

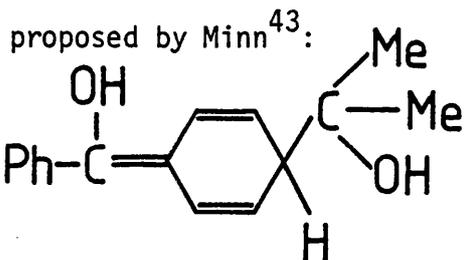
Evidence of Hammond and Moore³⁹ has shown that the triplet state was responsible for reaction. Further mechanistic studies in oxygen-free systems have been carried out by many groups of workers^{40 - 43}, identifying the intermediates involved. The quantum yield for photoreduction has been shown to approach 2⁴⁴. The reaction is generally considered to proceed via free radical intermediates according to the following Scheme - 8, for the photoreduction of benzophenone by isopropanol.

Scheme 8



The precise mechanism is still a matter of some controversy.

Weiner⁴⁵ has pointed out that the key coloured intermediate



A later study by the same group⁴⁹ found that the presence of increasing amounts of methyl methacrylate in the reaction mixture led to the conclusions that:

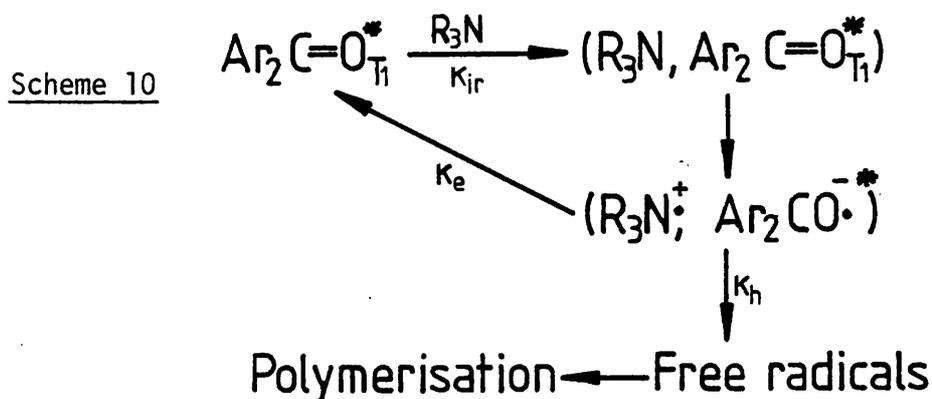
- i. the quantum yield for production of the primary radicals is not altered by concentration of methyl methacrylate, but the percentage of tetrahydrofuran radicals which react with methyl methacrylate increases with increasing proportion of the methyl methacrylate.
- ii. the proportion of primary radicals which combine to give an adduct remains constant, but the rate of primary radical formation decreases with increased methacrylate concentration because of the quenching action by methyl methacrylate on benzophenone triplets.

These conclusions would lead, in the first case, to an increase in the order of the reaction and, in the second case, to a decrease. It was found that the second conclusion was not true for certain benzophenone derivatives, thus efficiency of polymerisation could be influenced by whether the excited state of the ketone is quenched by the monomer, as well as the extent of chain termination by semi-pinacol radicals.

Initiation by electron transfer

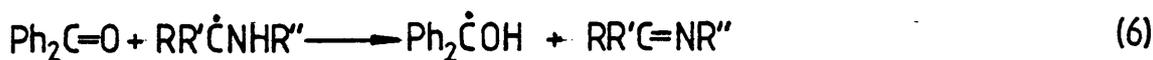
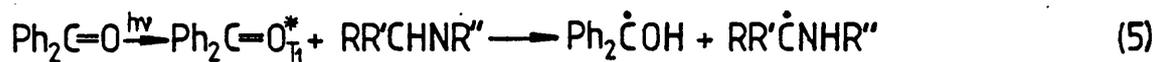
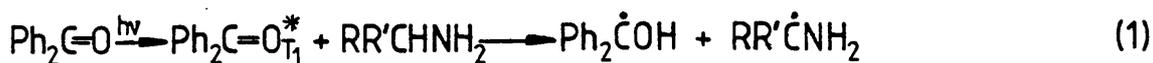
Aromatic carbonyl compounds can be efficiently reduced by a variety of electron donor molecules, especially amines. This reaction will occur from both the $n-\pi^*$ and the $\pi-\pi^*$ excited ketone. The marked difference between the photoreductivity of alcohols and amines is that, for alcohols the excited triplet carbonyl

attacks hydrogen on carbon α to the hydroxyl in preference to more distant hydrogen, and this abstraction is facilitated by electron donation by oxygen in a polar contribution to the transition state⁵⁰. Whilst the nitrogen of amines may behave similarly, reduction by amines appears to proceed by rapid initial interaction of the lone pair of electrons on the heteroatom leading to a charge transfer complex⁵¹. This is followed by either transfer of α hydrogen and formation of radicals or quenching by spin inversion and charge destruction. A generalised mechanism can be outlined - as below in Scheme 10.



A substantial part of the barrier to hydrogen abstraction can be overcome in the initial charge-transfer interaction, a process which also allows for subsequent quenching. This results in a decrease in the quantum yield to less than two. The quantum yields of photoreduction of amines are determined by the relative values of k_e and k_h because k_{ir} is very high. The photoreduction of benzophenone by amines was first reported by Cohen and Baumgarten⁵² who showed that reduction by primary and secondary amines produced benzpinacol and the imines I and II in the following reaction pathway (11):

Scheme 11



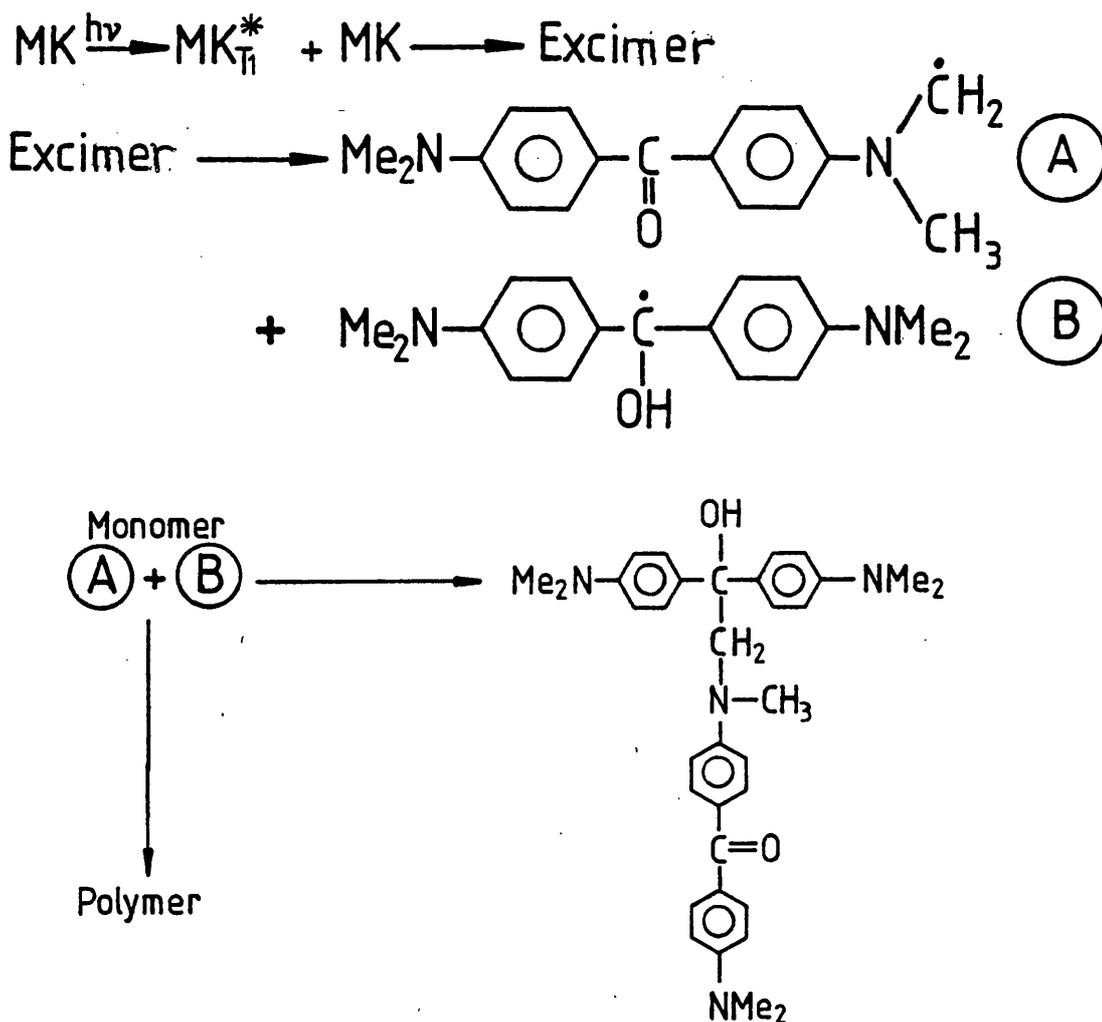
The effects of structure and oxidation potential of the amine can be studied by looking at rates of photoreduction of ketones

Sandner et al⁵³ observed that addition of small amounts of triethylamine enhanced the photo-induced polymerisation of methyl acrylate by benzophenone. Photoinitiation was not effected by triethylamine alone. Quantum yields obtained from the reaction suggested that the methyl acrylate acted as a quencher of the benzophenone excited state. The quenching action only having a small affect on the interaction of the excited ketone with the amine.

Efficient formation of an excited electron-transfer complex from triplet benzophenone and ground state amine was postulated, but initiation by the complex was discounted. It was proposed that initiating radicals resulted from the collapse of the complex following proton transfer.

Michlers Ketone

There has been many reports of improved light sensitivity of photopolymerisable systems on the addition of Michlers Ketone (4,4'-dimethylaminobenzophenone) especially in conjunction with benzophenone^{54,55}. Tertiary amines are potent electron donor sites for photoexcited aryl ketones, thus Michlers Ketone could act as electron donor and excited ketone. The exact mechanism by which Michlers Ketone acts in simple systems is unclear, but the most probable route is via an intermolecular exciplex or encounter complex. There is evidence that the photoinduced self condensation of Michlers Ketone (MK)⁵⁶ proceeds as shown in the following reaction scheme (Scheme 12).



RESULTS AND DISCUSSION

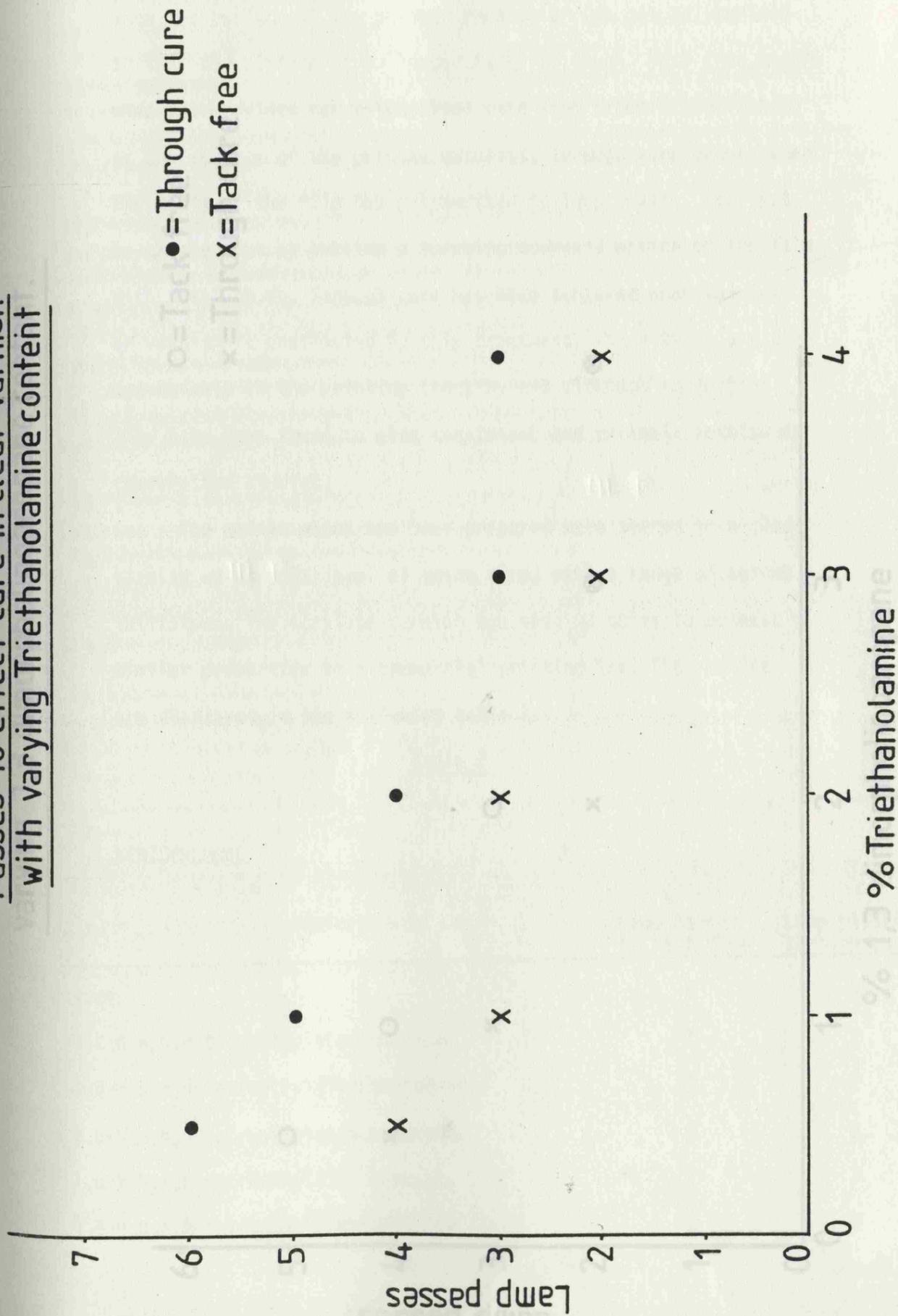
Preliminary studies on the photo-reactions of amines have been carried out by R.S. Davidson et. al.⁵⁶. They found that the reactivity of diamines was greater than two equivalents of a mono-amine. This observation was thought worthy of further investigation especially in the field of ultra-violet light initiation of polymerisation involving free radicals.

A series of tertiary α - ω diamines and tertiary polyamines. Methylations were carried out on the corresponding primary amines using the Eschweiler-Clarke⁴ procedure. N,N,N,N- α - ω -tetraethyl-diaminoalkanes were prepared by the reaction of the α - ω dibromoalkanes with diethylamine. Other α - ω diamines were prepared in a similar manner using the α - ω dibromoalkane and a secondary amine.

The amines were studied initially, as co-initiators with diaryl ketones in the polymerisation of acrylates using thin films of a printing varnish, printed on card. A preliminary study was made to investigate the optimum amine content in the varnish. The level of diaryl ketone initiator was maintained at 5% weight for weight. The results of the experiments which were carried out using triethanolamine and 1,3-dimorpholinopropane are illustrated overleaf, figures 1 and 2. The optimum amount of amine is a balance between the fastest cure rate and the cost of additional quantities of amine. For triethanolamine the optimum percentage was 3%, the same was true for 1,3-dimorpholinopropane.

The terms tack free and through cure used in the figures

Passes to effect cure in clear varnish with varying Triethanolamine content



Passes to effect cure in clear varnish with varying 1,3 dimorpholinopropane content.

O = Tack free
 x = Through cure

and later in the chapter can be related to the extent of polymerisation in the system. Tack free is the condition of the film when the surface of the printed varnish or ink has polymerised so that the surface is no longer tacky to touch. Tack free occurs when the acrylate has polymerised into long cross-linked chains at the surface of the printed material. Through cure occurs when the whole of the film has polymerised to long chains. The test is carried out by putting a screwing downward motion on the film with the thumb. Through cure has been achieved when the ink or varnish is unaffected by this treatment. These tests are used extensively in the printing industry and although subjective, they have been found to give consistent and reliable results in comparative studies.

The amines which had been prepared were tested in a clear varnish using a 3% level of amine along with a range of ketone initiators. The acrylate varnish was made up so as to possess similar properties to a commercial printing ink. The results are displayed in the following table 2.

Table 2

Amine	Lamp passes to tack free	Lamp passes to through cure
None	6	
1,2-N,N,N,N-tetraethylidiaminopropane	2	1
1,3-N,N,N,N-tetraethylidiaminopropane	2	2
1,5-N,N,N,N-tetraethylidiaminopropane	2	2
1,6-N,N,N,N-tetraethylidiaminopropane	3	3
1,8-N,N,N,N-tetraethylidiaminopropane	3	3

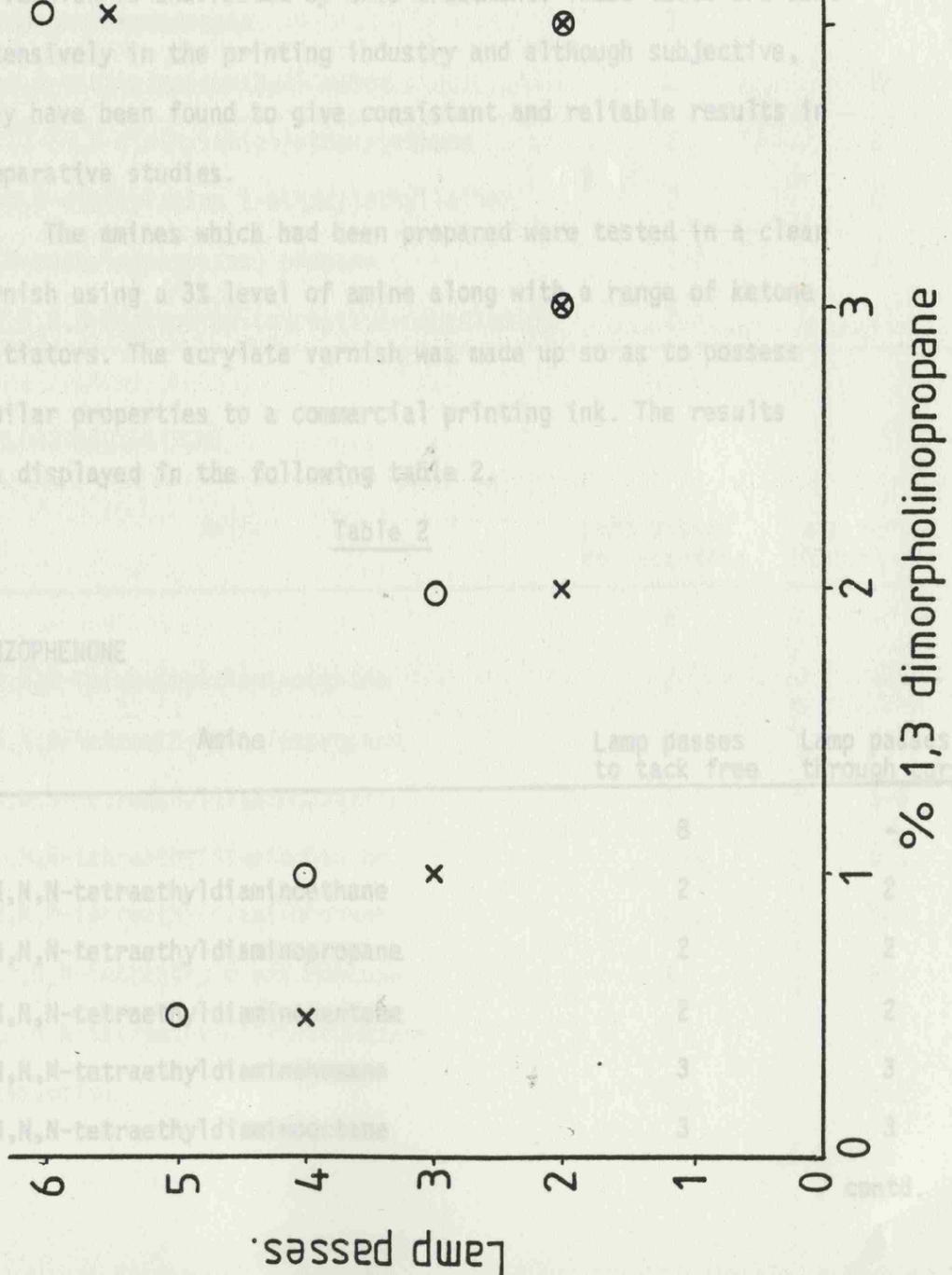


Figure 2

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Table 2

1. BENZOPHENONE

Amine	Lamp passes to tack free	Lamp passes to through cure
None	8	-
1,2-N,N,N,N-tetraethyldiaminoethane	2	2
1,3-N,N,N,N-tetraethyldiaminopropane	2	2
1,5-N,N,N,N-tetraethyldiaminopentane	2	2
1,6-N,N,N,N-tetraethyldiaminohexane	3	3
1,8-N,N,N,N-tetraethyldiaminooctane	3	3

/ contd.

Amine	Lamp passes to tack free	Lamp passes to through cure
1,10-N,N,N,N-tetraethyldiaminodecane	3	3
1,12-N,N,N,N-tetraethyldiaminododecane	3	4
triethanolamine	2	2
1,2-dimorpholinoethane	3	4
1,3-dimorpholinopropane	2	2
1,6-dimorpholinohexane	3	3
1,8-dimorpholinooctane	3	3
1,10-dimorpholinodecane	3	3
1,12-dimorpholinododecane	3	3
bis(2-N,N-diethylaminoethyl) ether	2	2
1,2-bis(2-(N,N-diethylamino)ethoxy)ethane	2	2
bis(2-(N,N-diethylamino 2-ethoxy)ethyl)ether	2	2
1,3-di(N-methylpiperazino) propane	1-2	2
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	2	2

2. 2-CHLOROTHIOXANTHONE

Amine	Lamp passes to tack free	Lamp passes to through cure
None	8	-
1,2-N,N,N,N-tetraethyldiaminoethane	2	4-5
1,3-N,N,N,N-tetraethyldiaminopropane	2	4-5
1,5-N,N,N,N-tetraethyldiaminopentane	2	5-6
1,6-N,N,N,N-tetraethyldiaminohexane	2-3	5-6
1,8-N,N,N,N-tetraethyldiaminooctane	2-3	5-6
1,10-N,N,N,N-tetraethyldiaminodecane	3	6
1,12-N,N,N,N-tetraethyldiaminododecane	3	6
triethanolamine	2	4-5

/ contd.

Amine	Lamp passes to tack free	Lamp passes to through cure
1,2-dimorpholinoethane	2	4
1,3-dimorpholinopropane	1	2
1,6-dimorpholinohexane	2	2
1,8-dimorpholinooctane	2	2
1,10-dimorpholinodecane	2	2-3
1,12-dimorpholinododecane	2	3
bis (2-N,N-diethylaminoethyl) ether	1	2
1,2-bis(2-(N,N-diethylamino)ethoxy) ethane	1-2	3-4
bis(2-(N,N-diethylamino 2-ethoxy)ethyl) ether	2	4
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	2	6

3. MICHLERS KETONE

Amine	Lamp passes to tack free	Lamp passes to through cure
None	4	-
1,2-N,N,N,N-tetraethyldiaminoethane	2	5
1,3-N,N,N,N-tetraethyldiaminopropane	2	7
1,5-N,N,N,N-tetraethyldiaminopentane	2-3	8
1,6-N,N,N,N-tetraethyldiaminohexane	3	9
1,8-N,N,N,N-tetraethyldiaminooctane	3	10
1,10-N,N,N,N-tetraethyldiaminodecane	3	10
1,12-N,N,N,N-tetraethyldiaminododecane	3	10
triethanolamine	2-3	8
1,2-dimorpholinoethane	2	8
1,3-dimorpholinopropane	2	4
1,6-dimorpholinohexane	2	7
1,8-dimorpholinooctane	2-3	7

/ contd.

Amine	Lamp passes to tack free	Lamp passes to through cure
1,10-dimorpholinodecane	2-3	6
1,12-dimorpholindodecane	2-3	7
bis(2-N,N-diethylaminoethyl)ether	1-2	4
1,2-bis(2-(N,N-diethylamino)ethoxy)ethane	2	4-5
bis(2-(N,N-diethylamino 2-ethoxy)ethyl)ether	2	5-6
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	2	5

4. FLUORENONE

Amine	Lamp passes to tack free	Lamp passes to through cure
None	> 10	-
1,2-N,N,N,N-tetraethyldiaminoethane	> 10	-
1,3-N,N,N,N-tetraethyldiaminopropane	> 10	-
1,5-N,N,N,N-tetraethyldiaminopentane	> 10	-
1,6-N,N,N,N-tetraethyldiaminohexane	> 10	-
1,8-N,N,N,N-tetraethyldiaminooctane	> 10	-
1,10-N,N,N,N-tetraethyldiaminodecane	> 10	-
1,12-N,N,N,N-tetraethyldiaminododecane	> 10	-
triethanolamine	7	7-8
1,2-bis(2-(N,N-diethylamino)ethoxy)ethane	6	6
bis(2-(N,N-diethylamino 2-ethoxy)ethyl)ether	6	6
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	7	7

The table of results provides several pieces of information. Firstly, that the type of ketone photoinitiator has a considerable effect on the rate of cure of the varnish. Michlers Ketone was the best photoinitiator tested. The reason for this can be seen from

observation that Michlers Ketone, without an amine co-initiator cured the varnish faster than the other ketone photoinitiators without amine present. This is because Michlers Ketone can react with itself via a charge transfer mechanism, (as described in the introduction) a ketone group from one molecule and an amine group from another molecule interacting to produce an exciplex, which breaks down, leading to radicals and consequently initiation of polymerisation. Therefore for Michlers ketone there is effectively a ketone / amine initiator before any alkyl amines are added. Michlers Ketone however does possess a problem in its use in varnishes that the material is coloured.

Benzophenone in conjunction with the amines was the next most effective ketone initiator followed by 2-chlorothioxanthone and finally fluorenone. Benzophenone and 2-chlorothioxanthone both react via the $n \rightarrow \pi^*$ transition whereas fluorenone is known to react via the lower energy $\pi \rightarrow \pi^*$. Cohen et. al.⁵⁷ have stated that ketones reacting from the $\pi \rightarrow \pi^*$ are generally less reactive than those which reacted from the $n \rightarrow \pi^*$, this can be seen in some of Cohen's results⁵⁷ which showed that fluorenone was not photo-reduced efficiently by alcohols.

The effect of different chain length between the two amine groups in the diamines was to diminish the speed of cure as the chain length increased. This does not necessarily reflect a lowering in reactivity of the amine, the difference in cure rate may have been due to a lower concentration of amine in the varnish. (A result of using weight for weight ratio of materials.) Thus triethanolamine which effects cure faster than 1,8-N,N,N,N-tetraethyl diamino octane does not do so because of higher reactivity but because of a much greater ^{molar} concentration. In the printing

industry the use of weight for weight comparisons between different materials is more important than mole for mole comparisons used in the laboratory because it measures cost effectiveness, thus materials are normally evaluated in this way. The results also show that the presence of an oxygen atom in the amine molecule enhanced the cure speed of the varnish. No explanation could be found for this observation.

Some of the amines were tested under similar conditions except using the amines in equimolar quantities, to investigate the effect of different amine reactivity on speed of cure. The results are displayed below in table 3.

Table 3

BENZOPHENONE

Amine	Lamp passes to tack free	Lamp passes to through cure
None	16	-
triethanolamine	3	6-7
1,8-diaminooctane	10	14
1,8-N,N,N,N-tetramethyldiaminooctane	3	4
1,8-N,N,N,N-tetraethyldiaminooctane	6	7
1,6-N,N,N,N-tetraethyldiaminohexane	4	7-8
N,N,N,N,N,N-hexamethyltriethylenetetramine	2	3
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	2	3
bis(2-N,N-diethylaminoethyl)ether	1	2

The results shown in the table above suggest that tertiary amines are more effective in thin film acrylate polymerisations

than primary amines. In addition the nature of the amine substituents appears to be relevant. A methyl group on nitrogen causing a faster reaction than an ethyl substituent. This observation of the difference in cure speed on changing substituent may reflect the ease with which hydrogen is abstracted from the amine. There appears to be only a small acceleration in the rate of cure as the chain length between the amine groups diminishes in the systems studied. An interesting feature of the polymerisations of the dimorpholino compounds was that 1,3-dimorpholinopropane effects a cure faster than 1,2-dimorpholinoethane, this was due to poor interaction of the amine groups. The amine groups being kept in an orthogonal position relative to each other, allowing only one of the amine groups to react rather than both of them.

Experiments were carried out to look at the rate of cure in a pigmented system using triethanolamine, escalol (n-butyl 4-N,N-dimethylaminobenzoate) which are used in commercial printing inks and 1,3-dimorpholinopropane which was selected because it possessed good curing characteristics in the varnish. The results are shown below in table 4.

Table 4

BLUE INK.

Photoinitiator	Amine	Tack free	Through cure
benzophenone	none	> 10	-
benzophenone	triethanolamine	4	7
benzophenone	escalol	4	7
benzophenone	1,3-dimorpholinopropane	2-3	7
2-chlorothioxanthone	none	> 10	-
2-chlorothioxanthone	triethanolamine	2	3

/ contd.

Photoinitiator	Amine	Tack free	Through cure
2-chlorothioxanthone	escalol	2	2
2-chlorothioxanthone	1,3-dimorpholinopropane	2	2
2-isopropylthioxanthone	none	>10	-
2-isopropylthioxanthone	triethanolamine	2	3
2-isopropylthioxanthone	escalol	2	3
2-isopropylthioxanthone	1,3-dimorpholinopropane	2	2

RED INK.

Photoinitiator	Amine	Tack free	Through cure
benzophenone	none	8	>10
benzophenone	triethanolamine	3	6
benzophenone	escalol	3-4	7
benzophenone	1,3-dimorpholinopropane	3	5
2-chlorothioxanthone	none	8	>10
2-chlorothioxanthone	triethanolamine	3	3
2-chlorothioxanthone	escalol	2	3
2-chlorothioxanthone	1,3-dimorpholinopropane	3	3

It is obvious that the pigment in the ink has some effect on the rate of polymerisation, the red ink requiring more light to effect a cure than the blue ink. The reason for this may be that the red pigment absorbs more light in the region of the photoinitiator absorption than the blue ink and does not sensitise the initiator, thus it is in competition with the initiator for the available light. The results as regards to the amines show little difference compared with each other on going from a clear varnish to a pigmented ink.

A further experiment was performed in which the bisphenol 'A'

epoxy acrylate prepolymer was substituted for the special acrylate prepolymer. The results are shown in the table 5 below.

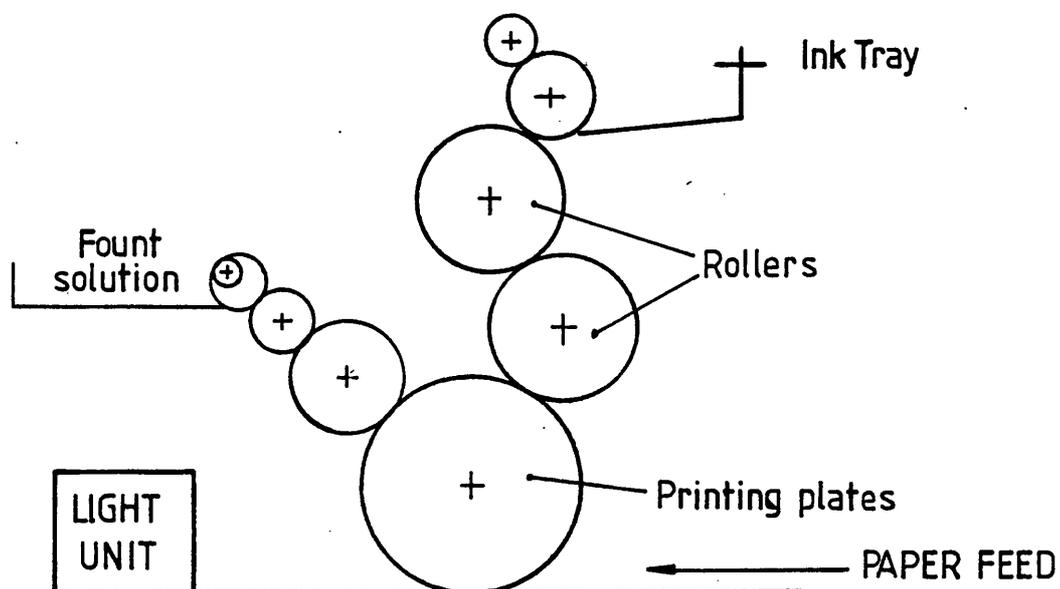
Table 5

BLUE INK.

Photoinitiator	Amine	Tack free	Through cure
benzophenone	escalol	3-4	7
benzophenone	1,3-dimorpholinopropane	2	5
2-chlorothioxanthone	escalol	2	5-6
2-chlorothioxanthone	1,3-dimorpholinopropane	2	3

The results establish that the resin type has had little effect on the rate of polymerisation in the systems under examination.

There are several problems to be overcome for printing ultra-violetlight initiated printing inks when employing a lithographic press as opposed to the offset printing used in the experiments outlined on the previous pages. A diagram of a lithographic press is shown below.



The ink which is applied to a roller near the top is transferred across the lower rollers to the printing plate. The reason for transfer over several rollers is to obtain an even distribution of ink across the printing plate. The printing plate has two types of surface, hydrophobic areas and hydrophilic areas. The printing ink which is hydrophobic, sticks to this part of the plate. This then rotates and is applied to the printing substrate, e.g. paper, card etc. In order to prevent the ink from smearing on to the non-image areas of the plate, which are hydrophilic, a fount solution based on water is also applied. The printed material then passes under the lamp, or lamps, polymerisation of the acrylate resin occurs and the dry print is stacked. Since the fount solution is water based, amines with good water solubility will be leached from the ink and into the fount. As the preliminary experiments illustrate, a reduction in the concentration of amine in the ink reduces cure speed as this is a prime consideration in printing this has to be avoided. Most amines because of their polar character are very soluble in water and thus are not suitable for use in lithographic printing. The presence of an oxygen atom in the molecules also seems to improve the rate of polymerisation as was shown in the experiments using clear varnishes. The α - ω -N,N,N,N tetraethyl diamino alkanes and the amines based on glycols, e.g. bis (2 - N,N diethylamino ethyl) ether have good solubility in water. The 1,3-dimorpholinopropane alkanes are much less soluble in water and thus may be suitable for lithographic printing. U.V. curing printing inks for lithographic printing are currently based on aromatic amines and suffer from toxicological problems. 1,3 dimorpholinopropane and 1,6 dimorpholinohexane were selected as being the best choice of amine, and were incorporated into

a black printing ink and compared with an ink using Michlers ketone as the amine component. In addition to a print trial, the amount of water taken into the ink was measured as was the pH of the water that did not enter the ink. An odour panel test was also carried out because printing inks are used on food packagings and the odour may taint the food. The scale is from 0 - 5 with 0 having the least odour. The results of these tests are shown below in Table 6.

Table 6.

Initiator	Amine	Water Uptake %	pH	Odour Test
benzophenone	Michlers ketone	58	5.6	2.4
2 -chlorothioxanthone	1,3 dimorpholinepropane	44	7.7	2.6
2 -chlorothioxanthone	1,6 dimorpholinohexane	60	8.1	2.6

The print test showed that the two test inks had poor curing characteristics, but were equally good in every other respect. The water uptake result does not provide any reason why the ink does not cure. The main indication as to the reason for the poor initiation of polymerisation is the pH reading for the supernatant from the water uptake test. The alkaline reading suggests that some of the amine had leached out of the ink, this has probably occurred on the printing press, thus the speed of cure has been reduced.

A further print test was carried out on a blue ink comparing escalol 1,3 dimorpholinopropane and triethanolamine. It was found that the ink containing triethanolamine would not polymerise to produce a polymerised coating. The inks with 1,3 dimorpholinopropane and escalol cured with two lamps at 4000 feet per minute. The ink

made with 1,3 dimorpholinopropane as the amine component was found to key to the paper it was printed on better than the escolol containing ink. An example of the printing is shown overleaf.

The ink used in this trial had different water carrying properties to the black ink previously used. The water uptake of the ink was 29% for escolol ink, 28% for the 1,3 dimorpholinopropane ink and 40% for the triethanolamine ink.

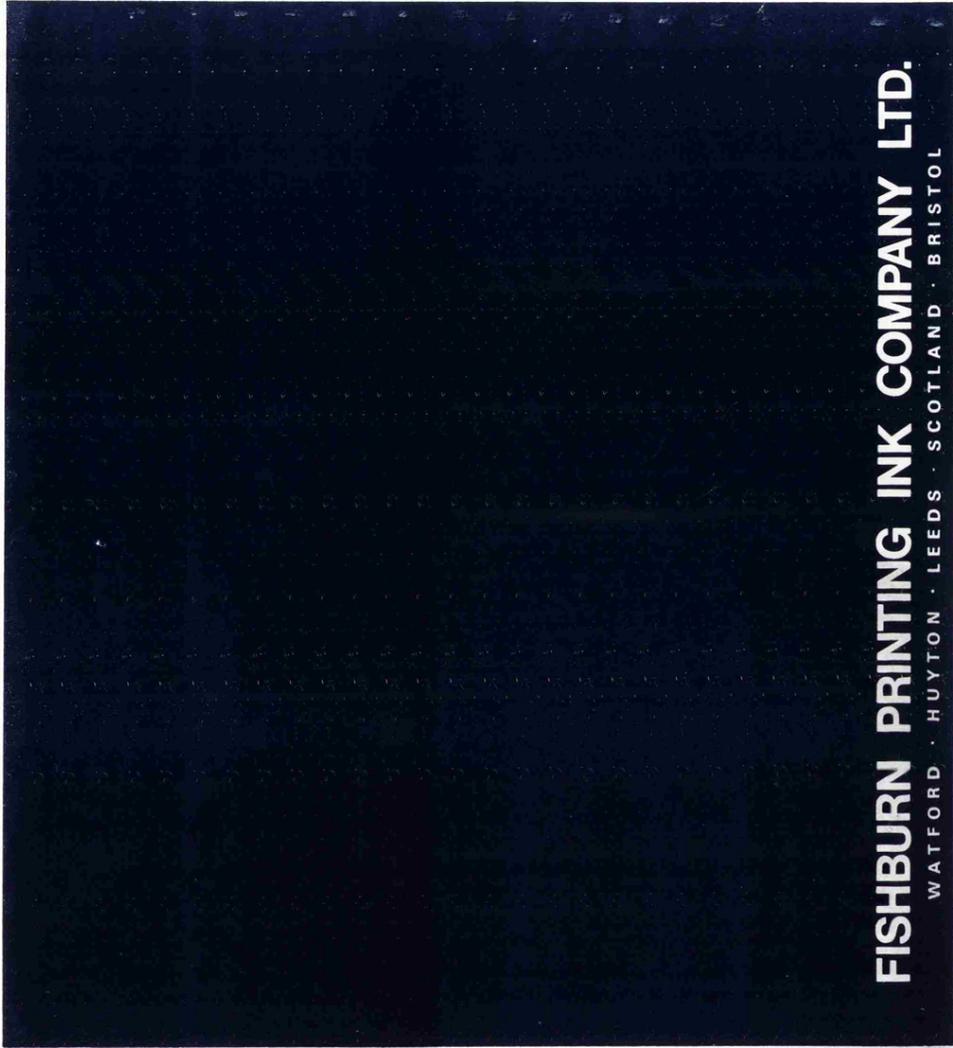
A rub test was carried out on the inks, this test is a measure of the hardness of the coating. The cured inks all gave similar results. Only a small amount of ink being removed from the surface coating.

In order to try to understand the reasons for the difference in rates of acrylate polymerisation, the photoreduction of fluorenone and benzophenone by selected amines, and the photoxygenation of the amines were studied.

An initial study was made of the photoreduction of benzophenone by several amines. It was found that the reaction proceeded very rapidly. The rapidity of the reaction prevented easy differentiation of reactivity of the amines. See Table 7 below.

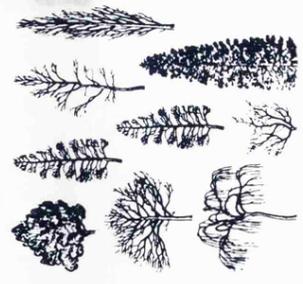
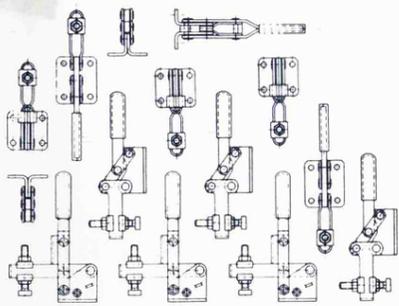
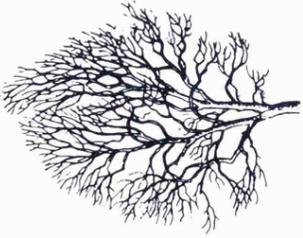
Table 7.

Amine	Rate (moles/second)
1,2-N,N,N,N-tetraethyldiaminoethane	3.5×10^{-5}
1,3-N,N,N,N-tetraethyldiaminopropane	4.8×10^{-5}
1,6-N,N,N,N-tetraethyldiaminohexane	3.1×10^{-5}



FISHBURN PRINTING INK COMPANY LTD.
 WATFORD · HUYTON · LEEDS · SCOTLAND · BRISTOL

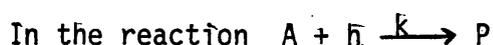
THIS INK HAS BEEN PRINTED ON A STANDARD
 NORMAL LITHOGRAPHIC CONDITIONS USING FPI INKS. THIS PLATE IS DESIGNED TO SHOW
 THE PERFORMANCE OF AN INK UNDER ANY CONDITIONS IT IS LIKELY TO BE SUBJECTED TO.



In addition, it has been reported that the photoreduction of benzophenone by secondary and tertiary amines is accompanied by formation of light absorbing transients and by products in benzene solution.⁵⁸ This observation may lead to erroneous results.

Walling and Gibian⁵⁹ have previously reported this technique as a method of measuring the reactivity of different bonds and compounds towards Benzophenone. Consequently the technique has been applied to the photoreduction of fluorenone. Fluorenone photoreduction has been carried out by several groups of workers using tri-n-butyl tin^{hydride}, xanthene and triethylamine.^{60,61} Evidence has been presented that the low lying $\pi \rightarrow \pi^*$ excited singlet and triplet states are responsible for reaction. The reactivity of the amine will be reflected in the rate constant for the abstraction of hydrogen by the fluorenone..

The rate constants were determined by studying the variation in quantum yield for photoreduction with change in hydrogen donor concentration. The reaction was followed by measuring the decrease in the ultra-violet absorption at 294 nm by high performance liquid chromatography and comparing it with previously obtained standards.



the rate of disappearance of A is given by

$$\frac{-d[A]}{dt} = k[A] I \quad (1) \text{ Where } I = \text{light intensity}$$

Some examples of the curve for rate of disappearance of fluorenone with time are given on the following pages.

The quantum yield for the disappearance of A is given by

$$\phi = \frac{\text{rate of disappearance}}{\text{light intensity}} \quad (2)$$

The light intensity used in the reactions can be found using a reaction in which the quantum yield for the reaction has already been determined. Cohen et.al.⁶² have determined the quantum yield for the photoreduction of fluorenone by triethylamine. This reaction was carried out in our photochemical reactor using a triethylamine concentration of 0.1 molar. The quantum yield as determined by Cohen is 0.91. Therefore the quantum yield for the reduction of fluorenone by an amine is given by

$$\phi = \frac{\text{Rate of disappearance with amine} \times \phi \text{ for triethylamine}}{\text{Rate of disappearance with triethylamine}}$$

A curve for the disappearance of fluorenone in the photoreduction with triethylamine is shown overleaf.

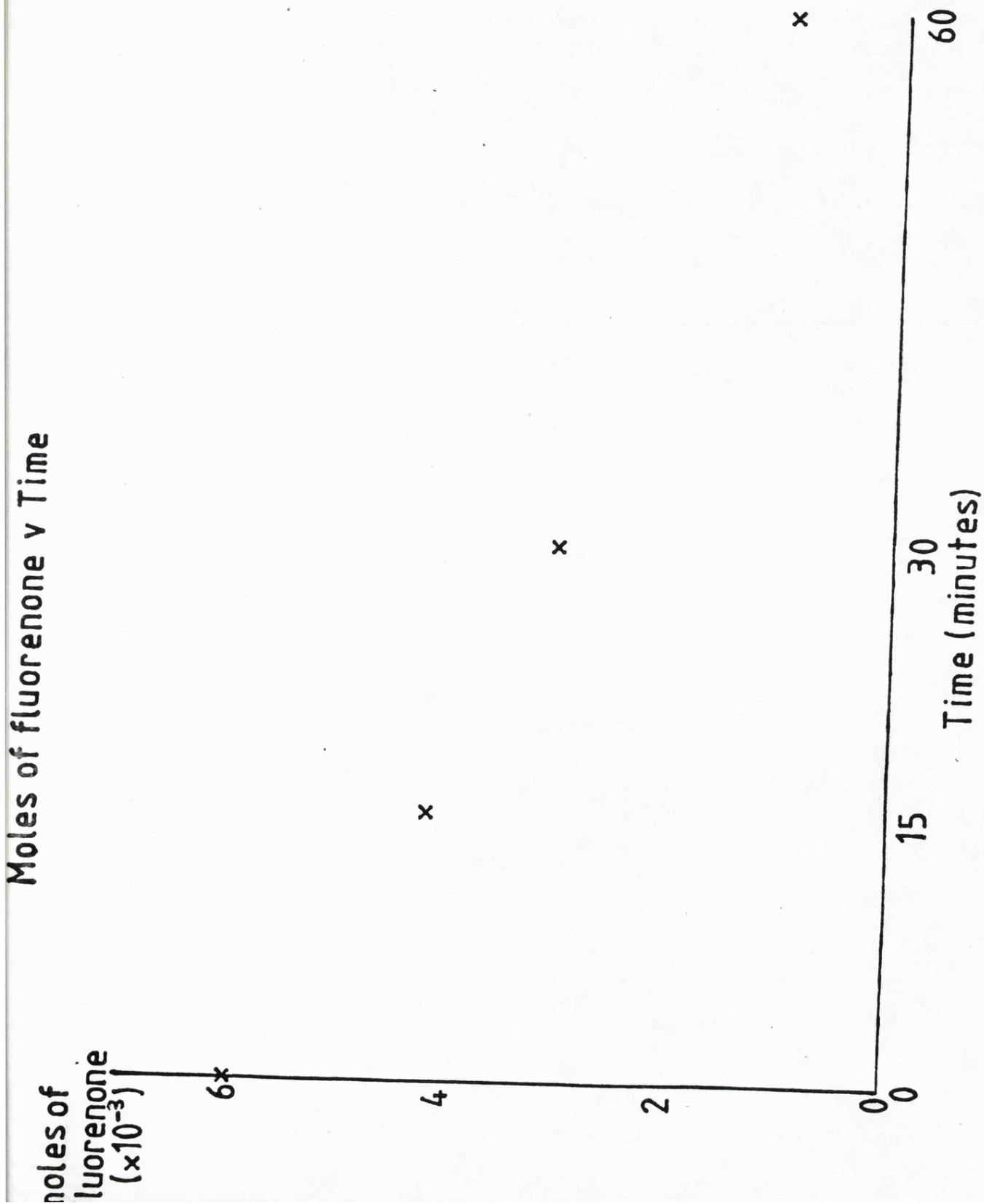
The relationship between quantum yield for photoreduction and the concentration of hydrogen donor are given by the Stern-Volmer equation (see introduction).

$$\frac{1}{\phi} = \frac{1}{a} + \frac{k_d}{a k_r [\text{Amine}]}$$

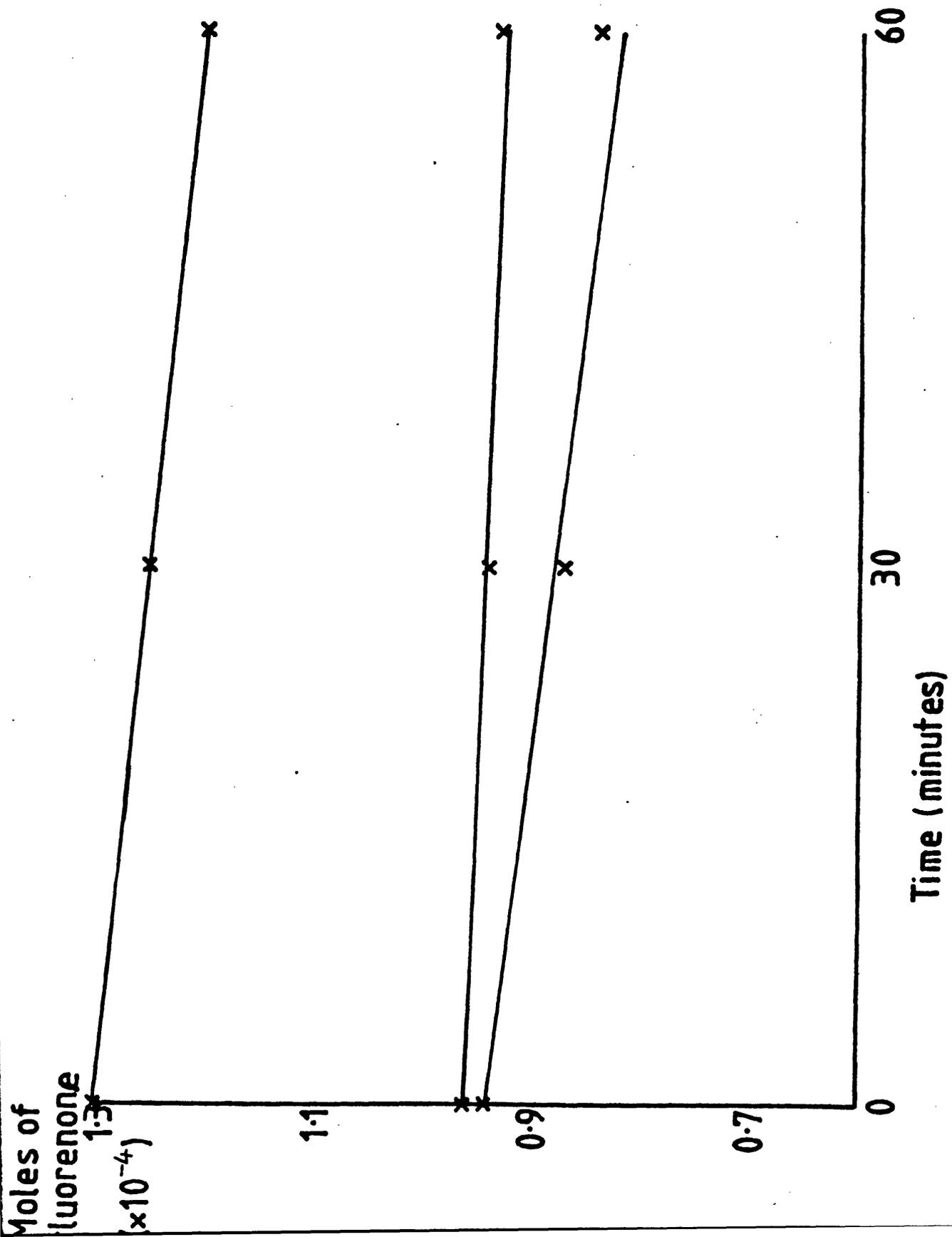
Where a is the quantum yield for triplet formation, this has been taken as 1. k_d is the rate constant for deactivation of the triplet state and k_r is the rate constant for the hydrogen-abstraction reaction. From the slope the value for k_r can be calculated. A value of 2.2×10^5 was used for k_d . The rate constants for hydrogen abstraction, demonstrate the reactivity of the amine.

Some examples are given overleaf of the Stern-Volmer plots for the amines studied. Three different concentrations of each amine were used in the determinations and table 7 overleaf is given of the values obtained.

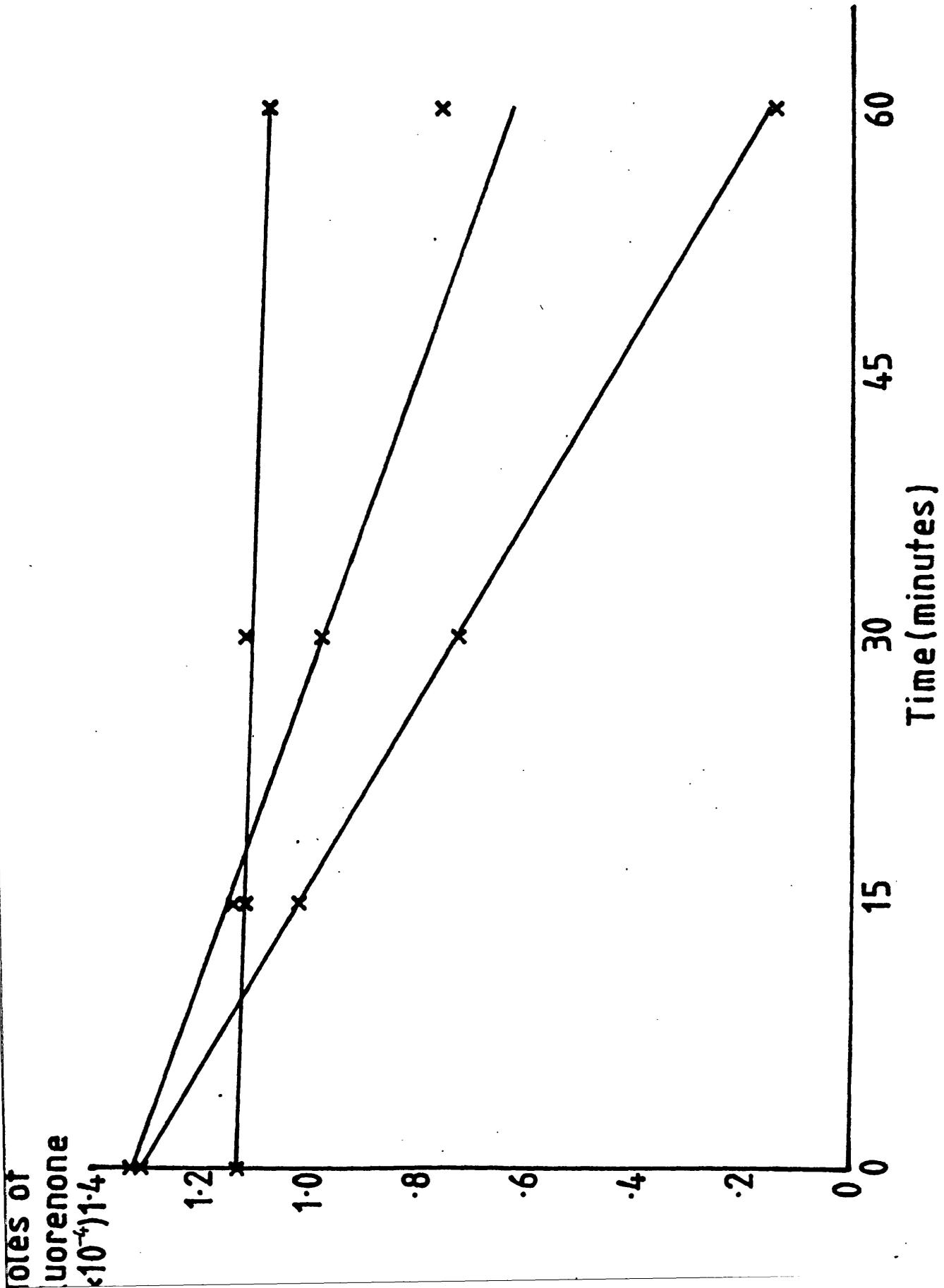
The Photo-reduction of Fluorenone by Triethylamine.



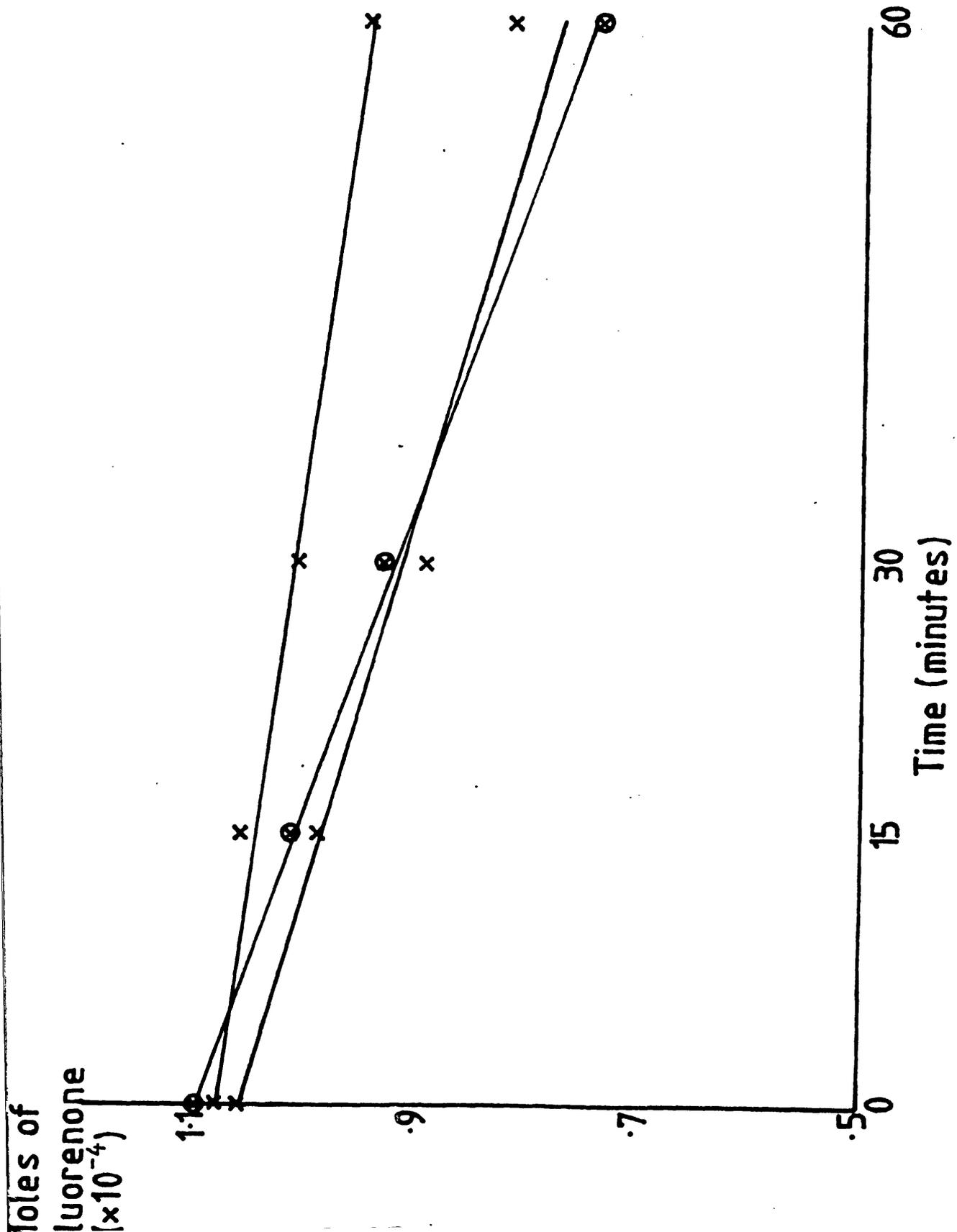
The Photo-reduction of Fluorenone by Triethanolamine



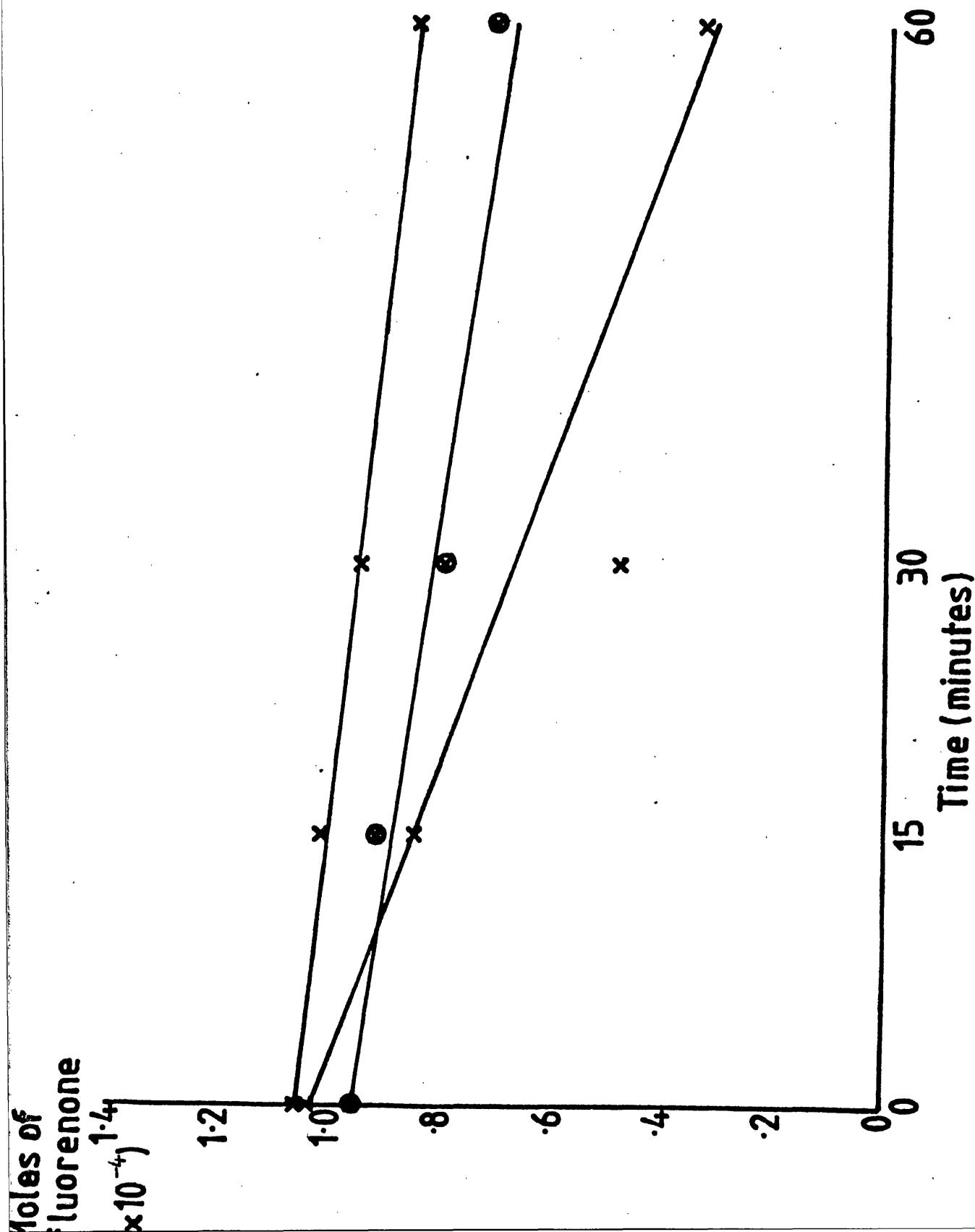
The Photoreduction of Fluorenone by 1,8-diaminooctane



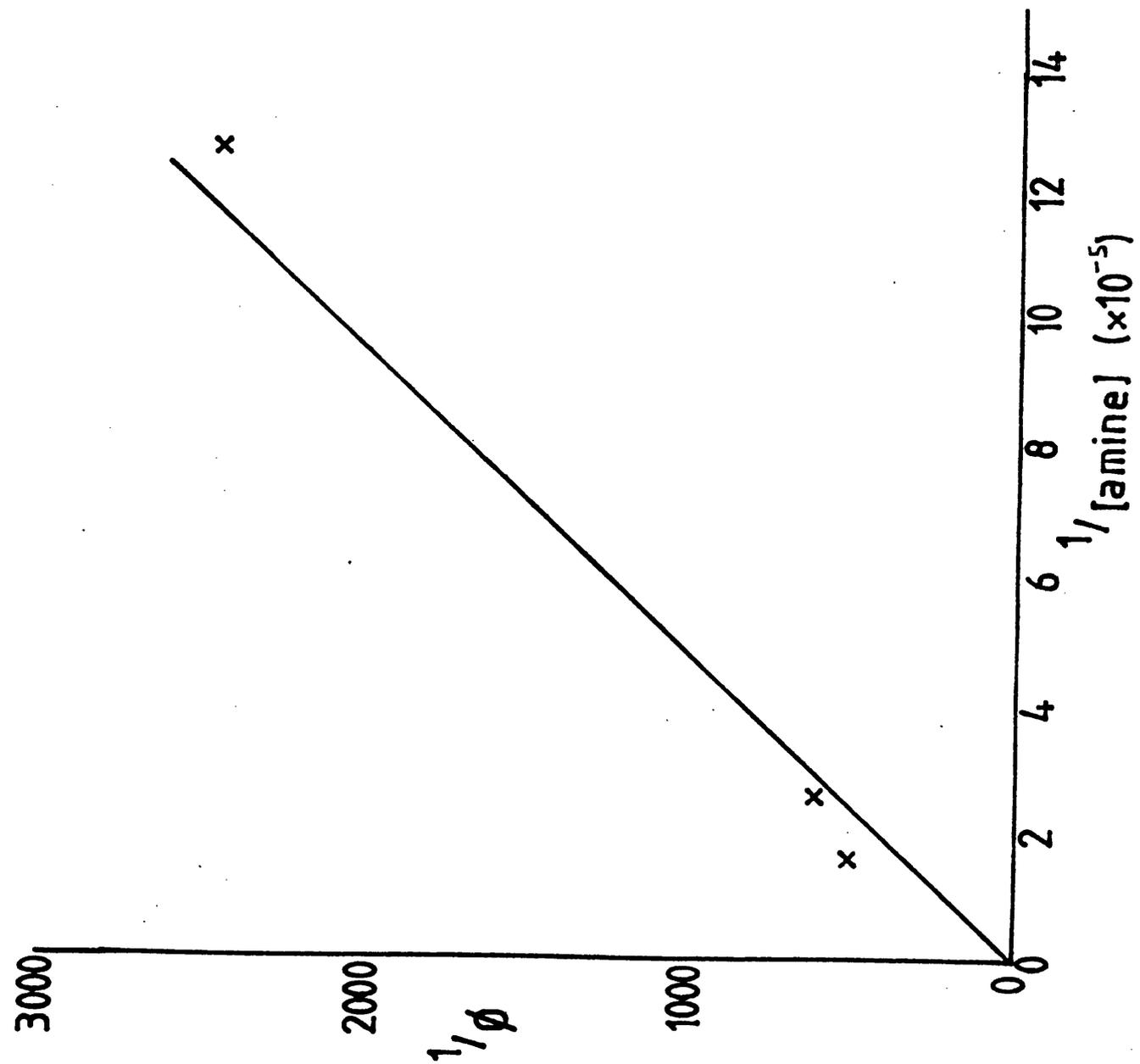
The Photoreduction of Fluorenone by N,N,N,N,N,N-hexamethyl-triethylenetetramine



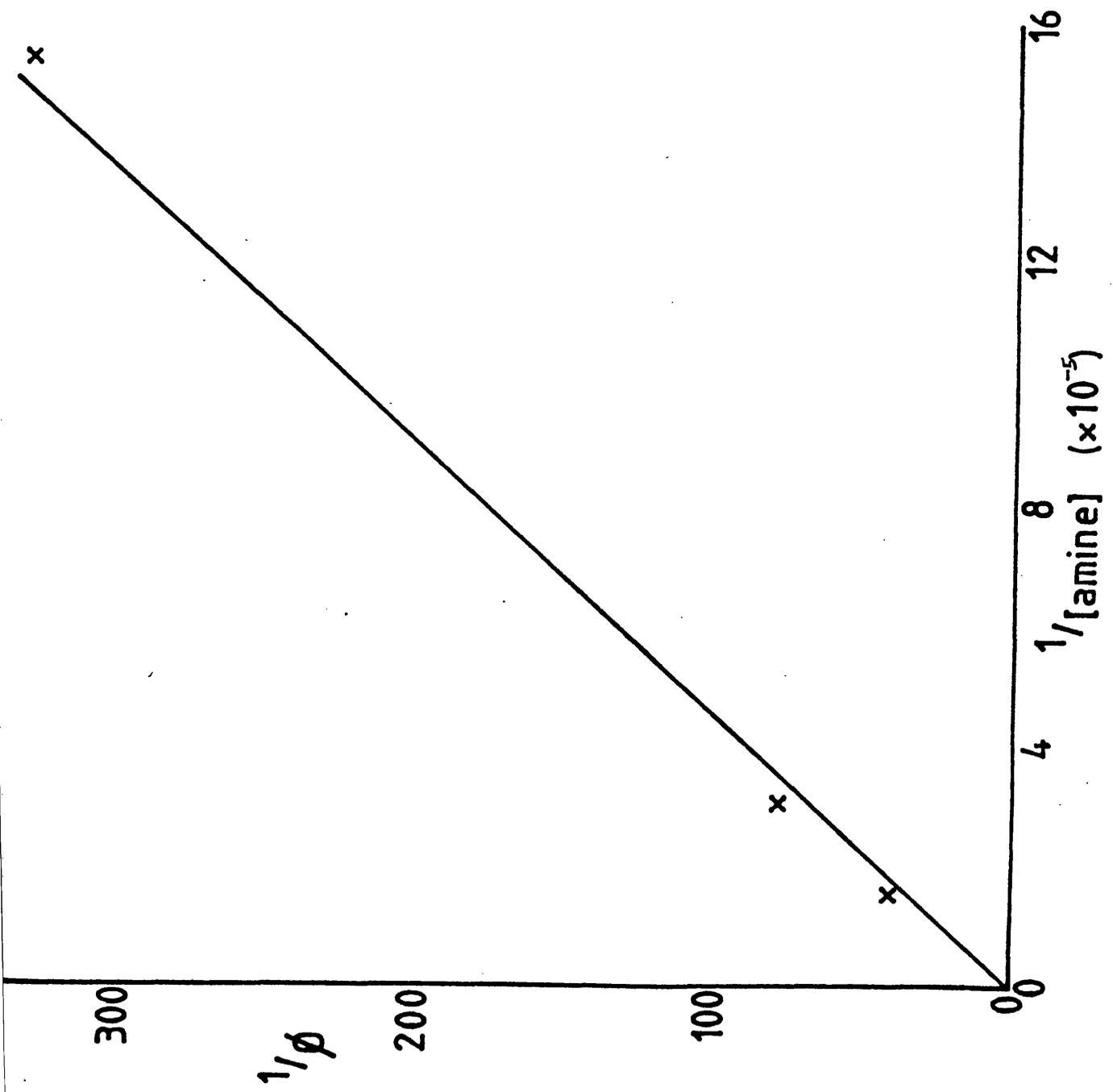
The Photoreduction of Fluorenone by 1,2-bis(2-(N,N-diethyl-
aminoethyl)ethoxy)ethane



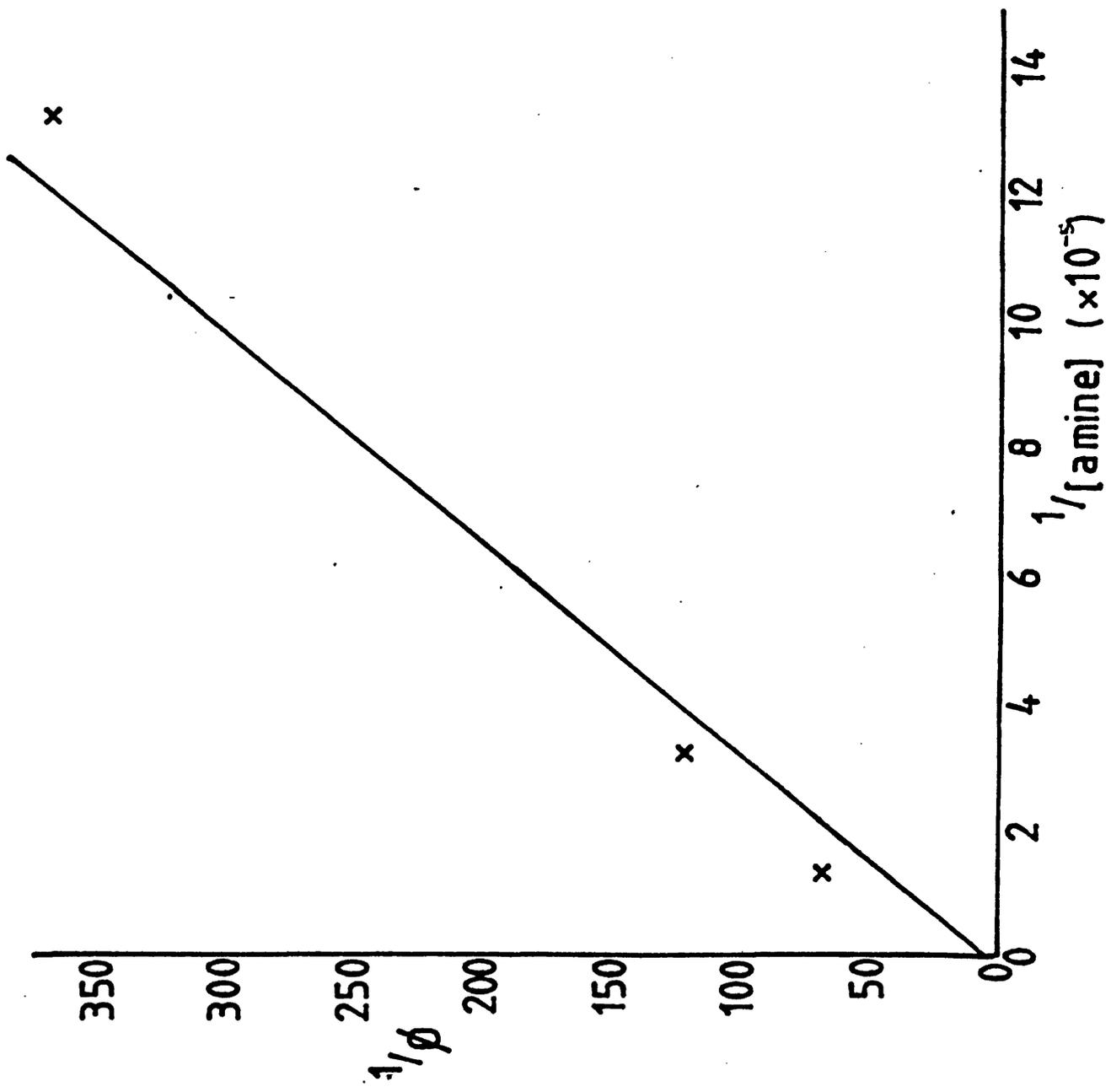
Stern-Volmer Plot of Photoreduction of Fluorenone by Triethanolamine



Stern-Volmer Plot of Photoreduction of Fluorenone by 1,10-N,N,N,N-tetraethyldiaminodecane



Stern-Volmer Plot of Photoreduction of Fluorenone by 1,6-dimorph-
-olinohexane



Stern-Volmer Plot of Photo-reduction of Fluorenone by bis(2-(N,N-diethylamino-2-ethoxy)ethyl)ether

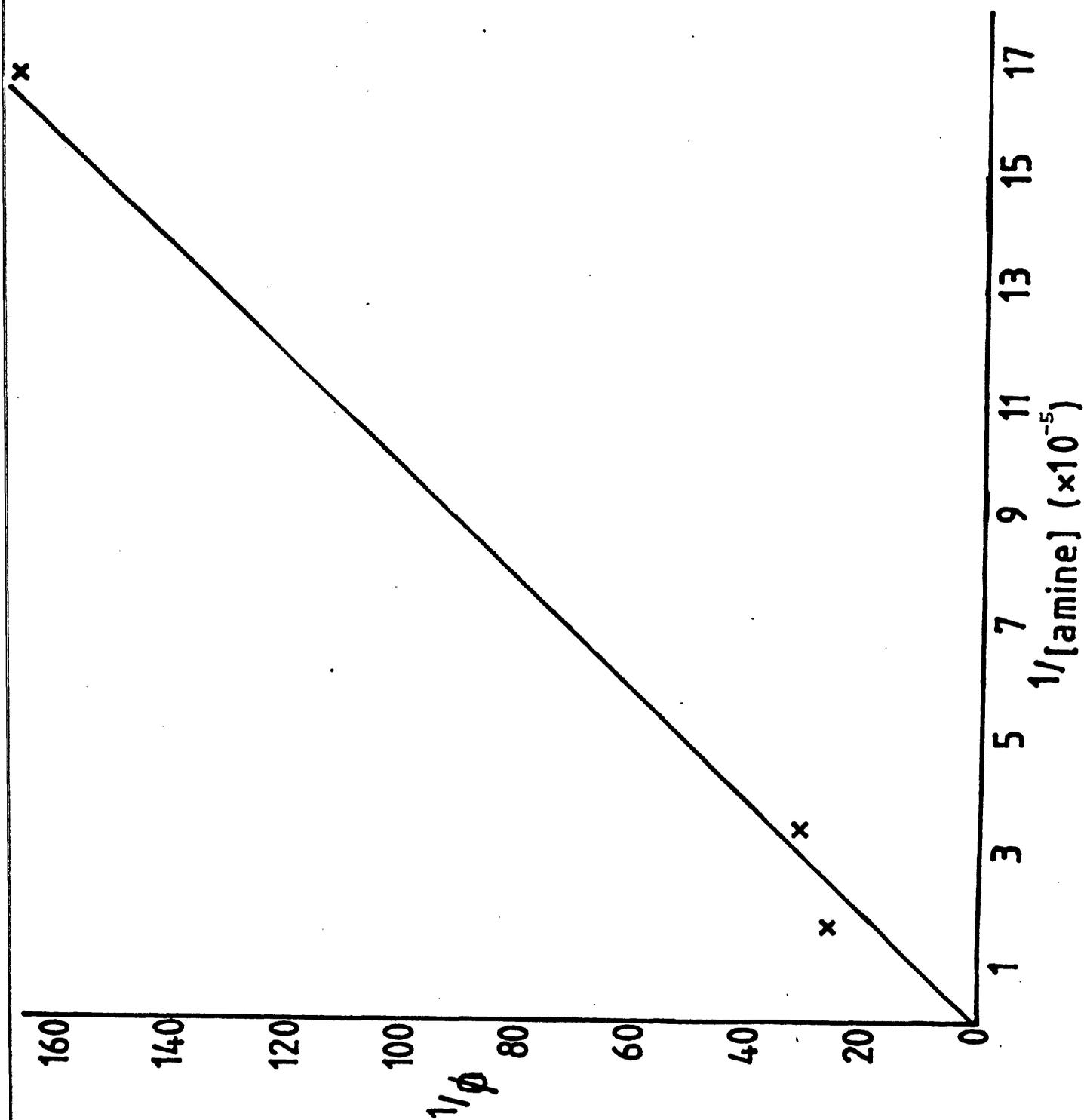


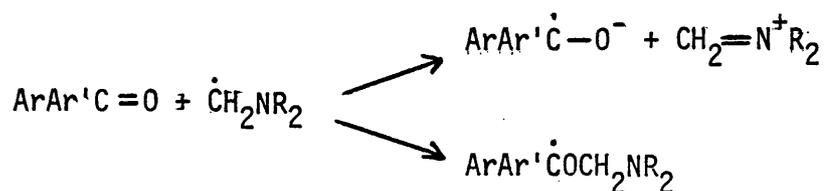
Table 7

Amine	k_r (sec^{-1})
Triethanolamine	$8.37 \times 10^5 \pm 2.93 \times 10^5$
N-methyldiethanolamine	$1.53 \times 10^6 \pm 6.7 \times 10^5$
N,N-dimethylethanolamine	$5.61 \times 10^7 \pm 3.06 \times 10^7$
1,3 dimorpholinopropane	$1.47 \times 10^6 \pm 1.17 \times 10^6$
1,6 dimorpholinohexane	$6.15 \times 10^6 \pm 1.94 \times 10^6$
1,10 dimorpholinodecane	$1.03 \times 10^6 \pm 0.46 \times 10^6$
1,3-N,N,N,N tetraethyldiaminopropane	$2.41 \times 10^7 \pm 1.55 \times 10^7$
1,8 -N,N,N,N tetraethyldiaminooctane	$1.37 \times 10^7 \pm 0.38 \times 10^7$
1,10-N,N,N,N tetraethyldiaminodecane	$9.19 \times 10^6 \pm 0.11 \times 10^6$
1,8-N,N,N,N-tetramethyldiaminooctane	$4.13 \times 10^7 \pm 2.69 \times 10^7$
1,8-diaminooctane	$4.92 \times 10^6 \pm 1.75 \times 10^6$
bis (2-N,N-diethylaminoethyl) ether	$7.25 \times 10^7 \pm 3.75 \times 10^7$
1,2-bis (2-(N,N-diethylamino)ethoxy) ethane	$2.75 \times 10^7 \pm 1.75 \times 10^7$
bis (2-(N,N-diethylamino 2-ethoxy)ethyl) ether	$1.8 \times 10^7 \pm 0.39 \times 10^7$
N,N,N,N,N,N-hexamethyltriethylenetetramine	$5.62 \times 10^6 \pm 3.46 \times 10^6$
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	$1.79 \times 10^7 \pm 1.02 \times 10^7$
bis (2-morpholinoethyl) ether	$3.69 \times 10^6 \pm 1.23 \times 10^6$
1,3-di(N-methylpiperazino) propane	$2.63 \times 10^7 \pm 1.42 \times 10^6$

A low concentration of amine was used to avoid quenching of the singlet state of fluorenone. The points on the Stern-Volmer plots did not always represent a straight line with an intercept of one. Generally it was the point representing the highest concentration of amine that was not on the line. This suggests that at these concentrations some quenching of the fluorenone singlet was taking place.

is also followed by transfer of a second reducing group to the ground state ketone leading to the formation of the immonium ion or to an addition product, both of which may be hydrolysed to afford the observed products. This is shown in the following reaction scheme 13.

Scheme 13

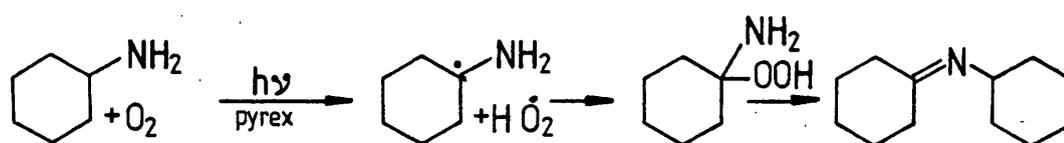


However comparison of the results of the photoreductions with those obtained from the thin film polymerisations show that there is little correlation between reactivity as measured by photoreduction, and efficiency of photo-induced polymerisation. For example, triethanolamine is more effective than the α - ω N,N,N,N-tetraethyldiaminoalkanes but it has a much lower rate constant for photoreduction. The ether type amines do exhibit both high rate constants for the photoreduction and also initiate polymerisation of the acrylate thin films efficiently. These results can be rationalised by the fact that an oxygen atom in the amine molecule is necessary for efficient photoinitiated free radical polymerisations of thin films. Once this condition is satisfied the reactivity of the amine can have an influence on the speed of cure.

An investigation was carried out on the rate of photo-oxygenation of the amines studied previously, using benzophenone as a sensitizer and benzene as the solvent. Irradiation of

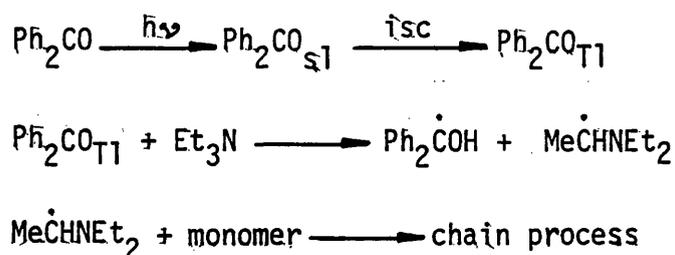
amines in the presence of oxygen has been studied by Kulevsky et. al.⁶⁵. They showed that the reaction proceeded through a contact charge-transfer complex between the amine and molecular oxygen to afford a hydroperoxide, which via subsequent reactions led to a range of products. A schematic representation is shown below for cyclohexylamine.

Scheme 14

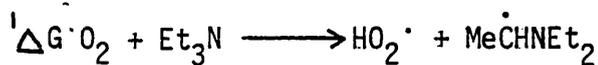
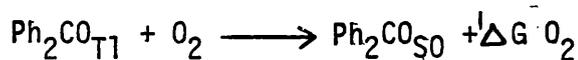


The mechanism of photo-oxygenation reactions has been the subject of a recent review⁶⁶. The rate of photo-oxygenation is amine dependant and the difference in the relative rates may have a bearing on the rate of photoinitiated polymerisation. Oxygen acts as a quencher in radical reactions and an ink or varnish contains large amounts of oxygen dissolved in them. Atmospheric oxygen may also be important. The presence of amine is able to counteract some of the oxygen inhibition of polymerisation. The scheme 15 following illustrates some of the processes important in radical initiated polymerisation.

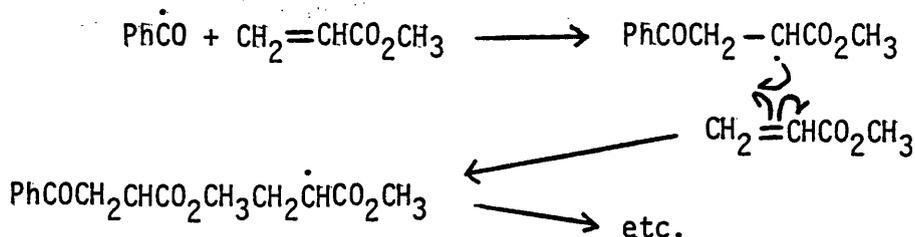
Scheme 15



also



chain process,



The rate of oxygenation was measured as a rate of oxygen uptake using a manometer, the results for equal concentration of amine (2×10^{-4} moles) are shown below in table 8.

Table B

Amine	Oxygen uptake ($\times 10^{-3} \text{ cm}^3 \text{ seconds}^{-1}$)
Triethanolamine	0.30
N-methyldiethanolamine	1.55
N,N-dimethylethanolamine	1.45
1,2-dimorpholinoethane	2.35
1,3-dimorpholinopropane	6.60
1,6-dimorpholinohexane	3.45
1,10-dimorpholinodecane	3.00
1,3-N,N,N,N-tetraethyldiaminopropane	2.90
1,8-N,N,N,N-tetraethyldiaminooctane	3.50
1,10-N,N,N,N-tetraethyldiaminodecane	4.15
1,8-N,N,N,N-tetramethyldiaminooctane	4.55
1,8-diaminooctane	0.20

/ contd.

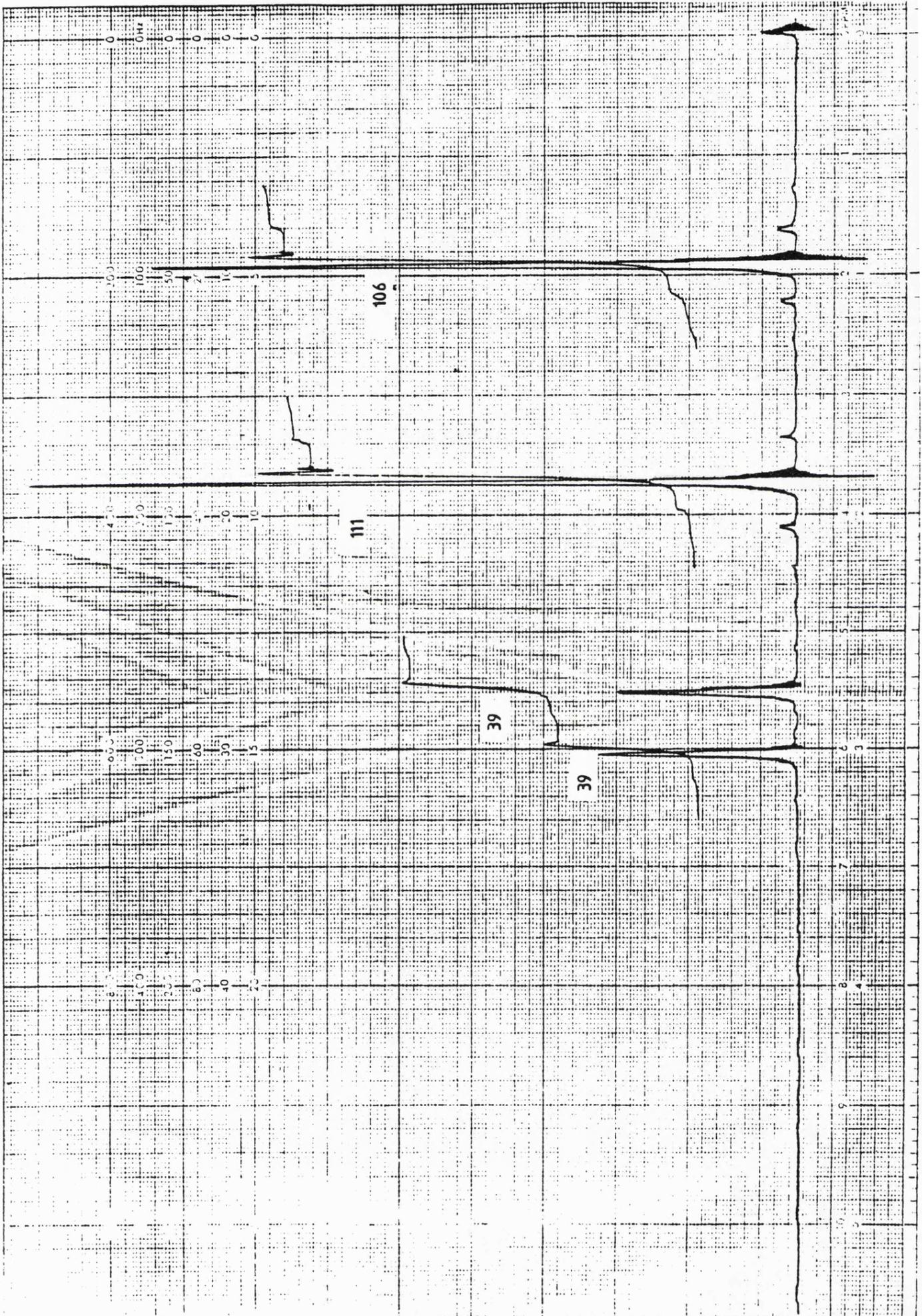
Amine	Oxygen uptake ($\times 10^{-3} \text{ cm}^3 \text{ seconds}^{-1}$)
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	3.35
bis(2-morpholinoethyl)ether	2.00
1,3-di(N-methylpiperazino)propane	3.85
bis(2-N,N-diethylaminoethyl)ether	1.40
1,2-bis(2-(N,N-diethylamino)ethoxy)ethane	2.55
bis(2-(N,N-diethylamino-2-ethoxy)ethyl)ether	3.80

Comparison of the results above with those for the photo-reductions show that there is little correlation between them. Neither is there any similarity between the rate of photo-oxygenation and the speed of cure in thin film acrylate polymerisations.

A series of bulk polymerisations were carried out using equimolar amounts of amine and photoinitiator to polymerise methyl methacrylate. The degree to which polymerisation took place was estimated as a percentage of the amount of methyl methacrylate used for the polymerisations. The amount of polymer formed was measured by precipitating the polymer in petroleum ether.

Several other methods of estimating the amount of polymer formed in the reaction were tried, including proton nuclear magnetic resonance spectroscopy. This method did not work because little change in the integral of the peaks for methyl methacrylate occurred during the polymerisation despite the fact that large amounts of polymer could be precipitated. The ^1H n.m.r. spectrum of methyl methacrylate before polymerisation and after irradiation (when polymerisation had taken place) are shown in the diagram overleaf.

¹H n.m.r. of methyl methacrylate, 0 & 30 mins. irradiation.



The results of the precipitation method for measuring polymerisation when benzophenone was used as a photoinitiator are shown in the table 9 below.

Table 9

Amine	% Polymethyl methacrylate
Triethanolamine	13.6
N-methyldiethanolamine	14.6
N,N-dimethylethanolamine	34.0
1,3-N,N,N,N-tetramethyldiaminopropane	28.7
1,5-N,N,N,N-tetraethyldiaminopentane	20.3
1,6-N,N,N,N-tetraethyldiaminohexane	20.5
1,8-N,N,N,N-tetraethyldiaminooctane	21.0
1,10-N,N,N,N-tetraethyldiaminodecane	21.0
Tetraethylenepentamine	2.3
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	31.9
1,3-dimorpholinopropane	22.8
1,6-dimorpholinohexane	19.5

The results show that there is a measure of agreement between reactivity as measured by the rate of photoreduction of fluorenone and the rate of bulk polymerisation. The more reactive amines causing the formation of larger amounts of polymethyl methacrylate than amines of lower reactivity. An experiment was carried out to study the effect of different ketone initiators on the amount of polymer formed. These results are described overleaf in table 10.

Table 10

Amine	Photoinitiator	% Polymethyl methacrylate
1,3-dimorpholinopropane	Benzophenone	21.0
1,3-dimorpholinopropane	2-isopropylthioxanthone	17.5
1,3-dimorpholinopropane	fluorenone	2.2
triethanolamine	Benzophenone	11.9
triethanolamine	2-isopropylthioxanthone	11.0
triethanolamine	fluorenone	2.5
triethylamine	Benzophenone	30.2
triethylamine	2-isopropylthioxanthone	28.0
triethylamine	fluorenone	1.1

Examination of the results described in table 10 show that benzophenone is the best photoinitiator of bulk polymerisation and fluorenone the least efficient. These results are in agreement with the scale of reactivities of the ketones already described.

The observations of Cardenas and O'Driscoll⁶⁷ using ethyl methacrylate polymerised in bulk suggested that little difference should be observed between acrylate polymerisations in bulk and curing of commercial photocure formulations. Walling⁶⁸ found that gel points occurred at around 5% conversion of the prepolymer in typical commercial formulations. However a more recent study by Brown⁶⁹ showed that a conversion of prepolymer to polymer of 63% was required before the coating would appear dry. The results of the bulk polymerisations may not then represent very closely the curing of commercial acrylate systems. The bulk polymerisations may show generalised trends in behaviour of the different systems. An experiment was carried out to investigate the effect of oxygen on the extent of polymerisation, the results

given below in table 11 showed that polymerisation occurred to a greater extent when oxygen was excluded. This result is in agreement with the results obtained by Van Neerbos⁷⁰.

Table 11

<u>Initiator</u>	<u>Amine</u>	<u>Atmosphere</u>	<u>% Polymer</u>
Benzophenone	triethanolamine	air	22.0
Benzophenone	triethanolamine	argon	26.3
2-isopropylthioxanthone	triethanolamine	air	15.0
2-isopropylthioxanthone	triethanolamine	argon	19.2

From the various results obtained, the ability of an amine to accelerate cure cannot be measured in terms of its reactivity towards ketones in photoreduction reactions, nor the rate of photo-oxygenation. The results have shown that the structure of the amine affects cure in photopolymerisable systems. One cannot predict which amines will be most effective as synergists in ketone / amine initiated polymerisations using photoreduction or photo-oxygenation reactions of the amines.

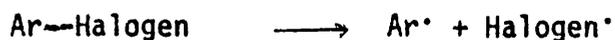
Chapter 3.

***Dehalogenation
of Haloaromatic
Compounds***

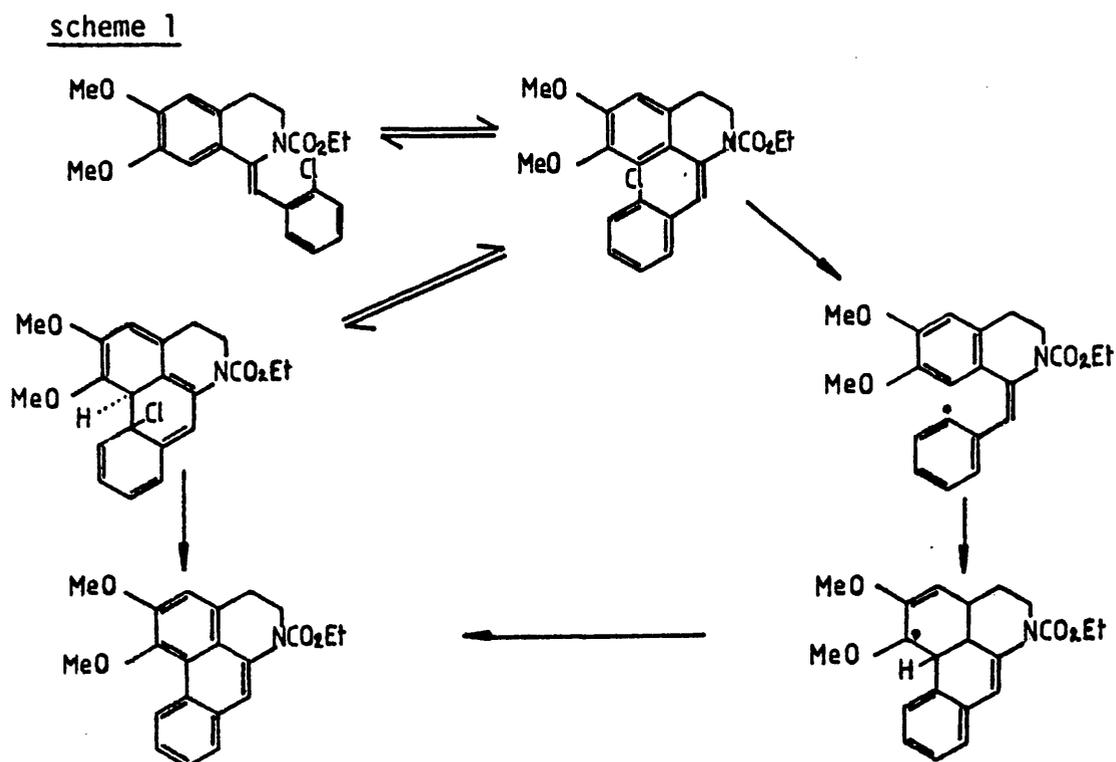
INTRODUCTION

There are many references to the photochemistry of haloaromatic compounds in the published literature with particular emphasis being placed on iodoaromatic compounds^{71,72}. The topic has been the subject of several reviews^{73,74,75} in the early 1970's describing both mechanistic and synthetic uses of the reaction.

It has been established that aryl halides, on photolysis undergo a homolytic cleavage of the carbon-halogen bond to afford aryl radicals and halogen atom radicals⁷⁶.

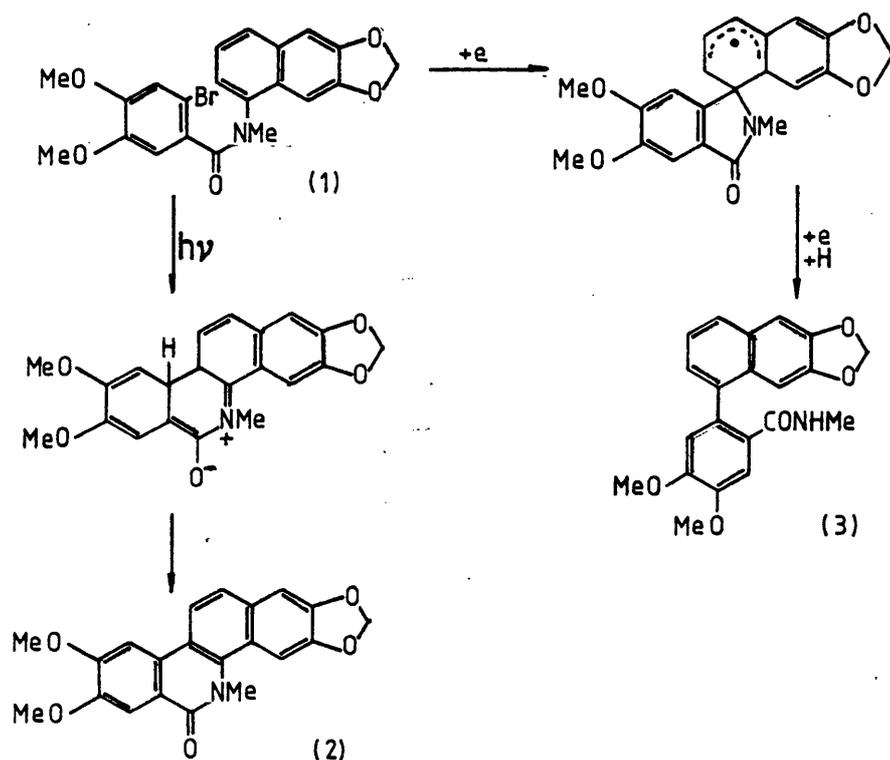


The question of the excited state responsible for the reaction is of considerable importance. In some cases it has been found that bond homolysis is in competition with an electrocyclic reaction. Cava et al.⁷⁷ presented evidence for an electrocyclic reaction in the photo-cyclisation of halogenated stilbenes to the dehydroaporphine ring system. (scheme 1)



This example also illustrates the conformational factors which can affect the outcome of reactions. Begley and Grimshaw⁷⁸ showed that electrocyclic reactions could take place to the exclusion of homolytic cleavage of the carbon-halogen bond.

scheme 2



They demonstrated that (1) photo-cyclises to produce (2) as the only product. The exclusive product of an electrochemical reduction is (3) which arises from an aryl radical. The lack of formation of (3) in the photochemical reaction confirms that the electrocyclic reaction is taking precedence over the radical reaction. The capacity for the electrocyclic reaction to compete would depend on the activation energy, the energy available for the reaction and steric factors. There is a greater probability of steric crowding in the transition state of an electrocyclic reaction.

The nature of the halogen should also affect the degree to which the electrocyclic reaction can compete with homolytic

fission, homolysis becoming progressively easier as the halogen substituent changes from $F \rightarrow Cl \rightarrow Br \rightarrow I$. This is largely a result of the reduction in bond strength of the carbon-halogen bond as shown in table 1.⁷⁹

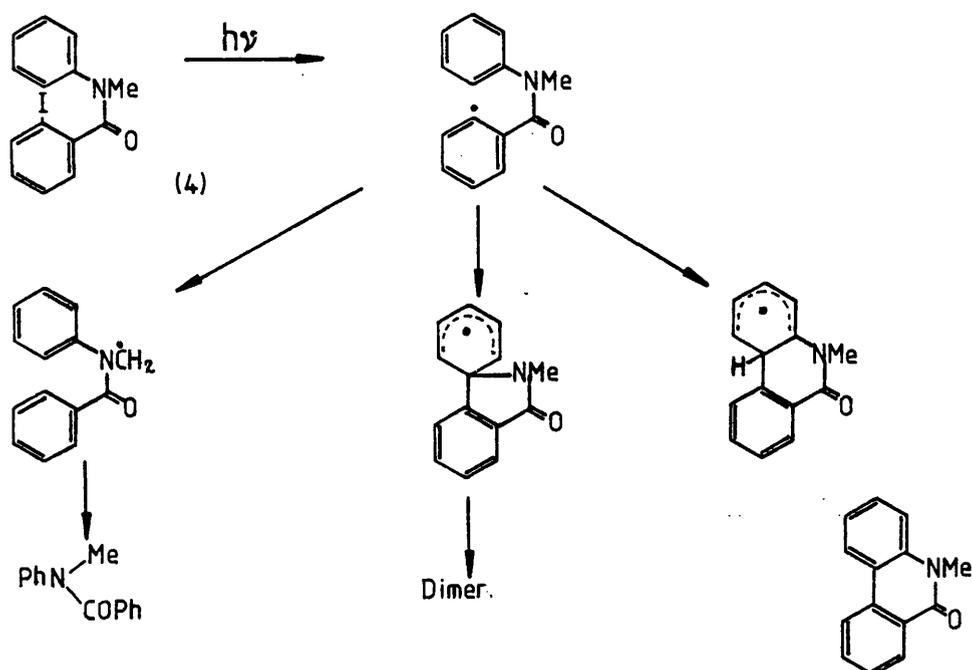
Table 1

Bond dissociation energies of carbon-halogen bonds.

Bond	Energy (Cal.mole ⁻¹)
C_2H_5-Cl	80.8
C_2H_5-Br	67.6
C_2H_5-I	53.2
C_6H_5-Cl	94.5
C_6H_5-Br	79.2
C_6H_5-I	64.4
$C_6H_5CH_2-Cl$	69.4
$C_6H_5CH_2-Br$	54.7
$C_6H_5CH_2-I$	40.0
$C=C-Cl$	88.8
$C=C-Br$	76.4
$C=C-I$	63.0

This point is illustrated in the example (scheme 3) in which the products of the photolysis were shown to be derived from radical intermediates as a result of bond homolysis.⁸⁰ The formation of cyclised products is accounted for by the fact that the favoured conformation for (4) is that for the cis form.

Scheme 3



A further consideration is that halogen substituents enhance intersystem crossing both from the excited singlet to the excited triplet state and from the excited triplet state to the singlet ground state.

The different aryl groups have differing triplet energies, e.g. naphthalene 61 Cal mole^{-1} , anthracene 43 Cal mole^{-1} , benzene 84 Cal mole^{-1} , some of these have triplet energies lower than the carbon-halogen bond dissociation energy thus the triplet state may not be responsible for reaction.

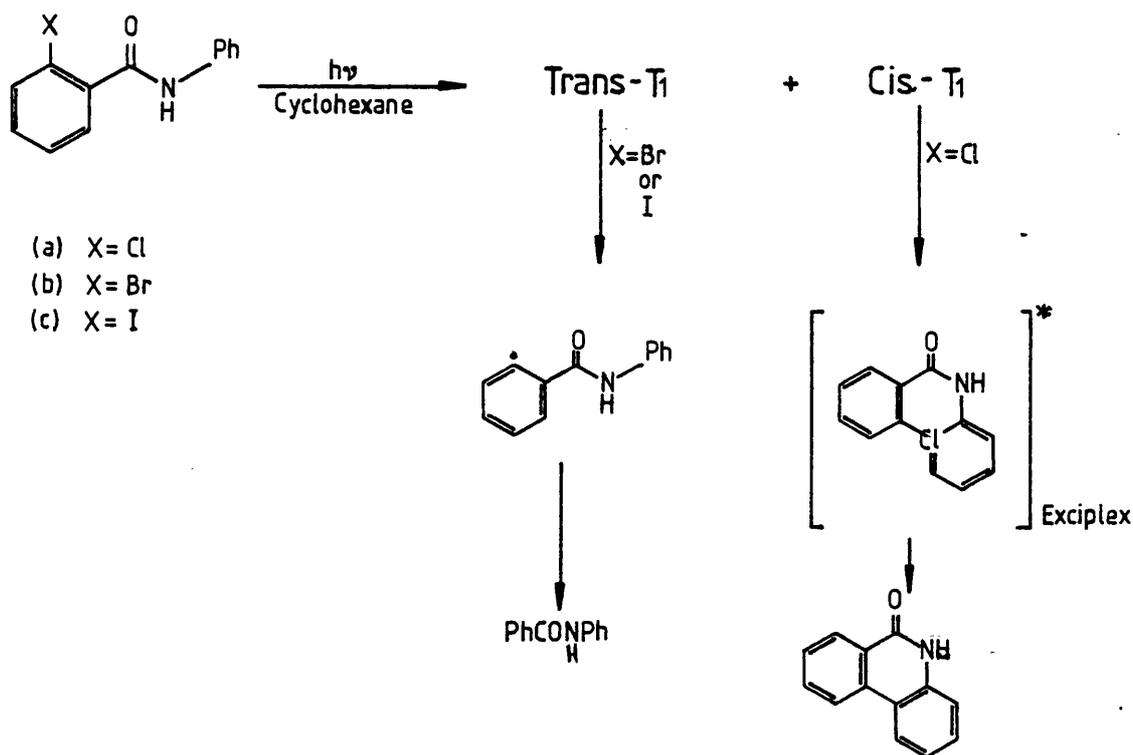
CHLOROBENZENES

A. Shimoda and his coworkers⁸¹ measured the fluorescence lifetimes in the vapour phase of the various dichlorobenzenes. They showed that a fast non-radiative decay of the excited singlet state was caused by the chlorine substituent and prop-

They showed that (5) dechlorinates inefficiently. The compound also shows an exciplex emission, therefore the formation of an intramolecular exciplex leads to energy wastage, reducing the efficiency of the homolysis reaction. Vernon and Robinson⁸⁴ found a similar stability for the biphenyl (6) and 1-naphthyl (7) cases.

In 1980 Grimshaw⁸⁷ showed that the formation of exciplexes between chlorobenzene and benzene and its derivatives can be exploited in photocyclisation reactions.

Scheme 5

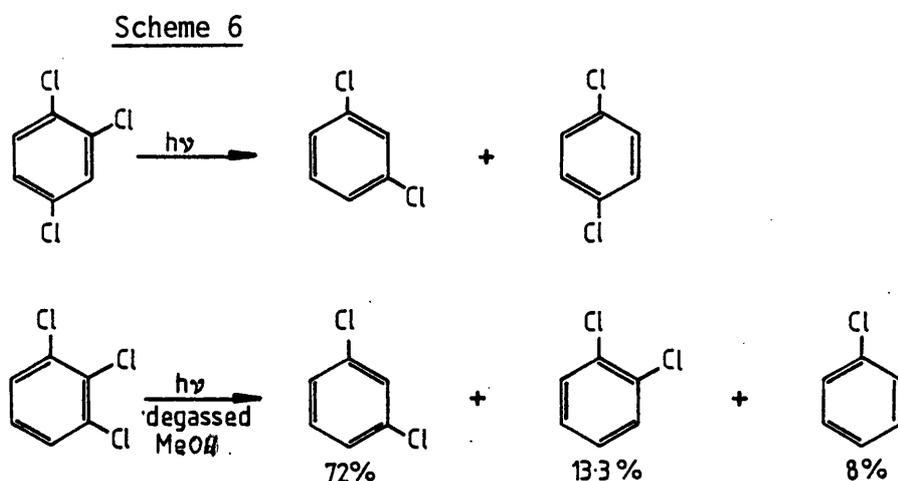


The bromo and iodo compounds dehalogenate. The explanation for these observations was that an exciplex was formed between the chlorine atom in the cis conformer and the other aromatic group in the triplet state. Carbon-chlorine bond

homolysis occurring from this intermediate resulting in cyclisation. The carbon-bromine and carbon-iodine bonds are weaker than the carbon-chlorine bond and homolysis can occur from the trans conformer which is the preferred ground state conformer.

An intriguing observation was the reduction in reactivity on addition of polar solvents to the cyclohexane solution. This indicated the excited state has some charge-transfer character which could be solvated, thus lowering its energy below that needed for formation of the intramolecular exciplex. Grimshaw assigned the triplet state as being responsible for reaction; this was based on quenching and sensitization studies.

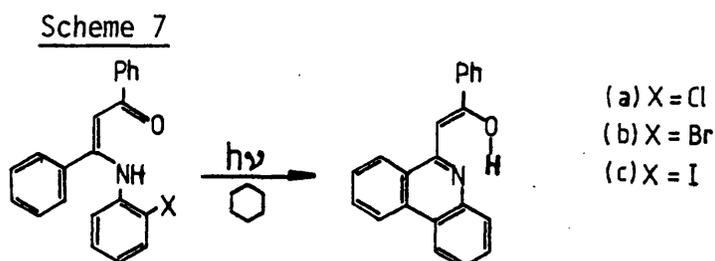
Several groups of workers^{88,89} have made observations concerning the photochemistry of trichlorobenzenes. It was found that reaction occurred in such a way to relieve the interaction between ortho chlorines.



This relief of steric congestion was thought to play a part in the energetics of the homolysis reaction. Evidence was also found supporting the fact that both singlet and triplet manifolds were reactive. Product distribution was found to change when triplet sensitization was carried out. The excited singlet state exhibiting less regioselectivity than the lower

energy triplet state.

The importance of carbon-halogen bond strength relative to the energy of the excited state undergoing reaction has been examined by Grimshaw et al.⁹⁰ as shown in scheme 7.



The quantum yield for reaction showed considerable wavelength dependence (Table 2:)

Table 2

Wavelength /nm	Quantum Yield		
	X=Cl	$10^4 \phi$ X=Br	X=I
254	1.2	110	460
315	0.2	4.0	90
335	0.4	0.4	9.0
370	0.1	1.0	4.0

It was proposed that the wavelength dependence was the result of dissociation from either the second excited singlet state or from a vibrationally excited singlet state. Reaction from the second excited singlet state could only take place if the energy entered the aryl group via a $\sigma-\sigma^*$ transition rather than the lower energy $\pi-\pi^*$ transition, leading to bond cleavage.

CHLORINATED BIPHENYLS

The photochemistry and photophysics of chlorinated biphenyls have been more extensively studied than the chlorobenzenes as a result of environmental considerations^{91.92.93.}

Biphenyl in the ground state is a twisted molecule because of steric interaction at the ortho positions in a planar configuration increases the energy of the molecule. On excitation however, biphenyl produces a non-planar excited singlet state which relaxes and forms a planar excited singlet state and excited triplet state. The photophysics has been studied extensively by Bunce and his co-workers^{94.} Their results are summarised in table 3.

Table 3
Photophysical Parameters and Quantum Yields for
Dechlorination of Chlorinated Biphenyls

POSITION OF SUBSTITUTION	ϕ_F	ϕ_P	$T(10^{-8}s)$	ϕ_R
2	0.09	0.46		0.39
3	0.07	0.27		0.001
4	0.07	0.60		0.007
2,4	0.02			0.62
2,5	0.06			0.73
2,2'	0.01	0.95		0.16
2,4,5	0.11			0.43
2,4,6	0.003			0.14
2,2',4,4'	0.02	0.94	0.78	0.45
2,2',3,3'			0.77	0.007
2,2',5,5'	0.001		0.67	0.005
2,2',6,6'			0.70	

3,3',4,4'	0.08	.	2.20	0.005
3,3',5,5'	0.02	0.41	1.91	0.001
2,2',4,4',6,6'	0.003	1.0		

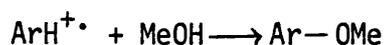
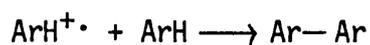
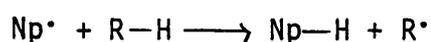
Bunce reported that for all examples intersystem crossing was efficient and this was particularly so with those possessing a chlorine atom in the ortho position. The ortho chlorine atom increasing the energy of activation needed to achieve planarity. Thus the loss of such a substituent was found to lead to a greater relief of strain than a meta or para chlorine atom. Compounds of this type were subsequently observed to have a shorter triplet lifetime than the corresponding meta or para compounds. This may be a result of homolytic bond cleavage being an important non-radiative decay route. Product studies⁹⁵ showed that ortho chlorine substituents were lost preferentially. It was suggested on the basis of quenching studies⁹⁶ utilising cyclohexa-1,3-diene that the triplet manifold was responsible for reaction. However the authors pointed out that the diene also quenches the excited singlet state of the chlorinated biphenyls. If this occurred curvature of the Stern-Volmer plots would have been observed, this is not the case. Some credence to triplet state involvement in the reaction is given by use of the heavy_{atom} effect. The yield of triplet product however does not provide very convincing evidence for this.⁹⁴.

CHLORONAPHTHALENES

Bunce and his co-workers⁹⁷ have irradiated several different chloronaphthalenes in hydrogen donating solvents such as methanol. The photolysis producing naphthalene as the major product. Some nucleophilic substitution also took place to afford

methoxynaphthalene. The amount of substitution was found to be increased when a nucleophile such as water was used in solution in acetonitrile. Bunce on the basis of results of oxygen quenching experiments assigned the reaction to occur from the excited triplet state. Further experiments by the same author⁹⁸ resulted in the assignment of the singlet state as being responsible for reaction. A mechanism involving excimers was proposed when it was found that the carbon-chlorine bond energy was higher than the energy available and spectroscopic evidence for such a species was provided. In addition, it was shown that the quantum yield for dechlorination increased as the concentration of the chloro compound was increased, and the same result was produced by the addition of a non-absorbing additive, 4-chlorobiphenyl. The following reaction scheme was proposed.

Scheme 8

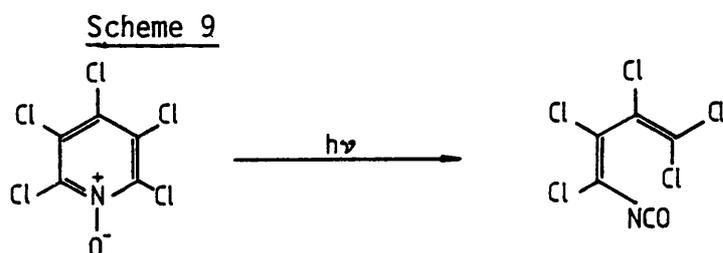


This mechanism accounted for the formation of methoxynaphthalenes from the irradiation of chloronaphthalene in methanol.

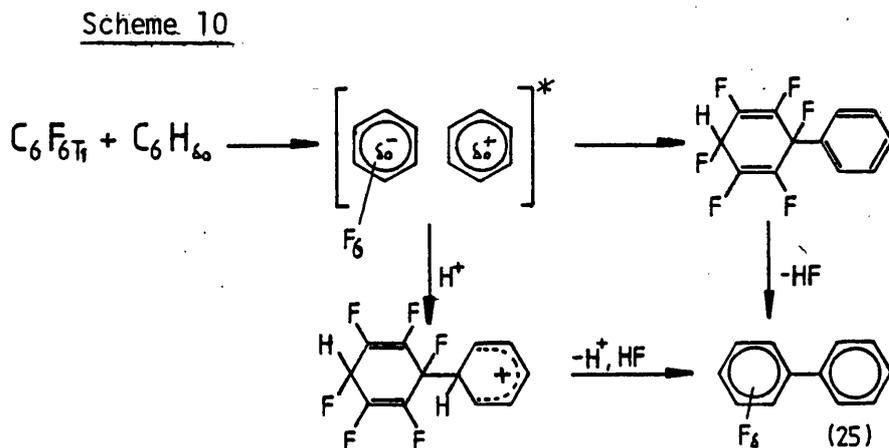
Investigations have been carried out on polychlorinated naphthalenes⁹⁹; the same type of product distribution as for 1-chloronaphthalene being observed.

DEHALOGENATION OF OTHER RELATED COMPOUNDS

Pentachloropyridine has been found to undergo dechlorination regiospecifically to give 2,3,4,6-tetrachloropyridine on irradiation in ethers¹⁰⁰. The reason for specific reactivity at the 5 position^{is not} fully understood. The N-oxide derivative however did not dehalogenate but formed an isocyanate as illustrated below in scheme 9.



An interesting reaction was discovered by Bryce-Smith and his co-workers¹⁰¹. Irradiation of hexafluorobenzene and benzene in a solvent afforded 2,3,4,5,6-pentafluorobiphenyl as shown in scheme 10.

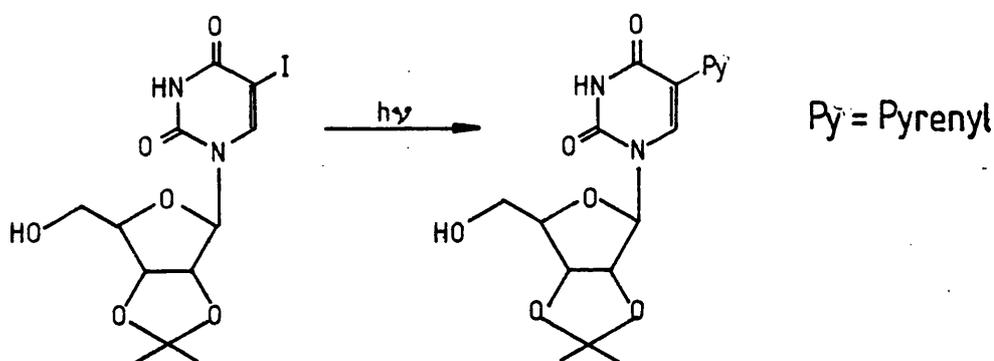


An exciplex intermediate was postulated on the basis of an increase in product yield with increase in solvent polarity and

concentration of benzene. However studies utilising deuterated solvents did not lead to incorporation of deuterium, implying free radical ions were not involved. The excited state responsible for reaction was suggested as being the excited triplet state, this conclusion was drawn from quenching studies. Homolysis of the carbon-fluorine bond does not appear to take place in this reaction and defluorination appears to take place by a similar mechanism to the electrocyclic reactions, by elimination of hydrogen halide.

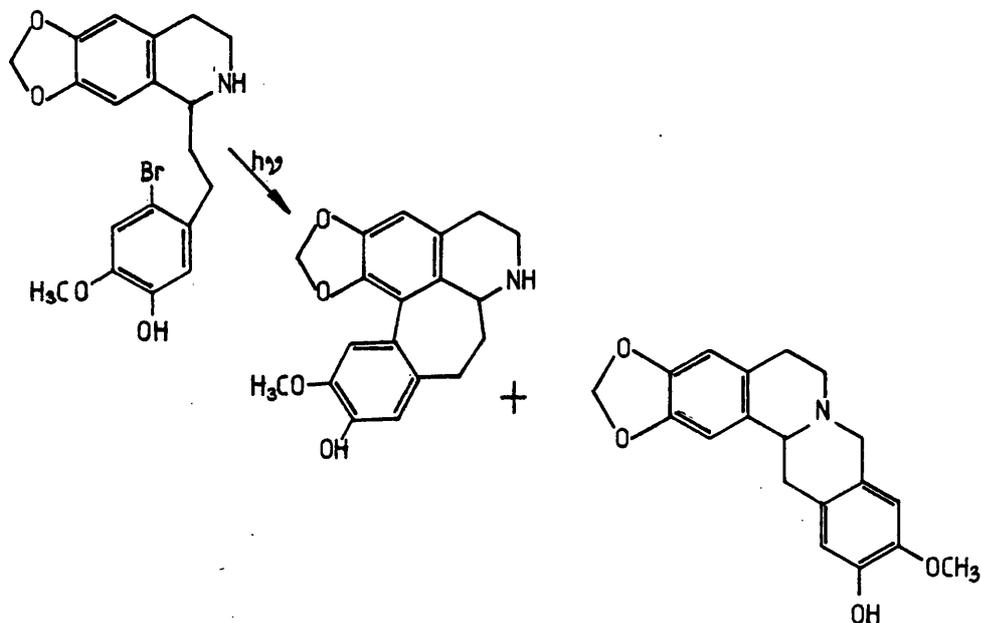
An important use the dehalogenation reaction is in the production of a fluorescent label¹⁰². Irradiation of iodouridine with pyrene resulted in a highly fluorescent adduct as shown below in scheme 11.

Scheme 11



The synthetic utility of the dehalogenation reaction has also been exploited in the field of alkaloid synthesis. Govindichari et al¹⁰³ utilised this reaction in the following example.

Scheme 12



BROMO AND IODO COMPOUNDS

Table 1 indicates that the carbon-halogen bond strength of bromo and iodo aromatic compounds is substantially lower than the aryl-chlorine bond dissociation energy, falling below the energy for the excited singlet state of the benzenoid compounds. In addition the $\sigma-\sigma^*$ absorption bands of carbon-bromine and carbon-iodine bonds have a tail which extends beyond 254 nm. Thus irradiation of the compounds at these short wavelengths could lead to reaction via population of the $\sigma-\sigma^*$ transition as well as the more usual $\pi-\pi^*$ transition. The work of C.P. Andrieux et al.¹⁰⁴ using electron paramagnetic resonance spectroscopy to study the radical anions derived from simple halobenzenes showed the lowest antibonding orbital to be the σ^* orbital.

It was also found that the introduction of groups having negative resonance effects or with electron withdrawing substituents

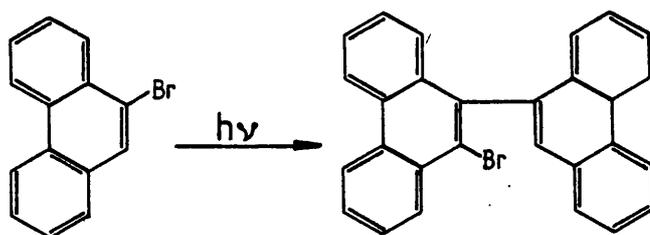
e.g. nitro groups, reduced the energy of the π^* orbital to below that of the σ^* orbital.

The fact that the aryl-iodine bond is much weaker than the carbon-bromine bond (see table 1) would lead to the expectation of a higher product yield, this was found to be the case in a study by Sharma and Kharasch⁷⁴.

The photolysis of bromobiphenyls has been examined by Bunce et al.¹⁰⁵, they found that 2-bromobiphenyl is more reactive than the 4-bromo compound. The reason for this observation is the same as that for 2-chlorinated biphenyls, i.e. relief of steric strain.⁹⁴. Irradiation of 3,5-dibromobiphenyl led to loss of bromine from the 5 position to afford the more stable 3-bromobiphenyl.

U. Weiss and his co-workers¹⁰⁶ photolysed 9-bromophenanthrene as shown in scheme 13. The product of the irradiation, which was carried out in hexane, was a dimer type product.

Scheme 13



The mechanism for the reaction was postulated as occurring via attack by 9-phenanthryl radicals on the starting material. The fact that hydrogen abstraction from the solvent did not take place suggested to the authors that the phenanthryl radicals may be produced from an excimer made up of two molecules of 9-bromophenanthrene.

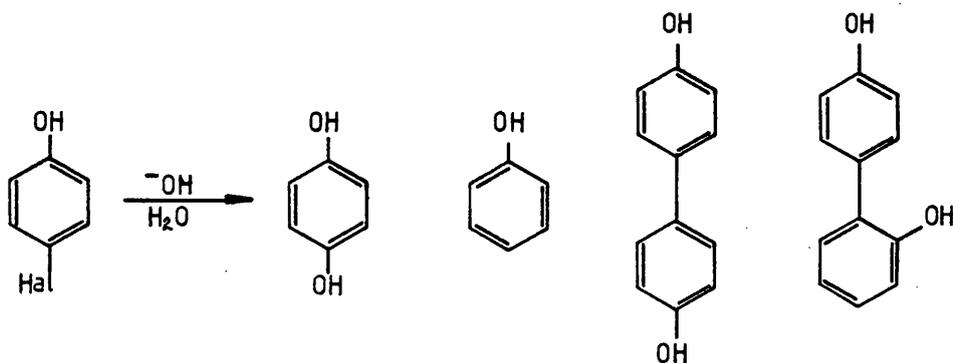
SODIUM BOROHYDRIDE ASSISTED DEHALOGENATION OF HALOGENATED
AROMATIC MOLECULES

Sodium borohydride was shown by Pratt et al.^{107.} to accelerate the photo-induced dechlorination of 3-chloro and 4-chlorobiphenyl. Evidence for the mechanism of this reaction has been provided by the work of Bartrop and Owers^{108.}, who showed that sodium borohydride photoreduces excited 1-cyano-naphthalene via hydride attack. The chlorinated aromatic compounds were assumed to undergo reduction by a similar mechanism.

PHOTO-INDUCED NUCLEOPHILIC SUBSTITUTION REACTIONS

Photochemical nucleophilic substitution reactions have been recently reviewed by Havinga^{109.}. There is a plethora of examples of displacement of a halogen by hydroxides and amines^{110.111.}. Radical processes have a role in some of these reactions, for example, the reactions of 4-halogenated phenols^{112.} as shown in the following reactions, scheme 14.

Scheme 14



Miller et al.,^{113.} irradiated a series of halogenated

quinolines and isoquinolines in methanol solution containing hydroxyl ions. They found that the bromo compounds, but not their chloro counterparts dehalogenate on irradiation. The rate of photoreduction is dependant upon the concentration of hydroxyl ions. It was found that utilising deuterated solvent and deuterium oxide did not lead to deuterium incorporation into the product. The explanation for this was that the hydroxyl ion acted as an electron donor producing a bromoquinoline radical ion which undergoes dehalogenation. The mechanism by which hydroxyl ions act as electron donors to excited states has also been suggested by Parkanyi and Lee¹¹⁴. However no explanation for the lack of reactivity of chloroquinolines was suggested.

AMINE ASSISTED DEHALOGENATION OF HALO-AROMATIC COMPOUNDS

The literature contains many examples concerned with the formation of excited complexes between aromatic hydrocarbons and tertiary amines^{115,116}. The reduction potentials for haloaromatic compounds have been shown to be similar to the parent aromatic compounds¹¹⁷ and may form excited complexes or radical ions with electron donors. Fluorescence form complexes between 1-chloronaphthalene and triethylamine have been observed by Bunce et al.⁹⁸. Many examples of quenching of fluorescence of haloaromatics¹¹⁸ and haloheterocycles¹¹⁹ by triethylamine are known. The debromination of bromopyrimidines was reported by Nasielski¹²⁰, acceleration being effected by secondary aliphatic amines as well as tertiary amines.

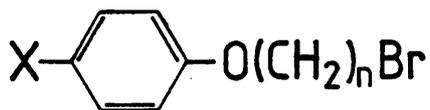
The fluorescence of aromatic amines, for example N,N-dimethyl aniline, is quenched by haloaromatic compounds such as chloro and bromobenzene and exciplex emission has been

observed by Tosa and his co-workers¹²¹. They also irradiated N,N-dimethyl aniline in the presence of halobenzenes, the products of the photolysis were benzene, biphenyl, N-methylaniline and phenylated N,N-dimethylaniline. The product distribution was accounted for by the postulation of aryl radical intermediates.

DISCUSSION AND RESULTS

The mechanism of the photo-induced homolysis of aryl halides has been studied to try to elucidate the excited state responsible for reaction.

A series of ω -(4-halophenoxy) alkyl bromides were synthesised using the method of B.Jones¹²². Irradiation of ω -(4-halophenoxy) alkyl bromides (1,2) in methanol afforded phenoxy alkyl bromides (3) as the major products.



1) X = Br

2) X = Cl

3) X = H

The yields of products from the irradiations are presented in the table 4 shown overleaf.

In addition to the products shown in the table (4) 4-chlorophenol was found in 2% yield on irradiation of 2-(4-chlorophenoxy) 1-bromo ethane and in 0.5% yield on irradiation of 3-(4-chlorophenoxy) 1-bromo propane.

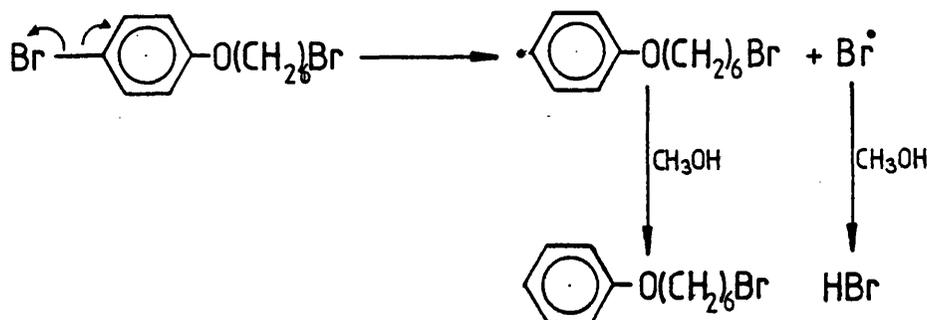
The homolytic cleavage of the aryl carbon-bromine bond proceeded preferentially to alkyl carbon-bromine bond homolysis and gave good yields of the phenoxy alkyl bromides. The mechanism by which the phenoxy alkyl bromides are formed is presumably via homolytic cleavage of the aryl-bromine or aryl-chlorine bond to afford an aryl radical, followed by hydrogen abstraction from the solvent to give the product. This scheme 15 is outlined

Table 4

Halogen (X)	Chain length (n)	Irradiation time (hrs)	Starting material (%)	Product (%)	Product (%)
Cl	2	3	56.5	PhO(CH ₂) ₂ Br 15.5	Phenol 25.0
Cl	3	3	46.0	PhO(CH ₂) ₃ Br 26.5	Phenol 20.0
Cl	8	4	53.0	PhO(CH ₂) ₈ Br 40.0	
Cl	10	6	60.0	PhO(CH ₂) ₁₀ Br 38.0	
Br	2	2	52.0	PhO(CH ₂) ₂ Br 35.0	Phenol 25.0
Br	3	4	5.0	PhO(CH ₂) ₃ Br 81.0	Phenol 10.0
Br	6	4	20.0	PhO(CH ₂) ₆ Br 74.0	
Br	8	4	39.0	PhO(CH ₂) ₈ Br 59.0	
Br	10	4	47.0	PhO(CH ₂) ₁₀ Br 50.0	

below using 1-bromo-6-(4-bromophenoxy) hexane as an example.

Scheme 15



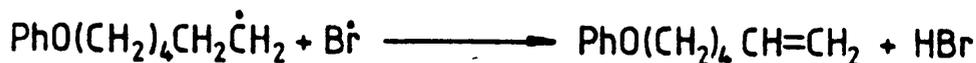
Since the incident energy is gathered by the aryloxy moiety, the lack of reaction alkyl-bromine bond could be due to inefficient energy transfer along the alkyl carbon chain to the $\text{CH}_2\text{-Br}$ bond. Inter-molecular energy transfer does not occur during these irradiations because of the low concentration of material used. Precedent exists however for sensitization of the alkyl-bromine bond. Kropp et al.¹²³ were able to sensitize cleavage of this bond in 1-bromonorbornane using benzene. The possibility of sensitization was investigated using 1-bromo-6-phenoxy hexane and utilising benzene as the sensitizer. The photolysis yielded the products shown in the following table 5.

Table 5

Solvent	Photolysis time(hr)	Phenol(%)	1-hexylphenylether(%)	1-hexenylphenylether
benzene	6	7.0	15.0	8.0

As a result of the high concentration of benzene used virtually none of the incident light would be absorbed by the 1-bromo-6-phenoxy hexane. The products indicate sensitization has taken

place. 1-hexyl phenyl ether was produced as a result of the following reaction sequence, scheme 16.



The reaction does not appear to involve the solvent in a hydrogen abstraction step as no phenylated products were observed, nor was biphenyl which would be formed if aryl radicals were present, by gas chromatography.

The reaction does not supply any evidence as to the excited state involved, as the multiplicity of the excited species effecting sensitization was not characterised.

The fluorescence spectra of the series of ω -phenoxy-alkyl bromides and their related ethers were studied, the table 6 below details the ratio of quantum yield of fluorescence of ether to quantum yield of fluorescence for the corresponding bromide. Absolute quantum yields were determined from a methyl phenyl ether standard.

Table 6

Chain length (n)	ϕ_f ether / ϕ_f bromide
2	2.086
3	1.159
4	1.136
6	1.038
10	1.311

These quantum yields for ethers and bromides were plotted against chain length on a graph (figure 1. see overleaf.)

The results show that for a chain length of two carbons and to a lesser extent when $n = 3$ and $n = 4$ the terminal bromine atom interacts with the aryloxy group quenching fluorescence. The observation that quenching was most efficient when the length of carbon chain was small is not unexpected in the light of recent work on excimers and exciplexes¹¹⁵. For ω -(4-halophenoxy) alkyl bromides having a carbon chain longer than three carbons, the bromine atom on the alkyl chain does not come close enough to the aryloxy moiety to interact and sensitize bond homolysis.

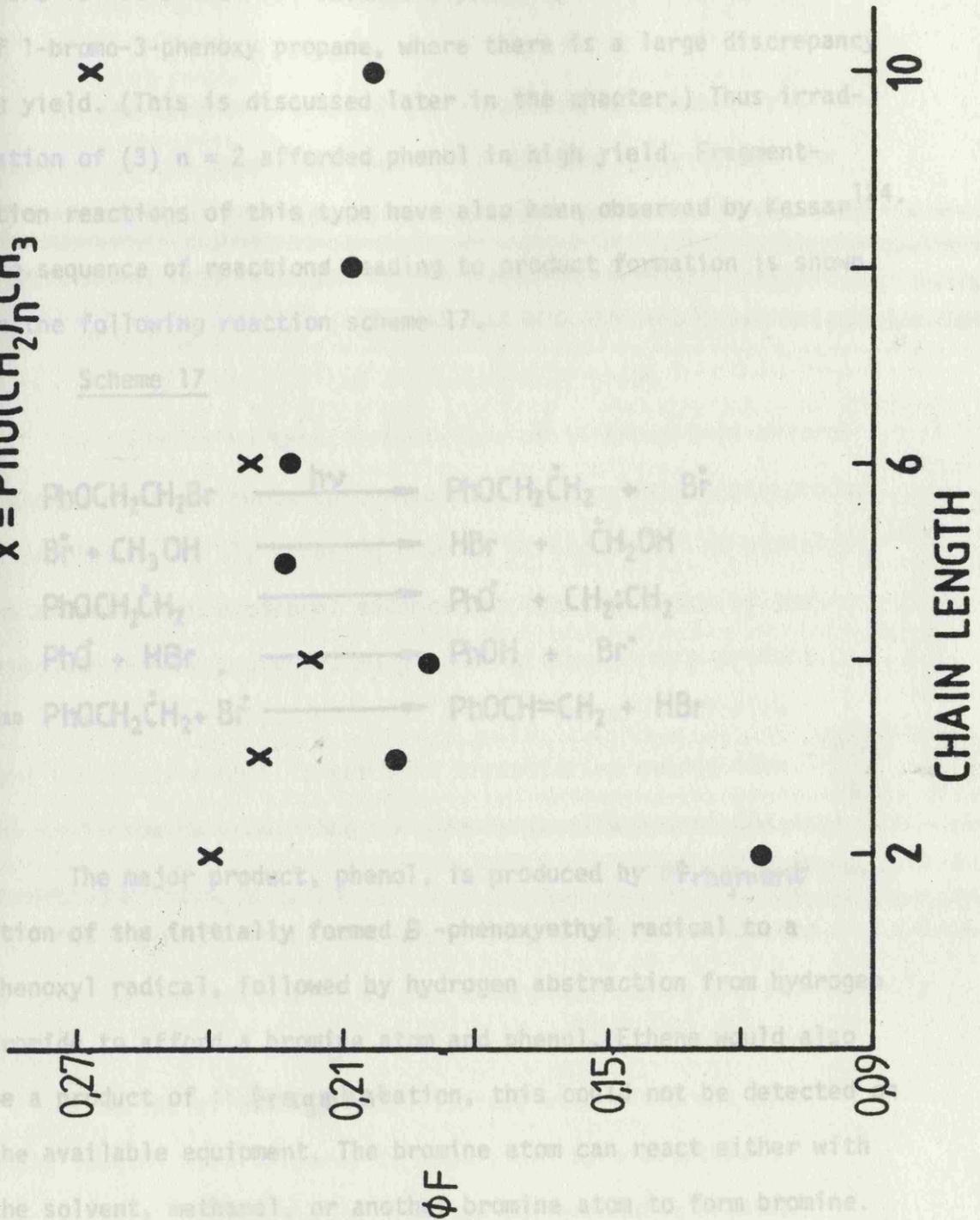
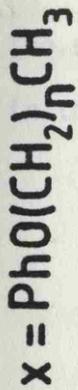
Irradiation of phenoxy alkyl bromides (3) in methanol led to reaction and product yields are shown in the following table 7.

Table 7

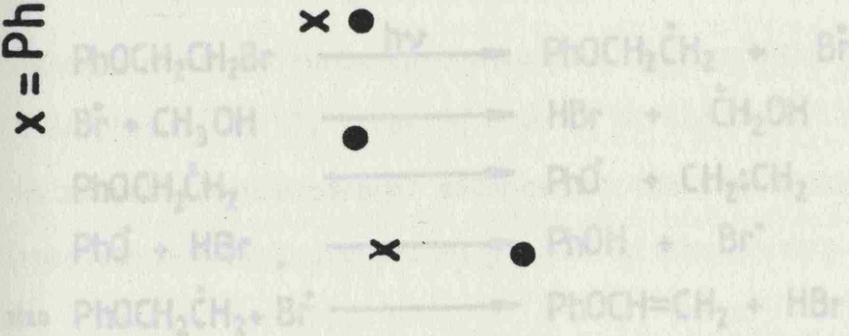
Chain length (n)	Photolysis time (hrs)	Starting material (%)	Phenol (%)	1-alkenyl-phenyl ether (%)
2	6	12	80	5
3	6	15	65	3
4	6	52	16	18
6	6	57	8	33
10	24	100	0	0

These results show that intra-molecular sensitized homolysis of alkyl-bromine bonds can occur for compounds having $n = 2$ and $n = 3$. That this phenomenon takes place is shown by the high reactivity of 1-bromo-2-phenoxy ethane and 1-bromo-3-phenoxy propane compared with other members of the series

Fluorescence Yields for w-phenoxyalkyl bromides.



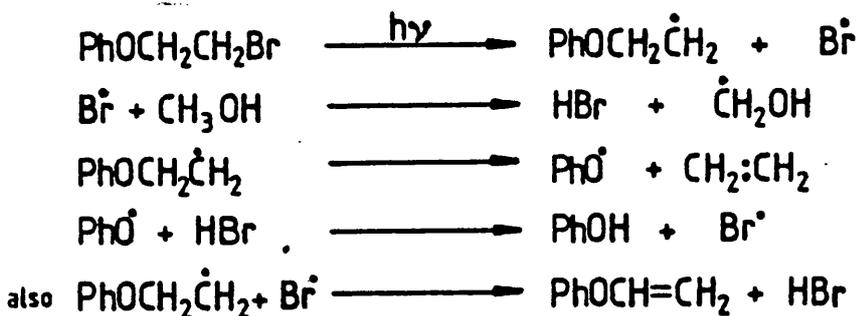
Scheme 17



The major product, phenol, is produced by fragmentation of the initially formed β -phenoxyethyl radical to a phenoxy radical, followed by hydrogen abstraction from hydrogen bromide to afford phenol and a bromine atom. Ethanol would also be a product of hydrogen abstraction, this could not be detected with the available equipment. The bromine atom can react either with the solvent, methanol, or another bromine atom to form bromine. Bromine was detected in solution using the fluorescein test. For phenoxy alkyl bromides where the chain length is > 2 the

possessing longer carbon chains, i.e. $n = 3$. Reaction cannot take place through light being absorbed directly into the alkyl-bromine bond because no reaction is observed in compounds of long chain length e.g. $\text{PhO}(\text{CH}_2)_{10}\text{Br}$. It should be noted that there is not a material balance especially for the photolysis of 1-bromo-3-phenoxy propane, where there is a large discrepancy in yield. (This is discussed later in the chapter.) Thus irradiation of (3) $n = 2$ afforded phenol in high yield. Fragmentation reactions of this type have also been observed by Kessar¹²⁴. The sequence of reactions leading to product formation is shown in the following reaction scheme 17.

Scheme 17



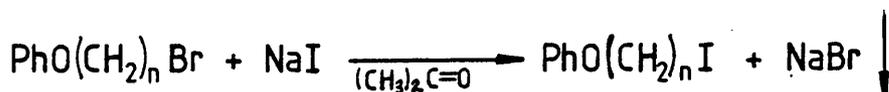
The major product, phenol, is produced by fragmentation of the initially formed β -phenoxyethyl radical to a phenoxy radical, followed by hydrogen abstraction from hydrogen bromide to afford a bromine atom and phenol. Ethene would also be a product of fragmentation, this could not be detected on the available equipment. The bromine atom can react either with the solvent, methanol, or another bromine atom to form bromine. Bromine was detected in solution using the fluorescein test. For phenoxy alkyl bromides where the chain length is > 2 the

the alkene product of the reaction is higher boiling, despite this fact the compounds could not be detected by gas chromatography. The phenoxy radical is more likely to abstract hydrogen from hydrogen bromide than the solvent as the energy requirement is less (H-Br bond dissoc. energy $87.4 \text{ Cal.mole}^{-1}$, H-CH₂OH = 94 Cal.mole^{-1} .) to form phenol.

In the case of 1-bromo-2-(4-bromophenoxy) ethane, fragmentation of the type described above was not observed and the aryl-bromine bond was cleaved to the total exclusion of the alkyl-bromine bond. This demonstrates that aryl-bromine bond homolysis takes place very rapidly and is responsible for the short lifetime of the excited states of the 4-bromoaryloxy group.

In contrast to this, irradiation of 1-bromo-2-(4-chlorophenoxy) ethane affords chlorophenol as the primary photo-product. Chlorophenol rapidly breaking down to afford phenol on photolysis¹²⁶. The amount of chlorophenol detected at the completion of the irradiation represents a steady state of the primary product. The rationale for these observations is, the aryl-chlorine bond possesses a much larger bond dissociation energy than the aryl-bromine bond, thus the homolytic cleavage of the aryl-halogen bond will be slower for 1-bromo-2-(4-chlorophenoxy) ethane than for 1-bromo-2-(4-bromophenoxy) ethane. As a consequence of this the excited states of the chloro derivative are sufficiently long lived to allow energy transfer to the alkyl-bromine bond.

A series of phenoxy alkyl iodides with different alkyl chain lengths were prepared in good yield by a metathesis reaction with sodium iodide from the corresponding bromides.



The iodides were shown to be pure by gas-liquid chromatography confirming confirming that there was no starting bromide present prior to irradiation.

Photolysis of the phenoxy alkyl iodides using a low pressure mercury lamp resulted in elimination of hydrogen iodide to afford ω -phenoxy alk-1-enes as the major product of the reaction as can be seen in the table 8 shown below.

Table 8

PhO(CH ₂) _n I	Chain length (n)	Photolysis time (mins.)	Starting material (%)	Phenol (%)	Alkene (%)
	2	60	36.5	6.0	57.5
	3	60	57.2	1.9	35.9
	4	60	53.8	1.35	44.2
	6	60	39.5	4.2	53.2
	10	60	70.0	1.0	28.8

The results displayed in the table show that a different product distribution is obtained when phenoxy alkyl iodides are irradiated compared with those obtained on photolysis of the corresponding bromides (see table 4.) In addition, reaction takes place even when there is a long chain of carbons between the aryloxy group and the carbon-iodine bond. there are several possible reasons to account for this observation. The most plausible explanation is that light is being absorbed directly by the carbon-iodine bond. The light is therefore being partitioned between this bond and the aryloxy chromophore. A further possibility is that the iodine atom enhances intersystem crossing, R.Beer et.al.^{127.} and Watkins^{128.} have shown that halide ions quench the excited singlet states of aromatic hydrocarbons.

A further study by Ruzo and his co-workers¹²⁹. examined the dehalogenation of 1-bromonaphthalene and 1-iodonaphthalene with added lithium halides. They found the efficiency of retardation of reaction by the ions was $I^- > Br^- > Cl^-$. They also found that the quenching did not lead to triplet production. This observation of retardation of reaction may indicate that the added ions were quenching the excited singlet state and that reaction was occurring from this state.

The difference in product distribution may reflect that reaction occurs in the iodo compounds from both singlet and triplet states and the quenching of the singlet state by the iodine atom influences product distribution.

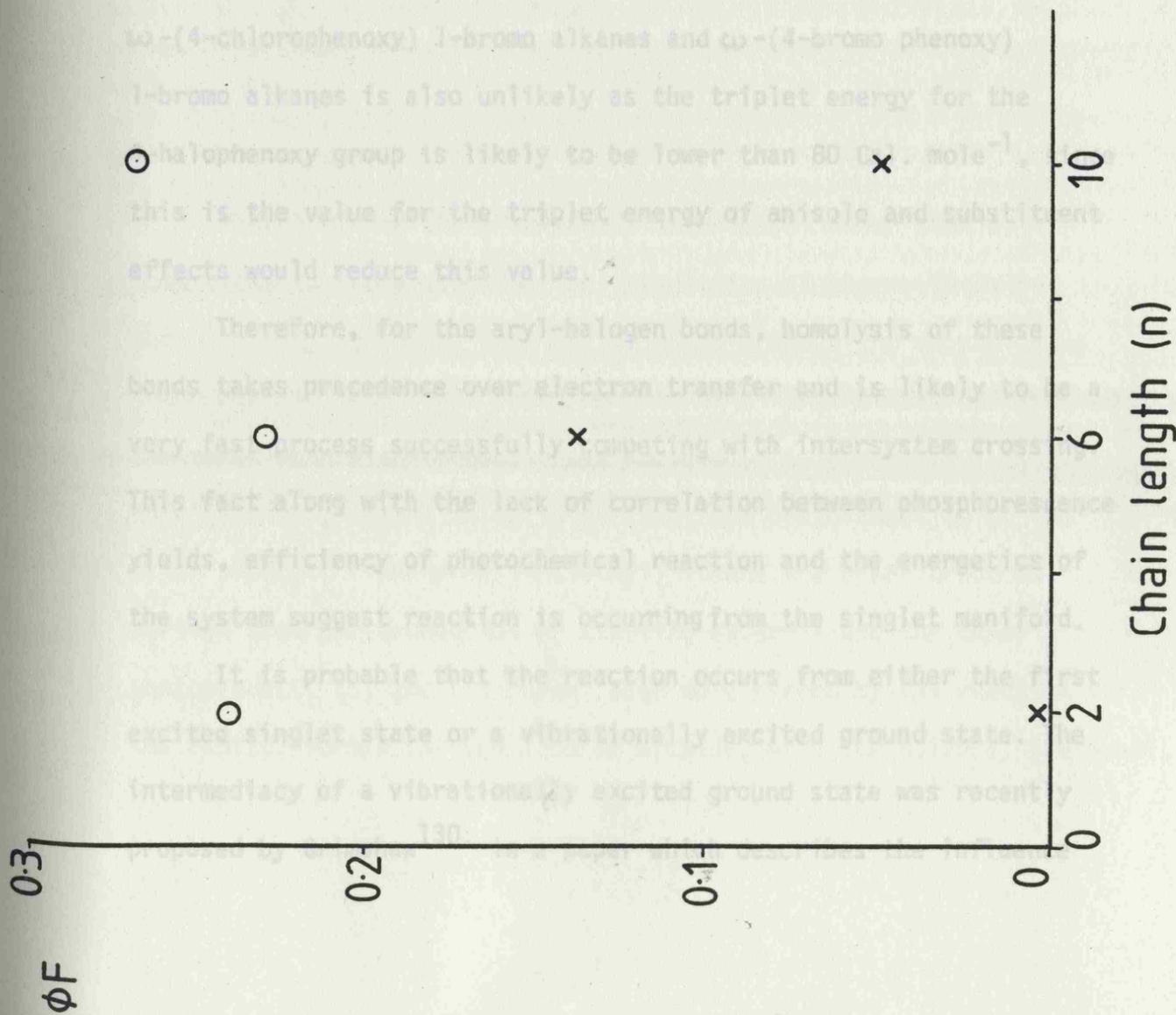
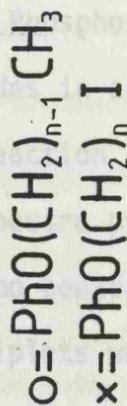
The fluorescence spectra of several iodides were recorded along with their corresponding ethers, the values are shown in diagramatic form overleaf.

The fluorescence quenching of the iodine was estimated by taking the ratio of fluorescence quantum yield for the ether and dividing this value by the fluorescence quantum yield for the iodide derivative of the parent ether. These results are shown in the following table 9.

Table 9.

PhO(CH ₂) _n I Chain length (n)	ϕ_f ether / ϕ_f iodide
2	60.54
6	2.04
10	3.99

From the graph and table it can be seen that the iodides appear to have a similar pattern of quenching with chain length i.e. most quenching occurs for PhO(CH₂)₂I and a minimum value is obtained when



$n = 6$. However in all cases the quenching ability of the iodine is enhanced, the ratios being considerably larger than the bromide in all cases examined.

Phosphorescence spectra were recorded for several aryl bromides in an attempt to determine the excited state responsible for reaction in the ω -(4-halo phenoxy) 1-bromo alkanes. Accordingly the spectra produced by 4-bromo anisole, 1,4-dibromo benzene and 4-bromo benzonitrile were examined. In all these cases the yield of triplet was low and in the case of 4-bromo anisole the spectrum was barely detectable. The data described here and that obtained by

Bunce⁹⁴ on chlorinated biphenyls show that there is little correlation between the quantum yields for phosphorescence and reaction.

The intermediacy of triplet states in the reactions of ω -(4-chlorophenoxy) 1-bromo alkanes and ω -(4-bromo phenoxy) 1-bromo alkanes is also unlikely as the triplet energy for the

halophenoxy group is likely to be lower than $80 \text{ kcal mole}^{-1}$, this is the value for the triplet energy of anisole and substituent effects would reduce this value.

Therefore, for the aryl-halogen bonds, homolysis of these bonds takes precedence over electron transfer and is likely to be a very fast process successfully competing with intersystem crossing. This fact along with the lack of correlation between phosphorescence yields, efficiency of photochemical reaction and the energetics of the system suggest reaction is occurring from the singlet manifold.

It is probable that the reaction occurs from either the first excited singlet state or a vibrationally excited ground state. The intermediacy of a vibrationally excited ground state was recently

n = 6. However in all cases the quenching ability of the iodine is enhanced, the ratios being considerably larger than the bromide in all cases examined.

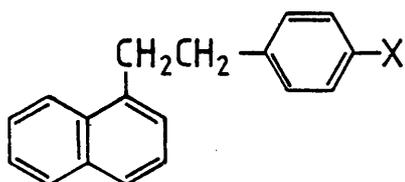
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Therefore, for the aryl-halogen bonds, homolysis of these bonds takes precedence over electron transfer and is likely to be a very fast process successfully competing with intersystem crossing. This fact along with the lack of correlation between phosphorescence yields, efficiency of photochemical reaction and the energetics of the system suggest reaction is occurring from the singlet manifold.

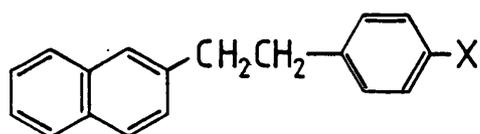
It is probable that the reaction occurs from either the first excited singlet state or a vibrationally excited ground state. The intermediacy of a vibrationally excited ground state was recently proposed by Grimshaw¹³⁰ in a paper which describes the influence

of solvent viscosity on reaction yields.

In order to substantiate that reaction did not occur from a triplet state 1-naphthyl 2-(4-bromophenyl) ethane (4a) was synthesised by a Wittig reaction of 1-naphthaldehyde with 4-bromobenzyltriphenyl phosphonium bromide. The corresponding 2-naphthyl compound (5a) was prepared by the same route.

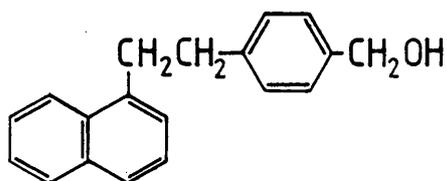


4(a) X = Br
(b) X = H

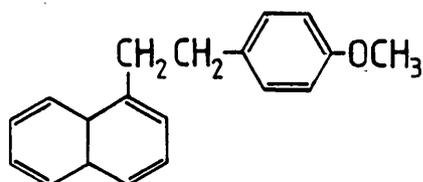


5(a) X = Br
(b) X = H

Photolysis of these compounds in methanol under similar conditions to those used for the irradiation of the ω -(4-halo-phenoxy) alkyl bromides gave as the major product the debrominated compounds (4b) and (5b). Trace amounts of a range of radical derived compounds were also formed, these included:- 1-phenyl-2-(1-(1,2-dihydronaphthyl) ethane which is derived from photoreduction of the major product, 1-phenyl-2(1-naphthyl) ethane and other products derived from photoreduction of starting material and the major photoproduct. (6) and (7) shown over were formed by the reaction of the radical formed through loss of bromine, with the solvent, (methanol.)

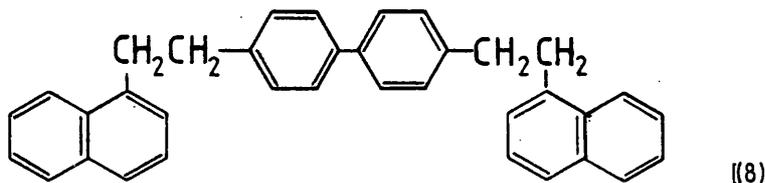


(6)



(7)

The coupling product (8) was also detected by mass spectrometry.

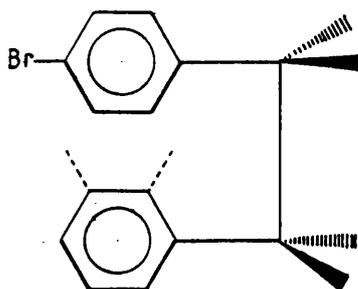


(8)

The observation of product (8) is unusual when one considers that the low concentration of the irradiated starting material should be so low as to make the chance of coupling of two radicals derived from this compound negligible.

The formation of 1-phenyl-2-(1-naphthyl) ethane as the major photoproducts would indicate that homolysis of the aryl-bromine bond has successfully competed with energy transfer from the aryl group to the naphthalene nucleus despite the fact that deactivation of the excited states of the bromophenyl group as shown in the scheme (17) below.

Scheme 17



This observation implies that the photo-dehalogenation can only take place via an excited singlet state as triplet formation and reaction would be too long an event to compete with energy transfer. Since cleavage of the aryl-bromine bond is very fast and competes effectively with intramolecular energy transfer and inter-system crossing the photolysis of multifunctional compounds should lead to phenyl radicals which if substitution is appropriate undergo intramolecular reactions. This preferential activity has been utilised in the elegant work of Grimshaw¹³⁰ and Kametani¹³¹.

It was not possible to elucidate the nature of the singlet state responsible for reaction. The products of the photolysis being similar if reaction took place from either a vibrationally excited singlet ground state or the first excited singlet state.

The excited state responsible for reaction in cleaving alkyl-halogen bonds is harder to determine. For phenoxy alkyl halides there is evidence to suggest participation of both singlet and triplet excited states. In order to try to elucidate the responsible state, a series of naphthyloxy alkyl bromide compounds were synthesised from 1-naphthol, by formation of the naphtholate anion followed by reaction with the dibromoalkane. Fluorescence spectra were recorded of two of the compounds and the related ethers. The table (10) below shows the results of the relative fluorescence quenching.

Table 10.

$\text{NpO}(\text{CH}_2)_n\text{Br}$ Chain length (n)	ϕ_f ether / ϕ_f bromide
2	2.59
6	1.11

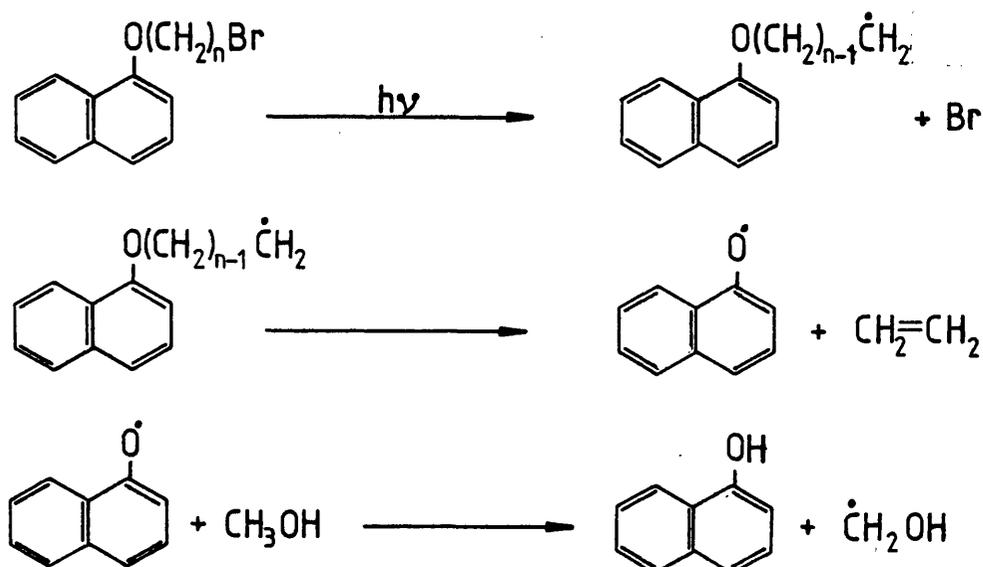
From the limited number of results, firm conclusions cannot be drawn. However a similar pattern of quenching to that seen for the phenoxy alkyl bromides was observed. A series of 1-bromo- ω -naphthylalkanes were irradiated in methanol. The photolyses produced the photoproducts shown in the following table (11).

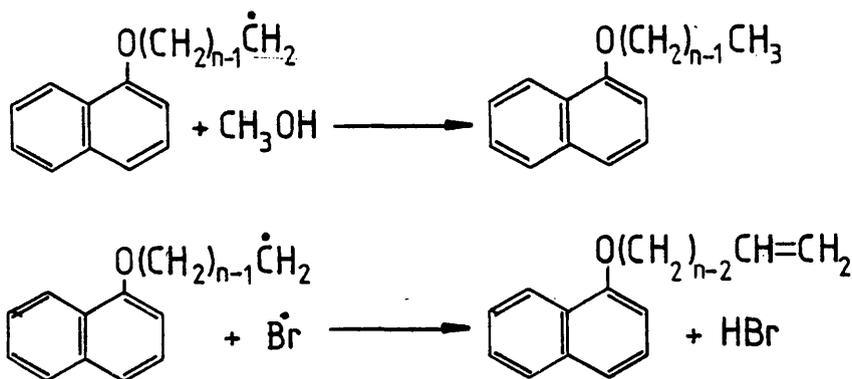
Table 11

Substrate	Photolysis time (hrs)	Starting material (%)	1-naphthol (%)	naphthyl-alkyl ether (%)
1-NpOCH ₂ CH ₂ Br	6	3.5	44.7	3.1
1-NpO(CH ₂) ₆ Br	6	65.3	17.5	1.0
1-NpO(CH ₂) ₈ Br	6	97.8	2.0	0.0
1-NpO(CH ₂) ₁₀ Br	6	99.8	0.0	0.0
1-Np(CH ₂) ₁₂ Br	6	100.0	0.0	0.0

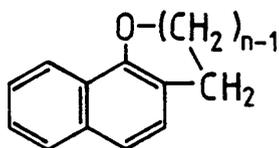
A further series of photoproducts were formed when $n = 2, 6,$ and 8 were irradiated. These products were the unsaturated derivatives 1-NpO(CH₂) _{$n-2$} CH=CH₂, which were identified by mass spectrometry. The major product, 1-naphthol, was formed via the following reaction sequence, scheme 19.

Scheme 19





It was assumed that these compounds corresponded to one of the peaks on the high performance liquid chromatograph. This could not be confirmed because of the lack of suitable standards. It is possible that the radical $\text{NpO(CH}_2\text{)}_{n-1}\text{CH}_2\cdot$ could undergo ring closure to afford a cyclic product,



however no evidence for this product was found.

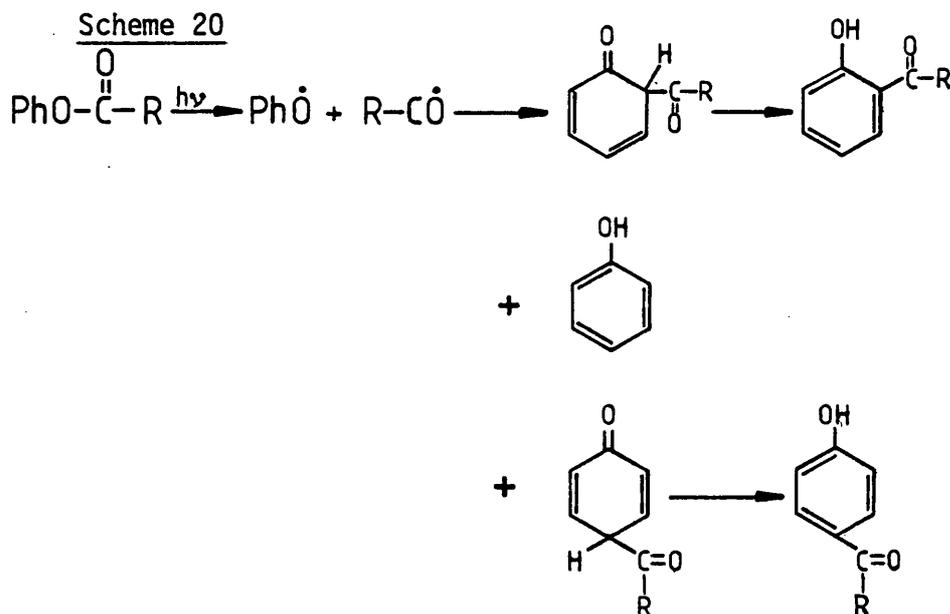
The product distribution was fairly similar to that obtained for the phenoxy alkyl bromides. Since the triplet energy of the naphthalene group is $60.8 \text{ Cal. mole}^{-1}$ ¹³², and the bond dissociation energy of the alkyl-bromine bond is $67.6 \text{ Cal. mole}^{-1}$ on energetic grounds it is extremely unlikely that the triplet state can be responsible for reaction. The first excited singlet state energy for naphthalene is $99.0 \text{ Cal. mole}^{-1}$, thus the reaction would at least be energetically favourable from this state.

It is possible that the phenol and 1-naphthol produced in the photolyses of the phenoxy alkyl bromides and 1-naphthoxy alkyl bromides resulted from the ethers which were detected in small amounts, or the products which resulted from the elimination of hydrogen bromide from the starting material, i.e. phenol and

and 1-naphthol are secondary photoproducts, the reaction being catalysed by hydrogen bromide. Anisole was therefore irradiated in the presence of hydrogen bromide, in methanol under the same conditions as the phenoxy alkyl bromides, no reaction occurred, this implied that the ether was not a precursor of the phenol or 1-naphthol.

The possibility that the phenol was derived from the ω -phenoxy alk-1-enes was also investigated.

The photo-Fries rearrangement is the light induced rearrangement of phenolic esters¹³³. It is predominantly an intramolecular free radical process and phenol is always a side product. The generalised mechanism is illustrated in the diagram, scheme 20, below.

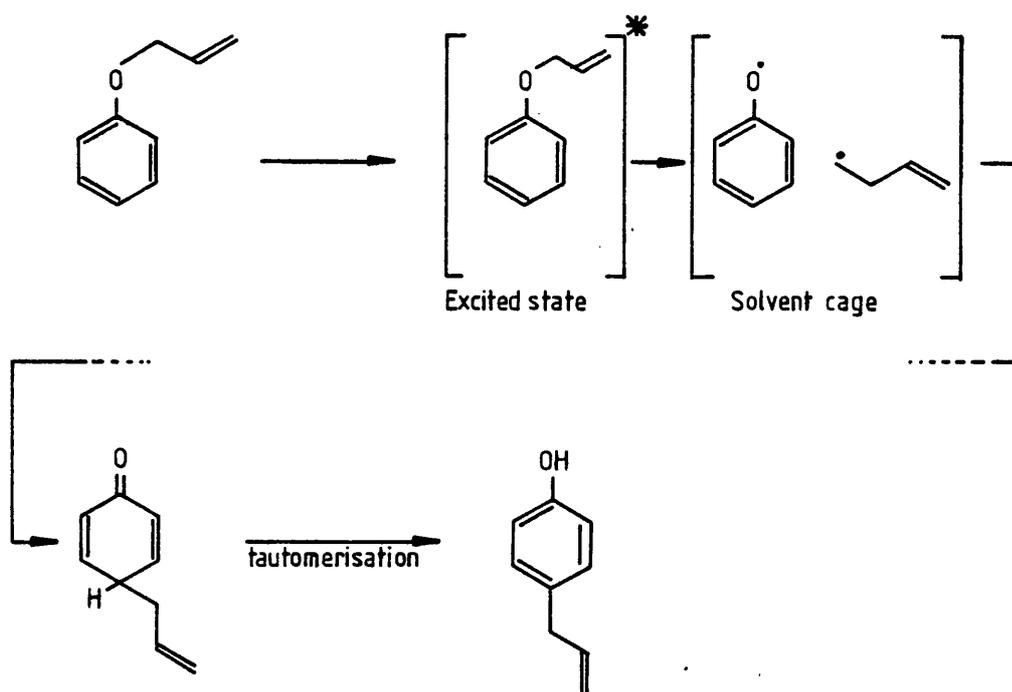


In support of the mechanism, Hammond et. al.¹³⁴ have shown that in the gas phase, (no solvent cage,) phenyl acetate on irradiation affords good yields of phenol but no rearranged products. Kalmus and Hercules¹³⁵ showed that phenoxy radicals are formed in the reaction, by experimental~~ation~~ utilising flash photolysis of phenyl acetate in solution. Absorption spectra

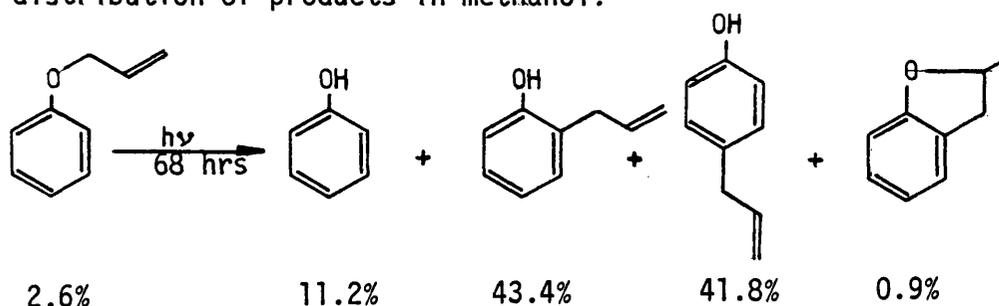
corresponding to the phenoxy radical and that of the acyl substituted cyclohexa-2-4-dienone were detected.

A related reaction the photo-Claisen rearrangement¹³⁶ has received less attention. This reaction has been applied to phenolic ethers by Kelly et. al.¹³⁸. A more thorough investigation was carried out by H.Waespe and his co-workers on the photo-reaction of allyl aryl ethers¹³⁹. They studied the effects of solvent and deuterium incorporation on the reaction, and found evidence for the radical nature of the reaction and discounted any possible concerted processes. Their results suggested that all the products were derived from homolytic cleavage of the alkyl carbon-oxygen bond in the singlet state of the ethers to yield intermediate radicals. This was followed by radical recombination of the two fragments. They found that the major products were 2-allyl phenol and 4-allyl phenol. The mechanism for the formation of the allyl phenols from allyl phenyl ether is shown in the reaction scheme 21 below.

Scheme 21



Phenol is always found as a side product of the reaction being derived from the aryloxy radicals which escape from the solvent cage and then abstract hydrogen from a neighbouring solvent molecule. That phenol is a product of photolysis of allyl phenyl ether would suggest that some if not all of the phenol found on irradiation of ω -phenoxy alkylhalides originated from ω -phenoxy alk-1-enes. It was noted that the length of time used for effecting the photo-Claisen rearrangements carried out by Waespe et.al.¹³⁹ were considerably longer than the irradiation times employed in the photolysis of ω -phenoxy-alkyl halides. Waespe and his co-workers¹³⁹ found the following distribution of products in methanol.

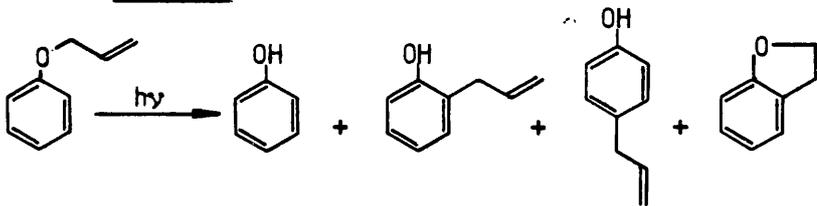


These observations do not mean that phenol found in the photolysis of the ω -phenoxy alkyl halides could not have derived from a photo-Claisen rearrangement because hydrogen bromide which is formed in the photolysis may affect the reaction. For example, the presence of hydrogen bromide may produce an acceleration of the side reaction which forms phenol, via a break-down of the solvent cage which leads to radical recombination. If this was the case an increase in the yield of phenol would be observed and a corresponding decrease in yield of rearranged products. Accordingly the photolysis of several ω -phenoxy alk-1-enes was carried out in the presence of hydrogen bromide.

Control reactions were also performed. For phenyl vinyl ether it was established that after six hours irradiation 5% phenol had been formed in the presence of hydrogen bromide. There was no evidence for the formation of phenol when the corresponding photolysis was performed in the absence of hydrogen bromide.

Allyl phenyl ether broke down to give a range of products on irradiation, these are shown in the table 9 below.

Table 9

Solvent	
Methanol	75 6 hrs. 5 10 7 1.0
Methanol + HBr	80 6 hrs 5 7.5 5 0.5

The results show that the ratio of phenol to rearranged products increases only to a smaller extent on addition of hydrogen bromide to the solution to be irradiated. Phenol forming 27.8% of the photoproducts on irradiation with hydrogen bromide and 21.7% in its absence. The overall rate of reaction with hydrogen bromide present is reduced however. From these results it can be concluded that allyl phenyl ether is not a significant precursor of phenol in the photolysis of 1-bromo-3-phenoxy propane. The discrepancy in product yield for the photolysis of 1-bromo-3-phenoxy propane is likely to be due to the formation of 2-allyl phenol and 4-allyl phenol the photo-Claisen rearrangement products.

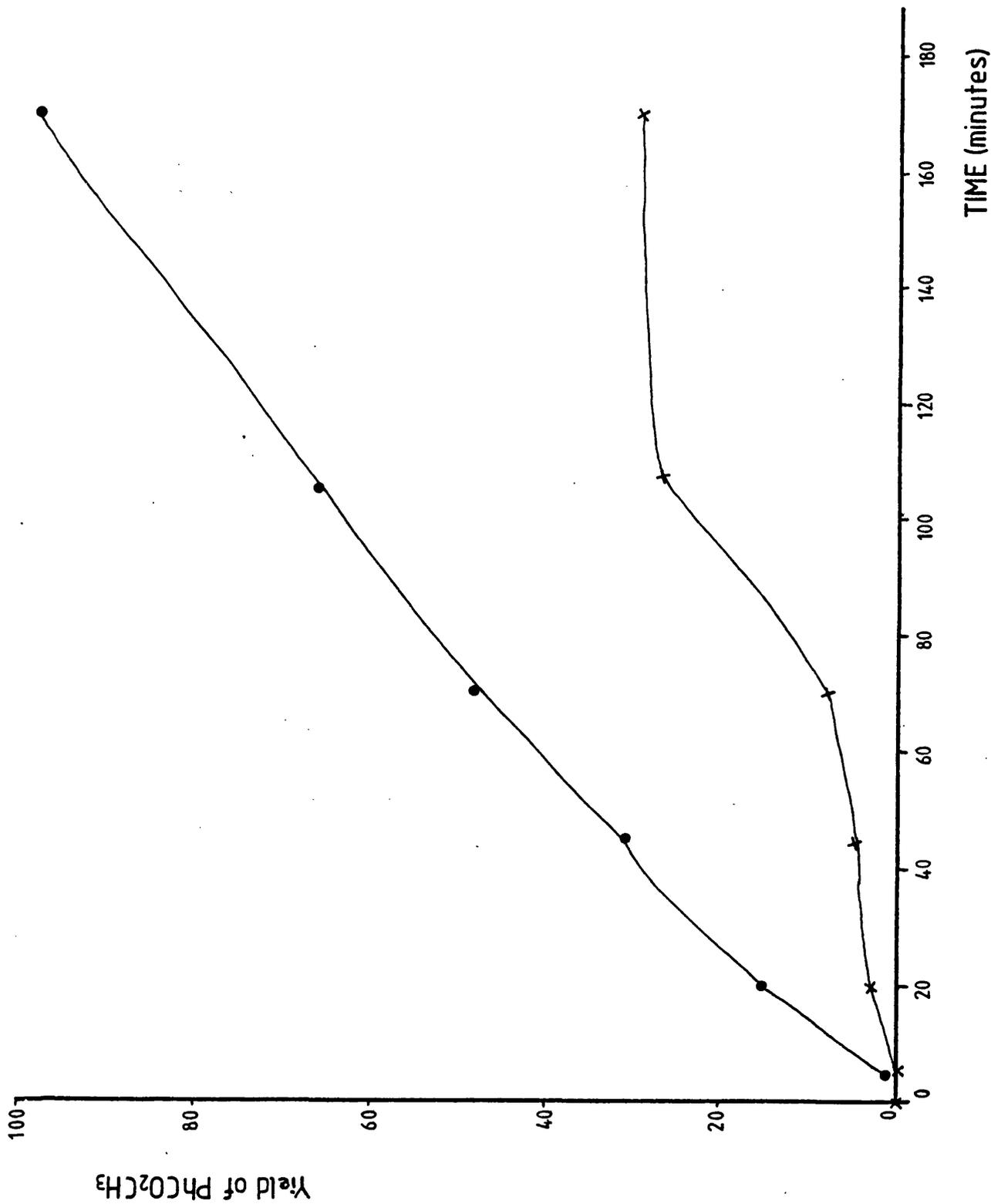
Photolysis of 5-phenoxy pent-1-ene was carried out under

similar conditions to those used for ω -phenoxy alkyl bromides, both in the presence and absence of hydrogen bromide. Analysis by gas liquid chromatography and mass spectrometry after the irradiation showed that no reaction had taken place. Thus, 5-phenoxy pent-1-ene cannot be responsible for the production of phenol which was found when 1-bromo-5-phenoxy pentane was irradiated simultaneously. The yield of phenol in this case was 22%. The case of 5-phenoxy pent-1-ene is more similar to the photolysis of an alkyl aryl ether than allyl phenyl ether. Rearrangement has been observed in alkyl aryl ethers but reaction is considerably slower than for the photo-Claisen rearrangement.

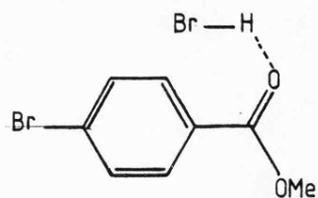
Methyl 4-bromobenzoate

Methyl benzoate emerged as the sole product on irradiation of methyl 4-bromobenzoate in methanol, confirming the earlier work of Nikishin and Cheltsova¹⁴⁰. This substrate was also irradiated in the presence of hydrogen bromide. The results of these reactions are displayed in the diagram shown overleaf. The diagram shows that in the absence of hydrogen bromide the rate of product formation is far from linear. The acceleration after approximately seventy minutes may be attributed to the accumulation of hydrogen bromide. Confirmation of this can be seen if one considers the curve of product formation with time when the irradiation is carried out in the presence of hydrogen bromide. The curve is almost linear and the photolysis appears to be accelerated. The mechanism for this reaction is possibly that accumulated hydrogen bromide hydrogen bonds

see table for exact numbers



to the ester group as shown below.



This has the effect of raising the energy of the $n-\pi^*$ transition relative to the $\pi-\pi^*$ transition allowing carbon-bromine bond homolysis to occur efficiently.

AMINE ASSISTED DEHALOGENATION OF HALOAROMATIC COMPOUNDS

An investigation into some mechanistic aspects of amine assisted photo-induced dehalogenation of halo-aromatic compounds have been carried out.

Parkanyi and Lee¹¹⁴. with work on bromoquinolines and Bunce et. al.⁹⁴. studying chlorinated biphenyls found that photo-induced dehalogenation was accelerated by the addition of triethylamine.

Photolyses of 3-bromoanisole were carried out in methanol containing differing amounts of amine to analyse the rate of reaction with concentration of triethylamine. The results of these experiments are shown below in table 12.

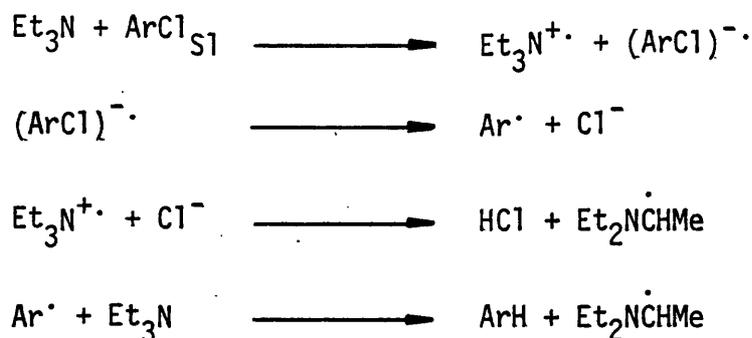
Table 12

Amine concentration (moles)	Starting material (%)	Anisole (%)
None	64.0	35.5
$5.3 \cdot 10^{-5}$	64.9	34.1
$5.3 \cdot 10^{-4}$	40.9	60.0
$4.2 \cdot 10^{-3}$	23.7	76.1

The percentages given are for one hundred and twenty minutes irradiation. The product of the reaction was anisole. The results show that an excess of amine led to the fastest rate of debromination, however the effect was only a two-fold increase in the rate of reaction. It has been proposed by Bunce et. al.⁹⁸. that the acceleration is due to the amine reacting with the excited singlet state of the halo-aromatic compound to give a radical anion, which breaks down to afford an aryl radical and a chlorine

anion according to the following scheme 22.

Scheme 22



A series of substituted bromobenzenes were irradiated in methanol containing an excess of triethylamine (8 molar), the results are shown in the table 13 overleaf.

The acceleration in rate of reaction varied between 1.1 and 2.1 times faster in the presence of triethylamine. Two reasons can be put forward to account for the small effects triethylamine has on the rate of debromination of these compounds. In many cases the reduction potentials of the halo-aromatic compounds are similar to the parent benzenoid molecule¹⁴⁰, and therefore, the excited singlet state of these compounds may form excited complexes or radical ions with electron donors. However, the presence of the halogen atom may affect the probability of such reactions occurring by enhancing intersystem crossing to such an extent that the excited singlet state has a very short lifetime. Therefore there would be little chance of participation of such a species in bimolecular reaction. Thus, if the triplet state does not react with the amine, the addition of amine will have little effect. The other possibility is that the photo-induced homolysis process has a very large rate

Table 13

Compound	Amine	Irradiation time (mins)	Product	(%)	Acceleration
Bromobenzene	None	75	Benzene	13.0	1.8
Bromobenzene	Triethylamine	75	Benzene	23.5	
Methyl 4-bromobenzoate	None	120	Methyl benzoate	42.9	1.2
Methyl 4-bromobenzoate	Triethylamine	120	Methyl benzoate	51.4	
1,4-dibromobenzene	None	45	Bromobenzene + Benzene	43.0	1.1
1,4-dibromobenzene	Triethylamine	45	Bromobenzene + Benzene	48.0	
4-bromobenzonitrile	None	60	Benzonitrile	54.0	1.1
4-bromobenzonitrile	Triethylamine	60	Benzonitrile	61.0	
4-bromoanisole	None	15	Anisole	19.5	1.6
4-bromoanisole	Triethylamine	15	Anisole	32.0	
3-bromoanisole	None	120	Anisole	35.5	2.1
3-bromoanisole	Triethylamine	120	Anisole	76.1	

constant thus attenuating the singlet lifetime and consequently reaction with the amine will be inefficient.

Several substituted chlorobenzenes were irradiated under similar conditions to the bromo compounds, the results are displayed in the table 14 below.

Table 14

Compound	Amine	Photolysis time (hrs)	Product (%)	Acceleration
4-chlorobenzonitrile	None	1	Benzonitrile 20.0	
4-chlorobenzonitrile	Triethylamine	1	Benzonitrile 60.0	
4-chloroanisole	None	1	Anisole 21.0	
4-chloroanisole	Triethylamine	1	Anisole 28.7	1.4

These results show that on the one hand there is little acceleration in the rate of dehalogenation for 4-chloroanisole whereas on the other hand the dechlorination of 4-chlorobenzonitrile only proceeds when triethylamine is present. This dichotomous behaviour may be due to the inefficiency of the homolysis reaction allows the bimolecular reaction with the amine to compete. Thus it would seem that any substituents other than the halogen also affect the rate of amine assisted dechlorination.

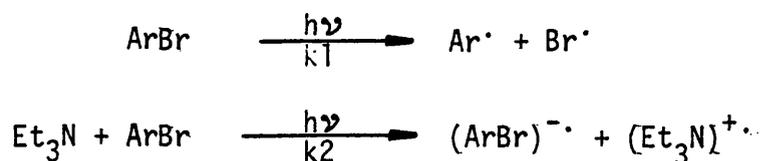
Since the reactivity of triethylamine may be reduced by hydrogen bonding to methanol the small amount of acceleration observed in some cases may be due to this phenomenon. Accordingly a cross-section of substituted halobenzenes were irradiated with triethylamine in solvents of widely differing solvating character, namely cyclohexane, methanol and acetonitrile. The

results of the irradiations are outlined in the following table 15.

Table 15

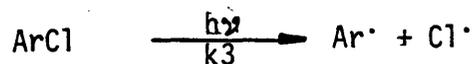
Substrate	Product	Comparative Rate Of Product Formation		
		Acetonitrile	Methanol	Cyclohexane
4-chloroanisole	Anisole	3.4	1.3	1.0
4-chlorobenzonitrile	Benzonitrile	11.7	3.75	1.0
4-bromobenzonitrile	Benzonitrile	1.25	1.1	1.0
4-bromoanisole	Anisole	1.8	1.6	1.0

The results clearly demonstrate that the greatest acceleration of triethylamine assisted dehalogenations occurred in acetonitrile, whereas the least effect on the amine assisted reaction occurred in cyclohexane. This result is what one would expect if the amine was reacting with the aromatic molecule via an electron transfer process. The effect of solvation on electron has been noted in previous studies by Brimage and Davidson¹⁴². The acceleration of rate of reaction is also more pronounced for chloro compounds than it is for their bromine counterparts. For the bromo compounds (see tables 13 and 14) the reaction is probably exogenic, thus homolysis of the carbon-bromine bond will compete effectively with the reaction with triethylamine. The competing reactions would therefore be:-



Evidence would suggest therefore that $k_1 [\text{ArBr}^*] > k_2 [\text{ArBr}^*][\text{Et}_3\text{N}]$

As the homolytic cleavage of chloro compounds is energetically less favourable, (see table 1 of bond dissociation energies) the rate constant k_3



should be less than k_1 and therefore make the reaction with triethylamine more competitive.

A second factor is that because of the heavy atom effect the lifetimes of the excited states of bromo-aromatics are shorter than those of the corresponding chloro compounds. Consequently, bromo compounds are less likely to undergo bimolecular reactions than chloro compounds.

A number of halogenated polycyclic aromatic compounds were irradiated in solvents of different solvating character in the presence of triethylamine at a concentration of 3×10^{-2} molar. The results of the photolyses are detailed below in table 16.

Table 16

Substrate	Product	Comparative Rate Of Product Formation		
		Acetonitrile	Methanol	Cyclohexane
1-chloronaphthalene	Naphthalene	34.5	4.1	1.0
1-bromonaphthalene	Naphthalene	12.4	4.3	1.0
4-chlorobiphenyl	Biphenyl	32.0	11.5	1.0
4-bromobiphenyl	Biphenyl	6.9	4.6	1.0
9-chloroanthracene	Anthracene	10.3	4.4	1.0
9-bromoanthracene	Anthracene	4.8	3.1	1.0
1-iodonaphthalene	Naphthalene	1.3	1.1	1.0

The difference in rate of product formation with changing

solvent, in triethylamine assisted reactions is much more marked on going from benzenoid compounds to naphthalene, biphenyl and anthracene compounds. The reduction potentials for benzene and naphthalene have been determined by L.Meites and P.Zuman¹⁴³, the values obtained were, benzene $E_{\frac{1}{2}} = 2.4$ versus the standard calomel electrode and naphthalene $E_{\frac{1}{2}} = 1.7$ versus the standard calomel electrode. Thus the different accelerating affect of triethylamine in the various solvents may be due to the lower reduction potentials of the naphthyl, biphenyl and anthracenyl compounds compared with the benzenoid compounds, which would favour the electron transfer process. Furthermore the dehalogenation of the polycyclic aromatic compounds would be less exogonic than the benzenoid compounds and therefore the bimolecular reaction with the amine has more chance to compete with the homolysis reaction.

From the results in tables 15 and 16 it can be seen that in general the accelerating effect of triethylamine increases as the unassisted reaction becomes less favourable energetically and also if polar aprotic solvents are used. The latter observation is consistent with triethylamine undergoing an electron transfer reaction with the halo-aromatics in such solvents.

An investigation into the effect of primary, secondary and tertiary amines on the rate of dehalogenation of 1-bromonaphthalene was carried out and is displayed overleaf on table 17.

The photolyses showed that primary, secondary and tertiary amines all increase the rate of dehalogenation over the rate for the non-assisted reaction. The tertiary amine is the most effective in promoting dehalogenation. This result is not unexpected as the higher oxidation potentials of primary and secondary amines compared with tertiary amines makes them less likely to participate in electron

transfer reactions.

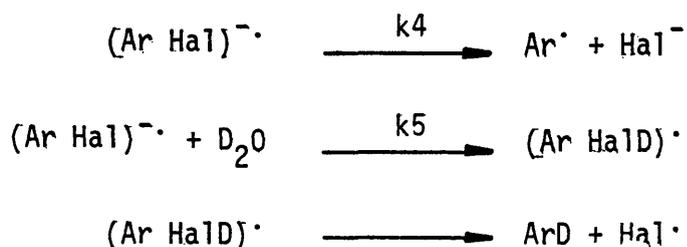
Table 17

Amine	Naphthalene
None	12.2
Primary	34.6
Secondary	36.6
Tertiary	44.1

Despite this the ease of reduction of 1-bromonaphthalene may help the thermodynamics of the process. Nasielski et.al.¹²⁰ have previously reported that secondary amines assist debromination in bromopyrimidines; they postulated radical ions as intermediates in the reaction.

Another method of ascertaining whether radical ions are intermediates in the amine assisted dehalogenations is to carry out the reactions using an acetonitrile / deuterium oxide solvent mixture. The usefulness of this type of reaction can be illustrated in the following reaction scheme 23.

Scheme 23



If the radical anions are sufficiently long lived deuterium incorporation should be observed,

$$\text{i.e. } k_4 [\text{Ar Hal}^{\cdot-}] > k_5 [\text{D}_2\text{O}] [\text{Ar Hal}^{\cdot-}]$$

A selection of substituted halobenzenes were photolysed using acetonitrile / deuterium oxide as solvent (MeCN : D₂O; 5 : 1 v/v) in the presence of triethylamine as shown below in table 18.

Table 18

<u>Substrate</u>	
4-chloroanisole	
4-chlorobenzonitrile	No
1,4-dichlorobenzene	Deuterium
4-bromoanisole	Incorporation
4-bromobenzonitrile	
4-bromotoluene	

No deuterium incorporation was detected either in unreacted starting material nor in dehalogenated product. That 4-chlorobenzonitrile did not dehalogenate with deuterium incorporation was somewhat surprising when one considered that triethylamine was essential for reaction to occur. No plausible explanation could be found to account for this observation.

Irradiation of 1-chloronaphthalene, 1-bromonaphthalene, 1-iodonaphthalene, 9-chloroanthracene, 9-bromoanthracene, 4-chlorobiphenyl, 4-bromobiphenyl and 1-bromopyrene were carried out under similar conditions to those used for the benzenoid compounds but in these cases deuterium incorporation was observed, the results are shown in table 19 overleaf.

Deuterium incorporation could have arisen by two processes:-
1) by the process outlined on the previous page or
2) by photo-induced electron transfer reactions of the dehalogenated product with the amine¹⁴⁴.

Table 19

Compound	Deuterium Incorporation Into Product					
	n=0	n=1	n=2	n=3	n=4	n=5
$C_{10}H_{8-n}D_n$						
1-chloronaphthalene	1.0	0.35	0.085	0.066	0.038	-
1-bromonaphthalene	1.0	1.16	0.605	0.243	0.103	-
1-iodonaphthalene	1.0	0.29	0.054	0.054	0.015	-
$C_{12}H_{10-n}D_n$						
4-chlorobiphenyl	1.0	0.665	0.346	0.622	0.45	0.088
4-bromobiphenyl	1.0	0.239	0.039	0.011	0.002	0.002
$C_{14}H_{10-n}D_n$						
9-chloroanthracene	1.0	0.128	-	-	-	-
9-bromoanthracene	1.0	0.478	-	-	-	-
$C_{16}H_{10-n}D_n$						
1-bromopyrene	1.0	0.356	-	-	-	-

It is not without precedent that polycyclic aromatic hydrocarbons are photoreduced by tertiary amines¹¹⁵ and unusually 3-chlorobiphenyl is reduced to afford 1,4-dihydro-3-chlorobiphenyl¹⁴⁵. In order to ensure that the deuterium incorporation occurred during dehalogenation and not through reaction of the photoproduct, naphthalene was irradiated under similar conditions to the halogenated compounds, except that the irradiation period was doubled, this led to the production of deuterium labelled naphthalene. Pyrene was labelled in the same way. The results are displayed overleaf in table 20. Although the concentration of naphthalene in this control reaction was greater than that produced in the dehalogenation reactions, there is less deuterium incorporation

than in the dehalogenation reactions.

Table 20

Compound	Deuterium Incorporation Into Product				
	n=0	n=1	n=2	n=3	n=4
Naphthalene	1.0	0.29	0.054	0.054	0.015
Pyrene	1.0	0.091			

This test however was not particularly close to the conditions for photolysis used in the dehalogenation reactions as all the light was absorbed by the naphthalene. Therefore a further test was designed to look at deuterium incorporation into the aromatic photoproduct.

A mixture of the halogenated material and methyl substituted hydrocarbon, e.g. 4-phenyltoluene, in the ratio of starting material to product found after one hours photolysis of the halogenated material. The mixture was irradiated for one hour in an acetonitrile /deuterium oxide mixture similar to that used for the other deuterium incorporation experiments as well as triethylamine. The results are shown in the table 21 below.

Table 21

Compound	Deuterium Incorporation Into Product					
	0D	1D	2D	3D	4D	5D
1-methylnaphthalene	1.0	0.32	0.11	0.07	-	-
Naphthalene	1.0	0.71	0.30	0.16	0.04	-
4-phenyltoluene	1.0	0.508	0.243	0.13	0.073	0.040
Biphenyl	1.0	0.736	0.510	0.317	0.120	0.063
9-methylanthracene	1.0	0.108	0.10	-	-	-
Anthracene	1.0	0.231	0.132	-	-	-

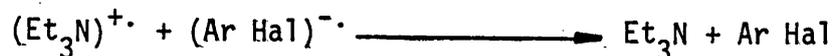
If the figure for deuterium incorporation into the methyl substituted hydrocarbon is taken from the result obtained for the unsubstituted aromatic hydrocarbon photoproduct, a value is obtained which is representative of the deuterium incorporation occurring during the dehalogenation. This estimate would be a lower limit for this value provided the methyl group and its electron donation does not have any effect on the rate of reaction of the methyl substituted hydrocarbon. The values obtained are shown below in table 22.

Table 22

Compound	Deuterium Incorporation				
	n=1	n=2	n=3	n=4	n=5
Naphthalene	0.39	0.19	0.09	0.04	-
Biphenyl	0.228	0.267	0.187	0.047	0.023
Anthracene	0.123	0.032	-	-	-

Thus it is evident that the observed deuterium incorporation in the dehalogenation reactions is due at least in part, to the interception of radical ions by deuterium oxide. Some of the ways by which this can occur are shown in the reaction scheme 24 overleaf.

Since no deuterium incorporation into the haloaromatic compounds occurred it appears that the back electron transfer

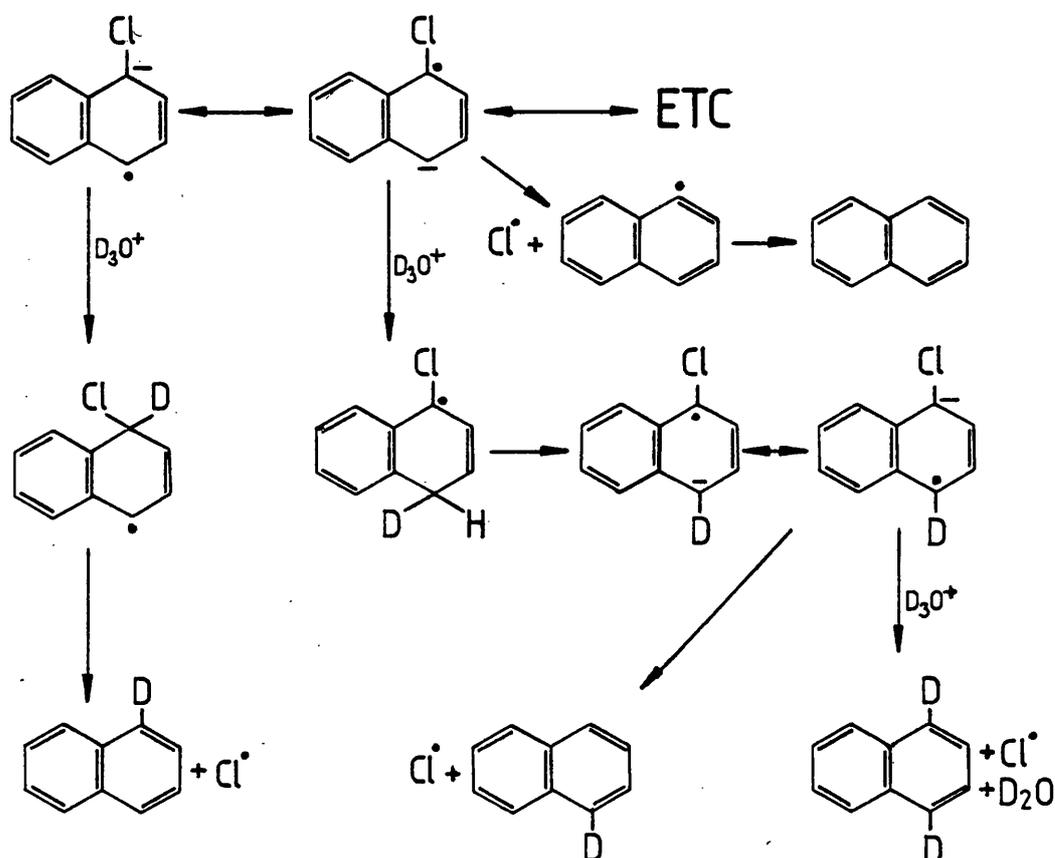


does not occur. This probably reflects the ease with which $(\text{Ar Hal})^{\cdot-}$ expels halogen⁻.

The deuterium incorporation studies show that the halogenated polycyclic aromatic compounds which do not readily dehalogenate

undergo photo-induced electron transfer reactions with triethylamine.

Scheme 24

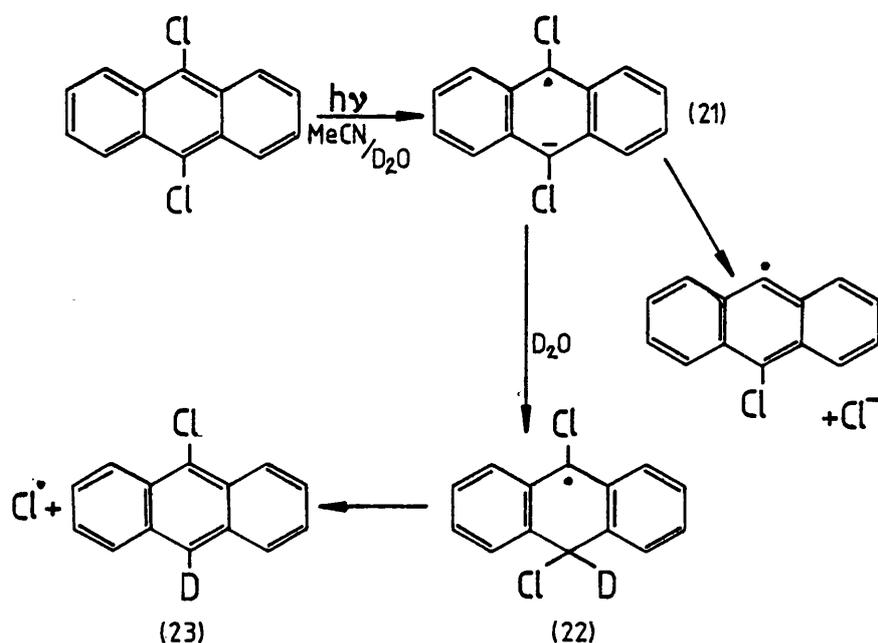


It is anticipated that reactive halogenated aromatic compounds such as 2,4-dichlorobiphenyl will not show this effect to any marked degree. The lack of deuterium incorporation into the halogenated benzenoid compounds is probably a manifestation of the ease with which the radical anions of such species break up to yield halide ions¹⁴⁶. The electron transfer reaction with triethylamine may also be less important with these compounds since the dehalogenation is exogonic.

Recent related work by Saltiel et. al.¹⁴⁷ on diene assisted

dehalogenations has shown that irradiation of 9,10-dichloroanthracene with 2,5-dimethylhexa-2,4-diene in acetonitrile led to dechlorination and formation of 9-chloroanthracene. If deuterium oxide was used with acetonitrile as solvent, deuterium incorporation into the 9-chloroanthracene was observed as shown in scheme 25, below.

Scheme 25



This suggests that the interaction of the diene with the excited anthracene gave rise to extensive electron transfer, to afford radical ions.

Chapter 4.

Photoinitiation
of Cationic
Polymerisation

INTRODUCTION

Cationic polymerisation by strong acids or Friedel-Crafts catalysts was discovered in 1839 by Deville¹⁴⁸, when he studied the polymerisation of styrene using tin (IV) chloride as a catalyst for the reaction. A more rigorous investigation was carried out in the late 1920's and early 1930's by Staudingers¹⁴⁹ school,

Cationic photoinitiation of polymerisation has only received attention over the last fifteen years. The major reason for this being the dearth of suitable photoinitiators.

The advantages of photoinitiated cationic polymerisations are the high reaction rates which have been attributed to a lack of chain terminating side reactions. Thus low viscosity monomers can be polymerised as easily as high viscosity materials. In addition, cations do not react with oxygen, which would inhibit polymerisation, therefore, the polymerisations can be carried out efficiently in air.

Many of the early photoinitiators were capable of polymerising only one or two monomer systems. Included in this type of photoinitiator are several inorganic and organo-metallic salts. Asai and his co-workers¹⁵⁰ found that gold (III) halide salts were capable of photoinitiating the polymerisation of N-vinylcarbazole. They suggested that the mechanism for the reaction proceeded via a redox couple and that the initiating species was a transient gold (III) species or a halogen atom. The same group of workers also reported that silver perchlorate¹⁵¹ would initiate polymerisation, the reaction involving an N-vinylcarbazole-silver perchlorate complex. McDonald et. al,¹⁵² reported that silver and copper salts having large non-nucleophilic

anions were capable of photoinitiating polymerisation of tetrahydrofuran. These compounds could also initiate polymerisation thermally. Evidence for the cationic nature of the polymerisations was provided by experiments which showed that triethylamine and other bases inhibited polymerisation but the system was insensitive to oxygen.

It has been found that dicyclopentadienyl titanium dichloride was able to photoinitiate the cationic polymerisation of vinyl ethers and initiate polymerisation of styrene by free radicals¹⁵³.

Friedel-Crafts catalysts have been utilised as polymerisation catalysts¹⁵⁴, as have several charge-transfer complexes formed between electron donating monomers and electron acceptor initiator molecules. The mechanism for this type of photoinitiation of cationic polymerisation was investigated by Irie et. al.¹⁵⁵ using α -methylstyrene complexed with tetracyanobenzene. Their experiments showed that the photo-induced electron-transfer from the donor to the acceptor molecule produced radical cations and radical anions. Polymerisation occurred from the contact-ion pair or solvent separated pair. Charge-transfer complexes have also been used to polymerise isobutyl vinyl ether¹⁵⁶.

The photoinitiated polymerisation of epoxides by the photoinitiators previously mentioned has not been studied, however this type of monomer has been extensively used in studies investigating the use of nearly every other type of cationic photoinitiator. Only two inorganic compounds have been used which catalyse epoxide polymerisation efficiently, these are silver trifluoromethane sulphonate¹⁵⁷ and silver salts of boron halides¹⁵⁸.

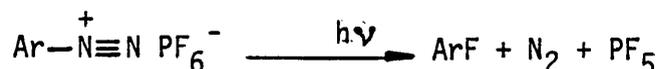
DIAZONIUM SALTS

Aryl diazonium salts were the first organic photoinitiators found to be capable of initiating cationic polymerisation in a wide range of cationically polymerisable substrates. The salts were easily prepared by the diazotization of aromatic amines with nitrous acid.



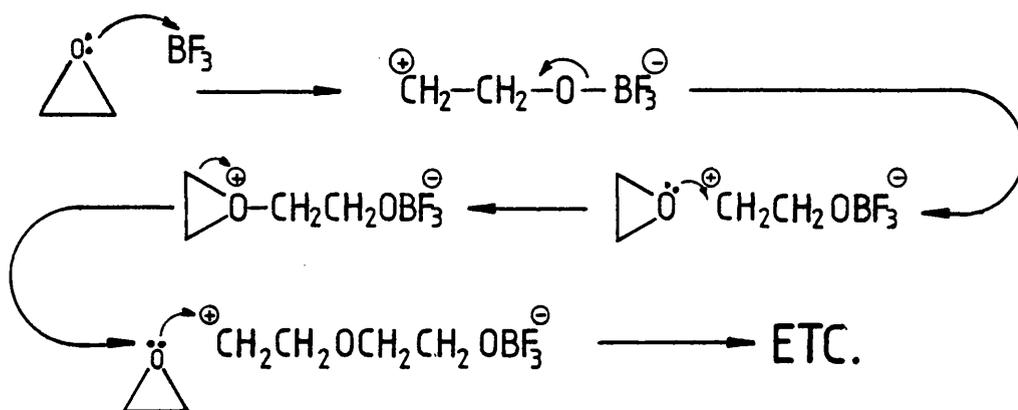
These compounds were found to be photo-sensitive and on photolysis afforded aryl halides¹⁵⁹. Irradiation of diazonium salts bearing a complex metal halide anion such as the hexafluorophosphate anion afforded as one of the products a Lewis acid, phosphorus pentafluoride, as shown in the following reaction scheme 1.

Scheme 1



In the presence of a polymerisable monomer, the Lewis acid produced, initiates polymerisation as shown in the following reaction scheme 2.

Scheme 2



Diazonium salt photoinitiators have been used mainly in the

polymerisation of epoxides, much of the literature has appeared in patent form^{160.161.}

Photoinitiators which produce Lewis acids on irradiation differ from free radical initiators in that the polymerisation continues for a long period after the light ceases to impinge on the initiating molecule. These photoinitiators have a further advantage in being insensitive to oxygen, this factor is of special importance in the field of printing inks where oxygen is in contact with much of the material to be polymerised.

It has been found that modification of the aromatic part of the diazonium salts could be easily achieved, this has been investigated in order to alter the absorption spectrum characteristics. This has led to the appearance in the literature of many different diazonium salts and it has been reported by Schlessinger^{162.} that compounds have been produced which between them were capable of absorbing light from the ultra-violet through to the visible spectrum.

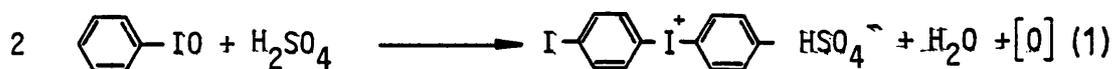
Schlessinger has further reported^{163.} that for a series of aryl diazonium salts there was a noticeable variation in efficiency of polymerisation with the type of Lewis acid produced on irradiation of the salt. The hexafluorophosphate anion was found to be four times more effective than the tetrafluoroborate anion despite the fact that the quantum efficiency was similar for the two salts.^{163.} Diazonium salts possessing several other anions have been investigated, examples include the silicotungstate and the tungsto-germanate anions^{164.}, these also produced Lewis acids on irradiation however, these proved to be less reactive than the tetrafluoroborate anion.

There are several disadvantages inherent in aryl diazonium salt photoinitiation of polymerisation which limit its use. The major disadvantage of these salts is that on irradiation of diazonium salts nitrogen is produced, in printing inks this manifests itself as small bubbles and pinholes in cured films greater than 0.2 mm. thick. A further problem is the thermal instability of this type of photoinitiator, the tendency being to decompose even at room temperature causing polymerisation to occur in the storage of the ink^{164a}; and despite the development of stabilising additives such as nitriles¹⁶⁵, a printing ink employing a diazonium salt photoinitiator can only be stored for approximately two weeks at room temperature.

DIARYLIODONIUM SALTS

Diaryliodonium salts were first prepared in 1894 by Hartmann and Meyer^{165a} condensing two molecules of iodosobenzene as shown in the scheme 3 below.

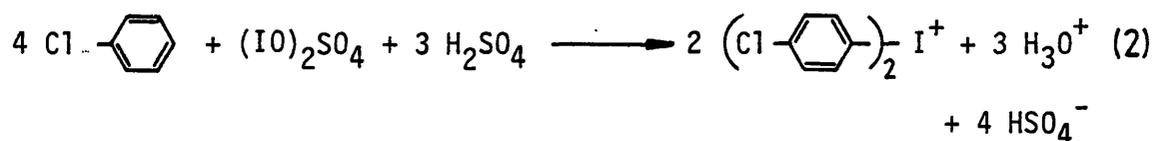
Scheme 3



Extensive work by Beringer et. al.^{166,167} has led to the development of several synthetic pathways to this class of compound. Recently a number of new synthetic routes have been developed, leading to diaryliodonium salts bearing many types and positions of substitution. The choice of method used being dependant on the nature and position of the substituent. For salts having

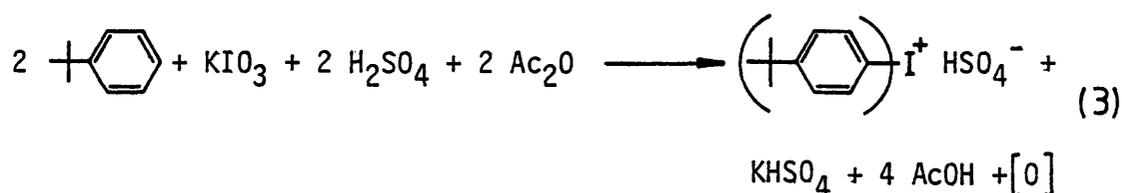
symmetrically positioned substituents, two methods involving the coupling of two molecules of an aromatic substrate by an electrophilic substitution mechanism have been developed. The first method designed by Masson and his co-workers¹⁶⁸. can be also utilised for aromatic molecules possessing deactivating substituents such as nitro groups or halogens. The equation for this reaction is described below in scheme 4.

Scheme 4



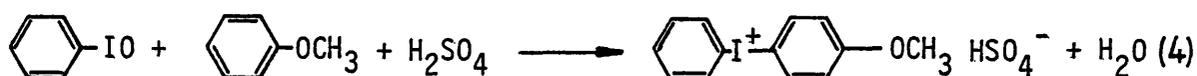
Diaryliodonium salts having electron donating substituents were prepared by the coupling of the aromatic precursors using an alkali metal iodate in a mixture of sulphuric acid, acetic acid and acetic anhydride¹⁶⁹. as shown in the following scheme 5.

Scheme 5



Unsymmetrical iodonium salts were prepared by the reaction of an aromatic compound with an iodoso compound in the presence of a strong acid¹⁷⁰. as shown in scheme 6.

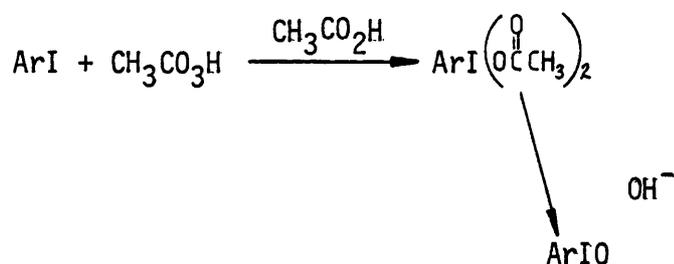
Scheme 6



The aromatic iodoso compounds were synthesised by the

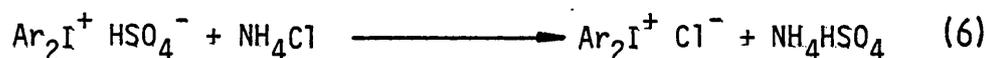
oxidation of the corresponding iodo-compounds with peracetic acid followed by hydrolysis, as shown in scheme 7.

Scheme 7



The salts prepared by these methods have as their counter-ions the hydrogensulphate anion. These were difficult to characterise as a result of their instability and the fact they are hygroscopic. Therefore the stable halide salts were usually isolated, these were prepared by a metathesis reaction as shown in scheme 8.

Scheme 8



These compounds were not suitable as photoinitiators because cationic species produced by the photolyses of diaryliodonium halides would react with the halide ion to form a stable bond rather than reacting with monomer molecules present. For this reason, iodonium salts having large non-nucleophilic anions such as ClO_4^- , BF_4^- , CF_3SO_3^- , which do not react with cationic species were required.

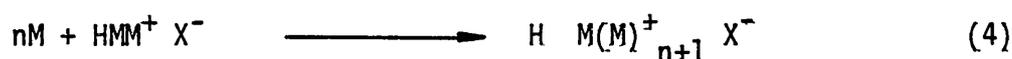
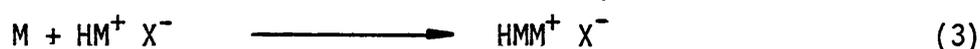
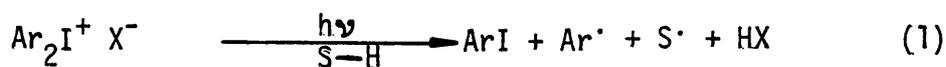
Salts of this kind could be prepared by either of two techniques, reaction of the halide salts with basic silver oxide to form the hydroxide, followed by acidification with the acid from which the required anion was derived^{171,172.} or

directly by metathesis of the hydrogensulphate salts with acids such as HPF_6 , HSbF_6 , or their alkali metal salts¹⁷³.

Several groups of workers have reported that these salts are highly efficient photoinitiators of cationic polymerisations¹⁷⁴⁻¹⁷⁶.

The mechanism by which diaryliodonium salts function as photoinitiators in the cationic polymerisation of monomers is displayed in the scheme 9 below.¹⁷⁷

Scheme 9



M = monomer, S H = solvent.

The acid produced in the first reaction, protonates the monomer M, this is the initiation step. Further monomer molecules add to the protonated species resulting in chain growth. Termination only occurs by reaction with basic or nucleophilic impurities present. Thus the polymers produced in 'clean' systems are living polymers.

HALONIUM SALTS

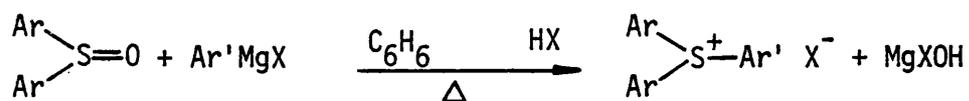
In addition to iodonium salts, bromonium and chloronium salts^{178,179} have been prepared and have been found to initiate cationic polymerisation. However the compounds have no commercial interest because they could only be prepared in very low yields, approximately 3%, in addition to this they are unstable.

SULPHONIUM SALTS

Triarylsulphonium salts of non-nucleophilic complex anions have been shown to be efficient photoinitiators of cationic polymerisation¹⁸⁰. A variety of synthetic methods have been utilised in their synthesis.

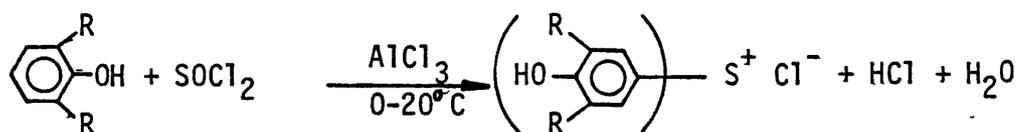
D.S.Wildi and his co-workers¹⁸¹ found that diphenyl sulphoxide could be reacted with a Grignard reagent to produce a triarylsulphonium salt. The non-nucleophilic anion could then be substituted by a metathesis reaction as illustrated in scheme 10 below.

Scheme 10



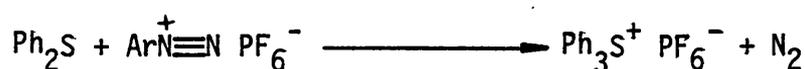
Several groups of workers¹⁸²⁻¹⁸⁴ have used reactions employing aluminium chloride as a catalyst to produce triaryl-sulphonium salts, they employed a range of starting materials. An example is shown below in scheme 11.

Scheme 11



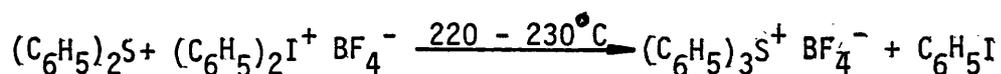
Diazonium salts have been used as intermediates in the synthesis of triarylsulphonium salts to produce good yields of the compounds but the diazonium salts could only be used in small quantities. The equation is shown in scheme 12.¹⁸⁵

Scheme 12



The most widely utilised method for obtaining triaryl-sulphonium salts has been that employing diaryliodonium compounds. In 1957 Nesmeyanov et. al.¹⁸⁶. discovered that diphenyl sulphide could be arylated using diaryliodonium tetrafluoroborate as shown below in scheme 13.

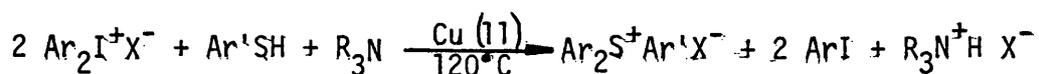
Scheme 13



Modification of Nesmeyanov's procedure¹⁸⁶. was carried out by Knapczyk and McEwen¹⁸⁷., by using milder conditions they were able to obtain a yield of 64% of the triarylsulphonium salt. The yield of of sulphonium salt was found to be dependant on the substitution on the aryl rings.

Using an observation made by Beringer¹⁸⁸. that copper (II) compounds accelerate the rate of decomposition of diaryliodonium salts, Crivello and Lam have added copper (II) compounds to the reaction mixture of diaryliodonium salt and diphenyl sulphide, to produce triarylsulphonium salts in better yields than have previously been obtained¹⁸⁹. A similar procedure was found to arylate thiophenol¹⁹⁰. producing a good yield of triphenylsulphonium salt. Further to this they found that a further additive triethylamine increased the yield of the product. The stoichiometry of the reaction is shown below in scheme 14.

Scheme 14



The triarylsulphonium salts have been found to be useful photoinitiators for cationic polymerisation of a wide variety

of monomers¹⁹¹. Further studies have shown that the sulphonium salts have good thermal stability, only decomposing at temperatures in excess of 350°C.

RESULTS AND DISCUSSION

Since the patent literature concerning the photoinitiation of polymerisation by triarylsulphonium salts is extensive^{192.193.}, and trialkylsulphonium salts absorb ultra-violet light only at short wavelengths, the synthesis of diarylalkylsulphonium salts, S-alkylthioxanthylum salts and S-alkylthioxanthonium salts was embarked upon.

Several methods were found in the literature outlining the synthesis of sulphonium salts. Speziale et. al.^{193.} prepared such salts by mixing equimolar quantities of dimethyl sulphide and ethylbromo acetate. An attempt was made to synthesise the diphenyl sulphide analogue by this method, however no reaction occurred even at elevated temperatures.

ElieI and Willer^{194.} were able to synthesise trialkylsulphonium salts by reacting iodomethane (in excess) with dimethyl sulphide. However the reaction could not be utilised in the preparation of S-methylthioxanthylum iodide, as the required product could not be detected. A possible reason as to why these approaches failed to alkylate diarylsulphides is that there may be steric hindrance. For diphenylsulphide the aromatic rings are placed orthogonal to each other, thus preventing attack. A further reason may be that the alkylating agents used were not strong enough to alkylate the sulphur atom.

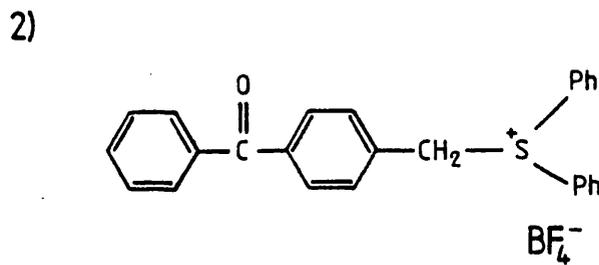
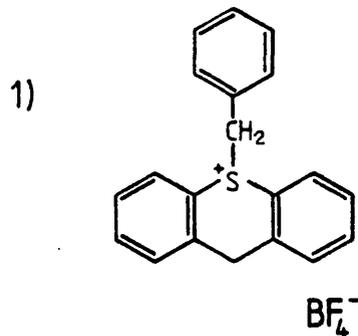
The recent literature showed that a class of strong alkylating agents, trialkyloxonium salts^{195.} were capable of alkylating thiophene to make S-alkylthiophenium salts^{196.} and

Dennerly¹⁹⁷. utilised this approach to S-alkylate penam sulphides to prepare penam sulphonium salts.

Triethyl and trimethyloxonium hexafluorophosphate were synthesised by the method of Olan et. al.¹⁹⁸, affording high yields (in excess of 100%) of the oxonium salts. The alkylation of diphenyl sulphide using triethyloxonium hexafluorophosphate was attempted. Diphenylethylsulphonium hexafluorophosphate was isolated but in very low yield. The alkylation of thiophenol was carried out using a similar procedure, this afforded a 26% yield of diethylphenylsulphonium hexafluorophosphate. Thioxanthene was alkylated under similar conditions and also gave the sulphonium salt derivative. Alkylations of thioxanthene-9-ol and thioxanthone were also achieved using triethyloxonium hexafluorophosphate as the alkylating agent. Several alkylations utilising trimethyloxonium hexafluorophosphate were also successful.

In order that the alkyl substituent on sulphur could be varied so as to include all types of alkyl groups another method of alkylation was required. Brumlick et. al.¹⁹⁹. have reported the S-methylation of thiophene by methyl iodide and silver perchlorate. As a result of the explosive nature of perchlorates the silver perchlorate was replaced with silver tetrafluoroborate in similar syntheses by Acheson and Harrison.¹⁹⁶. (Note, this material is also not without risk²⁰⁰.)

A series of alkylations of thioxanthene and thioxanthone were successfully carried out utilising this method, however, only moderate yields of the required compounds were obtained. Several of the compounds (1 and 2) shown overleaf, prepared by this method proved unstable under laboratory conditions, decomposing rapidly in the presence of light and air.



Diphenyliodonium salts were also prepared using the method of Berry et. al.¹⁶⁹ affording a moderate yield of the tetrafluoroborate salt. A table of yields of the sulphonium and iodonium is given below.

Table 1

Cation	SALT	
	Anion	% Yield
diphenylethylsulphonium	PF_6^-	7.0
diethylphenylsulphonium	PF_6^-	26.0
S-ethylthioxanthylium	PF_6^-	43.0
S-ethylthioxanthonium	PF_6^-	14.6
S-ethyl-9-ethoxythioxanthylium	PF_6^-	52.0
S-methylthioxanthylium	BF_4^-	29.0
S-methylthioxanthonium	BF_4^-	65.5
S-benzylthioxanthonium	BF_4^-	30.0
S-n-butylthioxanthylium	BF_4^-	6.0
S-n-hexylthioxanthylium	BF_4^-	4.3
S-phenylthioxanthylium	BF_4^-	68.0
diphenyliodonium	BF_4^-	43.0

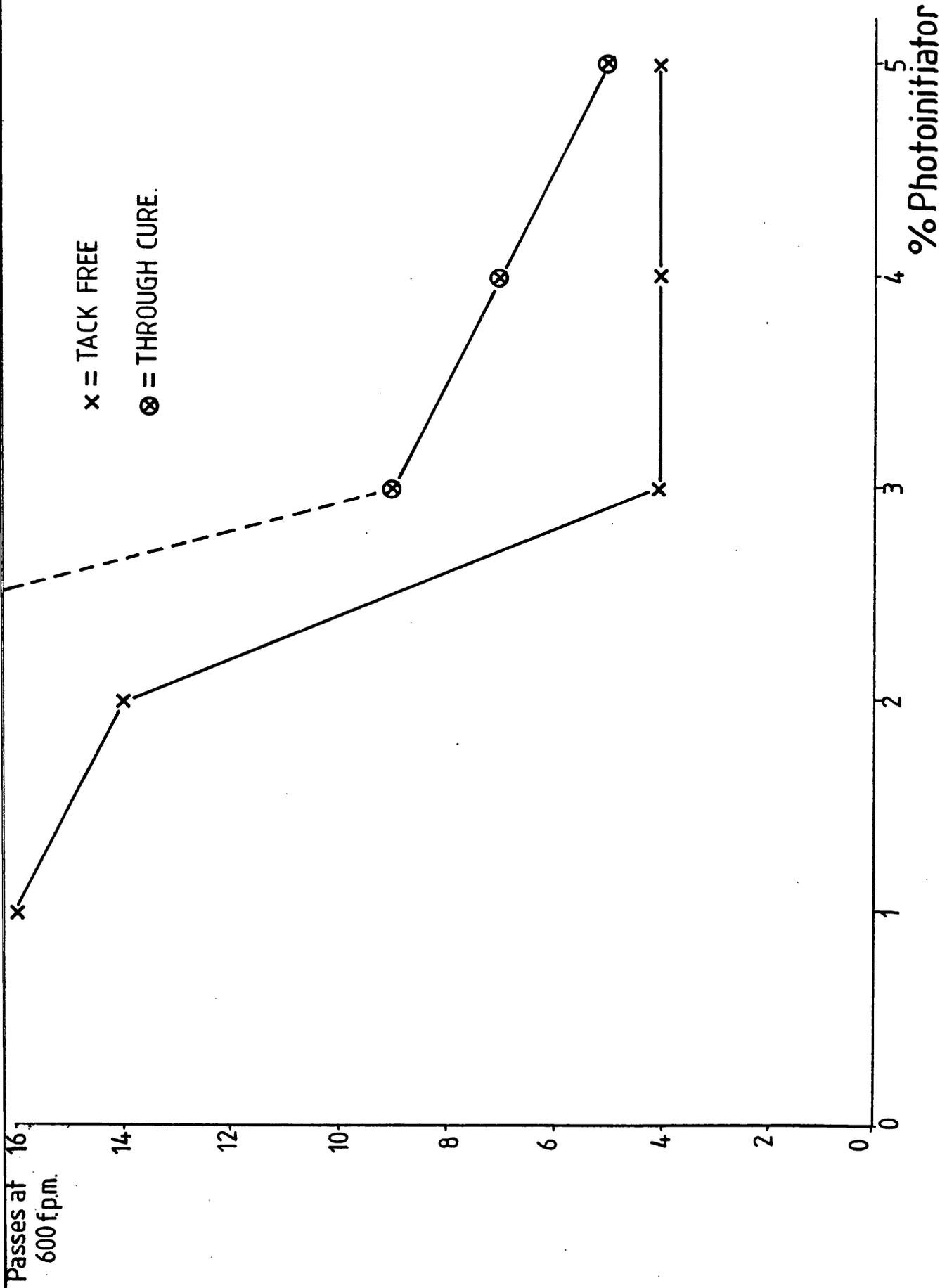
The table shows that the oxonium salt alkylations led to higher yields of the sulphonium salts than the silver tetra-

fluoroborate / iodoalkane method. The last method also proved less effective as the alkane chain increased in length, the yields going from 29% for the methyl group to 4.3% for the hexyl group.

The salts were tested in a commercial white ink, a preliminary study was made using diphenyliodonium tetrafluoroborate to discover the optimum photoinitiator content for the ink. This determination was carried out in a similar manner to that described in the chapter on free radical initiation of polymerisation. A graph of this is shown overleaf. The optimum percentage of photoinitiator was found to be 3%. Using 3% photoinitiator a series of sulphonium and iodonium salts were tested in a white ink containing an epoxy resin. The results of the tests are shown below in table 2.

Table 2

Photoinitiator		Lamp passes to tack free	Lamp passes to through cure
Cation	Anion		
diphenyliodonium	BF_4^-	4	9
diphenyliodonium	PF_6^-	1-2	5
triphenylsulphonium	PF_6^-	2	5
S-methylthioxanthonium	BF_4^-	12	15
S-methylthioxanthylum	BF_4^-	16	20
S-ethylthioxanthylum	BF_4^-	10	15
S-n-hexylthioxanthylum	BF_4^-	13	15
S-ethylthioxanthylum	PF_6^-	2	6
S-ethyl-9-ethoxythioxanthylum	PF_6^-	4	7



The results showed that the rate of cationic photoinitiation of epoxide polymerisation was more dependant on the nature of the anion used rather than the type of cation. The hexafluorophosphate salts curing more rapidly than the tetrafluoroborate salts. Similar observations have been made by Ketley et. al.²⁰¹. they found that the rate of epoxide polymerisation was dependant on the type of anion and that the hexafluoroantimonate anion was more efficient than the hexafluoroarsenate anion than the hexafluorophosphate anion than the tetrafluoroborate anion. The mechanism by which the epoxides react with the initiators has already been described in the introduction to the chapter..

A study by Crivello¹⁷⁷. has shown that the rate of decomposition of iodonium and sulphonium salts was independant of the nature of the anion. Odian²⁰². using carbonium salts has made similar observations that whilst the rate of decomposition of the salts was independant of the anion, the rate of cure of epoxides was dependant on the nature of the photoinitiator anion. Odian explained his results in terms of the degree of separation between the ion-pair. The SbF_6^- anion is the largest anion and is thus most loosely bound, the BF_4^- anion is the smallest and consequently the most tightly bound.

The table 2 did show that there was a degree of cation dependance. The diphenyliodonium salts being more effective initiators than the sulphonium salts, this may be due to the difference in the strength of the aryl-iodine and aryl-sulphur bonds. There is also some dependance on the structure of the cation on the rate of cure of the ink. The thioxanthonium salt effecting a faster cure than the thioxanthylum salts.

The inks used to test the cationic photoinitiators were found to undergo considerable post cure, i.e. the ink which was not completely cured during the irradiation was found to cure on standing. The rate of post cure was found to increase if the temperature was raised after the irradiation. This is good evidence for the existence of living polymers in cationic polymerisations. An example of a cationic polymerised ink is shown overleaf. An advantage of cationic inks over free radical inks is that they adhere to the printed substrate more strongly.

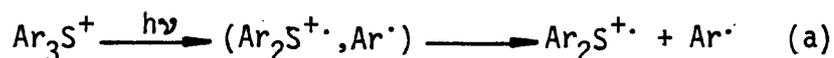
The decomposition of sulphonium salts on irradiation in methanol was studied. Triarylsulphonium salts were irradiated using low pressure mercury lamps. The products of the photolysis are shown below in table 3.

Table 3

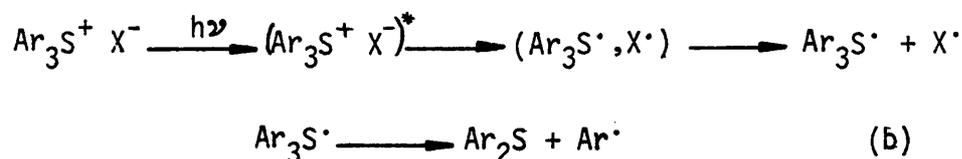
Salt	Photolysis time (hrs)	Starting material	Products (%)				
			PhH	PhOCH ₃	Biphenyl	Ph ₂ S	PhF
Ph ₃ S ⁺ BF ₄ ⁻	61	23.8	12	8	1.0	60.5	30
Ph ₃ S ⁺ PF ₆ ⁻	61	22.0	15	6	0.8	65.0	35

A yellow insoluble film was also formed on the sides of the reaction vessels. On completion of the photolysis the solution was acid to litmus.

The stoichiometry of the reaction was found to be straightforward, one mole of sulphide being formed for each mole of triarylsulphonium salt destroyed. Several mechanisms may be possible to account for the decomposition. The initial step may be either,



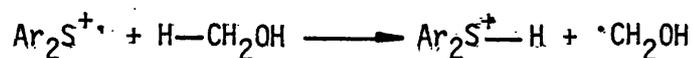
or



Mechanism b represents an electron transfer reaction similar to that postulated by Walsh and Long²⁰³, and Griffin et. al.²⁰⁴, for anilinium and phosphonium salts. This mechanism can be discounted however as it does not account for the production of acid in the reaction.

Mechanism a involves the formation of a diarylsulphinium cation radical via photochemical homolytic cleavage of one of the sulphur-carbon bonds. Cation radicals of this type have been observed by Shine and his co-workers²⁰⁵, in the oxidation of aryl sulphides. Maycock and Berchtold²⁰⁶, have suggested their intermediacy in the photolysis of phenacylsulphonium tetrafluoroborates. The cation radical may then undergo the reactions outlined below in scheme 15.

Scheme 15

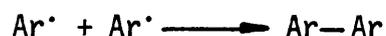


These reactions would account for the presence of acid in the photosylate. The acid if produced in a polymerisable medium such as an epoxy resin would be capable of initiating polymerisation. The other products can be accounted for by invoking further

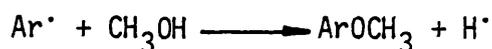
reactions of the aryl radical..Benzene by hydrogen abstraction from the solvent;



biphenyl by coupling of two aryl radicals;



anisole by reaction with the solvent, thus;



Fluorobenzene formation may occur by a similar process to that occurring in the photo-decomposition of aryldiazonium tetrafluoroborates.

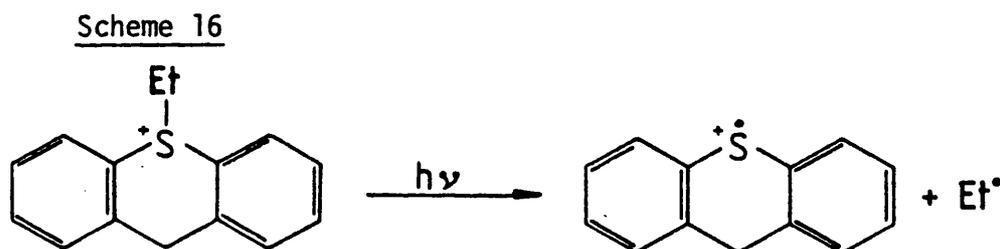
Several of the thioxanthylum and thioxanthonium salts were also irradiated, the only identifiable product was thioxanthene or thioxanthone. The results are displayed in the table 4 below.

Table 4

Sulphonium salt		%	Product (%)			
S-methylthioxanthylum	BF ₄ ⁻	16.9	thioxanthene	81		
S-ethylthioxanthylum	PF ₆ ⁻	17.5	thioxanthene	82		
S-phenylthioxanthylum	BF ₄ ⁻	15.5	thioxanthene	83	C ₆ H ₆	41 C ₆ H ₅ F 25
S-methylthioxanthonium	BF ₄ ⁻	23.1	thioxanthone	75		
S-ethylthioxanthonium	PF ₆ ⁻	14.0	thioxanthone	84		
S-n-butylthioxanthylum	BF ₄ ⁻	8.2	thioxanthene	88		

A red or yellow insoluble polymeric film formed around the sides of the reaction vessels during the photolyses. An acid

was also a product of the reaction. Examination of the results in table 4, shows that the S-alkylthioxanthylum and S-alkylthioxanthonium salts decompose at a similar rate on irradiation in methanol. The S-phenylthioxanthylum^{salt} which was prepared by the method of Crivello et. al.¹⁹⁰ gave thioxanthene as the major product of the photolysis. Within the photosylate in addition to thioxanthene, benzene and fluorobenzene were found. A similar mechanism to that proposed for the triaryl-sulphonium salts would be likely to occur. The thioxanthylum salts undergoing homolytic cleavage of the carbon-sulphur bond to afford a thioxanthene cation radical as shown in scheme 16 below.



The cation radical could then undergo further reactions to yield thioxanthene. It would seem likely that as no other products were detected on the gas chromatograph under the conditions available, cleavage of the alkyl carbon-sulphur bond occurs. The primary alkyl radical formed then hydrogen abstracts from the solvent, for example,



As a result of the volatility of the alkane this product could not be detected.

The photolysis of diaryliodonium salts in methanol using low pressure mercury lamps was carried out. The results are

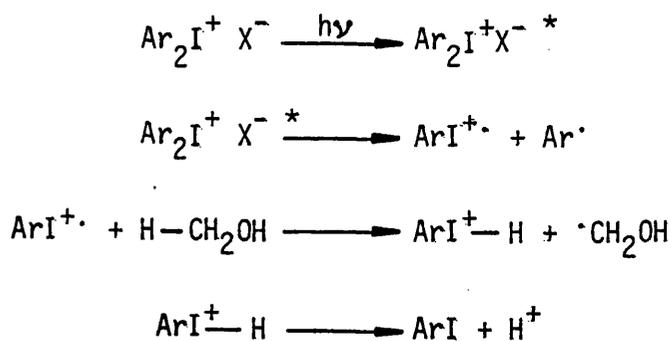
shown below in table 5.

Table 5

Cation	Anion	Products (%)					
diphenyliodonium	BF ₄ ⁻	benzene	68	fluorobenzene	17	biphenyl	10
diphenyliodonium	PF ₆ ⁻	benzene	70	fluorobenzene	16	biphenyl	12

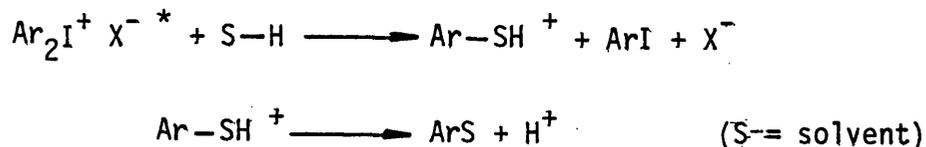
Neither of the photosylates contained any starting material. An acid was detected in the reaction mixture in addition to the other products. The mechanism for the decomposition of the diaryliodonium salts is probably similar to that for the sulphonium salts. Homolytic cleavage of the carbon-iodine bond to produce an aryl radical and an iodobenzene radical cation ArI⁺·-H. This rapidly deprotonates to afford iodobenzene and a hydrogen ion. A reaction scheme describing this is shown below.

Scheme 17

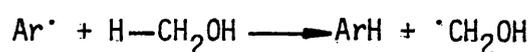


Crivello et. al.¹⁷⁴ have proposed that in addition to this route a minor pathway also operates as shown below in scheme 18.

Scheme 18



This reaction scheme involved nucleophilic attack by the solvent on the excited iodonium salt. The collapse of this species generating iodobenzene, a proton and Ar-S. However under the conditions of our photolysis no product corresponding to attack on the solvent, neither anisole nor benzyl alcohol were detected. Examination of table 5 shows that iodobenzene was not detected in the photo-sylate this is probably a result of dehalogenation of the iodobenzene to afford benzene, this reaction occurring very rapidly. (See

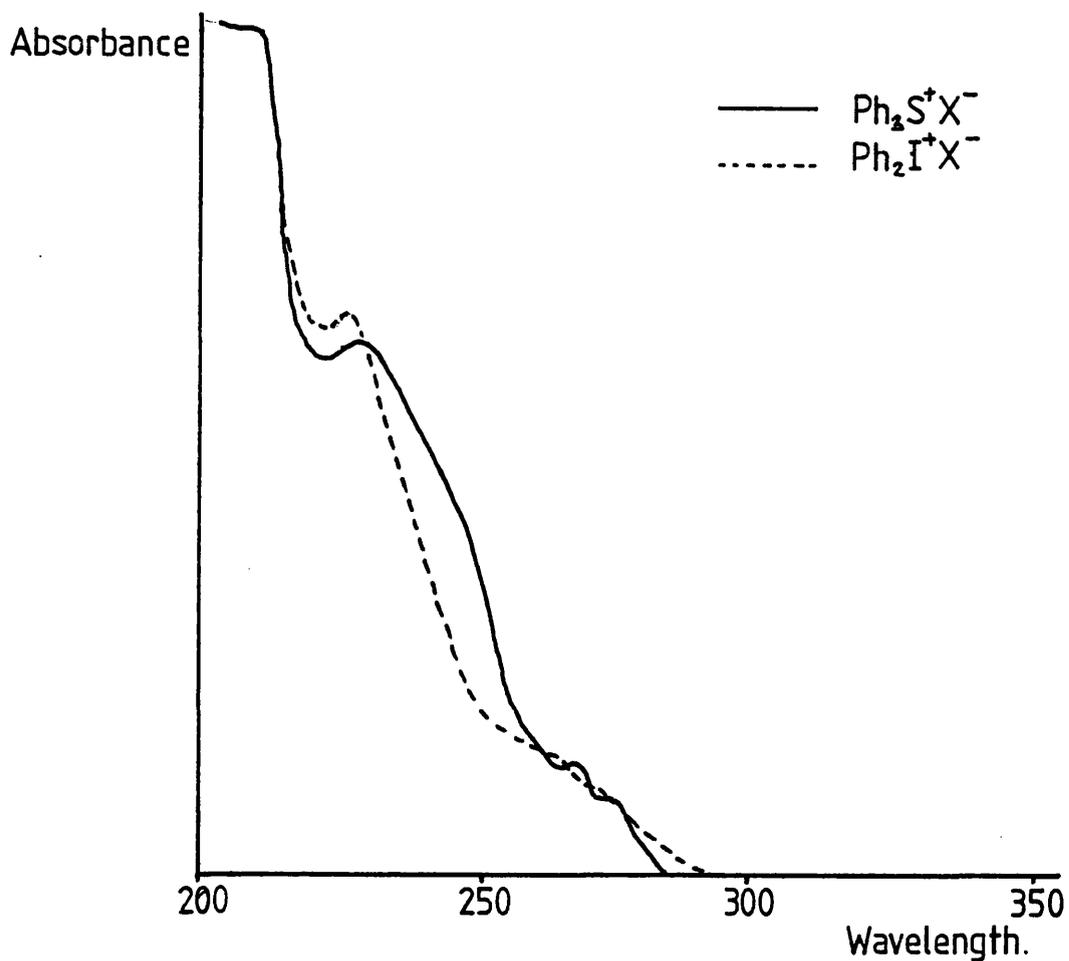


chapter 3.)

The acids produced from both sulphonium and iodonium salts on irradiation would be capable of initiating cationic polymerisation.

PHOTOSENSITIZATION OF CATIONIC PHOTOINITIATORS

Diaryliodonium salts and sulphonium salts do not absorb ultra-violet light appreciably, beyond 275 nm. as can be seen in the spectrum below.

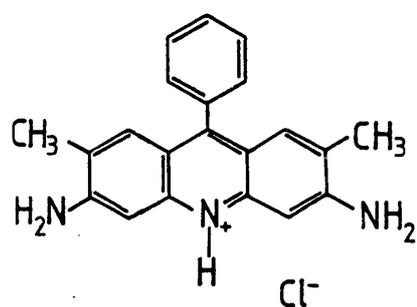


Since in commercial applications the most commonly used source of light is a medium pressure mercury lamp or tungsten halogen doped lamps with most of their output at wavelengths longer than 275 nm. much of the light is wasted.

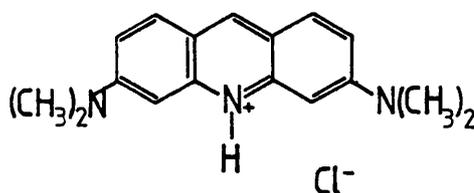
An additional reason for utilising longer wavelength light is that the energy requirement is less, and hence the cost of running the lamp is less. Therefore it would be advantageous

to be able to sensitize the decomposition of iodonium and sulphonium salts using compounds which absorb light at longer wavelengths.

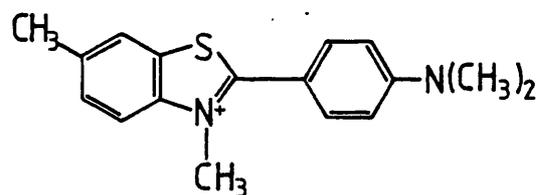
Crivello and Schroeter²⁰⁷. have found that iodonium salts decomposition can be sensitized by the use of certain dyes, for example, benzoflavin λ max. 460 nm. , acridine orange λ max. 539 nm. and setoflavin λ max 380 nm. The structures of these molecules are shown below.



Benzoflavin



Acridine Orange



Setoflavin

Crivello found that only small quantities of dye were necessary to sensitize diaryliodonium salt decomposition and accelerate cure in photoinitiated cationic polymerisations using these salts. They also noted an interesting concentration effect, that above a certain concentration the sensitizer ceased to accelerate decomposition and instead decreased the rate of photodecomposition. This effect has been observed in other applications where sensitizers have been used, for example the use of dyes to sensitize silver halide emulsions. The effect

has been explained as being due to dye-dye quenching and or dye screening effects²⁰⁸.

It was found that whilst the dyes accelerated iodonium salt decomposition and iodonium salt initiated polymerisations they had no effect in sulphonium salt photo-decomposition.

DISCUSSION AND RESULTS

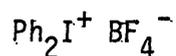
It has been found that dyes could only sensitize the photo-decomposition of diaryliodonium salts and not sulphonium salts. As a result of this lack of general applicability an investigation has been carried out of compounds thought to be likely sensitizers of the photo-decomposition and hence the curing of cationic polymerisations of epoxy resins initiated by diaryliodonium and aromatic sulphonium salts.

A series of substituted polyaromatic compounds and related compounds were added to white inks containing either of the sulphonium or iodonium photoinitiators. The ink contained an epoxide resin which was capable of being polymerised, the curing was carried out as previously described. The results of these experiments are detailed below in table 5. Throughout the experiments the sensitizer level was kept at 1% w/w whilst the initiator level was 3% w/w.

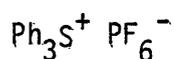
Table 5

$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	Sensitizer	Lamp passes to tack free	Lamp passes to through cure
	None	1-2	5
	Thioxanthone	1	4-5
	Anthracene	1	4
	9,10-dimethylantracene	1	3
	2-ethyl-9,10-dimethoxyanthracene	1	2
	2,6-dimethylnaphthalene	1	4-5
	2,5-diphenyl-1-3-4-oxadiazole	1	4

Table 5 contd.



Sensitizer	Lamp passes to tack free	Lamp passes to through cure
None	4	9
Anthracene	4	7
2-ethyl-9,10-dimethoxyanthracene	4	5



Sensitizer	Lamp passes to tack free	Lamp passes to through cure
None	4	6
Xanthpinacol	4	6
Perylene	4	4
2,6-dimethylnaphthalene	3	6
1,2-benzanthracene	3	4
Anthracene	2	3
9-nitroanthracene	3	5
9,10-dimethylanthracene	2	3
2-ethyl-9,10-dimethoxyanthracene	1	2
Thioxanthone	4	4
2,5-diphenyl-1-3-4-oxadiazole	2	2

From the table it can be seen that most of the compounds accelerate the rate of cure for both sulphonium and iodonium salt photoinitiated reactions. Xanthpinacol and thioxanthone were not very effective as promoters of the polymerisations of epoxides. Both of these compounds would be sources of free radicals, and it has been reported by Ledwith and his co-workers²⁰⁹.

optimum amount of sensitizer for effecting the most rapid speed of cure. Therefore, a study was made of the amount of sensitizer needed to effect cure most efficiently. The results of using increasing amounts of sensitizer are displayed in the following table, and in graphical form overleaf.

Table 6

Initiator: diphenyliodonium tetrafluoroborate.

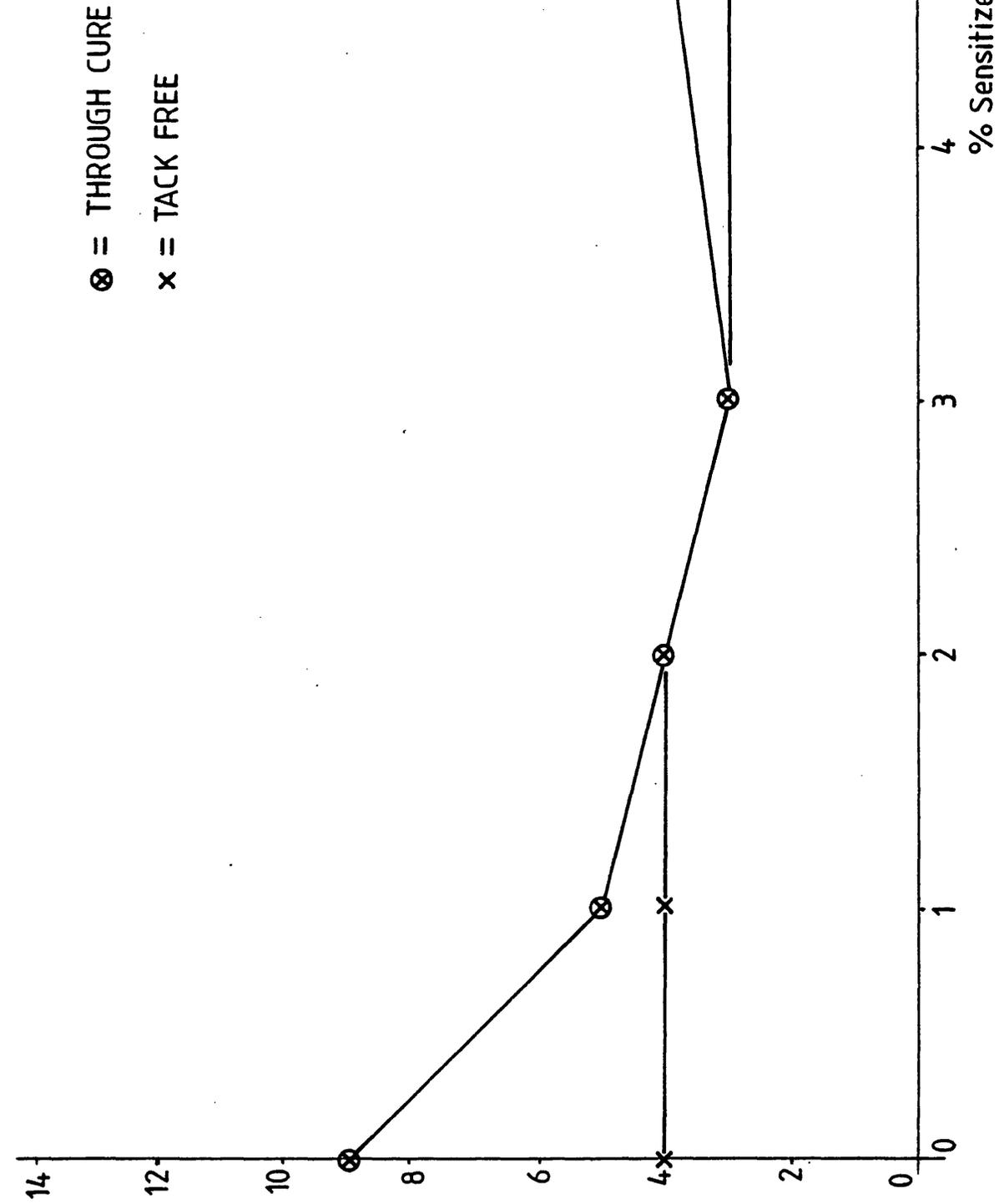
Sensitizer: 2-ethyl-9,10-dimethoxyanthracene.

% Sensitizer	Lamp passes to tack free	Lamp passes to through cure
0	4	9
1	4	5
2	4	4
3	3	3
5	3	4

The results in the table show that the fastest speed of cure was obtained when 3% w/w of sensitizer was used. However this level of incorporation into the ink would not be economic and a 1% loading would be most cost effective. As with the results obtained by Crivello²⁰⁷, using dyes, the speed of cure began to diminish at higher concentrations of the sensitizer.

The compounds used to sensitize sulphonium and iodonium salt initiation of cationic polymerisation all had significant quantum yields of fluorescence and phosphorescence making it difficult to identify which excited state was responsible for the sensitization.

The fluorescence spectrum of 9,10-dimethylantracene was recorded and Stern-Volmer plots made of the quenching of its fluorescence by a variety of sulphonium and iodonium salts,



Cure rate passes at 600 f.p.m.

The values for the gradient of the line and for k_q are shown below in table 7 and the Stern-Volmer plots are shown on the following pages. A value of 16.2×10^{-10} s was used for the lifetime of 9,10-dimethylantracene in the absence of quencher.

Table 7

Quencher	Slope	k_q ($\times 10^{10}$)
diphenylmethylsulphonium BF_4^-	78.02	4.82
triphenylsulphonium PF_6^-	296.94	18.32
S-methylthioxanthylum BF_4^-	63.08	3.89
diphenyliodonium BF_4^-	164.66	10.16

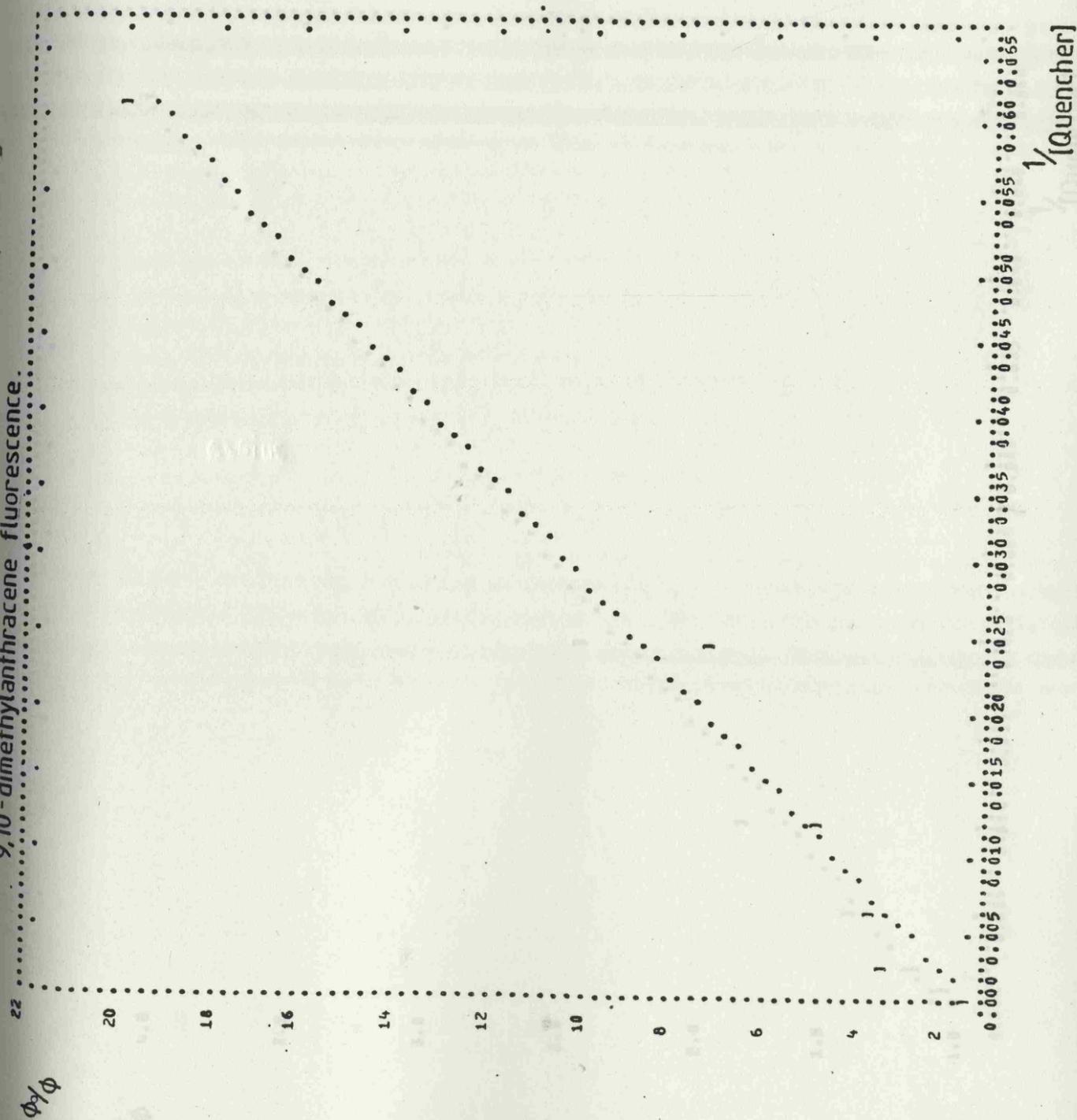
In all cases k_q was diffusion controlled. These results whilst not eliminating the triplet state as being responsible for the sensitization show that the sensitization occurs at least in part from the excited singlet state.

Since the sensitization occurred to some extent from the singlet state several compounds were tested that have quantum yields of fluorescence of almost unity. The compounds studied absorbed ultra-violet light with maxima at approximately 315 nm. At this wavelength the light output of the lamps normally used is highest. The sensitizers were tested in a white ink using a sulphonium salt as a photoinitiator. The results are displayed below in table 8.

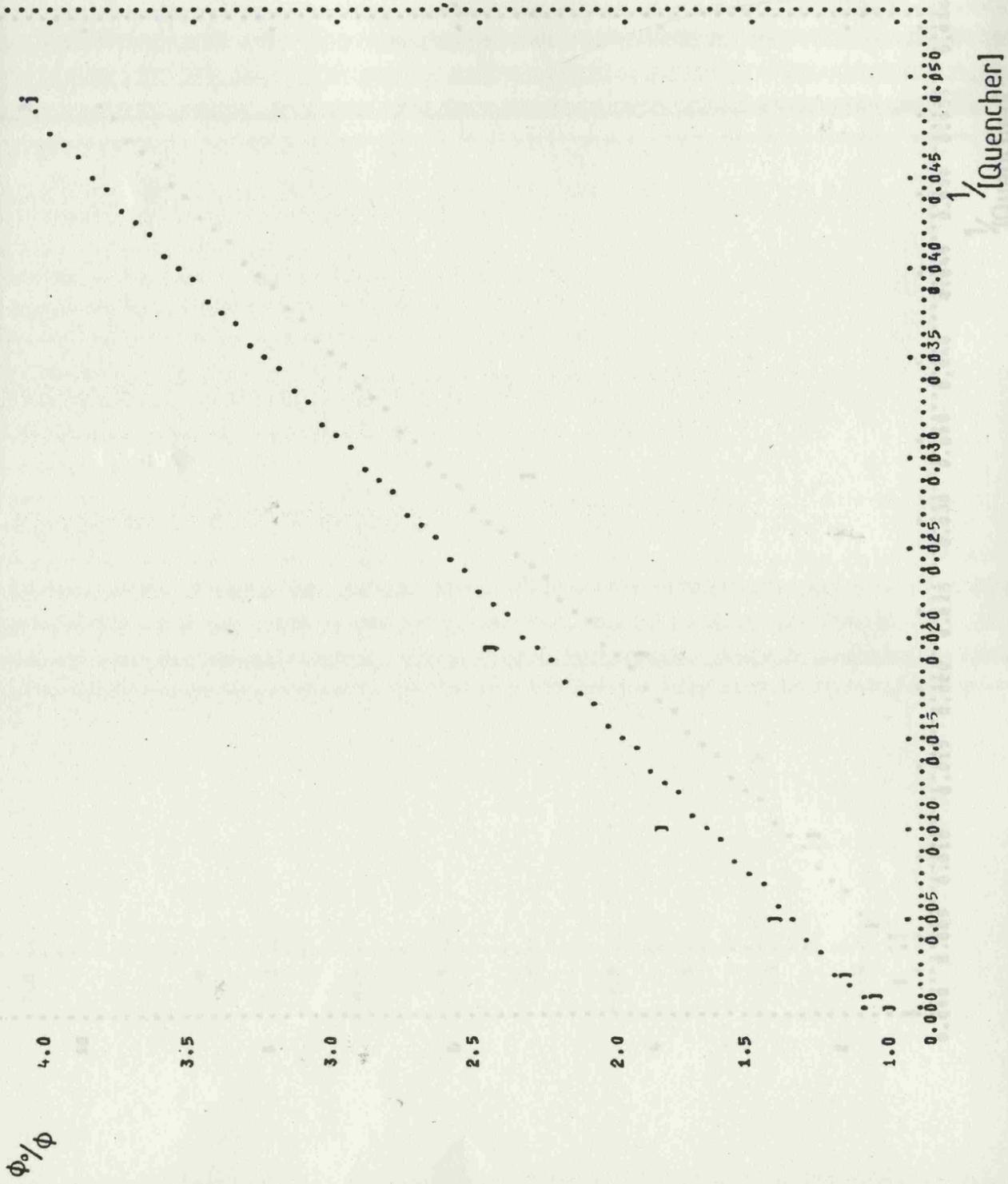
Table 8

Sensitizer	Lamp passes to tack free	Lamp passes to through cure
None	2	2
2-phenyl-5-(4-biphenyl)-1-3-4-oxadiazole	1	2

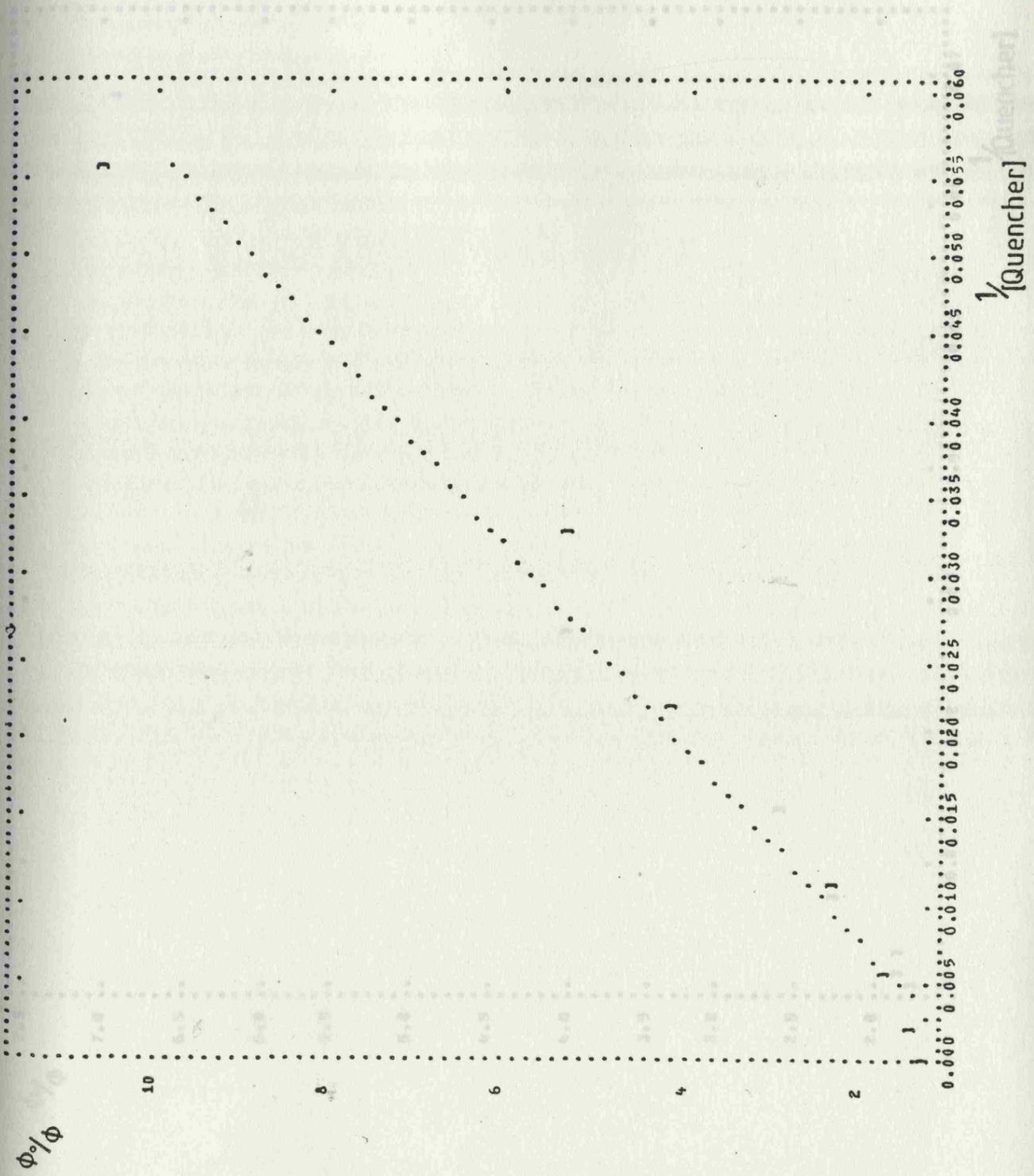
Stern-Volmer plot of triphenylsulfonium PF₆⁻ quenching of 9,10-dimethylantracene fluorescence.



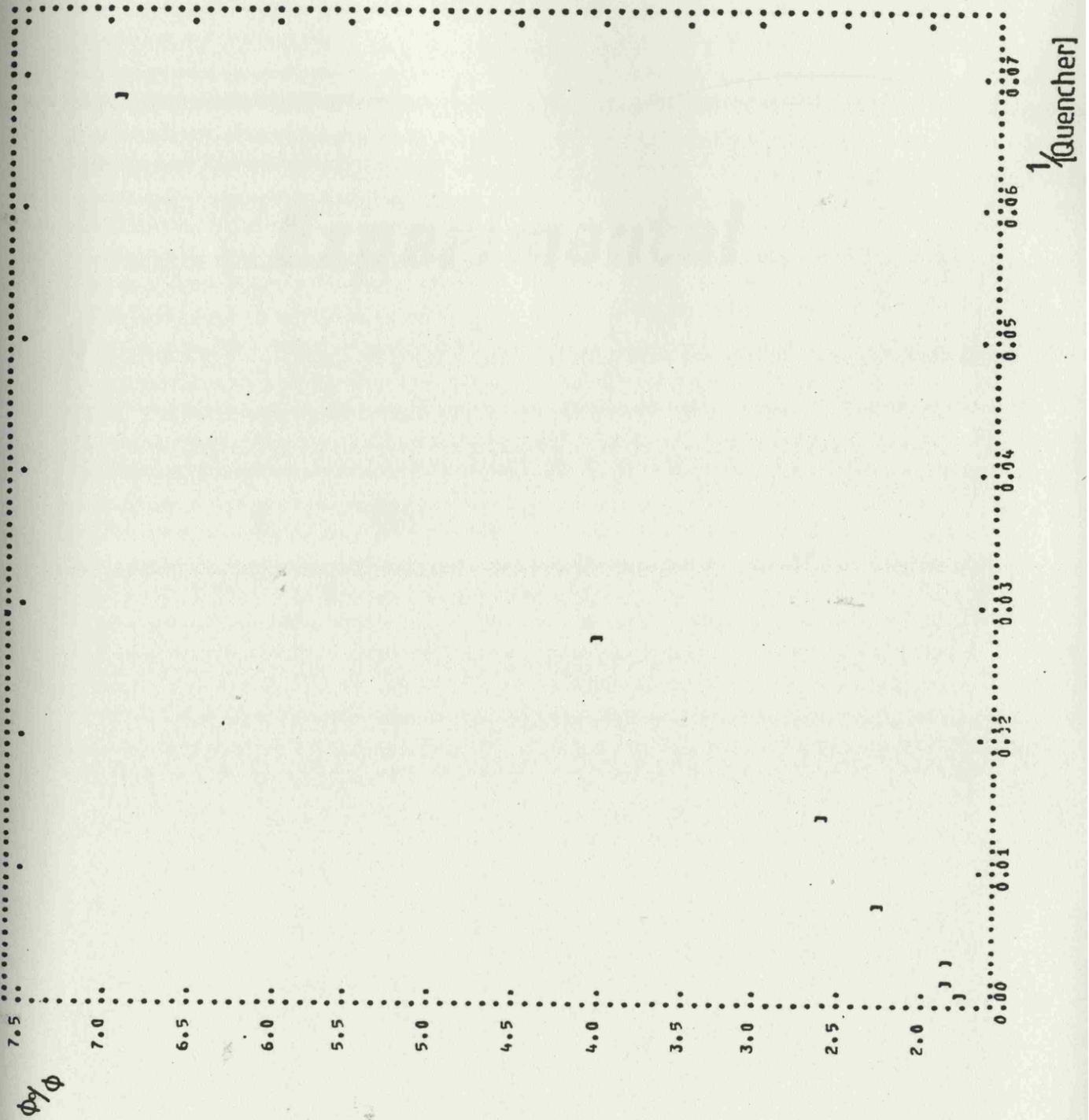
Stern-Volmer plot of S-methylthioxanthylum BF₄⁻ quenching of 9,10-dimethylanthracene fluorescence.



Stern-Volmer plot of diphenyliodonium BF₄⁻ quenching of 9,10-dimethylantracene fluorescence.



Stern-Volmer plot of diphenylmethylsulphonium BF₄⁻ quenching of 9,10-dimethylantracene fluorescence.



Sensitizer
Lamp passes to tack free
Lamp passes to through cure

2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole

The results show that cure was accelerated by these compounds and that these compounds sensitize the sulphonium and iodonium salt photoinitiation of polymerisation via the excited singlet state.

Sensitizer	Lamp passes to tack free	Lamp passes to through cure
2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole	1	2

The results show that cure was accelerated by these compounds and that these compounds sensitize the sulphonium and iodonium salt photoinitiation of polymerisation via the excited singlet state.

Chapter 5.

Experimental

EXPERIMENTAL

INSTRUMENTATION AND GENERAL DETAILS

Melting points were determined on a Kofler Block or a Gallenkamp melting point apparatus, and are uncorrected.

Infra-red spectra were carried out on a Perkin Elmer 237 or Perkin Elmer 457 grating spectrophotometers as KBr discs or thin films. Proton nuclear magnetic resonance spectra were recorded on either a Varian model T60, a Perkin Elmer EM390 or a Jeol PS100, in deuteriochloroform solution, using tetramethylsilane as an internal reference, unless stated. The following abbreviations have been used:

s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

¹³Carbon and ³¹Phosphorus n.m.r. spectra were obtained on a Jeol FX60.

Ultra-violet spectra were carried out on a Unicam SP800 spectrophotometer.

Mass spectra were performed on a Micromass MS30/76 Kratos spectrometer fitted with a G.L.C./mass spectrometer interface.

Gas-liquid chromatography was performed on a Pye-Unicam series 104 and a Perkin Elmer Sigma 3. Preparative gas-liquid chromatography was carried out on a Pye Unicam 105 chromatograph.

High performance liquid chromatography was carried out using a Waters model 6000A solvent delivery system and a Cecil CE2012 variable wavelength UV monitor.

Elemental analyses were determined by C, H and N Analysis Ltd., Wigston and P Hemming., City University.

Solvents were prepared by the following methods, prior to use: Benzene, cyclohexane, diethyl ether, ethyl acetate, carbon disulphide and all grades of petroleum ether were distilled and dried over sodium wire.

Dichloromethane, nitromethane, 1,2-dichloroethane, acetonitrile and dimethyl sulphoxide were distilled and stored over molecular sieves.

Methanol and ethanol were distilled from calcium hydride. Chloroform was distilled and ethanol added as a stabiliser.

Analar acetone was used as received.

Solvents for fluorescence spectroscopy were obtained as spectroscopic grade and used as supplied.

Reagents were used as supplied by the manufacturer, except for triethylamine which was stored over molecular sieves. Liquid reagents were distilled prior to use only if discoloured or an impurity was detected by chromatography in non-preparative experiments.

1. PREPARATION OF N,N,N,N,N,N, HEXAMETHYLTRIETHYLENETETRAMINE

Triethylenetetramine (10g.0.097 moles) was dissolved in water (100cm³), formaldehyde solution 40% (21g.0.7 moles) and formic acid (61.9g.1.34 moles) were added and the mixture heated under reflux for six hours. The solution was evaporated in vacuo to one third of the original volume and then saturated with potassium hydroxide. A dark red oil which appeared was separated from the aqueous layer which was then extracted with diethyl ether (3 x 25 cm³). The extracts were combined, dried (MgSO₄) and then solvent removed to leave a red oil which was distilled to yield a colourless oil. (Yield 7.1g, 59%).

b.p. 120-122°C at 6mm of Hg. (Lit. 130°C at 11m.m. of Hg)²¹¹.

¹H n.m.r. (CDCl₃) : 2.5 δ (12H,d); 2.2 δ (18H,s).

I.R. ν_{max} (thin film) 3350, 2920, 2800, 1660, 1460, 1045 cm⁻¹.

2. PREPARATION OF N,N,N,N,N,N,N, HEPTAMETHYLTETRAETHYLENEPENTAMINE

Tetraethylenepentamine (10g. 0.053 moles) was dissolved in water (30cm³) and formaldehyde solution 40% (28.2g. 0.94 moles) and formic acid (73.2g. 1.59 moles) added. The mixture was heated under reflux for four hours. The solution was evaporated to half the original volume and saturated with potassium hydroxide. The organic components were extracted with diethylether (3 x 30cm³). The combined extracts were dried (MgSO₄) and the solvent evaporated off to leave a yellow oil, this was distilled to yield a colourless oil. (Yield 7.5g, 49.3%).

b.p. 129°C at 3mm of Hg²¹².

¹H n.m.r. (CDCl₃) : 2.5 δ (16H,d); 2.2 δ (24H,s).

I.R. ν_{max} (thin film) 3350, 2920, 2760, 1650, 1450, 1050 cm⁻¹.

3. PREPARATION OF 1,8-N,N,N,N. TETRAMETHYLDIAMINOCTANE

1,8 - diaminoctane (2g. 0.01 moles) was dissolved in water (10cm³) and added to a mixture of formic acid (9.2g. 0.2 moles) and formaldehyde, 40%, (2.65g. 0.09 moles). The solution was heated under reflux for four hours. On cooling 1 mole equivalent of hydrochloric acid was added. Excess formic acid and formaldehyde were removed by evaporation. The mixture was then made basic with sodium hydroxide and the organic

components extracted with dichloromethane (3 x 20cm³). The combined extracts were dried (MgSO₄) and the solvent removed at the pump to leave a yellow oil which was distilled to give a colourless oil as product. (Yield 1.5g. 60%).

b.p. 100-102°C at 0.9mm of Hg (Lit 117-117.5°C at 10mm of Hg)²¹³.

¹H n.m.r. (CDCl₃) : 2.25 δ (16H,s); 1.3 δ (12H,s).

I.R. ν max (thin film) 2920, 2845, 2765, 1670, 1465, 1380,
1260, 1040, 840 cm⁻¹.

4. PREPARATION OF 1,3-N,N,N,N TETRAETHYLDIAMINOPROPANE

1,3 dibromopropane (20g. 0.1 moles) and diethylamine (excess) were heated under reflux for six hours. A white crystalline mass was formed over this period. After cooling, water (5cm³) was added, this dissolved the crystalline material. The solution was then saturated with potassium hydroxide. The amine was extracted with diethyl ether (3 x 15cm³), the combined extracts were dried (MgSO₄) and the solvent removed in vacuo to afford a pale yellow oil which was distilled to give a colourless oil. (Yield 8.85g. 48%).

b.p. 80-82°C at 7mm of Hg (Lit 95-100°C at 15mm of Hg)²¹⁴.

¹H n.m.r. (CDCl₃) : 2.5 δ (12H,q); 1.6 δ (2H,m); 1.0 δ (12H,t).

I.R. ν max (thin film) 2970, 2930, 2790, 1465, 1380, 1280,
1200, 1065, 760, 730 cm⁻¹.

5. PREPARATION OF 1,2-N,N,N,N, TETRAETHYLDIAMINOETHANE

Experimental procedure as in Preparation 4, using 1,2 dibromoethane (20g 0.106 moles) and excess diethylamine. (Yield 4.72g. 25.5%).

b.p. 68°C at 6.5mm of Hg. (Lit $82-5^{\circ}\text{C}$ / ?)²¹⁴.

^1H n.m.r. (CDCl_3): 2.5 δ (12H,q); 1.0 δ (12H,t).

I.R. ν max (thin film) 2970, 2930, 1465, 1380, 1280, 1200
1065, 760, 730 cm^{-1} .

6. PREPARATION OF 1,6-N,N,N,N, TETRAETHYLDIAMINOHEXANE

The preparation was carried out as outlined in Experiment 4, using 1,6-dibromohexane (5g. 0.02 moles) and excess diethylamine. (Yield 3.5g. 76%)

b.p. 88°C at 1mm of Hg. (Lit 135°C at 13mm of Hg)²¹⁵.

^1H n.m.r. (CDCl_3) : 2.5 δ (12H,m); 1.4 δ (8H, broad s); 1.05 δ (12H,t).

I.R. ν max (think film) 2970, 2790, 1460, 1380, 1280, 1200,
1065, 760, 730 cm^{-1} .

7. PREPARATION OF 1,8-N,N,N,N, TETRAETHYLDIAMINOCTANE

Methodology as in Experiment 4, using 1,8 dibromooctane (20g. 0.074 moles) and excess diethylamine. (Yield 16.9g. 89.7%)

b.p. $112-114^{\circ}\text{C}$ at 1mm of Hg.

^1H n.m.r. (CDCl_3): 2.4 δ (12H,m); 1.4 δ (12h,broad s); 1.0 δ (12H,t).

I.R. ν max (thin film) 2970, 2930, 2850, 2790, 1465, 1380,
1280, 1200, 1065, 760, 730 cm^{-1} .

8. PREPARATION OF 1,10-N,N,N,N, TETRAETHYLDIAMINODECANE

Experimental procedure was carried out as detailed in Experiment 4,
using 1,10-dibromodecane (20g 0.067 moles) and excess diethylamine.
(Yield 13.5g 71.3%)

b.p. 120-122 $^{\circ}\text{C}$ at 1mm of Hg. (Lit 186-188 $^{\circ}\text{C}$ at 16mm of Hg)²¹⁶.

^1H n.m.r. (CDCl_3) 2.4 δ (12H,m); 1.4 δ (16H,broad s,); 1.0 δ (12H,t).

I.R. ν max (thin film) 2970, 2930, 2850, 2790, 1465, 1380, 1280,
1200, 1065, 760, 730 cm^{-1} .

9. PREPARATION OF 1,12-N,N,N,N, TETRAETHYLDIAMINODODECANE

The procedure utilised was similar to that in Experiment 4, using
1,12 dibromododecane (20g. 0.061 moles) and excess diethylamine.
(Yield 10.5g 52.2%)

b.p. 140 $^{\circ}\text{C}$ at 0.5mm of Hg. (Lit 125-128 $^{\circ}\text{C}$ at 0.01mm of Hg)²¹⁵.

^1H n.m.r. (CDCl_3): 2.4 δ (12H,m); 1.4 δ (20H, broad s); 1.0 δ (12H,t).

I.R. ν max (thin film) 2970, 2930, 2850, 2790, 1465, 1380, 1280,
1200, 1065, 760, 730 cm^{-1} .

10. PREPARATION OF 1,5-N,N,N,N, TETRAETHYLPENTANENEDIAMIDE

Pentanedioic dichloride (20g 0.118 moles) was added drop-wise with stirring to excess diethylamine. When the addition had been completed the mixture was heated under reflux for eighteen hours. On cooling, water (20cm³) was added, the organic components were extracted with diethyl ether (4 x 30cm³). The combined extracts were dried (MgSO₄) and the solvent and excess diethylamine were removed at the pump to leave a dark oil which was distilled to yield a yellow oil. (Yield 13.5g 47.7%

b.p. 150°C at 0.2mm of Hg. (Lit 205°C at 760mm of Hg)²¹⁷.

¹H n.m.r. (CDCl₃) 3.4 δ (8H,m); 2.4 δ (6H,t); 1.2 δ (12H,m).

I.R. ✓ max (thin film) 3500, 2960, 1630, 1450, 1380, 1260,
1220, 1140, 1070, 790 cm⁻¹.

11. PREPARATION OF 1,5-N,N,N,N, TETRAETHYLAMINOPENTANE

Lithium aluminium hydride (4.1g 0.174 moles) was added to diethyl ether (150cm³) to form a slurry. N,N,N,N, tetraethylpentadiamide (13.0g 0.054 moles) was added drop-wise with stirring, under nitrogen, whilst being cooled in an ice-water bath. When addition was complete the reaction mixture was allowed to warm to room temperature and then heated under reflux for four hours. On cooling, water was added cautiously until all the excess lithium aluminium hydride had been destroyed. The liquid portion was decanted from the alumina and separated. The ethereal layer was dried (MgSO₄) and the solvent removed on a rotary evaporator to leave a pale yellow oil which was distilled. (Yield 7.2g. 62.5%)

b.p. 80°C at 1.5mm of Hg (Lit $68-71^{\circ}\text{C}$ at 0.2mm of Hg) ²¹⁸.

^1H n.m.r. (CDCl_3) 2.5 δ (12H,m); 1.4 δ (6H, broad s); 1.05 δ (12H,t).

I.R. ν max (thin film) 2920, 2790, 1450, 1370, 1200, 1060, 765 cm^{-1} .

12. PREPARATION OF BIS(2-BROMOETHYL) ETHER

Phosphorus tribomide (20g. 0.074 moles) was added drop-wise with stirring to bis(2-hydroxyethyl) ether (7.8g. 0.074 moles) and pyridine (5cm^3). The mixture was stirred overnight at room temperature and then poured into water (30cm^3). A yellow oil formed which was extracted with diethyl ether ($2 \times 25\text{cm}^3$). The extracts were combined, dried (MgSO_4), and the solvent removed on a rotary evaporator to leave a yellow oil. This was distilled to give the product. (Yield 12.2g. 71.5%)

b.p. $75-77^{\circ}\text{C}$ at 5mm of Hg.

^1H n.m.r. (CDCl_3) 3.83 δ (4H,t); 3.43 δ (4H,t).

I.R. ν max (thin film) 2980, 2890, 1450, 1360, 1280, 1120, 670 cm^{-1} .

13. PREPARATION OF BIS(2-N,N DIETHYLAMINOETHYL) ETHER

Bis(2-bromoethyl) ether (4.3g. 0.0185 moles) and excess diethylamine were heated under reflux for twelve hours. A white crystalline mass formed. When cool the solid was filtered off and the liquid made basic with sodium hydroxide solution ($5\text{M}, 30\text{cm}^3$). The amine was extracted with diethyl ether ($2 \times 30\text{cm}^3$). The extracts were combined, dried (MgSO_4) and the solvent removed to leave a yellow oil which was colourless oil. (Yield 1.0g. 25%)

b.p. 65°C at 0.045mm of Hg.

¹H n.m.r. (CDCl₃) 3.55 δ (4H,t); 2.55 δ (12H,q) 1.0 δ (12H,t).

I.R. ν max (thin film) 2960, 2860, 1450, 1380, 1290, 1205,
1120, 1065 cm⁻¹.

Accurate Mass 216.2241

14. PREPARATION OF 1,2 - BIS(2-BROMOETHOXY) ETHANE

The title compound was prepared in a similar manner to compound 12. using phosphorus tribromide (30g 0.11 moles) and 1,2-bis (2-hydroxyethoxy) ethane (10g. .066 moles) to give a brown oil which was used without further purification. (Yield 12.7g, 69.6%)

¹H n.m.r. (CDCl₃) 3.74 δ (4H,t); 3.59 δ (4H,s); 3.39 δ (4H,t).

I.R. ν max (thin film) 2980, 2890, 1450, 1360, 1280, 1120, 670 cm⁻¹.

15. PREPARATION OF 1,2-BIS(2-(N,N DIETHYLAMINO)ETHOXY) ETHANE

1,2-bis(2-(N,N diethylamino)ethoxy)ethane was prepared as in Experiment 13 utilising 1,2-bis(2-bromoethoxy)ethane (4.5g. 0.0163 moles) and excess diethylamine to afford a yellow oil which was distilled to leave a colourless oil. (Yield 3.0g, 70%)

b.p. 92°C at 0.1mm of Hg.

¹H n.m.r. (CDCl₃) 3.5 δ (8H,m); 2.5 δ (12H,m); 1.0 δ (12H,t).

I.R. ν max (thin film) 2960, 2860, 2790, 1465, 1360, 1290,
1200, 1130, 1070 cm⁻¹.

16. PREPARATION OF BIS(2-(BROMO 2-ETHOXY)ETHYL) ETHER

The title compound was prepared by a similar method to that used in Experiment 12, using phosphorus tribromide (29.8g 0.11 moles) and bis(2-(Hydroxy 2-ethoxy)ethyl) ether (29g 0.149 moles). The reaction afforded a yellow oil which was distilled to give a colourless oil. (Yield 26.25g, 74.5%)

b.p. 110-120°C at 0.5mm of Hg

¹H n.m.r. (CDCl₃) 3.7 δ (16H,m)

I.R. ν max (thin film) 2980, 2890, 1450, 1360, 1280, 1120, 670 cm⁻¹.

17. PREPARATION OF BIS(2-(N,N-DIETHYLAMINO 2 - ETHOXY) ETHYL) ETHER

The title compound was prepared as in Experiment 13 using bis(2-(bromo 2-ethoxy)ethyl) ether (6g 0.019 moles) and diethylamine (excess) to yield a yellow oil which was distilled to give a colourless product. (Yield 4.1g, 71.9%)

b.p. 126°C at 3mm of Hg.

¹H n.m.r. (CDCl₃) 3.6 δ (12H,t); 2.55 δ (12H,q); 1.0 δ (12H,t).

I.R. ν max (thin film) 2960, 2860, 2790, 1460, 1370, 1270, 1200
1125, 1070 cm⁻¹.

Accurate Mass 304.2635

18. PREPARATION OF 1,2 DIMORPHOLINOETHANE

1,2 dibromoethane (5.0g, 0.026 moles) was added to excess morpholine and the mixture heated at 70°C for two hours. A white crystalline mass was formed during this time of morpholine hydrobromide. When the mixture was cool, water (15cm³) was added, this dissolved the crystals. Sodium hydroxide was added until the solution was saturated. The mixture was extracted with diethylether (4 x 30cm³), the combined extracts were dried (MgSO₄) and the solvent removed in vacuo to leave a white solid. This was distilled as further purification 80°C at 0.005mm of Hg. The resultant clear oil solidified to a white solid on standing. (Yield 3.0g, 57%)

m.p. 69-70°C (Lit b.p. 285°C)²¹⁹.

¹H n.m.r. (CDCl₃) 3.7 δ (8H,m); 2.5 δ (12H,m)

I.R. ν max (CH₂Cl₂ solution) 2845, 2800, 1270, 1110, 860 cm⁻¹.

19. PREPARATION OF 1,3 DIMORPHOLINOPROPANE

The title compound was prepared as outlined in Experiment 18, using 1,3 dimorpholinopropane (7.0g 0.035 moles) and morpholine (excess). When the solvent had been removed a yellow oil remained, this was distilled to give a colourless oil which was the desired product. (Yield 6.0g, 80%)

b.p. 124-127°C at 1.5mm of Hg (Lit 317°C)²¹⁹.

¹H n.m.r. (CDCl₃) 3.65 δ (8H,m); 2.35 δ (12H,m); 1.65 δ (2H,m)

I.R. ν max (thin film) 2940, 2805, 1445, 1400, 1360, 1325,
1270, 1110, 915, 865 cm⁻¹.

Analysis: required C 61.64%, H 10.35%, N 13.07%
found C 61.87%, H 10.61%, N 13.01%.

20. PREPARATION OF 1,6 DIMORPHOLINOHEXANE

1,6 dimorpholinohexane was prepared as described in Experiment 18, using 1,6 dibromohexane (5g 0.02 moles) and excess morpholine. The resultant oil was distilled 120°C at 0.005mm of Hg, the product solidified on standing. (Yield 4.0g, 76%)

m.p. 40-41°C. (Lit m.p. 35.5 - 38.5°C)²²⁰.

¹H n.m.r. (CDCl₃) 3.65 δ (8H,m); 2.35 δ (12H,m); 1.35 δ (8H, broad s)

I.R. ν max (KBr disc) 2920, 2850, 1445, 1400, 1265, 1255, 1155,
915, 870 cm⁻¹.

21. PREPARATION OF 1,8 DIMORPHOLINOCTANE

1,8 dibromooctane (5g, 0.018 moles) and morpholine (excess) were heated under reflux for 4 hours. When the mixture was cool, water (20cm₃) was added. A white precipitate formed on addition, this was filtered at the pump and dried in vacuo over sodium hydroxide to leave a white solid. (Yield 4.4g, 85%)

m.p. 44-45°C (Lit 46.5 - 47.5°C)²²⁰.

¹H n.m.r. (CDCl₃) 3.65 δ (8H,m); 2.35 δ (12H,m); 1.35 δ (12H, broad s).

I.R. ν max (CH₂Cl₂ solution) 2920, 2850, 2800, 1440, 1370, 1270,
1105, 860 cm⁻¹.

22. PREPARATION OF 1,10 DIMORPHOLINODECANE

The title compound was prepared as described in Experiment 18, using 1,10 dibromodecane (5g 0.016 moles) and morpholine (excess). The product was distilled b.p. 134°C at 0.005mm of Hg, a white crystalline solid formed on standing. (Yield 4.4g, 84.5%)

m.p. 47-48°C (Lit m.p. 48-49°C)²²⁰.

¹H n.m.r. (CDCl₃) 3.7 δ (8H,m); 2.4 δ (12H,m); 1.35 δ (16H, broad s)

I.R. ν max (CH₂Cl₂ solution) 2920, 2845, 2800, 1440, 1110, 865 cm⁻¹.

23. PREPARATION OF 1,12 DIMORPHOLINODODECANE

1,12 dibromododecane (5g 0.015 moles) and excess morpholine were used to prepare the title compound as described in Experiment 21, to give a white waxy solid. (Yield 4.8g, 92%)

m.p. 46 - 47°C

¹H n.m.r. (CDCl₃) 3.65 δ (8H,m); 2.4 δ (12H,m); 1.35 δ (20H, broad s)

I.R. ν max (CH₂Cl₂ solution) 2920, 2840, 2800, 1440, 1250,
1110, 860, 690 cm⁻¹.

24. PREPARATION OF 1,3-DI(N-METHYLPYPERAZINO) PROPANE

1,3 dibromopropane (5g 0.025 moles) was added drop-wise with stirring to N-methylpiperazine (20g, 0.2 moles). Stirring was continued overnight during which time a white crystalline mass formed. Water (10cm³) was added to the mixture, this dissolved the crystalline

material. The mixture was basified with sodium hydroxide (10g). The organic components were extracted with diethylether (4 x 30cm³). The combined extracts were dried (MgSO₄) and the solvent removed at the pump to leave a yellow oil. This was distilled and gave a colourless oil. (Yield 4.6g 80%)

b.p. 130^oC at 0.5mm of Hg

¹H n.m.r. (CDCl₃) 2.4 δ (20H,s); 2.1 δ (6H,s); 1.6 δ (2H,m)

I.R. ν max (thin film) 2960, 2795, 1510, 1375, 1285, 1170, 1015, 805 cm⁻¹.

Analysis: required C 64.95%, H 11.74%, N 23.31%

found C 64.05%, H 11.59%, N 23.01%

25. PREPARATION OF BIS(2-DIMORPHOLINOETHYL) ETHER

Bis-(2-chloroethyl) ether (5g .035 moles) was added drop-wise to morpholine (4 molar excess). The mixture was heated at 80^oC for 4 hours. After cooling, water (10cm³) was added, the mixture was then saturated with sodium hydroxide. The amine was extracted with diethyl ether (3 x 30cm³). The combined extracts were dried (MgSO₄) and the solvent removed in vacuo to afford a pale yellow oil. The oil was distilled to yield a colourless oil. (Yield 1.7g 20%)

b.p. 164^oC at 2mm of Hg.

¹H n.m.r. (CDCl₃) 3.6 δ (12H,m); 2.4 δ (12H,m).

I.R. ν max (thin film) 2800, 1660, 1440, 1300, 1270, 1100, 915, 855 cm⁻¹.

Analysis: required C 58.99%, H 9.9%, N 11.47%

found C 58.81%, H 9.82%, N 11.48%

26. PREPARATION OF 1,3 DIMORPHOLINOPROPANE (LARGE SCALE)

Morpholine (excess) was added dropwise with stirring to 1,3 dibromopropane (80g 0.396 moles) in a 500cm³ round bottomed flask fitted with a condenser. Within several minutes of addition a violent reaction took place necessitating cooling in ice. A brown black solid formed in the flask which was dissolved in sodium hydroxide solution. The basic solution was extracted with diethylether (6 x 100cm³), the combined extracts dried (MgSO₄) and the solvent removed on a rotary evaporator to leave a brown oil. This was distilled to afford a colourless oil. (Yield 65g 78%).

b.p. 142⁰C at 6mm of Hg.

¹H n.m.r. (CDCl₃) 3.6 δ (8H,m); 2.2 δ (12H,m); 1.6 δ (2H,m).

27. MODIFIED PREPARATION OF 1,3 DIMORPHOLINOPROPANE

1,3 dibromopropane (50g, 0.247 moles) was added dropwise with stirring to a solution of morpholine (70g 0.8 moles) in toluene (60cm³). After one hour, (during which time a white crystalline mass had formed), water (20cm³) was added and this was saturated with sodium hydroxide. The toluene layer was decanted off and the aqueous layer extracted further with toluene (3 x 50cm³). The extracts were combined, dried (MgSO₄), and the solvent removed on a rotary evaporator to give a pale yellow oil. This was distilled under reduced pressure to give a colourless oil. (Yield 39.5g 74.5%)

b.p. 124 - 127⁰C at 1.5mm of Hg

¹H n.m.r. (CDCl₃) 3.6 δ (8H,m); 2.2 δ (12H,m); 1.6 δ (2H,m).

28. ATTEMPTED PREPARATION OF 1,3 DIMORPHOLINOPROPANE FROM 1-BROMO-3-CHLOROPROPANE

1-bromo-3-chloropropane (15.75g 0.1 moles) was added dropwise to a solution of morpholine (4 molar excess) in toluene (25cm³). A white crystalline mass formed after two hours. Water (10cm³) was added to dissolve the crystals. The toluene layer was separated from the aqueous layer and sodium hydroxide added to the aqueous component. This was extracted with toluene (2 x 25cm³). The extracts were combined and the solvent removed by evaporation to give a yellow oil which was distilled to give a colourless product of 1-chloro-3-morpholinopropane. Analytically pure. (Yield 13.5g 63%).

¹H n.m.r. (CDCl₃) 3.7 δ (6H,m); 2.4 δ (6H,m); 1.9 δ (2H,m)

Analysis required	C:51.37%; H:8.62%; N:8.56%
found	C:51.63%; H:8.90%; N:8.68%

29. PREPARATION OF 1,3 DIMORPHOLINOPROPANE

1-chloro-3-morpholinopropane (5g 0.03 moles) and morpholine (excess) were heated under reflux for twenty four hours. When cool, water (25cm³) was added. This was saturated with sodium hydroxide and extracted with diethylether (3 x 20cm³). The combined extracts were dried (MgSO₄) and the solvent removed to afford a colourless oil. (Yield 2.42g 38%)

¹H n.m.r. (CDCl₃) 3.7 δ (8H,m); 2.3 δ (12H,m); 1.6 δ (2H,m).

Analysis required	C:61.64%; H:10.35%; N:13.07%
found	C:61.87%; H:10.61%; N:13.01%

AMINE ASSISTED FREE RADICAL PHOTOINITIATED POLYMERISATIONS OF THIN FILMS

All varnishes and inks prepared in these experiments were cured (polymerised) using an M.B. Laboratory Conveyor Drier fitted with a single primarc medium pressure mercury lamp with an output of 200 watts per inch. ($6.3 \times 10^{-2} \text{Jcm}^{-1}$) The conveyor speed for the polymerisations was 500 feet per minute, unless otherwise stated. Following each pass through the drier, the varnishes and inks were tested for tack free and through cure.

The test for tack free determined when the surface of the film has been cured, was achieved by running a finger across the surface of an irradiated sample. The sample was regarded as being tack free when the coating ceased to adhere to the finger.

The test for through cure was effected by a thumb-screw test. It consisted of twisting the thumb down on the film, through cure was achieved when the material was unaffected by the downward twisting motion. All the experiments were carried out in this way and comparisons were made of the number of passes through the drier needed to effect cure.

INVESTIGATION OF OPTIMUM AMINE CONTENT OF VARNISH FOR EFFECTING CURE.

A varnish was made up by melting together the following:

30%	Aliphatic trifunctional acrylate diluent
30%	Resin
11.5%	Aromatic monofunctional acrylate
25%	Bisphenol 'A' epoxy acrylate prepolymer containing 30% benzophenone

0.5% Silicon

97% weight for weight.

Either triethanolamine or 1,3 dimorpholinopropane were added to the varnishes in percentages between 0 and 4% weight for weight and a sample of each varnish drawn down black printed card with a No 2# bar and cured using a conveyer speed of 400 feet per minute.

<u>AMINE</u>	<u>AMINE %</u>	<u>PASSES TO TACK FREE</u>	<u>PASSES TO THROUGH CURE</u>
0	0	8	10
Triethanolamine	0.5	4	6
Triethanolamine	1.0	3	5
Triethanolamine	2.0	3	4
Triethanolamine	3.0	2	3
Triethanolamine	4.0	2	3
1,3 dimorpholinopropane	0.5	4	5
1,3 dimorpholinopropane	1.0	3	4
1,3 dimorpholinopropane	2.0	2	3
1,3 dimorpholinopropane	3.0	2	2
1,3 dimorpholinopropane	4.0	2	2

TO COMPARE THE EFFECT OF VARIOUS AMINES ON RATE OF CURE IN NON-PIGMENTED SYSTEM

A varnish was made up of 70% Bisphenol 'A' epoxy acylate prepolymer
30% Bisphenol 'A' epoxy acrylate monomer
 100%

Benzophenone 5% weight for weight was added and the mixture heated until the benzophenone dissolved. The amines were added at a 3% level to samples of the varnish and mixed in. A layer 38 μ thick was coated onto art paper and cured testing for tack free and through cure.

Similar experiments were performed using 5% 2-chlorothioxanthone, Michlers ketone and fluorenone as initiators instead of benzophenone.

TO EVALUATE PHOTOINITIATOR SYSTEMS IN PIGMENTED INKS

Inks were made up of the following formulation:

53%	Special acrylate prepolymer
24%	Blue pigment
18%	Bisphenol 'A' epoxy acrylate diluent
6%	Photoinitiator
3%	Wax
<u>3%</u>	Amine
107%	

The ink was made up except for amine and mixed on a three-roll mill.

The amine was added to samples of the ink. 0.4cm³ of each complete ink sample was printed on to hi-fidelity art paper using a Duncan-Lynch proof print tester and cured using a conveyer speed of 600 feet per minute.

The experiment was repeated substituting the special acrylate prepolymer with bisphenol 'A' epoxy acrylate prepolymer. A further experiment was carried out substituting the blue pigment with a red pigment.

PRINT TEST ON BLACK INKS

Three inks were made up utilising different photoinitiator systems, one of which was a standard formulation.

Standard ink	special acrylate prepolymer	35
	bisphenol 'A' epoxy acrylate diluent	16
	bisphenol 'A' epoxy acrylate diluent	5
	wax	1
	benzophenone	4
	calcium carbonate	1
	blue pigment	3
	black pigment	<u>12</u>
		77%

This was milled and the following mixed in:

resin containing Michlers ketone	13
bisphenol 'A' epoxy acrylate diluent	<u>4</u>
	94%

The test inks were made up of the following formulation. 1,6-dimorpholine-hexane being substituted for 1,3-dimorpholinopropane in the second ink:

special acrylate prepolymer	35%
bisphenol 'A' epoxy acrylate prepolymer	16
bisphenol 'A' epoxy acrylate diluent	5
2 - chlorothioxanthone	6
wax	1
calcium carbonate	1
blue pigment	3
black pigment	<u>12</u>
	79%

these were milled on a three roll mill and the following added:

bisphenol 'A' epoxy acrylate diluent	14
bisphenol 'A' epoxy acrylate prepolymer	3
1,3 dimorpholinopropane	<u>3</u>
	99%

The inks were tested first by curing 0.6ml of ink printed on board and then using a lithographic printing press.

Water uptake of the ink was measured by mixing 1 gram of ink with water (10cm³) and stirred for five minutes. The supernatant was decanted into a measuring cylinder and measured. The pH of the supernatant was also measured.

PRINT TEST ON BLUE INK

A blue base was made up on the following formulation:

special acrylate prepolymer	27.8%
stabilizer	0.2
resin	15.0
calcium carbonate in resin	3.0
blue pigment	10.0
violet pigment	10.0
black pigment	<u>5.0</u>
	71.0%

This was ground on a three roll mill and the following added:

2-chlorothioxanthone in resin	10.0
bisphenol 'A' epoxy acrylate diluent	10.0

The base was split into three and 5% of escorol, triethanolamine and 1,3 dimorpholinopropane added and milled-in. The inks were printed on to super star paper using 0.5mm³ of ink and cured using 3 lamps at 400 feet per minute, then tested on a lithographic printing press. Water uptake was measured by the method outlined in the previous experiment.

DETERMINATION OF THE RELATIVE RATES OF REDUCTION OF FLUORENONE BY VARIOUS AMINE:

The method used for determining the relative reactivities is illustrated for the photoreduction of fluorenone by 1,3 NNNN tetraethylaminopropane.

A standard reference curve was drawn in order to calculate the concentration of fluorenone at any given time. Solutions containing known amounts of ketone were made up in benzene and are shown in the following table:

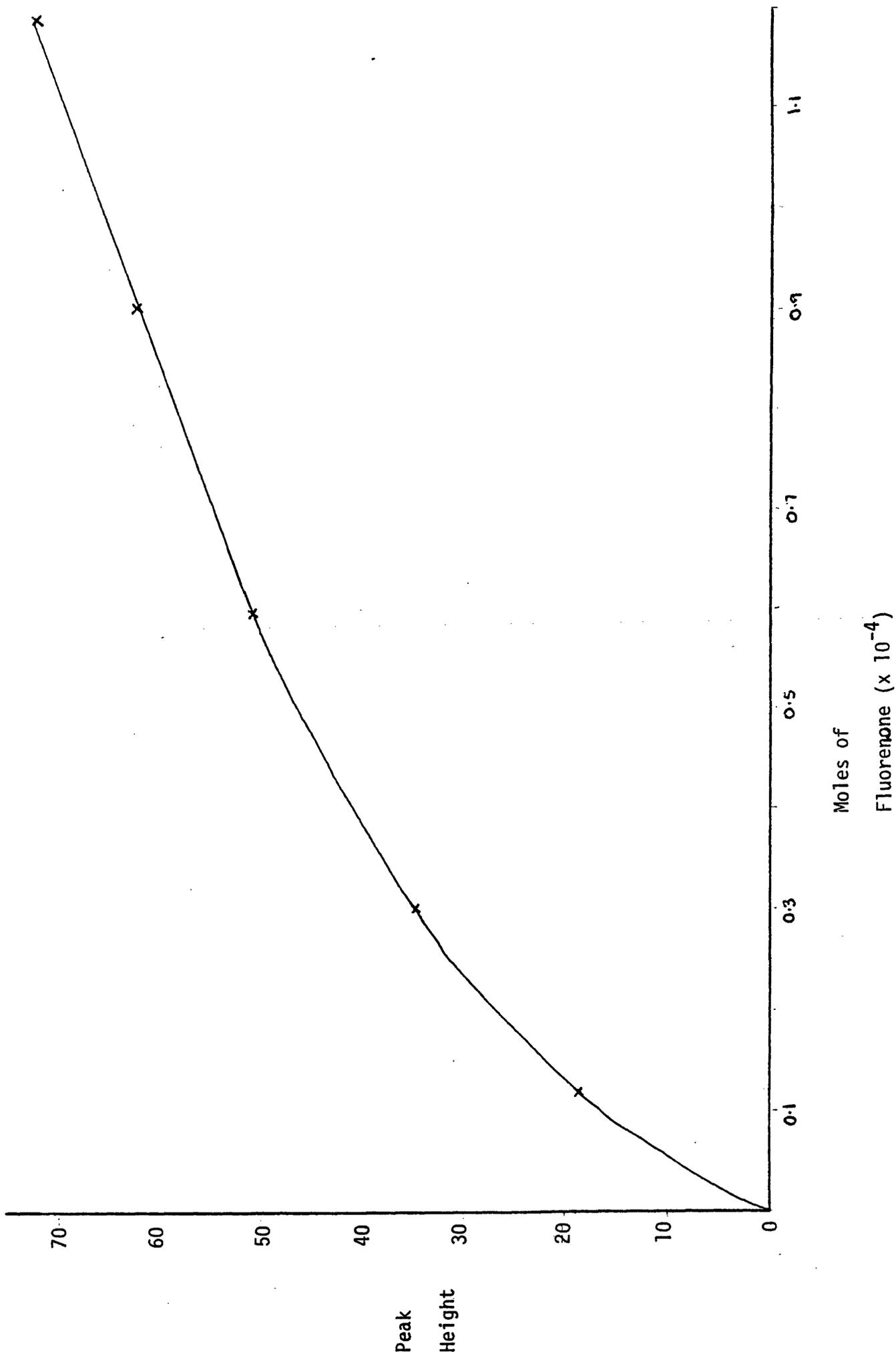
Weights of fluorenone (g)	0.0022	0.0054	0.0107	0.0162	0.351
Moles of fluorenone ($\times 10^{-4}$)	0.12	0.3	0.595	0.9	1.195
Peak Height	19	35	51	62.5	72

The solutions were run through an H.P.L.C. column and the peak height of the fluorenone absorption band at 294 n.m. was plotted against concentration of fluorenone, to give a standard curve. Shown overleaf for the fluorenone, 1,3 NNNN tetraethylaminopropane system (fig. 1). H.P.L.C. conditions were maintained for all the analyses and were as follows:

Column : Hypersil ODS 5 flow rate : 1cm^3 per minute
Injection loop : $20\mu\text{l}$ chart speed: 1 cm per minute
Detector wavelength : 294 nm.

For the various determinations and stock solution of fluorenone was made up of 0.897g in 500cm^3 of benzene. 20cm^3 of the stock solution and each of 0.1, 0.05 and 0.01 mole equivalents of amine in benzene (5cm^3) were poured into three photolysis tubes. The solutions were deoxygenated

Standard Curve for Fluorenone.



by bubbling dry nitrogen through the solutions for thirty minutes. An aliquot of 1cm^3 was taken from each of the tubes for analysis and the tubes irradiated in a Rayonet reactor fitted with blacklight lamps (emission 330-390nm), and a merry-go-round apparatus. Further aliquots of 1cm^3 were taken at time intervals and analysed by H.P.L.C., the absorption band was compared with the reference curve. The amount of remaining fluorenone could thus be determined. The amount of remaining fluorenone was plotted against time and the rate of reaction calculated. Examples of this are shown in the following graphs (Figs.p42ff)

The quantum yield for the reaction can be estimated with the knowledge of the rate of reaction, and the quantum yield of a previously determined photo reduction. The photo reduction chosen was that of fluorenone by triethylamine.

Fluorenone 0.3M (20cm^3) was deoxygenated by bubbling nitrogen through the solution for thirty minutes. Triethylamine was added to give a concentration of 0.1 Molar. The solution was irradiated and the resultant solutions analysed as above. A standard curve was drawn because of the higher concentrations of fluorenone used (Fig. p42).

Wt of fluorenone (g)	0.18	0.36	0.72	1.08
Moles of fluorenone ($\times 10^{-3}$)	1	2	4	6
Peak height (mm)	23	51	88	150

The disappearance of fluorenone was plotted against time to obtain the rate of photoreduction.

Time (minutes)	Moles of fluorenone remaining
0	6×10^{-3}
15	4.2×10^{-3}
30	3.05×10^{-3}
60	1×10^{-3}

This gave a value of 1.5×10^{-6} moles per second. The quantum yield of the reaction as determined by Cohen is 0.91. From these parameters and using equation (p 41) the quantum yield for disappearance of fluorenone was calculated for each concentration of amine. The results are given in the following table.

FLUORENONE/TRIETHANOLAMINE

Moles of fluorenone($\times 10^{-4}$) with amine concentration:

Time (minutes)	7.893×10^{-4} molar	3.947×10^{-4} molar	7.893×10^{-5} molar
0	0.94	1.30	
30	0.87	1.25	
60	0.84	1.20	
Rate (moles s^{-1})	3.33×10^{-9}	2.77×10^{-9}	
Quantum yield	1.95×10^{-3}	1.62×10^{-3}	

FLUORENONE/N-METHYLDIETHANOLAMINE

Time (minutes)	6.649×10^{-3}	3.325×10^{-3}	6.649×10^{-4}
0	1.10	0.90	0.90
$7\frac{1}{2}$	0.58	0.65	0.89
15	0.085	0.385	0.85
30	-	0.345	0.82
Rate (moles s^{-1})	1.13×10^{-7}	5.72×10^{-8}	4.44×10^{-9}
Quantum yield	6.61×10^{-1}	3.35×10^{-2}	2.60×10^{-3}

FLUORENONE/N,N-DIMETHYLETHANOLAMINE

Time (minutes)	5.753×10^{-4}	2.877×10^{-4}	5.753×10^{-5}
0	1.065	1.05	1.02
$7\frac{1}{2}$	0.52	0.75	0.91
15	0.04	0.4	0.875
30	-	0.355	0.7
Rate (moles s^{-1})	1.14×10^{-7}	7.22×10^{-8}	3.88×10^{-8}
Quantum yield	6.67×10^{-2}	4.22×10^{-2}	2.27×10^{-2}

FLUORENONE/1,3 DIMORPHOLINOPROPANE

Time (hours)	8.073×10^{-4}	4.037×10^{-4}	8.073×10^{-5}
0	1.025	1.01	0.915
1	0.39	0.75	0.90
3	0.09	0.515	0.885
Rate (moles s^{-1})	1.667×10^{-8}	6.173×10^{-9}	1.852×10^{-10}
Quantum yield	9.75×10^{-3}	3.61×10^{-3}	1.08×10^{-4}

FLUORENONE/1,6 DIMORPHOLINOHEXANE

Time (minutes)	7.473×10^{-4}	3.737×10^{-4}	7.473×10^{-5}
0	1.22	1.11	1.11
60	0.34	0.60	0.93
Rate (moles s^{-1})	2.44×10^{-8}	1.39×10^{-8}	4.7×10^{-9}
Quantum yield	1.43×10^{-2}	8.13×10^{-3}	2.75×10^{-3}

FLUORENONE/1,10-DIMORPHOLINODECANE

Time (minutes)	6.154×10^{-4}	3.077×10^{-4}	6.154×10^{-5}
0	1.0	1.2	1.0
60	0.63	1.0	0.99
180	0.25	0.98	0.98
Rate (moles s^{-1})	6.9×10^{-9}	2.77×10^{-9}	2.77×10^{-10}
Quantum yield	4.18×10^{-3}	1.62×10^{-3}	1.62×10^{-4}

FLUORENONE/1,3 - N,N,N,N TETRAETHYLDIAMINOPROPANE

Time (minutes)	6.239×10^{-4}	3.120×10^{-4}	6.239×10^{-5}
0	0.84	0.83	0.95
30	0.1	0.25	0.5
60	0.02	0.10	0.4
Rate (moles s^{-1})	4.11×10^{-8}	3.22×10^{-8}	1.94×10^{-8}
Quantum yield	2.4×10^{-2}	1.88×10^{-2}	1.13×10^{-2}

FLUORENONE/1,8 - N,N,N,N TETRAETHYLDIAMINOCTANE

Time (minutes)	6.344×10^{-4}	3.172×10^{-4}	6.344×10^{-5}
0	1.04	1.07	1.01
30	0.124	0.39	0.86
60	0.02	0.124	0.7
Rate (moles s ⁻¹)	4.89×10^{-8}	3×10^{-8}	8.61×10^{-9}
Quantum yield	2.86×10^{-2}	1.75×10^{-2}	5.04×10^{-3}

FLUORENONE/1,10-N,N,N,N- TETRAETHYLDIAMINODECANE

Time (minutes)	6.479×10^{-4}	3.240×10^{-4}	6.479×10^{-5}
0	0.85	0.775	0.875
30	0.12	0.3	0.78
60	0.05	0.16	0.70
Rate (moles s ⁻¹)	4.06×10^{-8}	2.17×10^{-8}	5.19×10^{-9}
Quantum yield	4.2×10^{-2}	7.9×10^{-3}	3.29×10^{-3}

FLUORENONE/1,8 - TETRAMETHYLDIAMINOCTANE

Time (minutes)	5.96×10^{-4}	2.98×10^{-4}	5.96×10^{-5}
0	1.06	1.065	1.18
15	0.205	0.27	0.79
30	0.135	0.225	0.72
Rate (moles s ⁻¹)	6.67×10^{-8}	5.56×10^{-8}	3.17×10^{-8}
Quantum yield	3.9×10^{-2}	3.25×10^{-2}	1.85×10^{-2}

FLUORENONE/1,8 DIAMINOCTANE

Time (minutes)	6.222×10^{-4}	3.111×10^{-4}	6.222×10^{-5}
0	1.31	1.33	1.13
15	1.03	1.15	1.12
30	0.74	0.99	1.12
60	0.18	0.77	0.99
Rate (moles s ⁻¹)	3.25×10^{-8}	1.94×10^{-8}	1.53×10^{-9}
Quantum yield	1.9×10^{-2}	1.13×10^{-2}	8.95×10^{-4}

FLUORENONE/N,N,N,N,N,N - HEXAMETHYLTRIETHYLENETETRAMINE

Time (minutes)	5.287×10^{-4}	2.644×10^{-4}	5.287×10^{-5}
0	1.095	1.065	1.08
15	1.01	0.985	1.065
30	0.93	0.895	1.01
60	0.735	0.82	0.945
Rate (moles s ⁻¹)	8.88×10^{-9}	6.94×10^{-9}	3.88×10^{-9}
Quantum yield	5.19×10^{-3}	4.06×10^{-3}	2.27×10^{-3}

FLUORENONE/N,N,N,N,N,N,N, - HEPTAMETHYLTETRAETHYLENEPENTAMINE

Time (minutes)	6.077×10^{-4}	3.039×10^{-4}	6.077×10^{-5}
0	1.08	1.04	1.025
15	0.85	0.85	0.905
30	0.425	0.69	0.785
60	0.215	0.55	0.71
Rate (moles s ⁻¹)	3.64×10^{-8}	1.94×10^{-8}	1.33×10^{-8}
Quantum yield	2.13×10^{-2}	1.13×10^{-2}	7.78×10^{-3}

FLUORENONE/BIS-(2-N,N, DIETHYLAMINOETHYL) ETHER

Time (minutes)	3.852×10^{-4}	1.926×10^{-4}	3.852×10^{-5}
0	1.275	1.13	1.17
15	0.325	0.57	0.95
30	0.2	0.44	0.85
Rate (moles s ⁻¹)	1.05×10^{-7}	6.22×10^{-8}	3.28×10^{-8}
Quantum yield	6.14×10^{-2}	3.64×10^{-2}	1.92×10^{-2}

FLUORENONE/1,2 - BIS(2-(N,N DIETHYLAMINE) ETHOXY) ETHANE

Time (minutes)	5.877×10^{-4}	2.939×10^{-4}	5.877×10^{-5}
0	1.04	0.965	1.06
15	0.855	0.93	1.025
30	0.47	0.8	0.95

60	0.34	0.725	0.855
Rate (moles s ⁻¹)	1.94 x 10 ⁻⁸	6.66 x 10 ⁻⁹	5.69 x 10 ⁻⁹
Quantum yield	1.13 x 10 ⁻²	3.89 x 10 ⁻³	3.33 x 10 ⁻³

FLUORENONE/BIS(2-(N,N, DIETHYLAMINO 2-ETHOXY)ETHYL) ETHER

Time (minutes)	5.987 x 10 ⁻⁴	2.994 x 10 ⁻⁴	5.987 x 10 ⁻⁵
0	0.65	0.82	0.91
15	0.055	0.325	0.8
30	-	0.15	0.725
Rate (moles s ⁻¹)	6.61 x 10 ⁻⁸	5.5 x 10 ⁻⁸	1.02 x 10 ⁻⁸
Quantum yield	3.87 x 10 ⁻²	3.22 x 10 ⁻²	5.96 x 10 ⁻³

FLUORENONE/BIS(2 DIMORPHOLINOETHYL) ETHER

Time (minutes)	8.0 x 10 ⁻⁴	4.0 x 10 ⁻⁴	8.0 x 10 ⁻⁵
0	1.15	1.1	1.04
15	1.05	1.04	1.025
30	0.875	0.985	0.985
Rate (moles s ⁻¹)	1.53 x 10 ⁻⁸	6.39 x 10 ⁻⁹	3.06 x 10 ⁻⁹
Quantum yield	8.95 x 10 ⁻³	3.74 x 10 ⁻³	1.79 x 10 ⁻³

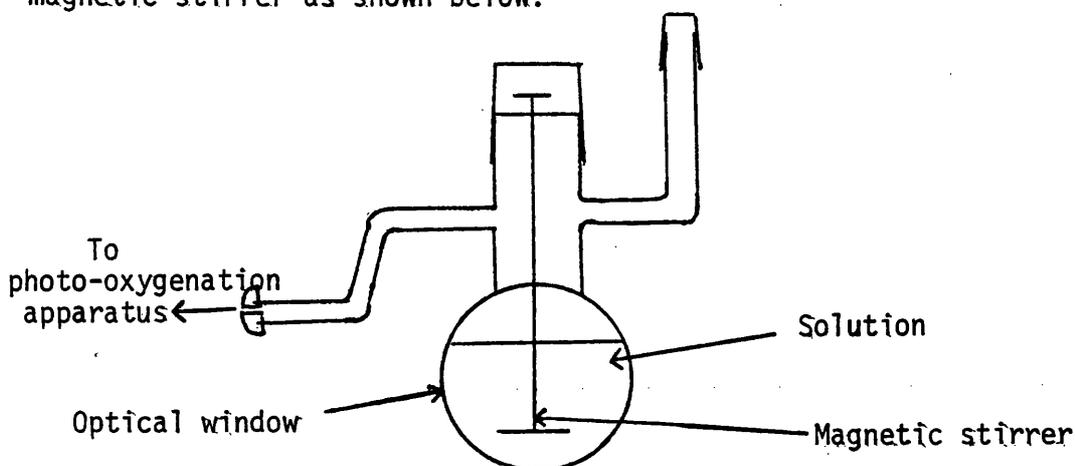
FLUORENONE/1,3 DI(N-METHYLPIPERAZINO) PROPANE

Time (minutes)	6.467 x 10 ⁻⁴	3.234 x 10 ⁻⁴	6.467 x 10 ⁻⁵
0	1.15	1.12	1.11
15	0.605	0.78	0.91
30	0.42	0.56	0.745
Rate (moles s ⁻¹)	6.06 x 10 ⁻⁸	3.11 x 10 ⁻⁸	2.08 x 10 ⁻⁸
Quantum yield	3.54 x 10 ⁻²	1.82 x 10 ⁻²	1.19 x 10 ⁻²

Stern-Volmer plots were drawn to obtain values for kr. (These are given in the results and discussion section, page 47).

DETERMINATION OF THE COMPARATIVE RATES OF PHOTO-OXYGENATION
OF AMINES

A solution of benzophenone (1 Litre) was made up so that the optical density was 0.4. Approximately 0.1 g of each amine was weighed out and added to an aliquot of 16 cm³ of the benzophenone solution. The solution was poured into a cell fitted with a magnetic stirrer as shown below.



The cell was placed in the photo-oxygenation apparatus illustrated overleaf, the key to which is given below:-

Key

- | | |
|----------------------------------|------------------------|
| 1. Battery charger, | 2. Mechanical stirrer, |
| 3. Medium pressure mercury lamp, | 4. Light reflector, |
| 5. Lens, | 6. Photolysis cell, |
| 7. Oxygen / air inlet, | 8. Electrolysis cell, |
| 9. Manometer, | 10. Scale, |
| 11. Trap, | 12. Manometer, |
| 13. Left hand tap, | 14. Centre tap, |
| 15. Right hand tap, | 16. Beer cooler, |
| 17. Water stirrer | 18. Ball joint, |
| 19. Shutter, | |

The apparatus was operated by using the following directions:-

1. Locate the filled cell (6) in the tank, to the ball joint (18).
2. Fill the water tanks with water.
3. Switch on beer cooler (16), and maintain the temperature at approximately 20 °C.
4. Switch on water stirrer.
5. With oxygen inlet tap (7) closed, evacuate the system to 85 cm. on manometer (12).
6. Allow oxygen into the system (7) until atmospheric pressure is attained. Repeat the last two instructions twice more.
7. Close tap (7) and turn the vacuum pump off.
8. Close right hand tap (15).
9. Turn electrolysis cell (8) on, this contains a potassium oxalate solution, with battery charger, this causes the release of carbon dioxide and forces the mercury onto the scale (10), when the mercury reaches the scale switch battery charger off.
10. Switch on cell stirrer (2) and lamp (3) whilst ensuring that the shutter (19) is closed. Allow the system to equilibrate (approx. 5 minutes.)
11. Measure temperature of both of the water baths ensuring that both are at the same temperature. Measure atmospheric pressure and measure the pressure on manometer (12).
12. Close centre and left hand taps (13 and 14) together. Manometer (9) should be level. Take reading on the scale (10)
13. Open shutter (19) allowing light into the cell. Maintain the manometer (9) so that the arms remain balanced by switching on the battery charger and thus activating the electrolytic cell. Take readings on the scale at intervals.

14. When the photo-oxygenation has been completed pull the shutter so that it is closed, and turn all the electrical appliances off.
15. Drain water from the tanks.
16. Open centre and left hand taps together, then right hand tap.
17. Allow air into the system and remove the cell.

The amount of oxygen taken up by the amine was plotted against time, a selection of these curves are shown in the following graphs (overleaf) and the rate of oxygen uptake determined. Comparisons were made of the rate of oxygen uptake at equal amine concentrations.

Triethanolamine.

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1086 g.	2	0.2
Moles of amine = 7.29×10^{-4} moles.	4	0.3
	6	0.4
	8	0.5
Rate = $0.07 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	0.7

N-methyldiethanolamine

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1158 g	2	1.0
Moles of amine = 9.73×10^{-4} moles.	4	1.9
	6	2.8
	8	3.6
Rate = $0.45 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.5

N,N-dimethylethanolamine

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1020 g.	2	0.9
Moles of amine = 1.15×10^{-3} moles	4	2.0
	6	3.0
	8	4.0
Rate = $0.5 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	5.0

1,2-dimorpholinoethane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1061 g.	2	0.8
Moles of amine = 5.25×10^{-4} moles	4	1.8
	6	2.7
	8	3.6
Rate = $0.45 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.7

1,3-dimorpholinopropane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1086 g.	2	1.5
Moles of amine = 4.38×10^{-4} moles	4	3.5
	6	5.5
	8	7.5
Rate = $1.00 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	9.6

1,6-dimorpholinohexane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1132 g.	2	0.8
Moles of amine = 4.38×10^{-4} moles	4	1.8
	6	2.8
	8	3.6
Rate = $0.45 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.6

1,10-dimorpholinodecane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1186 g	2	0.6
Moles of amine = 3.77×10^{-4} moles	4	1.2
	6	2.0
	8	2.6
Rate = $0.36 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	3.4

1,3-N,N,N,N-tetraethyldiaminopropane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1032 g	2	0.6
Moles of amine = 5.55×10^{-4} moles	4	1.6
	6	2.6
	8	3.6
Rate = $0.5 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.8

1,8-N,N,N,N-tetraethyldiaminooctane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1110 g	2	0.7
Moles of amine = 4.34×10^{-4} moles	4	1.7
	6	2.7
	8	3.7
Rate = $0.5 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.6

1,10-N,N,N,N-tetraethyldiaminodecane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1072 g	2	0.5
Moles of amine = 3.77×10^{-4} moles	4	1.3
	6	2.5
	8	3.6
Rate = $0.375 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	4.7

1,8-N,N,N,N-tetramethyldiaminooctane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.0458 g	2	0.6
Moles of amine = 2.29×10^{-4} moles	4	1.2
	6	1.9
	8	2.5
Rate = $0.3 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	3.1

1,8-diaminooctane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.0648 g.	2	0.0
Moles of amine = 4.5×10^{-4} moles	4	0.1
	6	0.1
	8	0.2
Rate = $0.03 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	0.3

N,N,N,N,N,N,N-heptamethyltetraethylenepentamine

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.0903 g.	2	0.7
Moles of amine = 3.15×10^{-4} moles	4	1.4
	6	2.0
	8	2.6
Rate = $0.33 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	3.2

bis(2-N,N-diethylaminoethyl)ether

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1340 g.	2	0.5
Moles of amine = 6.2×10^{-4} moles	4	1.0
	6	1.6
	8	2.1
Rate = $0.25 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	2.6

1,2-bis(2-(N,N-diethylamino)ethoxy)ethane

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1161 g.	2	0.6
Moles of amine = 4.47×10^{-4} moles	4	1.2
	6	1.8
	8	2.4
Rate = $0.3 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	3.2

bis(2-(N,N-diethylamino-2-ethoxy)ethyl)ether

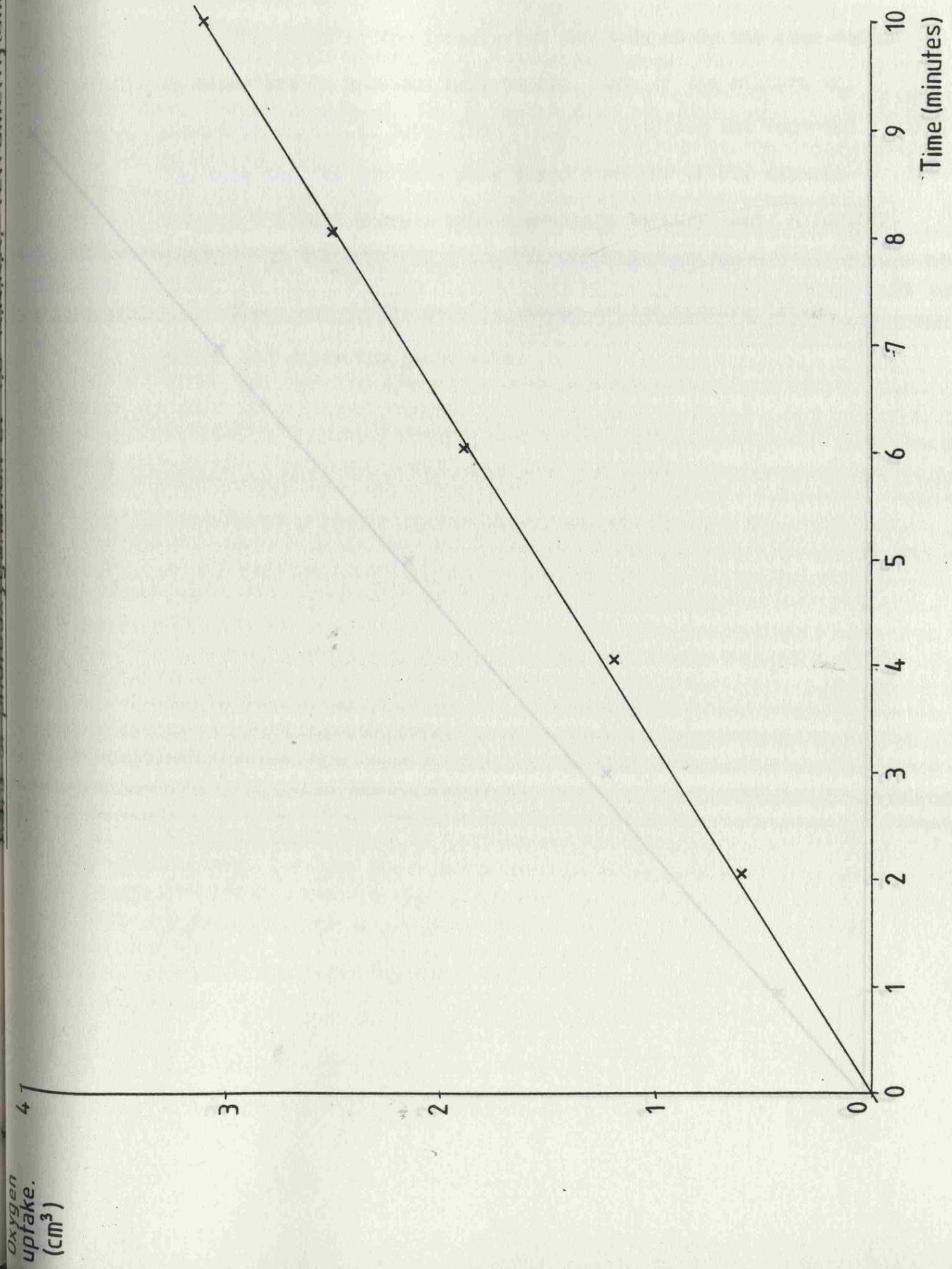
	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1009 g.	2	0.6
Moles of amine = 3.32×10^{-4} moles	4	1.4
	6	2.1
	8	3.0
Rate = $0.35 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	3.6

bis(2-morpholinoethyl)ether

	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.1057 g.	2	0.5
Moles of amine = 4.3×10^{-4} moles	4	1.0
	6	1.5
	8	2.1
Rate = $0.25 \text{ cm}^3 \text{ oxygen minute}^{-1}$	10	2.6

1,3-di(N-methylpiperazino)propane

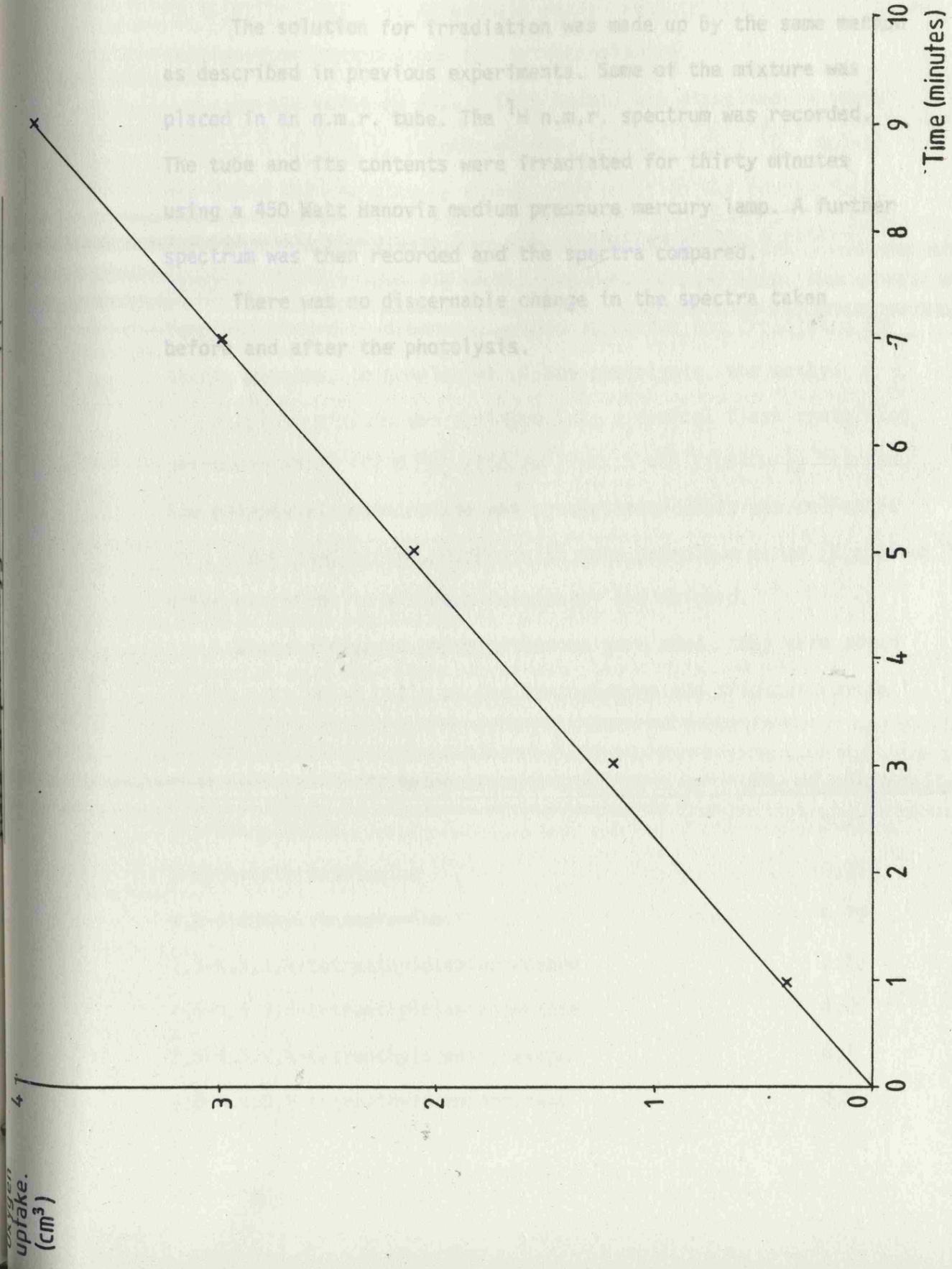
	Time (mins)	Oxygen uptake (cm ³)
Wt. of amine = 0.0904 g.	1	0.4
Moles of amine = 3.77×10^{-4} moles	3	1.2
	5	2.1
	7	3.0
Rate = $0.45 \text{ cm}^3 \text{ oxygen minute}^{-1}$	9	3.9



TO INVESTIGATE THE FREE RADICAL INITIATED BULK POLYMERISATION OF
METHYL METHACRYLATE BY ^1H N.M.R. SPECTROSCOPY

The solution for irradiation was made up by the same method as described in previous experiments. Some of the mixture was placed in an n.m.r. tube. The ^1H n.m.r. spectrum was recorded. The tube and its contents were irradiated for thirty minutes using a 450 Watt Hanovia medium pressure mercury lamp. A further spectrum was then recorded and the spectra compared.

There was no discernible change in the spectra taken before and after the photolysis.



TO INVESTIGATE THE FREE RADICAL INITIATED BULK POLYMERISATION OF
METHYL METHACRYLATE BY ^1H N.M.R. SPECTROSCOPY

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There was no discernable change in the spectra taken before and after the photolysis.

GENERAL PROCEDURE FOR THE BULK POLYMERISATION OF METHYL METHACRYLATE

The procedure used for the bulk polymerisation experiments is described using as an example methyl methacrylate polymerisation initiated by benzophenone and triethanolamine.

Benzophenone (0.45g, 0.0025 moles) was dissolved in methyl methacrylate (20g). Triethanolamine (0.19g, 1.25×10^{-3} moles) was added and the mixture shaken. The solution was poured into a pyrex glass photolysis tube and irradiated using a water-jacketed 450 Watt Hanovia medium pressure mercury lamp. The tube was placed in a merry-go-round apparatus and irradiated for thirty minutes. On completion of the photolysis, the methyl methacrylate mixture was syringed into a conical flask containing petroleum ether (60-80°C) (100 cm³) which was vigorously stirred. The polymethyl methacrylate was precipitated, this was collected on a preweighed sinter, washed with more petroleum ether (2 x 25 cm³) dried overnight in a vacuum dessicator and weighed.

Where different photoinitiators were used, they were added in the same molar ratio as the benzophenone and triethanolamine.

Benzophenone

Amine	Wt. of polymer (g)
Triethanolamine	2.72
N-methyldiethanolamine	2.91
N,N-dimethylethanolamine	6.79
1,3-N,N,N,N-tetraethyldiaminopropane	5.73
1,5-N,N,N,N-tetraethyldiaminopentane	4.06
1,6-N,N,N,N-tetraethyldiaminohexane	4.1
1,8-N,N,N,N-tetraethyldiaminooctane	4.2

Amine	Wt. of polymer (g)
1,10-N,N,N,N-tetraethyldiaminodecane	4.2
Tetraethylenepentamine	0.45
N,N,N,N,N,N,N-heptamethyltetraethylenepentamine	6.38
1,3-dimorpholinopropane	4.56
1,6-dimorpholinohexane	3.9

Photoinitiator	Amine	Wt. of polymer (g)
Benzophenone	Triethanolamine	2.38
2-isopropylthioxanthone	Triethanolamine	2.2
Fluorenone	Triethanolamine	0.5
Benzophenone	Triethylamine	6.04
2-isopropylthioxanthone	Triethylamine	5.6
Fluorenone	Triethylamine	0.22
Benzophenone	1,3-dimorpholinopropane	4.2
2-isopropylthioxanthone	1,3-dimorpholinopropane	3.5
Fluorenone	1,3-dimorpholinopropane	0.44

TO STUDY THE EFFECT OF OXYGEN ON THE FREE RADICAL INITIATED BULK
POLYMERISATION OF METHYL METHACRYLATE

The experimental procedure was similar to that used in the previous experiment except that argon or air was passed through the solution for thirty minutes prior to the irradiation.

Initiator	Amine	Atmosphere	WT. of polymer (g)
Benzophenone	Triethanolamine	Air	4.4
Benzophenone	Triethanolamine	Argon	5.26
2-isopropylthioxanthone	Triethanolamine	Air	3.0
2-isopropylthioxanthone	Triethanolamine	Argon	3.84

31. PREPARATION OF 1-BROMO 6-PHENOXYHEXANE

1,6 dibromohexane (18.3g 0.075 moles) and phenol (5.6g 0.06 moles) were added to water (40cm³) and heated to 100°C. A solution of sodium hydroxide (2.25g 0.056 moles) in water (10cm³) was added to the boiling solution at a rate of 3cm³ per hour. The mixture was then heated under reflux for 14 hours. After cooling the aqueous solution was extracted with diethylether (3 x 30cm³), the combined extracts were dried (MgSO₄) and the solvent removed on a rotary evaporator to leave an orange oil. This was distilled to give a colourless oil. (Yield 7.4g 48%)

b.p. 146 - 152°C at 2.5mm of Hg (Lit b.p. 155 - 156°C)²²¹.

¹H n.m.r. (CDCl₃) 7.0δ (5H,m); 3.9δ (2H,t); 1.7δ (8H,m); 3.4δ (2H,t)

I.R. ν_{max} (thin film) 3010, 2905, 1580, 1460, 1285, 1235, 1170, 1025, 750, 690 cm⁻¹.

Mass Spectrum M⁺256

32. PREPARATION OF 1 BROMO 10-PHENOXYDECANE

Phenol (4.7g 0.05 moles) was added to a stirred solution of potassium hydroxide (5.6g 0.1 moles) in dimethyl sulphoxide (50cm³). The mixture was stirred for 40 minutes. This solution was added dropwise to a stirred solution of 1,10 dibromodecane (22.5g 0.075 moles) in dimethylsulphoxide (30cm³) and stirred for a further 24 hours. The mixture was poured into water (100cm³) and the organic components extracted with diethylether (3 x 50cm³). The combined extracts were backwashed with water (30cm³) and then dried (MgSO₄). Evaporation of the solvent left a colourless oil which was distilled in vacuo (Yield 5.3g 34%).

b.p. 178°C at 4.5mm of Hg (Lit b.p. 107 - 112°C at 0.2mm of Hg)²²².

¹H n.m.r. (CDCl₃) 7.0 δ (5,H,m); 3.9 δ (2H,t); 3.4 δ (2H,t; 1.3 δ (20h, broad singlet)

I.R. ν max (thin film) 2900, 2840, 1580, 1460, 1235, 1170, 1020
750, 685 cm⁻¹.

33. PREPARATION OF 1 - (4BROMOPHENOXY) 2-BROMOETHANE

4-bromophenol (8.7g 0.05 moles), 1,2 dibromoethane (14.1g 0.075 moles) were added to a solution containing sodium (1.5g 0.065 moles) in ethanol (100cm³), and heated under reflux for twenty hours. A white solid formed during the reaction. The mixture was allowed to cool and the solid filtered off. The filtrate was poured into water (200cm³) and the organic products extracted with diethylether (3 x 100cm³). The combined extracts were dried (MgSO₄) and the solvent removed to leave a colourless oil; this was distilled under reduced pressure. The highest boiling fraction solidified on standing and was recrystallised from petroleum ether (60 - 80). (Yield 2.25g 16%)

m.p. 53 - 54°C (Lit m.p. 58°C)¹²².

¹H n.m.r. (CDCl₃) 7.1 δ (4H,q); 4.3 δ (2H,t); 3.6 δ (2H,t)

I.R. ν max (KBr disc) 1570, 1450, 1220, 800, 500 cm⁻¹

U.V. λ max (methanol) 282nm., 289nm.

34. PREPARATION OF 1 - (4-BROMOPHENOXY) 3-BROMOPROPANE

4-bromophenol (8.7g 0.05 moles) was added under nitrogen to a stirred suspension of potassium hydroxide (5.6g 0.1 moles) in dimethylsulphoxide (50cm³).

The mixture was stirred for one hour and then added dropwise with stirring under nitrogen, to a solution of 1,3 dibromopropane (15g 0.074 moles) in dimethylsulphoxide (50cm^3). The mixture was stirred for twenty-four hours and then poured into water (100cm^3). The mixture was extracted with diethylether ($3 \times 50\text{cm}^3$), the extracts were combined and backwashed with water (50cm^3). The organic layer was dried (MgSO_4) and the solvent evaporated in vacuo to leave a colourless oil. This was distilled, the highest boiling fraction solidified on standing. This was recrystallised from petroleum ether (60 - 80) to give white crystals. (Yield 3.8g 26%)

m.p. $49 - 49.5^\circ\text{C}$ (Lit m.p. $49 - 49.5$)¹²².

^1H n.m.r. (CDCl_3) 7.0δ (4H,q); 4.0δ (2H,t); 3.5δ (2H,t); 2.2δ (2H,m)
I.R. ν max (KBr disc) 2870, 1570, 1460, 1220, 810, 620, 500 cm^{-1} .

35. PREPARATION OF 1 - (4-BROMOPHENOXY) - 6-BROMOHEXANE

The title compound was prepared as described in experiment 34 using 4-bromophenol (10.38g 0.06 moles) and 1,6 dibromohexane (18.3g 0.075 moles). Resultant oil was distilled $164 - 168^\circ\text{C}$ at 0.1mm of Hg; this solidified on standing and was recrystallised from petroleum ether (60 - 80) to give waxy white crystals. (Yield 12.4g 50%)

m.p. $43 - 44^\circ\text{C}$ (Lit m.p. $41 - 42^\circ\text{C}$)²²³.

^1H n.m.r. (CDCl_3) 7.05δ (4H,q); 3.95δ (2H,t); 3.4δ (2H,t); 1.6δ (4H,m)
I.R. ν max (KBr disc) 2840, 1540, 1220, 990, 815 cm^{-1} .

Mass Spectrum: M^+ 336.

36. PREPARATION OF 1 - (4-BROMOPHENOXY) 8 BROMOOCTANE²²³

1-(4-bromophenoxy) 8-bromooctane was prepared as outlined in experiment 34 using 4-bromophenol (10.38g 0.06 moles) and 1,8 dibromooctane (20.1g 0.075 moles). The product was distilled keeping fraction of boiling point 182 - 186⁰ at 0.1mm of Hg. The product solidified and was recrystallised from petroleum ether (60 - 80) to give white crystals. (Yield 6.7g 35%)

M.Pt 52.5 - 53⁰C.

¹H n.m.r. (CDCl₃) 7.05 δ (4H,q); 3.9 δ (2H,t); 3.35 δ (2H,t); 1.35 δ (12H, broad singlet).

I.R. ν max (KBr disc) 2910, 2840, 1550, 1460, 1230, 995, 815, 630 cm⁻¹.
Mass Spectrum M⁺364.

37. PREPARATION OF 1 - (4-BROMOPHENOXY) 10-BROMODECANE

1-(4-bromophenoxy) 10-bromodecane was prepared by similar experiment to that of preparation³⁴ using 4-bromophenol (8.7g 0.05 moles) and 1,10 dibromodecane (22.5g 0.075 moles). The resultant yellow solid was distilled, the product distilling between 180 - 240⁰C at 4mm of Hg. The colourless oil solidified on standing, this was recrystallised from petroleum ether (60 - 80) to afford white crystals. (Yield 10.1g 50%)

M.Pt 69 - 70⁰C (Lit b.p. 160 - 180⁰C at 0.15mm of Hg)²²³.

¹H n.m.r. (CDCl₃) 7.05 δ (4H,q); 3.9 δ (2H,t); 3.4 δ (2H,t); 1.35 δ (16H, broad singlet).

I.R. ν max (KBr disc) 2900, 2840, 1570, 1460, 1235, 995, 815, 625 cm⁻¹.
Mass Spectrum: M⁺393 and 391.

38. PREPARATION OF 1(4-BROMOPHENOXY) 12 BROMODECANE²²³

The title compound was prepared as described in experiment 34 using 4-bromophenol (4.35g, 0.025 moles) and 1,12 dibromododecane (12.3g 0.0375 moles). The solid which formed on removal of the solvent was distilled keeping the fraction 236-240⁰C at 2mm of Hg. This was recrystallised from petroleum ether (60 - 80) to give white crystals. (Yield 4.5g, 41%).

m.pt 75 - 78⁰C.

¹H n.m.r. (CDCl₃) 7.05 δ (4H,q); 3.9 δ (2H,t); 3.35 δ (2H,t); 1.3 δ (20H, broad singlet).

I.R. ν max (KBr disc) 2840, 1570, 1460, 1220, 995, 815 cm⁻¹.

39. PREPARATION OF 1(4-CHLOROPHENOXY) 2 BROMOETHANE

Sodium (1.5g, 0.065 moles) was dissolved in ethanol (100cm³) 4-chlorophenol (6.1g, 0.047 moles) and 1,2 dibromoethane (14.1g, 0.075 moles) was added and the mixture heated under reflux for twenty hours, a white precipitate formed of sodium bromide, this was removed by filtration. The filtrate was poured into water (200cm³) and the resultant aqueous solution was extracted with diethylether (3 x 50cm³). The combined extracts were dried (MgSO₄) and the solvent removed on a rotary evaporator to leave a mixture of an oil and a solid. The solid by-product of 1,2 di(4-chlorophenoxy) ethane was removed by filtration, and the oil was distilled bulb-to-bulb under reduced pressure. The resultant oil was crystallised from petroleum ether (60 - 80 fraction) to afford the desired product. (Yield 1.05g 9.5%).

m.p. 64 - 65⁰C.

(Lit m.p. 68⁰C)²²⁴.

^1H n.m.r. (CDCl_3) 8.08 δ (4H,q); 4.3 δ (2H,t); 3.62 δ (2H,t).

I.R. ν max (KBr-disc) 2920, 1600, 1580, 1490, 1280, 1240, 1080, 1010,
840 cm^{-1} .

40. PREPARATION OF 1(4 CHLOROPHENOXY)-3-BROMOPROPANE.

4-chlorophenol (5g, 0.039 moles) was added to a stirred suspension of potassium hydroxide (2.5g 0.045 moles) in dimethylsulphoxide (50cm^3). After stirring for one hour this solution was added dropwise with stirring under an atmosphere of nitrogen to a solution of 1,3 dibromopropane (15g 0.074 moles) in dimethylsulphoxide (25cm^3). When addition was complete the reaction mixture was stirred for a further twenty four hours. The resultant solution was poured into water (200cm^3) and this was extracted with diethyl ether ($3 \times 100\text{cm}^3$). The extracts were combined and back washed with water (50cm^3). The ethereal layer was dried (MgSO_4) and the solvent removed in vacuo to leave a colourless oil. This was distilled under reduced pressure and the resultant oil crystallised from petroleum ether (60 - 80) to give white crystals. (Yield 1.4g 14.4%)

m.p. 33 - 34 $^{\circ}\text{C}$.

(Lit m.p. 37 $^{\circ}\text{C}$) 224.

^1H n.m.r. (CDCl_3) 6.9 δ (4H,q); 4.0 δ (2H,t) 3.5 δ (2H,t); 2.23 δ (2H,m)

I.R. ν max (thin film) 2920, 1580, 1465, 1235, 1170, 1025, 925, 820 cm^{-1} .

41. PREPARATION OF 1(4 CHLOROPHENOXY)-8-BROMOOCTANE

The title compound was prepared in a similar manner to experiment using 4-chlorophenol (7.74g 0.06 moles) and 1,8 dibromooctane (20.1g 0.075 moles). The resultant oil was distilled 192 - 200 $^{\circ}\text{C}$ at 0.8mm of Hg.

This formed a white solid on standing. This was recrystallised from petroleum ether (60 - 80) to afford white crystals. (Yield 6.3g 33%)

m.p. 52 - 52.5^oC

¹H n.m.r. (CDCl₃) 6.9 δ (4H,q) 3.9δ (2H,t); 3.4δ (2H,t); 1.4δ (12H, broad singlet).

I.R. ν (KBr disc) 2840, 1575, 1460, 1230, 1000, 820, 660, 630, 500 cm⁻¹.

Mass Spectrum M⁺320.

Analysis: Required C:52.60%, H:6.31%

Found C:52.74%, H:6.30%

¹³C n.m.r. (CDCl₃) p.p.m. 157.65, 129.21, 125.19, 115.71, 68.18, 34.02, 32.72, 29.22, 28.70, 28.05, 25.97.

42. PREPARATION OF 1(4-CHLOROPHENOXY)-10-BROMODECANE

1(4 chlorophenoxy) 10 bromodecane was prepared utilising the method in experiment 40 using 4-chlorophenol (6.5g 0.05 moles) and 1,10 dibromodecane (22.5g 0.075 moles). The resultant solid was distilled and the fraction 236 - 242^oC of 4mm of Hg was crystallised from petroleum ether (60 - 80) affording white crystals. (Yield 9.2g 53%)

m.p. 55 - 56^oC

¹H n.m.r. (CDCl₃) 6.95δ (4H,q); 3.9δ (2H,t); 3.4δ (2H,t); 1.3δ (16H, broad singlet).

I.R. ν max (KBr disc) 2840, 1580, 1460, 1275, 1232, 1000, 820, 660, 630, 500 cm⁻¹.

Analysis: Required C:55.26%, H:6.96%

Found C:55.16%, H:7.14%

Mass Spectrum M⁺348.

43. PREPARATION OF 1-iodo, 2-phenoxyethane

1-bromo, 2-phenoxyethane (1.15g, 5.7×10^{-3} moles) was dissolved in acetone (20cm³). Sodium iodide (3g 0.02 moles) was added and the mixture agitated on a mechanical shaker for one week. The mixture was filtered to remove sodium bromide and the solvent removed from the filtrate by evaporation in vacuo to leave a yellow solid. Diethyl ether (30cm³) was added to the solid and the mixture filtered through cellite filter aid. The filtrate was dried (MgSO₄) and the solvent removed at the pump to leave a yellow oil which crystallised on standing. Recrystallisation from methanol gave white crystals. (Yield 0.92g 65%).

m.p. 30.5 - 31°C.

(Lit m.p. 30°C)²²⁵.

¹H n.m.r. (CDCl₃) 7.16 δ (5H,m); 4.20 δ (2H,t); 3.38 δ (2H,t).

I.R. ν max (thin film) 3040, 2920, 1595, 1490, 1235, 1170, 1070, 1028, 750, 690

¹³C n.m.r. (CDCl₃) p.p.m. 158.2, 129.82, 121.61, 115.04, 68.68, 1.3.

44. PREPARATION OF 1-iodo, 6-phenoxyhexane

1-iodo, 6-phenoxyhexane was prepared by the method employed in experiment 43 using 1 - bromo, 6 - phenoxyhexane (1.25g 0.005 moles) and sodium iodide (3.0g 0.02 moles). The crude product was recrystallised from methanol to afford white crystals (Yield 1.1g 72.4%).

m.p. 73 - 74°C

(Lit m.p. 25°C)²²⁶.

¹H n.m.r. (CDCl₃) 7.12 δ (5H,m); 3.90 δ (2H,t); 3.12 δ (2H,t); 1.6 δ (8H,m)

I.R. ν max (KBr disc) 2940, 1600, 1470, 1390, 1240, 1170, 1010, 750, 690 cm⁻¹.

¹³C n.m.r. (CDCl₃) p.p.m. 159.3, 129.6, 120.7, 114.6, 67.6, 33.4, 30.2, 29.1, 25.1, 6.9.

45. PREPARATION OF 1-IODO, 10-PHENOXYDECANE

The title compound was prepared in a similar manner to 1 - iodo 2 phenoxyethane, experiment 43 using 1 - bromo, 10 phenoxy decane (1.25g 4×10^{-3} moles) and sodium iodide (3.0g 0.02 moles). This afforded white crystals after recrystallisation from methanol. (Yield 1.13g 78.5%)

m.p. 40 - 41°C

^1H n.m.r. (CDCl_3) 7.2 δ (2H,m); 6.8 δ (3H,m); 3.9 δ (2H,t); 3.12 δ (2H,t)
1.3 δ (16H, broad singlet).

I. R. ν max (KBr disc) 2900, 2840, 1595, 1585, 1470, 1245, 1168,
745, 690 cm^{-1} .

^{13}C n.m.r. (CDCl_3) p.p.m. 159.4, 129.6, 120.6, 114.7, 67.9, 33.6, 30.5,
29.3, 28.5, 26.0, 7.1.

46. PREPARATION OF PHENYLVINYLETHER²²⁷.

1 - bromo, 2 - phenoxyethane (10g 0.05 moles) and potassium hydroxide (4g 0.072 moles) were heated to 154°C whereupon a colourless oil distilled off. This was collected and re-distilled bulb-to-bulb to give a colourless oil. (Yield 5.2g 85%)

b.p. 155 - 156°C

^1H n.m.r. (CDCl_3) 7.1 δ (5H,m); 6.6 δ (1H,m); 4.7 δ (2H,d)

47. PREPARATION OF ALLYLPHENYLETHER

Allyl phenyl ether was prepared by the method of L. Claisen²²⁸. Phenol (5g 0.053 moles) was dissolved in acetone (30 cm^3). Allyl

bromide (6.25g 0.051 moles) and potassium carbonate (5g 0.05 moles) were added and the mixture heated under reflux for three hours. After cooling the solid was removed by filtration. The solvent was evaporated in vacuo to afford a yellow oil, this was dissolved in diethylether (30cm³) then washed successively with base and water. The ethereal layer was dried (Na₂SO₄) and the solvent removed on a Büchi rotary evaporator to leave a colourless oil. (Yield 0.8g 11.1%)

¹H n.m.r. (CDCl₃) 7.28 δ (2H,t); 6.85 δ (3H,m); 6.0 δ (1H,m); 5.26 δ (2H,t);
4.48 δ (2H,d).

48. PREPARATION OF PHENYLPROPYLETHER²²⁹.

Phenol (2.35g 0.025 moles) was added to a stirred solution of potassium hydroxide (5.6g 0.1 mole) in dimethylsulphoxide (30cm³). The mixture was stirred for one hour and 1-bromopropane (12.3g 0.0 mole) added. The suspension was stirred overnight and then poured into water (100cm³). The aqueous solution was extracted with diethylether (3 x 30cm³). The extracts were combined and backwashed with water, dried (MgSO₄) and the solvent removed on a rotary evaporator to leave a colourless oil. (Yield 3.0g 88%)

¹H n.m.r. (CDCl₃) 6.9 δ (5H,m); 3.9 δ (2H,t); 1.65 δ (2H,m); 1.0 δ (3H,t).

49. PREPARATION OF PHENYLBUTYLETHER

Phenylbutylether was prepared utilising the same method as experiment using phenol (2.35g 0.025 moles), 1-bromobutane (13.7g 0.1 mole) and potassium hydroxide (5.6g 0.1 mole). This gave a colourless oil which was distilled to give the pure product. (Yield 3.0g 76%)

b.p. 115 - 117°C at 18mm of Hg. (Lit 210.3°C)²²⁹.

¹H n.m.r. (CDCl₃) 6.9δ (5H,m); 3.95δ (2H,t); 1.65δ (4H,m); 0.9δ (3H,t).

50. PREPARATION OF PHENYLHEXYLEETHER

The title compound was prepared by the same method as experiment 49 using phenol (4.7g 0.05 moles), 1-bromohexane (16.5g 0.1 mole) and potassium hydroxide (5.6g 0.1 mole) this gave a colourless oil which was distilled to give the desired product. (Yield 10.3g 80%)

b.p. 84°C at 1mm of Hg. (Lit 243 - 243.5)²³⁰.

¹H n.m.r. (CDCl₃) 6.9δ (5H,m); 3.9δ (2H,t); 1.4δ (8H, broad singlet)
0.95δ (3H,t).

51. PREPARATION OF PHENYLDECYLEETHER

Phenyl decylether was prepared in a similar manner to phenylpropylether using phenol (4.7g 0.05 moles), 1-bromodecane (11.05g 0.05 moles) and potassium hydroxide (5.6g 0.1 mole). This afforded a colourless oil which was distilled to give phenyldecylether. (Yield 11.3g 98%)

b.p. 136 - 138°C at 2mm of Hg. (Lit. b.p. 178°C at 15mm of Hg)²³¹.

¹H n.m.r. (CDCl₃) 6.9δ (5H,m); 3.9δ (2H,t); 1.3δ (16H, broad singlet,
0.9δ (3H,t).

52. PREPARATION OF 4 - BROMOBENZYLTRIPHENYLPHOSPHONIUM BROMIDE

Triphenylphosphine (1.1g 4.2×10^{-3} moles) and 4-bromobenzylbromide (1.0g 4×10^{-3} moles) were dissolved in benzene (20cm³). The mixture

was heated under reflux for four hours, during which time a white precipitate formed. When the solution had reached ambient temperature the solid was collected by filtration. (Yield 2.0g 98.5%)

m.p. 274 - 276°C. (Lit m.p. 278°C)²³².

¹H n.m.r. (CDCl₃) 7.2 δ (19H,m); 5.3 δ (2H,d)

53. PREPARATION OF 1 - (1 NAPHTHYL) 2 - (4 BROMOPHENYL) ETHENE²⁴².

Sodium (0.09g 3.9×10^{-3} moles) was dissolved in methanol (15cm³), 4 - bromobenzyltriphenylphosphonium bromide (2.0g $3 \times 9 \times 10^{-3}$ moles) and 1 - naphthaldehyde (0.6g 3.8×10^{-3} moles) were added and the mixture stirred for seventeen hours. The solid which formed was collected by filtration; a second crop of crystals being obtained by partial evaporation of the solvent in the filtrate. (Yield 0.6g 51%)

m.p. 99.5 - 100.5°C.

¹H n.m.r. (CDCl₃) 7.4 δ (11H,m); 7.0 δ (2H,d).

54. PREPARATION OF 1 - (1 NAPHTHYL) 2 - (4 BROMOPHENYL) ETHANE²⁴²

1 - (1 naphthyl) 2 - (4 bromophenyl) ethene (0.5g 1.6×10^{-3} moles) was added to a slurry of palladium on charcoal (0.2g), in acetic acid (25cm³). The slurry was stirred vigorously whilst ^{kept} under a blanket of hydrogen at atmospheric pressure until hydrogen ceased to be absorbed. The mixture was filtered through cellite filter aid and the solvent removed from the filtrate by evaporation to yield a colourless oil. (Yield 0.44g 88%)

¹H n.m.r. (CDCl₃) 7.2 δ (11H,m); 3.2 δ (2H,m); 2.9 δ (2H,m).

55. PREPARATION OF BENZYLTRIPHENYLPHOSPHONIUM BROMIDE

The title compound was prepared by a similar method to that used in experiment 52, utilising triphenylphosphine (2.6g 0.01 moles) and benzyl bromide (2.0g 0.11 moles). This reaction afforded a white solid. (Yield 3.0g 85%)

m.p. 268 - 270°C. (Lit m.p. 274 - 275°C)²³³.

56. PREPARATION OF 1 (1 - NAPHTHYL)-2-PHENYLETHENE²⁴²

1 - (1 naphthyl)-2-phenylethane was prepared by utilising the method of experiment 53, using benzyltriphenylphosphonium bromide (1.5g 4.25×10^{-3} moles) and 1 naphthaldehyde (0.5g 3.2×10^{-3} moles). This gave a colourless oil. (Yield 0.37g 51%)

¹H n.m.r. (CDCl₃) 7.4 δ (12H,m); 6.8δ (2H,d).

57. PREPARATION OF 1 - (1 NAPHTHYL)-2-PHENYLETHANE²³⁴.

1 - (1 naphthyl) 2 phenylethane was prepared by the method used in experiment 54, using 1 - (1 - naphthyl) 2 phenylethane (0.37g 1.6×10^{-3} moles). This gave a colourless oil. (Yield 0.26g 70%)

¹H n.m.r. (CCl₄) 7.2 δ (12H,m); 3.2 δ (2H,m); 2.9 δ (2H,m).

58. PREPARATION OF 1 BROMO 2 (1 - NAPHTHYLOXY) ETHANE²³⁵.

The title compound was prepared as in experiment 33, using sodium (0.34g 0.015 moles), 1 - naphthol (1.5g 0.01 moles) and 1,2 dibromo ethane (3.75g 0.02 moles). A brown oil was the result of the reaction, this was triturated with petroleum ether (60 - 80) and then distilled, fraction 154 - 156°C at 0.8mm of Hg was retained and crystallised from methanol to give a pink-white solid. (Yield 0.82g 32.7%)

m.p. 25°C

¹H n.m.r. (CDCl₃) 8.3δ (1H,m); 7.7δ (1H,m); 7.3δ (4H,m); 6.7δ (1H,m);
4.1δ (2H,t); 3.6δ (2H,t)

I.R. ν max (thin film) 3045, 1575, 1400, 1265, 1240, 1100, 790, 770 cm⁻¹.

59. PREPARATION OF 1 BROMO 6 (1-NAPHTHYLOXY) HEXANE

1 bromo 6(1 naphthyloxy) hexane was prepared by the same method as experiment 31 using 1 - naphthol (3.2g 0.022 moles), 1,6 dibromohexane (*excess*) and potassium hydroxide (2.5g, 0.044 moles). This afforded a red oil which was distilled to remove excess 1,6 dibromohexane, and crystallised from methanol to yield pink-white crystals. (Yield 3.0 g 45%)

m.p. 30 - 31°C

¹H n.m.r. (CDCl₃) 8.3δ (1H,m); 7.7δ (1H,m); 7.3δ (4H,m); 6.7δ (1H,m)
4.1δ (2H,t); 3.4δ (2H,t); 1.8δ (4H,m); 1.5δ (4H,m).

I.R. ν max (thin film) 2940, 1580, 1510, 1460, 1405, 1390, 1270, 1240,
1100, 790, 770 cm⁻¹.

60. PREPARATION OF ETHYL (1 NAPHTHYL) ETHER²³⁶.

Ethyl (1-naphthyl) ether was prepared in a manner similar to that in experiment 33, using 1-naphthol (1.0g 6.6 x 10⁻³ moles), 1 bromoethane (1.3g 0.012 moles) and sodium (0.3 g 0.013 moles). This afforded a colourless oil (Yield 0.8g 67%).

¹H n.m.r. (CDCl₃) 8.3δ (1H,m); 7.7δ (1H,m); 7.4δ (4H,m); 6.7δ (1H,m);

61. PREPARATION OF HEXYL (1-NAPHTHYL) ETHER

The title compound was prepared by the same method outlined in experiment 31, using 1-naphthol (1.5g 0.0104 moles) potassium hydroxide (1.5g, 0.027 moles) and 1-bromohexane (1.75g, 0.0106 moles). This gave a colourless oil which was distilled to remove excess 1-bromohexane. (Yield 2.04g 86%).

^1H n.m.r. (CDCl_3) 8.3 δ (1H,m); 7.8 δ (1H,m); 7.4 δ (4H,m); 6.8 δ (1H,m)
4.1 δ (2H,t); 1.9 δ (2H,m); 1.4 δ (6H, broad singlet);
0.9 δ (3H, broad singlet)

I.R. ν max (thin film) 2925, 1580, 1460, 1405, 1390, 1270, 1240, 1100,
790, 770 cm^{-1} .

GENERAL PROCEDURE FOR PHOTOLYSIS OF ω - (4 - BROMOPHENOXY) ALKYL BROMIDE

ω - (4 - bromophenoxy) alkylbromides (0.0006 moles) are dissolved in methanol (30cm³) in quartz glass photolysis tubes. The solutions were de-oxygenated, by bubbling a stream of dry nitrogen through them for thirty minutes. The photolysis tubes were stoppered and placed in a rayonet reactor fitted with low pressure mercury lamps, (main output 254 nm), and a merry-go-round apparatus to ensure equal light distribution. Aliquots of 1cm³ were taken from the tubes at various time intervals and analysed by H.P.L.C. under the following conditions:

Column : Partisil PXS 10/25 ODS (Analytical)

Wavelength : 275nm. Flow rate : 1cm³ per minute.

Injection size : 20 μ l Solvent : Methanol 70%, Water 30%.

The ω - (4 - bromophenoxy) alkylbromides were consumed during the reaction and phenoxyalkyl bromides and phenol formed. Appropriate standards of various concentrations were used to constructing standard curves and the amounts of products and starting material calculated. The values from the H.P.L.C analysis are shown in table

1. 1-bromo 2-(4-bromophenoxy)ethane

Time (minutes)	BrPhO(CH ₂) ₂ Br	PhO(CH ₂) ₂ Br	PhOH
0	206	0	0
10	186	32	2
20	151	43	7
30	133	56	15
45	113	68	25
60	67	74	40
120	44	77	60

2. 1-bromo 3-(4-bromophenoxy)propane

Time (minutes)	BrPhO(CH ₂) ₃ Br	PhO(CH ₂) ₃ Br	PhOH
0	141	0	0
10	122	15	0
20	126	32	1
30	106	42	1
45	90	67	3
60	68	88	5
120	35	84	12
240	15	116	25

3. 1-bromo 6-(4-bromophenoxy)hexane

Time (minutes)	BrPhO(CH ₂) ₆ Br	PhO(CH ₂) ₆ Br
0	126	0
30	70	64
60	56	88
90	42	109
120	33	129
180	24	149
240	22	152

4. 1-bromo 8-(4-bromophenoxy)octane

Time (minutes)	BrPhO(CH ₂) ₈ Br	PhO(CH ₂) ₈ Br
0	186	0
10	168	22
20	134	51
30	110	74
60	102	103
120	82	133
240	62	206

5. 1-bromo 10-(4-bromophenoxy)decane

Time (minutes)	BrPhO(CH ₂) ₁₀ Br	PhO(CH ₂) ₁₀ Br
0	177	0
30	160	34
60	121	49
120	85	84
240	60	117

PHOTOLYSIS OF 1 BROMO 2 - (4 - CHLOROPHENOXY) ETHANE

1-bromo 2 - (4 - chlorophenoxy) ethane (0.0006 mol) was dissolved in methanol (30cm³) in quartz glass photolysis tubes. The solution was de-oxygenated by passing a stream of dry nitrogen through the solution for thirty minutes. The solution was stoppered and irradiated using low pressure mercury lamps' light in a rayonet reactor fitted with a merry-go-round. Aliquots of 1cm³ were taken at time intervals and analysed by H.P.L.C. using the following conditions:

Column : Partisil PXS 10/25 ODS.

Wavelength : 275nm.

Flow rate : 1cm³ per minute.

Injection size 20μl

Solvent : Methanol 80%, Water 20%.

Chart speed : 120 cm per hour.

The amounts of product and starting material were calculated using appropriate standards. A similar method was used for the photolyses of 1-bromo 3 - (4 - chlorophenoxy) propane, 1-bromo 8 - (4 - chlorophenoxy) octane and 1-bromo 10 - (4 - chlorophenoxy) decane.

Photolysis time (hrs)	Chain length	Starting Material %	PhO(CH ₂) _n Br%	Phenol %	p-chloro phenol %
3	2	56.5	15.5	25	2
3	3	46	26.5	20	.5
4	8	53	40	-	-
6	10	60	38	-	-

FLUORESCENCE STUDIES OF ω -PHENOXY ALKYL BROMIDES AND PHENYL ALKYL ETHERS

Cyclohexane solutions were made up of the various halides and ethers so that the optical density of each solution was 0.1 at 270nm. The fluorescence spectra of the compounds were recorded on a Perkin Elmer MPF4 spectrophotometer under the following conditions:

Excitation wavelength : 270nm

Excitation slit : 2 μ

Grain : 10/3

Emission slit : 4 μ

Range : 270 - 365nm.

The relative quantum yield of fluorescence of the compounds was determined by measuring the area under the curve; this was achieved by cutting out the peaks and weighing them. Quantum yields were determined by using a compound of known fluorescence quantum yield, measuring the peak area and converting this to quantum yield. Multiplication of the relative quantum yields by this factor affording the quantum yields.

Compound	Weight of Peak	ϕ_F
PhOCH ₂ CH ₃	1.6086	0.240
PhO(CH ₂) ₂ CH ₃	1.5302	0.228
PhO(CH ₂) ₃ CH ₃	1.4479	0.216
PhO(CH ₂) ₅ CH ₃	1.536	0.229
PhO(CH ₂) ₉ CH ₃	1.787	0.267
PhO(CH ₂) ₂ Br	0.771	0.115
PhO(CH ₂) ₃ Br	1.32	0.197
PhO(CH ₂) ₄ Br	1.2750	0.19
PhO(CH ₂) ₅ Br	1.487	0.222
PhO(CH ₂) ₆ Br	1.480	0.221
PhO(CH ₂) ₈ Br	1.396	0.208
PhO(CH ₂) ₁₀ Br	1.363	0.203

GENERAL PROCEDURE FOR PHOTOLYSIS OF ω -PHENOXY ALKYL HALIDES

The procedure for photolysis of these compounds is described using 1-bromo-3-phenoxypropane as an example.

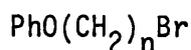
1-bromo-3-phenoxypropane (0.13g 0.0006 moles) was dissolved in methanol (30cm³) in a quartz glass photolysis tube. The solution was de-oxygenated by bubbling dry nitrogen through the solution for 30 minutes prior to the irradiation, which was carried out in a rayonet reactor fitted with a merry-go-round apparatus. The solutions were irradiated using low pressure mercury lamps (output 254nm). Samples of 1cm³ were taken and analysed by gas liquid chromatography under the following conditions:

Column : 3% O.V. 17.

Injection size : 0.4 μ l

Nitrogen flow rate : 10 lb per square inch. Oven temperature 120^oC.

Using appropriate standards the amounts of products and starting material were calculated by comparison of peak area.



Chain length (n=)	Irradiation time (hours)	Starting material %	Phenol %	Alkene %
2	6	12	80	5
3	6	15	65	3
4	6	60	16	18
6	6	68	8	23
10	24	100	0	0

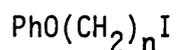
PHOTOLYSIS OF 1 - BROMO 6 - PHENOXYHEXANE IN BENZENE

1 - bromo 6 - phenoxyhexane (0.13g 0.0006 moles) was dissolved in methanol (25cm³) and benzene (5cm³) in a quartz glass photolysis tube.

Oxygen was removed from the solution by passing a stream of nitrogen through the solution for thirty minutes. The solution was irradiated for six hours in a rayonet photochemical reactor utilising low pressure mercury lamps. The reactor was also fitted with a merry-go-round apparatus. Aliquots of 1cm³ were removed for analysis by G.L.C. using the conditions outlined in the previous experiment. The reaction afforded three products - phenol 7%, hexyl phenylether 15% and phenyl 1 - hexenyl ether 8%

PHOTOLYSIS OF 1-IODO ω PHENOXYALKANES

The 1 -ωiodophenoxyalkanes (0.0006 moles) were dissolved in methanol (30cm³) and the solutions placed in quartz glass photolysis tubes. The solutions were de-oxygenated by bubbling a stream of argon through them for 30 minutes. The solutions were irradiated in a rayonet reactor fitted with low pressure mercury lamps and a merry-go-round apparatus. The solutions were irradiated for one hour and samples taken for analysis by gas liquid chromatography.



	Yield of phenol(%)	Yield of Alkene(%)	Starting material(%)
2	4.2	57.5	38.5
3	1.9	35.9	57.2
4	1.35	44.4	53.8
6	6.1	53.2	39.5
10	1.0	28.8	70.0

FLUORESCENCE SPECTROSCOPY OF 1 - IODO ω PHENOXYALKANES

Solutions of the iodides were made up in cyclohexane with an optical density of 0.1 at 270nm. The fluorescence spectra were recorded under the following conditions:

Excitation wavelength : 270nm

Excitation slit : 3 μ

Grain : 10/3

Emission slit : 4 μ

Range : 270 - 365nm

Chart speed : 60mm per minute.

Scan speed : 30nm per minute.

The fluorescence spectrum of a known standard was taken so that quantum yield of fluorescence could be determined.

Compound	Weight of Peak	ϕF
PhO(CH ₂) ₂ I	0.02657	0.004
PhO(CH ₂) ₆ I	0.9266	0.138
PhO(CH ₂) ₁₀ I	0.3347	0.050

PHOTOLYSIS OF PHENYLVINYLETHER WITH HYDROGEN BROMIDE

Phenylvinylether (0.15g 0.0013 moles) was dissolved in methanol (30cm³) and irradiated for 6 hours with low pressure mercury lamps in a rayonet reactor fitted with a merry-go-round apparatus. Dry nitrogen was passed through the solution for thirty minutes followed by hydrogen bromide gas for two minutes prior to the irradiation.

A control solution was set up which did not have hydrogen bromide bubbled through it - this was irradiated simultaneously. The solutions were analysed by gas liquid chromatography under the following conditions:

Column : 10% S.E.30

Temperature : 80°C

Nitrogen flow : 30cm³ per minute. Chart speed : 1cm per minute

Sample size : 0.5 μ l

Comparison of retention times with authentic material and by the use of standards, the products and their concentration were found.

It was assumed that the response of the gas-liquid chromatograph was identical for 2-allylphenol and 4-allylphenol. Standard solutions were prepared of starting material, phenol, 2-allylphenol and cyclised material in order to obtain percentage yields.

Photolysis of 5-phenoxy-pent-1-ene with hydrogen bromide

5-phenoxy-pent-1-ene (0.2 g, 1.23×10^{-3} moles) was dissolved in methanol (30 cm^3) in each of two quartz glass photolysis tubes. The solutions were deoxygenated by passing a stream of dry nitrogen through them for thirty minutes. Hydrogen bromide was bubbled slowly through one of the solutions for two minutes. Samples were taken from the solutions at intervals during the six hour irradiation in an 'Applied Photophysics' photochemical reactor with low pressure mercury lamps and fitted with a merry-go-round apparatus. The samples which were taken were analysed by gas-liquid chromatography under the following conditions:-

Column : 10% SE 30, Chart speed : 30 cm hour^{-1} ,
Nitrogen flow : $35 \text{ cm}^3 \text{ minute}^{-1}$, Oven temperature : $120 \text{ }^\circ\text{C}$,
Sample size : $0.5 \mu\text{l}$.

The chromatograph showed that no reaction had taken place,

Photolysis of 1-bromo-5-phenoxy-pentane

1-bromo-5-phenoxy-pentane (0.18 g, 7.4×10^{-4} moles) was dissolved in methanol (30 cm^3). The solution was deoxygenated, irradiated and analysed using a similar procedure to that used in the previous experiment. G.L.C. analysis for phenol was carried

out, and by the use of standards the percentage yield of phenol was determined.

Yield of phenol 22%.

PROCEDURE FOR THE PHOTOLYSIS OF ω -(1-NAPHTHYLOXY)ALKYL BROMIDES

The general procedure for the photolysis of the title compounds is illustrated using 1-bromo-2-(1-naphthyloxy)ethane as an example.

1-bromo 2-(1-naphthyloxy)ethane, (0.2 g, 8×10^{-4}) was dissolved in methanol (30 cm^3). The solution was placed in a quartz glass photolysis tube and deoxygenated by bubbling a stream of dry nitrogen through it for thirty minutes. The solution was placed in an 'Applied Photophysics' photochemical reactor fitted with a merry-go-round apparatus and irradiated for six hours using low pressure mercury lamps. A sample was taken from the solution before and after the irradiation, these were analysed by high performance liquid chromatography under the following conditions:-

Column : Hypersil O.D.S. 5 particle size.

Flow rate : $1 \text{ cm}^3 \text{ minute}^{-1}$ Chart speed : 500 cm hour^{-1}

Monitoring wavelength : 310 nm. Injection size : $20 \mu\text{l}$

Solvent mixture : 70% methanol / 30% water.

Range : 0.1

Standards of 1-naphthol and the corresponding ether were prepared for comparison of retention times and for estimation of the yield. After H.P.L.C. analysis, mass spectrometry was performed on the samples.

Compound	Starting material (%)	1-naphthol (%)	Ether (%)
1-NpOCH ₂ CH ₂ Br	3.5	44.7	3.1
1-NpO(CH ₂) ₆ Br	65.3	17.5	1.0
1-NpO(CH ₂) ₈ Br	97.8	2.0	-
1-NpO(CH ₂) ₁₀ Br	99.8	-	-
1-NpO(CH ₂) ₁₂ Br	100.0	-	-

Mass spectrometry showed the presence of ω -naphthyloxy-alk-1-enes but because of the lack of standards the percentage yields of these compounds could not be determined. Small amounts of unidentified material were also present in the photosylate.

FLUORESCENCE SPECTRA OF THE ω -(1-NAPHTHYLOXY)ALKYL BROMIDES

Solutions of the compounds under study were made up in cyclohexane so that the optical density at 310 nm. was 0.1. The fluorescence spectra were recorded under the following conditions :-

Excitation wavelength ; 310 nm. Gain : 3/3
 Excitation slit : 4 μ Emission slit : 4 μ
 Scan speed : 30 nm. minute⁻¹ Chart speed : 60 mm. minute⁻¹

The peaks were cut out and weighed and the relative fluorescence quantum yields determined.

Compound	Wt. of peak (g)	Relative ϕ_f
1-NpOCH ₂ CH ₃	0.9302 g	1.0
1-NpOCH ₂ CH ₂ Br	0.3590 g	0.33
1-NpO(CH ₂) ₅ CH ₃	0.7653 g	0.71
1-NpO(CH ₂) ₆ Br	0.6901 g	0.64

PHOTOLYSIS OF 1-(4-BROMOPHENYL)-2-(1-NAPHTHYL)ETHANE

1-(4-bromophenyl)-2-(1-naphthyl)ethane (0.1 g, 3.2×10^{-4} moles) was dissolved in methanol (30 cm^3) in a quartz glass photolysis tube and deoxygenated by passing a stream of nitrogen through the solution for thirty minutes. An aliquot of 1 cm^3 was taken and the remainder irradiated for one hour in an 'Applied Photophysics' photochemical reactor fitted with low pressure mercury lamps. On completion of the photolysis thin layer chromatography was carried out using petroleum ether ($60-80^\circ\text{C}$) as eluent. The chromatograph showed two spots of similar R_f 0.5. The solutions were analysed by H.P.L.C. under the following conditions :-

Column : Silica, normal phase Attenuation : 1
Solvent : cyclohexane Flow rate : $2 \text{ cm}^3 \text{ minute}^{-1}$
Injection size : $0.5 \mu\text{l}$ Chart speed : 1 cm minute^{-1}
Monitoring wavelength : 275 nm.

Standards of starting material and 1-phenyl 2-(1-naphthyl)ethane were used for comparison of retention times. Different concentrations of each compound were injected in order to determine the percentage yield of the components.

Compound	Retention time	(%)
1-(4-bromophenyl)-2-(1-naphthyl)ethane	4 minutes 48 seconds	90.5
1-phenyl-2-(1-naphthyl)ethane	4 minutes 24 seconds	9.0

Mass spectrometry was performed on the solution after photolysis this showed the presence of small amounts of the following compounds:-
1-phenyl-2-(1-(1,2-dihydronaphthyl)ethane,

1-(4-bromophenyl)-2-(1-(1,2-dihydronaphthyl)ethane,
1-phenyl-2-(1-(1,2,3,4-tetrahydronaphthyl)ethane,
1-(4-bromophenyl)-2-(1-(1,2,3,4-tetrahydronaphthyl)ethane,
1-(4-methoxyphenyl)-2-(1-naphthyl)ethane,
bis 4,4'-(1-ethyl(2-(1-naphthyl)biphenyl).

PHOTOLYSIS OF 1-(4-BROMOPHENYL)-2-(2-NAPHTHYL)ETHANE

The procedure for the photolysis of the title compound was similar to that for the previous experiment using 1-(4-bromophenyl)-2-(2-naphthyl)ethane (0.1 g, 3.2×10^{-4} moles). Product identification and distribution was found by a similar method to the previous experiment and showed that after one hours irradiation the following:- starting material 93%, 1-phenyl-2-(2-naphthyl)ethane 6.5%, and trace amounts of the materials similar to those described above except substituted in the two position of naphthalene.

PHOTOLYSIS OF ANISOLE WITH HYDROGEN BROMIDE

Anisole (0.65 g, 0.006 moles) was dissolved in methanol (30 cm³) in a quartz glass photolysis tube. The solution was deoxygenated in the usual manner. Hydrogen bromide was passed through the solution for two minutes prior to the irradiation, which was carried out in a 'Rayonet' photochemical reactor fitted with a bank of low pressure mercury lamps, for six hours. The photosylate was analysed by gas-liquid chromatography under the following conditions:-

Column : 3% APL.

Nitrogen flow : 7 lb. square inch⁻¹

Oven temperature : 103 °C

Chart speed : 600 mm. hour⁻¹

Injection size : 0.2 μl

The chromatograph showed that no reaction had taken place.

PHOTOLYSIS OF METHYL 4-BROMOBENZOATE WITH HYDROGEN BROMIDE

Methyl 4-bromobenzoate (0.1 g, 4.65×10^{-4} moles) was dissolved in methanol (12 cm³) in each of two quartz glass photolysis tubes. Dry nitrogen was passed through the solutions for thirty minutes prior to the irradiation to remove dissolved oxygen from the solution. Hydrogen bromide was passed through one of the solutions for two minutes. The irradiation was carried out in a 'Rayonet' photochemical reactor fitted with a bank of low pressure mercury lamps and a merry-go-round apparatus. Aliquots of 1 cm³ were taken at time intervals and analysed under the conditions described in the photolysis of anisole. The product of the photolysis was methyl benzoate.

No HBr		HBr	
Time (mins)	Product yield (%)	Time (mins)	Product yield (%)
5	0.0	5	2.0
20	3.0	20	16.8
45	5.4	45	31.1
70	8.5	70	48.2
107	28.0	107	66.6
170	31.9	170	98.0

62. PREPARATION OF 9-BROMOANTHRACENE

Anthracene (5.0 g, 0.028 moles) and copper II bromide (12.6 g, 0.056 moles) were added to carbon tetrachloride (75 cm³). The suspension was heated under reflux for twenty four hours. When cool the mixture was filtered, the solvent was removed from the filtrate by evaporation in vacuo. This afforded a yellow solid which was recrystallised from ethanol to give yellow crystals. (Yield 4.25 g, 59%)

m.p. 97.5-98.5 °C

(Lit. m.p. 101 °C)¹²⁵.

63. PREPARATION OF METHYL 4-BROMOBENZOATE

4-bromobenzoic acid (2.0 g, 1.0 x 10⁻³ moles), methanol (50 cm³) and concentrated sulphuric acid (2 cm³) were heated under reflux for four hours. When cool, the solvent was removed on a rotary evaporator to leave a white crystalline solid. The solid was dissolved in diethyl ether (50 cm³) and washed successively with sodium hydroxide solution (2M, 30 cm³) and water (30 cm³). The ethereal layer was dried (MgSO₄) and the solvent evaporated to afford a white crystalline solid which was recrystallised from petroleum ether (60-80 °C). (Yield 0.75 g, 35%)

m.p. 79.5-80.5 °C

(Lit. m.p. 81 °C)¹²⁵.

Amine amount	Time (mins)	Starting material (%)	Anisole (%)
Equimolar	120	40.9	60.0
Excess	120	23.7	76.1
None	240	48.0	47.4
Catalytic	240	44.4	53.5
Equimolar	240	14.9	84.8
Excess	240	0.0	100.0

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF BROMOBENZENE

Bromobenzene (0.2 g, 1.27×10^{-3} moles) was dissolved in methanol (25 cm³) in each of two quartz glass photolysis tubes. Triethylamine (4 cm³) was added to one of the tubes. The solutions were deoxygenated by passing a stream of dry nitrogen through them for thirty minutes. Irradiation of the solutions was carried out in a 'Rayonet' photochemical reactor using low pressure mercury lamps and fitted with a merry-go-round apparatus. Aliquots of 1 cm³ were taken from the tubes at time intervals and analysed by high performance liquid chromatography using the following conditions:-

Column : Hypersil O.D.S. Flow rate : 2 cm³ minute⁻¹
 Solvent mixture : methanol 50%, water 50%
 Chart speed : 1 cm minute⁻¹ Monitoring wavelength : 265 nm.

No Amine

Irradiation time (mins)	Bromobenzene (%)	Benzene (%)	Other products (%)
10	95.5	4.5	-
25	92.0	8.0	-
45	84.5	9.0	2.5

Irradiation time (mins)	Bromobenzene (%)	Benzene (%)	Other products (%)
75	71.5	13.0	6.5
180	35.0	28.5	15.5
250	18.0	52.0	30.0

With Amine

Irradiation time (mins)	Bromobenzene (%)	Benzene (%)	Other products (%)
10	95.5	4.5	-
25	88.5	10.0	1.5
45	74.0	17.5	8.5
75	58.5	23.5	16.0
180	21.0	37.5	41.5
250	12.5	41.5	46.0

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF METHYL 4-BROMOBENZOATE

Methyl 4-bromobenzoate (0.2 g , 9.3×10^{-4} moles) was dissolved in methanol (20 cm^3) in each of two quartz glass photolysis tubes. Triethylamine (8 molar excess) was added to one of the solutions. The solutions were deoxygenated by passing a stream of dry nitrogen through them for thirty minutes. The irradiations were carried out in a 'Rayonet' photochemical reactor fitted with a merry-go-round apparatus and low pressure mercury lamps. Aliquots of 1 cm^3 were removed at time intervals, these were analysed by G.L.C. chromatography using the following conditions:-

Column : 10% APL

Oven temperature : $110 \text{ }^\circ\text{C}$

Chart speed : 30 cm hour^{-1}

Injection size : $0.4 \mu\text{l}$

Nitrogen flow : $10 \text{ l} \text{ square inch}^{-1}$

No Amine

Irradiation time (mins)	Methyl 4-bromo-benzoate (%)	Methyl benzoate (%)
20	98.2	1.7
45	95.7	4.2
70	93.0	6.8
120	56.7	42.9
150	52.5	47.2
180	47.0	52.6

With Amine

Irradiation time (mins)	Methyl 4-bromo-benzoate (%)	Methyl benzoate (%)
25	94.2	5.7
45	85.3	14.6
75	72.6	27.1
120	48.2	51.4
180	24.3	75.4

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 1,4-DIBROMOBENZENE

1,4-dibromobenzene (0.147 g, 6.2×10^{-4} moles) was dissolved in methanol (25 cm^3) in each of two quartz glass photolysis tubes. Triethylamine (8 molar excess) was added to one of the solutions which were then deoxygenated by bubbling nitrogen through the solutions for thirty minutes. The solutions were irradiated using low pressure mercury lamps in a 'Rayonet' photochemical reactor fitted with a merry-go-round apparatus. Samples of 1 cm^3 were taken at time intervals and analysed for disappearance of the starting material by H.P.L.C. using the following conditions:-

Column : Partisil ODS (analytical column)

Solvent : methanol 65% / water 35%, Flow rate : $1 \text{ cm}^3 \text{ minute}^{-1}$

Injection size : $10 \mu\text{l}$ Chart speed : $120 \text{ seconds cm.}^{-1}$

Monitoring wavelength : 265 nm.

Without Triethylamine

Irradiation time (mins)	0	5	10	20	45	75	120
1,4-dibromobenzene (%)	100	94	86	71	57	31	15

With Triethylamine

Irradiation time (mins)	0	5	10	20	45	75	120
1,4-dibromobenzene (%)	100	97	85	72	52	26	12

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 4-BROMOBENZONITRILE

4-bromobenzonitrile (0.2 g, 1.1×10^{-3} moles) was dissolved in 25 cm^3 of each of methanol, acetonitrile and cyclohexane.

Triethylamine (5 cm^3) was added to the solutions and these were poured into quartz glass photolysis tubes. A control was set up consisting of 4-bromobenzonitrile (0.2 g, 1.1×10^{-3} moles) in methanol (30 cm^3). The solutions were deoxygenated by passing a stream of dry nitrogen through them for thirty minutes prior to the irradiation. Photolysis of the solutions was carried out in a 'Rayonet' reactor fitted with a merry-go-round apparatus and a bank of low pressure mercury lamps. Aliquots of 1 cm^3 were taken at various time intervals and these were analysed by gas-liquid chromatography using the following conditions:-

Column : 10% SE 30

Oven temperature : 80°C

Nitrogen flow : $30 \text{ cm}^3 \text{ minute}^{-1}$

Chart speed : $30 \text{ cm minute}^{-1}$

Standards were used to establish the identity and yield of the product and monitor the disappearance of starting material.

Solvent	Photolysis time (mins)	Starting material (%)	Benzonitrile (%)
Methanol	30	67	32
Acetonitrile	30	60	38
Cyclohexane	30	70	27
Control	30	74	26
Methanol	60	38	61
Acetonitrile	60	29	69
Cyclohexane	60	42	55
Control	60	42	54

PHOTOLYSIS OF 4-BROMOBENZONITRILE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

4-bromobenzonitrile (0.27 g, 1.4×10^{-3} moles) was dissolved in acetonitrile (25 cm^3) and deuterium oxide (5 cm^3) in a quartz glass photolysis tube. Oxygen was removed from the solution by passing a stream of dry nitrogen through it for thirty minutes. Triethylamine (4 cm^3) was added and the solution irradiated in an 'Applied Photophysics' photochemical reactor fitted with low pressure mercury lamps for one hour. The solution was analysed by mass spectrometry this showed a peak at 103.0337 corresponding to benzonitrile and a peak at 104.0389 which was that expected for the natural abundance of ^{13}C .

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 4-CHLOROBENZONITRILE

The photolysis was carried out as described in the experiment

into either the starting material or into the product-

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 4-BROMOANISOLE

The experiment was carried out as described^{p230} in the triethylamine assisted photolysis of 4-bromobenzonitrile using 4-bromoanisole (0.2 g, 1.07×10^{-3} moles). The samples taken from the photolyses were analysed by G.L.C. using the following conditions:-

Column : 10% SE30 Oven temperature : 120°C
Nitrogen flow : 30 cm³ minute⁻¹ Chart speed : 30 cm minute⁻¹
Injection size : 0.4 μl

Solvent	Photolysis time (mins)	Starting material (%)	Anisole (%)
Control	15	80.0	19.5
Methanol	15	67.0	32.0
Acetonitrile	30	29.2	70.5
Cyclohexane	30	59.0	40.0
Methanol	30	32.6	65.2
Control	30	61.0	38.0

PHOTOLYSIS OF 4-BROMOANISOLE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

The experiment was carried out in the same way as the experiment previously described which used deuterium oxide, using 4-bromoanisole (0.2 g, 1.07×10^{-3} moles). The mass spectrum showed a peak at 108.0534 corresponding to the molecular ion for anisole, and a peak at 109.0589 which was of an intensity which related to the content of ¹³C in the molecule.

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 4-CHLOROANISOLE

The photolysis was carried out in the same way as that described on page 229, using 4-chloroanisole (0.14 g, 9.8×10^{-4} moles) and the following solvent mixtures:- methanol, as control; methanol plus triethylamine; acetonitrile plus triethylamine; acetonitrile plus deuterium oxide 5:1 plus triethylamine; cyclohexane plus triethylamine. Analysis was carried out by G.L.C. using the following conditions:-

Column : 10% SE30

Oven temperature : 80°C

Chart speed : 30 cm hour⁻¹Nitrogen flow : 30 cm³ minute⁻¹Injection size : 0.5 μ l

Solvent	Additions	Irradiation time (mins)	4-chloro-anisole (%)	Anisole (%)
Methanol	Triethylamine	30	80.6	19.0
Acetonitrile	Triethylamine	30	53.8	46.0
Cyclohexane	Triethylamine	30	84.9	15.0
Methanol	-	60	78.8	21.0
Methanol	Triethylamine	60	71.3	28.7
Acetonitrile	Triethylamine	60	24.8	74.8
Cyclohexane	Triethylamine	60	77.8	22.0
Acetonitrile	Triethylamine D ₂ O	60	69.5	30.4

A mass spectrum was recorded of the photolysis using acetonitrile deuterium oxide as the solvent mixture, this showed a peak at 108.0559 corresponding to the molecular ion for anisole and a peak corresponding to the presence of a natural abundance of ¹³C. There was no deuterium incorporation into the product.

PHOTOLYSIS OF 4-BROMOTOLUENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

4-bromotoluene (0.25 g, 1.4×10^{-3} moles) was dissolved in acetonitrile (25 cm^3) and deuterium oxide (5 cm^3) in a quartz glass photolysis tube. The solution was deoxygenated in the usual way and triethylamine (4 cm^3) added. Irradiation of the solution was carried out in an 'Applied Photophysics' photochemical reactor fitted with low pressure mercury lamps. The solution was irradiated for one hour. G.C. mass spectrometry was used to analyse for deuterium incorporation. G.L.C. analysis showed that 47.8% of the starting material had been converted to toluene. The mass spectrum showed that deuterium incorporation had not taken place in either the product or the starting material.

PHOTOLYSIS OF 1,4-DICHLOROBENZENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

The photolysis was carried out as described in the previous experiment using 1,4-dichlorobenzene (0.22 g, 1.5×10^{-3} moles). The mass spectrum showed that deuterium incorporation had not taken place.

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 1-CHLORONAPHTHALENE

1-chloronaphthalene (0.25 g, 1.5×10^{-3} moles) was dissolved in each of cyclohexane, methanol, acetonitrile and acetonitrile / deuterium oxide 5:1 mixture, (30 cm^3) in silica glass photolysis tubes. The solutions were deoxygenated in the usual manner and triethylamine added (4 cm^3). The irradiation was carried out in

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
128.0569	C ₁₀ H ₈	1.0
129.0676	C ₁₀ H ₇ D	0.35
130.0794	C ₁₀ H ₆ D ₂	0.085
131.0753	C ₁₀ H ₅ D ₃	0.066
132.0937	C ₁₀ H ₄ D ₄	0.038

An allowance has been made in the results for the natural abundance of ¹³C in the product. There was no incorporation of deuterium into the starting material.

¹³C n.m.r. of the product of the photolysis showed a complex pattern suggesting the presence of several compounds.

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 1-BROMONAPHTHALENE

1-bromonaphthalene (0.2 g, 9.6 x 10⁻⁴ moles) was irradiated in each of acetonitrile, cyclohexane and methanol with triethylamine (4 cm³) using the same procedure as for the experiment with 1-chloronaphthalene. The chromatography conditions were also similar.

<u>Solvent</u>	<u>Irradiation time (mins)</u>	<u>Naphthalene (%)</u>
Methanol	15	7.4
Cyclohexane	15	1.8
Acetonitrile	15	20.4
Methanol	30	14.0
Cyclohexane	30	3.2
Acetonitrile	30	39.8

PHOTOLYSIS OF 1-BROMONAPHTHALENE WITH TRIETHYLAMINE AND DEUTERIUM
OXIDE

The photolysis was carried out as described in the experiment using 1-chloronaphthalene only with 1-bromonaphthalene (0.3 g, 1.5×10^{-3} moles). A mass spectrum showed that deuterium incorporation had taken place.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
128.0643	$C_{10}H_8$	1.0
129.0698	$C_{10}H_7D$	1.16
130.0787	$C_{10}H_6D_2$	0.605
131.0841	$C_{10}H_5D_3$	0.243
132.1016	$C_{10}H_4D_4$	0.103

An allowance has been made for the natural abundance of ^{13}C .

TO STUDY THE EFFECT OF PRIMARY, SECONDARY AND TERTIARY AMINES ON
THE RATE OF PHOTOLYSIS OF 1-BROMONAPHTHALENE

1-bromonaphthalene (0.8 g, 3.86×10^{-3} moles) was dissolved in methanol (25 cm³) in each of four photolysis tubes. Triethylamine, diethylamine and isopropylamine was each added to one of the tubes in 8 molar excess, the other tube being used as a control. Oxygen was removed from the solutions in the normal manner and the solutions irradiated in a 'Rayonet' photochemical reactor utilising low pressure mercury lamps, for thirteen hours. Samples were taken from the solutions before and after the irradiation and analysed by G.L.C. using the following conditions:-

Column : 10% E30

Oven temperature : 200°C

Chart speed : 600 mm. hour⁻¹

Nitrogen flow : 10 lb. square inch⁻¹

Injection size : 0.25 μ l

<u>Amine</u>	<u>Naphthalene (%)</u>	<u>Bromonaphthalene (%)</u>
None	12.2	87.8
Isopropylamine	34.6	65.3
Diethylamine	36.6	63.2
Triethylamine	44.1	55.9

PHOTOLYSIS OF NAPHTHALENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

Naphthalene (0.06 g, 5×10^{-4} moles) was dissolved in acetonitrile (12.5 cm³) and deuterium oxide (2.5 cm³). The solution was deoxygenated by passing a stream of dry nitrogen through it for thirty minutes. Irradiation of the solution was carried out in the same way as described for the photolysis of 1-chloronaphthalene except that the time period was two hours. G.C. mass spectrometry showed deuterium incorporation in the following way.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
128.0612	C ₁₀ H ₈	1.0
129.0682	C ₁₀ H ₇ D	0.141
130.0790	C ₁₀ H ₆ D ₂	0.018
131.0838	C ₁₀ H ₅ D ₃	0.005
132.0962	C ₁₀ H ₄ D ₄	0.002

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 1-IODONAPHTHALENE

The photolysis was carried out as described in the experiment with 1-chloronaphthalene, using 1-iodonaphthalene (0.2 g, 7.87×10^{-4}

moles). Gas-liquid chromatography showed that the conversion to naphthalene was 25.7% after thirty minutes with acetonitrile as solvent, 22.5% naphthalene with methanol as solvent, and 20% with cyclohexane as solvent.

PHOTOLYSIS OF 1-IODONAPHTHALENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

The photolysis was described in the photolysis of 1-chloronaphthalene with deuterium oxide except using 1-iodonaphthalene (0.2 g, 7.7×10^{-4} moles). Gas-liquid chromatography /mass spectrometry showed deuterium incorporation, an allowance was made for the natural abundance of ^{13}C .

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
128.0639	C_{10}H_8	1.0
129.0688	$\text{C}_{10}\text{H}_7\text{D}$	0.141
130.0783	$\text{C}_{10}\text{H}_6\text{D}_2$	0.018
131.0891	$\text{C}_{10}\text{H}_5\text{D}_3$	0.005
132.0963	$\text{C}_{10}\text{H}_4\text{D}_4$	0.002

PHOTOLYSIS OF 1-CHLORONAPHTHALENE WITH 1-METHYLNAPHTHALENE, TRIETHYLAMINE AND DEUTERIUM OXIDE

1-chloronaphthalene (0.16 g, 9.8×10^{-4} moles) and 1-methylnaphthalene (0.033 g, 2.32×10^{-4} moles) were dissolved in acetonitrile (25 cm^3) and deuterium oxide (5 cm^3). The solution was deoxygenated by passing a stream of dry nitrogen through it for thirty minutes. Triethylamine (4 cm^3) was added and the solution irradiated for one hour in an 'Applied Photophysics' photochemical reactor fitted with low pressure mercury lamps. Analysis of the mixture was achieved by

by mass spectrometry, this showed that deuterium incorporation had taken place. The natural abundance of ^{13}C was taken into account.

Molecular weight	Molecular formula	Deuterium incorporation
142.0770	$\text{C}_{11}\text{H}_{10}$	1.0
143.0759	$\text{C}_{11}\text{H}_9\text{D}$	0.32
144.0796	$\text{C}_{11}\text{H}_8\text{D}_2$	0.11
145.0956	$\text{C}_{11}\text{H}_7\text{D}_3$	0.07
128.0648	C_{10}H_8	1.0
129.0690	$\text{C}_{10}\text{H}_7\text{D}$	0.71
130.0811	$\text{C}_{10}\text{H}_6\text{D}_2$	0.30
131.1068	$\text{C}_{10}\text{H}_5\text{D}_3$	0.16
132.0888	$\text{C}_{10}\text{H}_4\text{D}_4$	0.04

TO STUDY THE EFFECT OF TEMPERATURE ON THE RATE OF DECHLORINATION IN
THE AMINE ASSISTED PHOTOLYSIS OF 1-CHLORONAPHTHALENE

1-chloronaphthalene (0.2 g, 8.5×10^{-4} moles) was dissolved in methanol (30 cm^3) in each of two quartz glass photolysis tubes. The solutions were deoxygenated by passing a stream of dry nitrogen through them for thirty minutes. Triethylamine (4 cm^3) was added and the tubes placed in a quartz glass jacket containing water which was maintained at 50°C by means of a heated and thermostated reservoir. The solutions were irradiated in a 'Rayonet' photochemical reactor fitted with low pressure mercury lamps. Aliquots of 1 cm^3 were taken at time intervals. Analysis by gas-liquid chromatography showed that there was no difference in the rate of dehalogenation.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
156.0899	$C_{12}H_8D_2$	0.039
157.0946	$C_{12}H_7D_3$	0.011
158.1056	$C_{12}H_6D_4$	0.002
159.1069	$C_{12}H_5D_5$	0.002

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 4-CHLOROBIPHENYL

The photolysis was carried out as described for 1-chloronaphthalene except using 4-chlorobiphenyl (0.18 g, 9.5×10^{-4} moles). Analysis was carried out by gas-liquid chromatography using the same conditions as for 4-bromobiphenyl.

<u>Solvent</u>	<u>Irradiation time (mins)</u>	<u>4-chlorobiphenyl (%)</u>	<u>Biphenyl (%)</u>
Acetonitrile	90	26.2	73.8
Cyclohexane	90	97.7	2.3
Methanol	90	74.0	26.0

PHOTOLYSIS OF 4-CHLOROBIPHENYL WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

The photolysis was carried out as described in the experiment with 1-chloronaphthalene except using 4-chlorobiphenyl (0.19 g, 1.0×10^{-3} moles). The mass spectrum showed that deuterium incorporation into the product had occurred, an allowance has been made for the natural abundance of ^{13}C .

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
154.0773	$C_{12}H_{10}$	1.0
155.0848	$C_{12}H_9D$	0.665
156.0890	$C_{12}H_8D_2$	0.346
157.0928	$C_{12}H_7D_3$	0.622
158.1036	$C_{12}H_6D_4$	0.45
159.1131	$C_{12}H_5D_5$	0.088

PHOTOLYSIS OF 4-CHLOROBIPHENYL AND 4-PHENYLTOLUENE WITH TRIETHYLAMINE
AND DEUTERIUM OXIDE

The procedure used for this experiment was similar to that used for 1-chloronaphthalene except using 4-chlorobiphenyl (0.14 g, 7.4×10^{-4} moles) and 4-phenyltoluene (0.041 g, 2.5×10^{-4} moles). The irradiation was carried out over a two hour period. The mass spectrum showed the following features:-

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
154.0835	$C_{12}H_{10}$	1.0
155.0867	$C_{12}H_9D$	0.736
156.0966	$C_{12}H_8D_2$	0.510
157.0999	$C_{12}H_7D_3$	0.317
158.1076	$C_{12}H_6D_4$	0.120
159.1194	$C_{12}H_5D_5$	0.063
168.0914	$C_{13}H_{12}$	1.0
169.1034	$C_{13}H_{11}D$	0.508
170.1089	$C_{13}H_{10}D_2$	0.243
171.1156	$C_{13}H_9D_3$	0.13

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
172.1271	$C_{13}H_8D_4$	0.073
173.1376	$C_{13}H_7D_5$	0.040

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 9-BROMOANTHRACENE

The photolysis was carried out as described in the experiment with 1-chloronaphthalene except using 9-bromoanthracene (0.1 g, 3.89×10^{-4} moles). Samples taken from the photosylates were analysed by high performance liquid chromatography using the following conditions:-

Column : Hypersil O.D.S. 5 Flow rate : $1 \text{ cm}^3 \text{ minute}^{-1}$
Injection size : $10 \mu\text{l}$ Chart speed : $500 \text{ mm. hour}^{-1}$
Monitoring wavelength : 340 nm

<u>Solvent</u>	<u>Irradiation time (mins)</u>	<u>Starting material (%)</u>	<u>Anthracene (%)</u>
Cyclohexane	60	97	2.7
Methanol	60	91	8.5
Acetonitrile	60	85	13.0

PHOTOLYSIS OF 9-BROMOANTHRACENE WITH TRIETHYLAMINE AND DEUTERIUM

OXIDE

The procedure utilised in this experiment was similar to that for 1-chloronaphthalene except using 9-bromoanthracene (0.15 g, 5.8×10^{-4} moles). A mass spectrum was recorded of the photosylate, this showed deuterium incorporation into the product. Allowance has been made for the natural abundance of ^{13}C .

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
178.0721	C ₁₄ H ₁₀	1.0
179.0786	C ₁₄ H ₉ D	0.478

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 9-CHLOROANTHRACENE

The photolysis was carried out as described in the experiment with 9-bromoanthracene except using 9-chloroanthracene (0.1 g, 4.7 x 10⁻⁴ moles)

<u>Solvent</u>	<u>Irradiation time (mins)</u>	<u>Starting material (%)</u>	<u>Anthracene (%)</u>
Cyclohexane	60	99	0.8
Methanol	60	96	3.5
Acetonitrile	60	91	8.2

PHOTOLYSIS OF 9-CHLOROANTHRACENE WITH TRIETHYLAMINE AND DEUTERIUM

OXIDE

The experimental details were similar to those for 1-chloro-naphthalene except using 9-chloroanthracene (0.1 g, 4.7 x 10⁻⁴ moles). A mass spectrum of the photosylate showed that deuterium incorporation into the product had occurred. An allowance was made for the natural abundance of ¹³C.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
178.0699	C ₁₄ H ₁₀	1.0
179.0750	C ₁₄ H ₉ D	0.128

PHOTOLYSIS OF 9-CHLOROANTHRACENE AND 9-METHYLANTHRACENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

The irradiation was carried out using the same procedure as for 1-chloronaphthalene except using 9-chloroanthracene (0.12 g, 5.65×10^{-4} moles) and 9-methylanthracene (0.07 g, 3.6×10^{-4} moles). The solution was irradiated for two hours, after this time an aliquot was taken and a mass spectrum run of this. The mass spectrum showed that deuterium incorporation had taken place. An allowance was made for the natural abundance of ^{13}C .

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
192.0936	$\text{C}_{15}\text{H}_{12}$	1.0
193.1047	$\text{C}_{15}\text{H}_{11}\text{D}$	0.108
194.1015	$\text{C}_{15}\text{H}_{10}\text{D}_2$	0.1
178.0711	$\text{C}_{14}\text{H}_{10}$	1.0
179.0761	$\text{C}_{14}\text{H}_9\text{D}$	0.231
180.0843	$\text{C}_{14}\text{H}_8\text{D}_2$	0.132

TRIETHYLAMINE ASSISTED PHOTOLYSIS OF 1-BROMOPYRENE

1-bromopyrene (0.2 g, 7.1×10^{-4} moles) was dissolved in cyclohexane (30 cm^3) and triethylamine (4 cm^3) added. The solution was deoxygenated by passing a stream of dry nitrogen through the solution for thirty minutes. The irradiation was carried out in an 'Applied Photophysics' photochemical reactor fitted with low pressure mercury lamps over a ten hour time period. Analysis was performed by high performance liquid chromatography using the following conditions:-

Column : Hypersil O.D.S. 5 Flow rate : 2 cm³ minute⁻¹
Chart speed : 500 mm hour⁻¹ Injection size : 20 μl
Monitoring wavelength : 277 nm.

The analysis showed a conversion of 44% to pyrene.

PHOTOLYSIS OF 1-BROMOPYRENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

1-bromopyrene (0.14g, 4.9×10^{-4} moles) was irradiated for eight hours utilising the same method as for 1-chloronaphthalene. A mass spectrum was taken of a sample of the solution this showed deuterium incorporation. An allowance was made for the natural abundance of ¹³C.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
202.1016	C ₁₆ H ₁₀	1.0
203.2131	C ₁₆ H ₉ D	0.356

PHOTOLYSIS OF PYRENE WITH TRIETHYLAMINE AND DEUTERIUM OXIDE

Pyrene (0.1g, 4.9×10^{-4} moles) was photolysed using a similar method to that used for naphthalene. The solution was irradiated for eight hours and a mass spectrum taken. Deuterium incorporation was observed, an allowance was made for the natural abundance of ¹³C.

<u>Molecular weight</u>	<u>Molecular formula</u>	<u>Deuterium incorporation</u>
202.0790	C ₁₆ H ₁₀	1.0
203.0355	C ₁₆ H ₉ D	0.091

63. PREPARATION OF TRIETHYLOXONIUM HEXAFLUOROPHOSPHATE²³⁷.

Diethylether (167cm³) was placed in a three necked round bottom flask, fitted with a gas inlet tube and a dropping funnel. Triethyl orthoformate (30.3g 0.205 moles) was allowed into the flask which was then flushed with nitrogen. The flask and contents were cooled to -78⁰C and the solution saturated with phosphorus pentafluoride. The reaction mixture was allowed to warm up to room temperature and left overnight. The white crystals formed during this time were collected by filtration under nitrogen and stored at -10⁰C. (Yield 56.9g 112%)

¹H n.m.r. (CDCl₃) 4.6 δ (6H,q); 1.6 δ (9H,t).

64. PREPARATION OF TRIMETHYLOXONIUM HEXAFLUOROPHOSPHATE²³⁷.

Trimethylorthoformate (3.0g 0.028 moles) was placed in a quickfit test tube and dimethylether (15cm³) condensed into it at liquid nitrogen temperature. The test tube was allowed to warm up to -78⁰C and phosphorus pentafluoride bubbled into the mixture until it was saturated. The reaction mixture was allowed to warm up to ambient temperature overnight, during this time a blanket of dry nitrogen was kept over the solution to prevent hydrolysis by water. The yellow solid which formed was collected by filtration and washed with petroleum ether (60 - 80⁰) and dichloromethane. The white crystals were stored at -10⁰C. (Yield 7.5g 130%)

m.p. 165⁰C (decomposed)

Due to the sparing solubility of the salt it could not be identified by spectroscopy and so was characterised by its reaction with phenol.

65. CHARACTERISATION OF TRIMETHYLOXONIUM HEXAFLUOROPHOSPHATE

Trimethyloxonium hexafluorophosphate (0.6g 0.003 moles) was dissolved in dichloromethane (15cm³). Phenol (0.3g 0.003 moles) was added to the suspension and the mixture heated under reflux for nine hours. When cool, water was added to remove excess oxonium salt. The organic layer was washed successively with sodium hydroxide solution (2 molar) and water. The dichloromethane solution was dried (MgSO₄) and the solvent removed on a rotary evaporator to yield a colourless oil. (Yield 0.23g 74%)

¹H n.m.r. (CDCl₃) 7.0 δ (5H,m); 3.8 δ (3H,s).

66. PREPARATION OF DIPHENYLETHYLSULPHONIUM HEXAFLUOROPHOSPHATE²⁴³

Diphenyl sulphide (1.5g, 6.45 x 10⁻³ moles) was added to triethyloxonium hexafluorophosphate (1.65g, 6.6 x 10⁻³ moles). The reaction vessel was attached to a vacuum pump to remove diethyl ether as it was formed. After thirty minutes the crystals which formed were collected by filtration and washed with petroleum ether (60-80°C). Recrystallisation from n-butanol afforded colourless crystals. (Yield 0.15g, 7%)

m.p. 216-217°C

¹H n.m.r. (CDCl₃) 7.65 δ (10H,m); 4.1 δ (2H,q); 1.45 δ (3H,t).

67. PREPARATION OF DIETHYLPHENYLSULPHONIUM HEXAFLUOROPHOSPHATE²⁴³

Thiophenol (0.8g, 7.2 x 10⁻³ moles) was dissolved in acetonitrile (10 cm³), triethyloxonium hexafluorophosphate (3.9g, 0.015 moles) was added and the mixture stirred for one hour under a blanket of nitrogen.

The solution became red as the reaction proceeded. The solvent was removed on a rotary evaporator to leave a red oil which was triturated with diethyl ether. The yellow-brown solid that remained was crystallised from ethanol to afford white crystals.

(Yield 0.59g, 26%)

m.p. 89-90°C

¹H n.m.r. (CD₂Cl₂) 7.95 δ (5H, broad s); 3.6 δ (4H, q); 1.4 δ (6H, t).

I.R. ν max. (KBr disc) 1410, 970.830 cm⁻¹

68. PREPARATION OF S-ETHYLTHIOXANTHYLIUM HEXAFLUOROPHOSPHATE

Thioxanthene (0.5g, 2.5 x 10⁻³ moles) was dissolved in dichloromethane (15 cm³) and triethyloxonium hexafluorophosphate (0.65g, 2.6 x 10⁻³ moles) added. The solution was stirred overnight under a blanket of dry nitrogen. The solvent was removed in vacuo, this left an orange oil which was triturated with diethyl ether. The resultant solid was recrystallised from ethanol to yield a white crystalline material. (Yield 0.38g, 43%).

m.p. 118-119°C

¹H n.m.r. (d⁶ acetone) 7.9 δ (8H, m); 4.7 δ (2H, s); 3.9 δ (2H, q); 1.4 δ (3H, t)

I.R. ν max. (KBr disc) 1400, 970, 825, 750 cm⁻¹

U.V. λ max. (CH₂Cl₂) 275, 285 nm.

Analysis: required C 48.39%, H 4.06%

found C 47.94%, H 4.02%

69. PREPARATION OF S-ETHYLTHIOXANTHONIUM HEXAFLUOROPHOSPHATE²⁴³

Thioxanthone (0.2g, 9.4 x 10⁻⁴ moles) was dissolved in acetonitrile

(20 cm³) and chloroform (2 cm³). Triethylxonium hexafluorophosphate (excess) was added. The mixture was stirred under nitrogen for fourteen hours during which time a white precipitate formed. The precipitated material was collected by filtration, washed with acetonitrile and dried in vacuo. (Yield 0.051g, 14.6%)
m.p. 222-222.5°C

¹H n.m.r. (d⁶ acetone) 8.3 δ (8H,m); 3.8 δ (2H,q); 1.6 δ (3H,t).
I.R. ν_{max}. (nujol mull) 1680, 1580, 1440, 1320, 1150, 1100,
815, 745 cm⁻¹.

70. PREPARATION OF THIOXANTHENE-9-OL

Thioxanthone (2.0g, 9.4 x 10⁻³ moles) was dissolved in methanol (45 cm³) and sodium borohydride (1.3g, 0.034 moles) added. The mixture was heated under reflux for six hours, after cooling the solvent was removed by evaporation. Water (30 cm³) was added slowly and the suspension which formed extracted with diethyl ether (3 x 25 cm³). The ethereal extracts were combined, dried (MgSO₄) and the solvent removed on a Büchi rotary evaporator to leave a yellow solid. The solid was recrystallised from petroleum ether (60-80°C) as pale yellow needles. (Yield 1.05g, 52%).

m.p. 100-102°C

(Lit. m.p. 104-105°C)²³⁸.

¹H n.m.r. (CDCl₃) 7.4 δ (8H,m); 5.4 δ (1H,d); 2.3 δ (1H, broad s).
I.R. ν_{max}. (KBr disc) 3300, 1580, 1430, 1300, 1160, 730 cm⁻¹

71. PREPARATION OF S-ETHYL-9-ETHOXYTHIOXANTHYLIUM HEXAFLUOROPHOSPHATE²⁴³

Thioxanthene-9-ol (0.5g, 2.3×10^{-3} moles) and triethyl-oxonium hexafluorophosphate (1.5g, 6×10^{-3} moles) were dissolved in dichloromethane (12 cm³). The solution was left overnight, during which time the solution changed colour from yellow to red. The solvent was removed in vacuo and the solid which remained was recrystallised from ethanol to afford white crystals.

(Yield 0.47g, 52%)

m.p. 237-239°C

¹H n.m.r. (CD₂Cl₂) 8.8 δ (2H,m); 7.8 δ (4H,m); 7.2 δ (2H,m); 4.4 δ (4H,m);
1.4 δ (6H,m)

I.R. ν max. (KBr disc) 1580, 1430, 1310, 1000, 725 cm⁻¹

72. PREPARATION OF S-METHYLTHIOXANTHYLIUM TETRAFLUOROBORATE

Thioxanthene (0.5g, 2.5×10^{-3} moles) and iodomethane (2.5g, 0.017 moles) were dissolved in 1,2-dichloroethane (20 cm³). A solution of silver tetrafluoroborate (0.5g, 2.6×10^{-3} moles) in 1,2-dichloroethane (15 cm³) was added dropwise with stirring, under nitrogen and in the absence of light. When addition was complete the reaction mixture was stirred overnight at room temperature. The mixture was then filtered through celite filter aid and the solvent removed on a rotary evaporator to leave a pale yellow solid. The solid was triturated with petroleum ether (60-80°C) and the reddish crystals recrystallised from n-butanol to yield white plates. (Yield 0.22g, 29%)

m.p. 184°C

^1H n.m.r. (d^6 acetone) 7.8 (8H,m); 4.7 (2H,s); 3.5 (3H,s);

I.R. ν_{max} . (KBr disc) 2930, 1410, 1280, 1040, 750 cm^{-1} .

U.V. λ_{max} . (CH_2Cl_2) 270, 278 nm.

Analysis : required C 56.03% H 4.36%

found C 55.95% H 4.29%

73. PREPARATION OF S-METHYLTHIOXANTHONIUM TETRAFLUOROBORATE²⁴³

Thioxanthone (0.5g, 2.35×10^{-3} moles) was dissolved in 1,2-dichloroethane (25 cm^3). A solution of iodomethane (3.1g, 0.021 moles) and silver tetrafluoroborate (0.5g, 2.6×10^{-3} moles) in 1,2-dichloroethane (10 cm^3) was added, during this operation the contents of the flask were kept under nitrogen. The mixture was stirred for twenty four hours in the absence of light. The suspension was filtered through celite filter aid. The filtrate, a pale yellow solution, was placed on a rotary evaporator to remove the solvent. The remaining solid was crystallised from 1,2-dichloroethane / diethyl ether as white needles. (Yield 0.45g, 65.5%)

m.p. 219-220°C

^1H n.m.r. ($\text{CF}_3\text{CO}_2\text{H}$) 8.3 (8H,m); 3.8 (3H,s).

I.R. ν_{max} . (nujol mull) 1680, 1580, 1440, 1325, 1310, 1150, 1100, 810, 750 cm^{-1} .

U.V. λ_{max} . (MeOH) 255, 285, 380 nm.

74. PREPARATION OF 4-BENZOYLDIPHENYLSULPHIDE

Benzoyl chloride (7.75g, 0.055 moles) was added to a suspension of aluminium chloride (10g, 0.075 moles) in carbon disulphide. The flask was cooled to 0°C and diphenyl sulphide (10.0g, 0.054 moles) added. The mixture was allowed to warm up slowly to room temperature and then heated under reflux for two hours. When cool, dilute sulphuric acid was added. The organic layer was separated and then washed successively with saturated sodium carbonate solution and water. The carbon disulphide was removed by evaporation in vacuo and the white crystalline material remaining was recrystallised from petroleum ether (60-80°C). (Yield 2.9g, 18.6%)

m.p. 67.5-68.5°C

(Lit. m.p. 70°C)^{23g}.

¹H n.m.r. (CDCl₃) 7.4 δ (14H, m)

I.R. ν max. (nujol mull) 2900, 1670, 1605, 1455, 1300, 860, 805,
745, 715 cm⁻¹.

75. PREPARATION OF S-METHYL, 4-BENZOYLDIPHENYLSULPHONIUM TETRAFLUOROBORATE²⁴³

4-Benzoyldiphenylsulphide (0.2g, 7.0 x 10⁻⁴ moles) was dissolved in 1,2-dichloroethane (10 cm³). Iodomethane (1.45g, 0.01 moles) and silver tetrafluoroborate (0.22g, 1.1 x 10⁻³ moles) in 1,2-dichloroethane were added whilst stirring the mixture. Stirring was continued overnight under nitrogen and in the absence of light. The mixture was then filtered to remove silver iodide and the filtrate evaporated on a rotary evaporator. The solid remaining was crystallised from 1,2-dichloroethane / diethyl ether. (Yield 0.081g, 29.6%)

^1H n.m.r. (CDCl_3) 7.8 s (1H,m); 3.8 s (3H,s);

The compound decomposed on standing in less than one hour.

76. PREPARATION OF S-BENZYLTHIOXANTHONIUM TETRAFLUOROBORATE

Thioxanthone (0.2g, 9.4×10^{-4} moles) was dissolved in dichloromethane (25 cm^3). Benzyl Bromide (1.71g, 0.001 moles) and silver tetrafluoroborate (0.22g, 0.001 moles) in dichloromethane added. The suspension was stirred for twenty four hours in the absence of light and whilst being kept under a blanket of nitrogen. The mixture was filtered through celite filter aid and the solvent removed from the filtrate at the pump. The remaining solid was crystallised from dichloromethane / diethyl ether to afford white crystals. (Yield 0.11g, 30%)

m.p. 215-216°C

^1H n.m.r. (CDCl_3) 8.6 s (2H,M); 7.4 s (13H,m).

I.R. ν_{max} . (nujol mull) 2800, 1630, 1585, 1430, 1320, 1160, 1100,
935, 735 cm^{-1}

The compound decomposed in one hour in the presence of light and air.

77. PREPARATION OF S-n-BUTYLTHIOXANTHYLIUM TETRAFLUOROBORATE ²⁴³

Thioxanthene (0.5g, 2.5×10^{-3} moles) was dissolved in 1,2-dichloroethane (20 cm^3). A suspension of 1-bromobutane (3.43g, 0.025 moles) and silver tetrafluoroborate (0.51g, 2.6×10^{-3} moles) in 1,2-dichloroethane (15 cm^3) added. The contents of the flask were stirred for twenty four hours in an atmosphere of nitrogen in the absence of light. The mixture was filtered

through celite filter aid and the solvent removed in vacuo to yield a red oil. The oil was triturated with petroleum ether (60-80°C) to remove unreacted thioxanthene and then recrystallised from n-butanol as needles. (Yield 0.05g, 6%)
m.p. 179-80°C

^1H n.m.r. (CDCl_3) 7.7 δ (8H,m); 4.5 δ (2H,s); 3.6 δ (2H,t); 1.4 δ (4H,m);
1.1 δ (3H,t).

I.R. ν_{max} . (KBr disc) 2970, 1640, 1585, 1430, 1315, 1170, 730 cm^{-1}

78. PREPARATION OF S-n-HEXYLTHIOXANTHYLIUM TETRAFLUOROBORATE²⁴³

The title compound was prepared using a similar method to that utilised in the previous experiment, except using thioxanthene (0.5g, 2.5×10^{-3} moles), 1-bromohexane (4.15g, 0.025 moles) and silver tetrafluoroborate (0.5g, 2.5×10^{-3} moles).

The compound was recrystallised from n-butanol. (Yield 0.04g, 4.3%)

m.p. 182-183°C

^1H n.m.r. (CDCl_3) 7.7 δ (8H,m); 4.5 δ (2H,s); 3.6 δ (2H,t); 1.6 δ (8H,m);
0.9 δ (3H,t).

79. PREPARATION OF DIPHENYLIODONIUM CHLORIDE¹⁸⁶.

Potassium iodate (20g, 0.093 moles), acetic anhydride (20 cm^3) and benzene (20 cm^3 , 0.2 moles) were placed in a three necked flask fitted with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was cooled to -5°C in a methanol-ice bath and a mixture of sulphuric acid (concentrated) (17 cm^3) and acetic anhydride (20 cm^3) were added dropwise with stirring.

When the addition had been completed the reaction mixture was allowed to warm up to room temperature and stirred for a further forty eight hours, the mixture was then re-cooled. Water (40 cm³) was added, a precipitate formed and this was removed by filtration. The filtrate was extracted with diethyl ether (1 x 30 cm³) and petroleum ether (1 x 30 cm³). Ammonium chloride (10.5g, 0.196 moles) was added to the aqueous solution, a yellow precipitate formed of diphenyliodonium chloride. The solid was collected by filtration and dried in air. (Yield 6.5g, 22%)
m.p. 146-152°C

80. PREPARATION OF DIPHENYLIODONIUM TETRAFLUOROBORATE

Silver oxide was prepared by mixing approximately equimolar solutions of silver nitrate and sodium hydroxide together. The aqueous solution was decanted off and the silver oxide washed several times with distilled water then collected by filtration.

Silver oxide (4.5g, 0.019 moles) and diphenyliodonium chloride (6.5g, 0.02 moles) and water (10 cm³) were mixed intimately with a pestle and mortar. The black-brown slurry which formed was put into a sinter funnel and the precipitate washed with water until approximately 70 cm³ of filtrate was obtained. The filtrate was frozen in a dry-ice / acetone bath (-78°C) and fluoroboric acid (40%) (8 cm³) added. The mixture was allowed to warm up to room temperature and the precipitate which formed was collected by filtration and dried in vacuo. (Yield 3.0g, 43%)

m.p. 134-136°C

(Lit. m.p. 136°C) 186.

81. PREPARATION OF DIPHENYLIODONIUM HEXAFLUOROPHOSPHATE

A solution of diphenyliodonium hydrogen sulphate was added to an equimolar solution of potassium hexafluorophosphate in water. A white precipitate formed, this was collected by filtration, washed with water and dried in vacuo.

m.p. 137-139°C (Lit. m.p. 138-141°C)²⁴⁰.

82. PREPARATION OF S-PHENYLTHIOXANTHYLIUM TETRAFLUOROBORATE¹⁸⁹

Thioxanthene (1g, 0.005 moles), diphenyliodonium tetrafluoroborate (1.89g, 0.005 moles) and copper II chloride (0.1g) were heated to 120 - 125°C for three hours, during this time the mixture was stirred and kept under a blanket of nitrogen. After cooling to room temperature the solid was triturated with diethyl ether several times in order to remove starting material and a by-product. The product was recrystallised from ethanol (Yield 1.23g, 68%)

m.p. 186-187°C

¹H n.m.r. (CDCl₃) 8.3 δ (5H,m); 7.6 δ (8H,m); 4.3 δ (2H,s).

I.R. ν max. (nujol mull) 1640, 1585, 1430, 1320, 1170, 935, 730 cm⁻¹.

CATION PHOTOINITIATION OF POLYMERISATION IN THIN FILMS

The inks and varnishes used in these experiments were printed and cured using the same conditions and equipment as that utilised for the free radical initiated polymerisations of thin films.

TO INVESTIGATE THE OPTIMUM CATIONIC PHOTOINITIATOR CONTENT FOR
POLYMERISATION

An ink was made up using the following formulation:-

45 % Mixture of high and low viscosity epoxy resins

45 % Titanium dioxide pigment

5 % Cycloaliphatic diepoxide diluent

95 %

The remainder of the ink was photoinitiator or cycloaliphatic diepoxide diluent, in different ratios.

The inks were milled on a three roll mill to obtain an even dispersion of pigment and photoinitiator. 0.5 cm³ of each ink was printed onto flamed tin plate. (to remove oil from the surface of the tin,) using a Duncan-Lynch proof print tester. Two coatings were applied, wet on wet. The inks were cured using a conveyer speed of 600 feet per minute. The photoinitiator used for the experiment was diphenyliodonium tetrafluoroborate. A graph is plotted overleaf of the percentage photoinitiator against lamp passes to achieve cure.

<u>Initiator (%)</u>	<u>Lamp passes to tack free</u>	<u>Lamp passes to through cure</u>
1	16	-
2	14	-

Initiator (%)	Lamp passes to tack free	Lamp passes to through cure
3	4	9
4	4	7
5	4	5

TO STUDY THE EFFECT OF DIFFERENT PHOTOINITIATORS ON THE SPEED OF CURE

Inks were made up to the same formulation of pigment and epoxy resins as in the previous experiment. 3% photoinitiator was added and the rest of the ink made up of cycloaliphatic diepoxide diluent. Printing and curing of the inks was also carried out in an analogous manner and the number of passes under the lamp to achieve cure was recorded. (See results and discussion, chapter 4.)

PHOTOLYSIS OF TRIPHENYLSULPHONIUM HEXAFLUOROPHOSPHATE

Triphenylsulphonium hexafluorophosphate (0.03g, 7.4×10^{-5} moles) was dissolved in methanol (3 cm^3). The solution was deoxygenated by three freeze, pump, thaw cycles and sealed under vacuum in a 12 mm. diameter quartz glass tube. Irradiation for 61 hours was carried out in an 'Applied Photophysics' photochemical reactor fitted with a bank of low pressure mercury lamps. The tube was opened and an aliquot of 1 cm^3 was removed and added to diethyl ether (40 cm^3) to precipitate unreacted starting material. After several hours the mixture was filtered through a preweighed sintered crucible, the crystals were dried in vacuo and the sinter reweighed. Gas liquid chromatography was performed on the remaining mixture using a 10% SE 30 column. G.C. mass spectrometry was used to confirm the identity of the products of the photolysis. The yields of products were determined by the use of appropriate standards.

PHOTOLYSIS OF S-METHYLTHIOXANTHYLIUM TETRAFLUOROBORATE

The photolysis was carried out in a similar manner to that described in the previous experiment except using S-methylthioxanthylum tetrafluoroborate (0.0256g, 6.88×10^{-5} moles).

PHOTOLYSIS OF S-ETHYLTHIOXANTHYLIUM HEXAFLUOROPHOSPHATE

The procedure for the irradiation of S-ethyl thioxanthylum hexafluorophosphate was similar to that used for triphenylsulphonium hexafluorophosphate except using (0.0266g, 6.88×10^{-5} moles) of the title compound.

PHOTOLYSIS OF S-PHENYLTHIOXANTHYLIUM TETRAFLUOROBORATE

The photolysis was carried out using the same method as described in the photolysis of triphenylsulphonium hexafluorophosphate, except using S-phenylthioxanthylum tetrafluoroborate (0.026g, 7.18×10^{-5} moles).

PHOTOLYSIS OF S-ETHYLTHIOXANTHONIUM HEXAFLUOROPHOSPHATE

S-ethylthioxanthonium hexafluorophosphate (0.0279g, 7.23×10^{-5} moles) was dissolved in methanol (5 cm^3). The solution was degassed by three freeze, pump, thaw cycles and then sealed into a quartz glass tube. The irradiation was carried out for 61 hours in a 'Rayonet' photochemical reactor fitted with low pressure mercury lamps. The tube containing the solution was opened and a 1 cm^3 aliquot added to benzene (50 cm^3), crystals of starting material were formed over a period of a few hours, these were collected on a preweighed sintered crucible, dried, then weighed. A further aliquot of 1 cm^3 was pipetted into diethyl ether (50 cm^3) and the crystals collected on a sinter and weighed. The amount of crystals represented unchanged starting material and thioxanthone formed in the photolysis. G.C. / mass spectrometry was performed on some of the remaining solution to detect any other products of the photoreaction. (See results section.)

PHOTOLYSIS OF S-METHYLTHIOXANTHONIUM TETRAFLUOROBORATE

The procedure for this photolysis was similar to that employed in the previous experiment, except using S-methylthioxanthonium tetrafluoroborate (0.022g, 7.01×10^{-5} moles).

PHOTOLYSIS OF S-n-BUTYLTHIOXANTHYLIUM TETRAFLUOROBORATE

The irradiation of the title compound was carried out as

described in the photolysis of triphenylsulphonium hexafluorophosphate, except using S-n-butylthioxanthylum tetrafluoroborate (0.0244g, 7.13×10^{-5} moles).

PHOTOLYSIS OF DIPHENYLIODONIUM HEXAFLUOROPHOSPHATE

Diphenyliodonium hexafluorophosphate (0.0292g, 6.85×10^{-5} moles) was dissolved in methanol (5 cm³) and degassed and irradiated by the same method as that used in the photolysis of triphenylsulphonium hexafluorophosphate. The amount of remaining starting material was determined by adding a 1 cm³ aliquot of the photosylate to diethyl ether (50 cm³), the crystals collected, dried and weighed by the same method as described previously. Analysis of the more volatile photoproducts was carried out by gas-liquid chromatography using a 10% SE 30 column. Yields were estimated by the use of standards.

PHOTOLYSIS OF DIPHENYLIODONIUM TETRAFLUOROBORATE

The photolysis was carried out as described in the previous experiment, except using diphenyliodonium tetrafluoroborate (0.029g, 7.88×10^{-5} moles).

83. PREPARATION OF BENZOHYDRAZIDE

Hydrazine hydrate (40 cm³, 40g, 0.8 moles) was dissolved in ethanol (80 cm³). Ethyl benzoate (40g, 0.27 moles) was added and the mixture heated under reflux for four hours. Approximately half the solvent was removed by evaporation and the product allowed to crystallise. The white needles which formed were collected by filtration, washed with ice-cold ethanol, then dried in vacuo. (Yield 22.4g, 62%)

m.p. 111°C (lit.m.p. 112°C)²⁴¹.

84. PREPARATION OF 2,5-DIPHENYL 1,3,4-OXADIAZOLE

Benzohydrazide (20g, 0.147 moles) was added to polyphosphoric acid (400g, excess) and the reaction mixture heated to 170°C. This temperature was maintained for forty minutes. The brown oil was allowed to cool to approximately 80°C and was then poured into ice-water (600 cm³). The mixture was stirred until a yellow-white solid precipitated, this was collected on a sinter and washed with water at about 0°C then dried in air. The white solid was recrystallised from ethanol to afford pink plates. (Yield 5.2g, 32%)

m.p. 136-137°C (Lit.m.p. 137-138°C)²⁴¹.

85. PREPARATION OF XANTHPINACOL

Xanthone (6.0g, 0.033 moles) was dissolved in hot benzene (100 cm³). The solution was added to a mixture of magnesium (4g, 0.16 moles) and iodine (15g, 0.11 moles) in diethyl ether (50 cm³)

and benzene (50 cm³). The mixture was heated until reaction started and was then allowed to cool to room temperature and stirred for a further twelve hours. Water was added to the solution and a yellow precipitate formed this was collected by filtration, washed with benzene to remove unreacted xanthone and recrystallised from toluene to give white plates. (Yield 3.3g, 51%)

m.p. 181-182°C

¹H n.m.r. (CDCl₃) 7.0 δ (16H,m); 3.4 δ (2H,s).

I.R. ν max. (nujol mull) 3540, 2920, 1600, 1470, 1450, 1225,
1060, 885, 765 cm⁻¹.

TO INVESTIGATE THE EFFECT OF SENSITIZERS ON THE RATE OF CURE USING
CATIONIC PHOTOINITIATORS

An ink was made using the following formulation:-

- 45% Titanium dioxide pigment
 - 45% Mixture of epoxide resins
 - 3% Photoinitiator (diphenyliodonium tetrafluoroborate)
-
- 93%

The remainder of the ink was made up of sensitizer and a cycloaliphatic diepoxide diluent. The sensitizer was 2-ethyl-9,10-dimethoxyanthracene. The inks were ground on a three roll mill and printed using the same method as described in previous experiments on thin film polymerisations. The number of passes through the conveyer drier to effect cure was recorded in the following table.

Initiator (%)	Lamp passes to tack free	Lamp passes to through cure
0	4	9
1	4	5
2	4	4
3	3	3
5	3	4

TO INVESTIGATE THE EFFECT OF DIFFERENT SENSITIZERS ON THE RATE OF
CURE OF CATIONIC PHOTOINITIATION OF POLYMERISATION

Inks were made up to the following formulation:-

- 45% Titanium dioxide pigment

45% Mixture of epoxide resins

6% Cycloaliphatic diepoxide diluent

3% Photoinitiator

1% Sensitizer

100%

Each ink was ground on a three roll mill to ensure an equal dispersion of photoinitiator and sensitizer in the ink. The inks were printed and cured by the same method previously described for thin film polymerisations (p 171.)

QUENCHING OF FLUORESCENCE OF 9,10-DIMETHYLANTHRACENE BY
CATIONIC PHOTOINITIATORS

A solution of 9,10-dimethylantracene was made up so that the optical density at 390 nm. was 0.1. The fluorescence spectrum was recorded of this solution with 5 cm³ of solvent added, (dichloromethane). Solutions of quencher were made up and added to a solution of 9,10-dimethylantracene so that the volume of solution was the same. The fluorescence spectrum was recorded. The area under the curve was calculated by cutting out the spectrum and weighing it. The ratio of the area with no quencher to the area with quencher was calculated and a graph plotted of this value against the reciprocal of quencher concentration. (This is a Stern-Volmer plot.) These plots are displayed in the results and discussion section, p150.

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ABSTRACT

A description of the absorption of light by organic molecules and the ways by which the energy gained can be lost by the excited compounds has been presented. The Stern-Volmer equation has also been described.

Free radical photoinitiation of polymerisation has been reviewed. An investigation has been carried out of ketone / amine photoinitiation of polymerisation of thin film and bulk polymerisations of acrylate esters. The photoreduction and photooxygenation of the amines used in the polymerisations, α - ω -dimorpholinoalkanes α - ω -N,N,N,N-tetraethyldiaminoalkanes and others have been carried out in an attempt to rationalise the observations made in the polymerisation experiments.

The dehalogenation of aryl halides has been described. The photolysis of ω -(4-halophenoxy)alkyl bromides and ω -phenoxyalkyl halides has been carried out and evidence presented for the nature of the excited state responsible for reaction. Criteria for the intervention of radical ions in the photoreactions of aromatic halides with triethylamine have been given and where appropriate evidence for the intermediacy of such species has been presented. The photo-Claisen rearrangement has been studied and the effect of hydrogen bromide on the reaction investigated.

The photoinitiation of cationic polymerisation by sulphonium and iodonium salts has been reviewed and a study carried out of thin film polymerisations in printing inks. The photochemistry of triaryl-sulphonium, thioxanthylum and diaryliodonium salts in methanol have been examined and a mechanism proposed for the decomposition. The photosensitization of photoinitiated cationic polymerisation has been investigated and Stern-Volmer plots recorded of the quenching of their fluorescence by cationic photoinitiators carried out.