The Photosensitised Oxidation of Amines.

A thesis presented for the degree of Doctor of Philosophy
in the Faculty of Science of the University of Leicester
by
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August 1971.

Statement.

The experimental work in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1968 and August 1971. The work has not been presented, and is not currently being presented for any other degree.

R.F. Bartholomew

University of Leicester,
August 1971.

The following published work is submitted in support of this thesis:

R.F.Bartholomew and R.S.Davidson, Chem. Commun., 1970, 1174.

R.F.Bartholomew and R.S.Davidson, J. Chem. Soc. (C), 1971, 2342, and 2347.

R.F.Bartholomew, R.S.Davidson, and M.J.Howell, J. Chem. Soc. (C), In press.

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R.F.Bartholomew.

Contents.

Section One: INTRODUCTION

Turro[1] conveniently divides the chronology of a photochemical sequence into three stages:

1. Absorption of light to produce an electronically excited state.
2. Primary photochemical processes; that is, processes involving excited states.
3. Thermal reactions of the various chemical species produced by the primary processes.

It is useful to discuss briefly the formation and nature of excited states before considering in more detail the primary processes and subsequent reactions that occur in photosensitised oxidations.

1.1. EXCITED STATES AND PHOTOPHYSICAL PROCESSES.

Electronic absorption falls generally in the region between 750 nm. in the red end of the visible spectrum to around 120 nm. in the far ultraviolet. Light useful for solution photochemistry is usually in the range 750 nm. to 200 nm. because of solvent absorption in the ultraviolet region. When a molecule absorbs light in this region, an electron from a filled or partially filled orbital in the molecule is promoted to an orbital of higher energy. This is a quantised process and is governed by selection rules.[2,3]

Electronic transitions of importance in photochemistry are usually those involving the orbitals of higher energy in a molecule. These higher molecular orbitals in, for example, formaldehyde, are:

$$(\pi_{co})^2\ (n_o)^2\ (\pi^*_{co})^o\ (\sigma^*_{co})^o$$

The orbitals are shown in order of increasing energy and the superscripts denote the electron distribution in the ground state. Clearly four transitions are schematically possible, but usually only two of these are involved in the photochemistry of carbonyl compounds. These are $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions, i.e.

Transitions	Configuration
$n \longrightarrow \pi^*$	$(\pi_{co})^2\ (n_o)^1\ (\pi^*_{co})^1\ (\sigma^*_{co})^o$
$\pi \longrightarrow \pi^*$	$(\pi_{co})^1\ (n_o)^2\ (\pi^*_{co})^1\ (\sigma^*_{co})^o$

Formaldehyde has a singlet ground state, that is, the spins of the electrons in the ground state orbitals are all paired. Most other organic molecules also have singlet ground states. The most probable electronic transitions are those in which spin inversion does not occur.[1,2,3] So the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions in formaldehyde produce species in which the spins of the electrons in the singly occupied orbitals are also paired. That is, the initial states formed on excitation are singlet states.

Each electronic state of a molecule has associated with it various allowed vibrational levels. As a consequence of the Franck-Condon principle[3] absorption of light usually produces an electronic state in a high vibrational level. This excess vibrational energy is usually lost rapidly to the surroundings within the time span of a few molecular vibrations.

The primary processes that an excited singlet state may be involved in are of four main types:

1. Fluorescence: the molecule may lose its excess electronic energy by emitting light to return to the ground state.
2. Internal conversion to the ground state: the excitation energy is dissipated as heat to the surroundings.
3. Chemical reaction: the excited state may react with, or transfer the whole of its electronic energy to, another molecule; or the excited state may react intramolecularly to produce new chemical species.
4. Intersystem crossing: an electron in a singly occupied orbital may invert its spin to produce a triplet state.

Triplet states are invariably of lower energy than the corresponding singlet states because of the reduced electron-electron repulsion following the Pauli principle.[1,2] Triplet states undergo similar primary processes to singlet states. They may phosphoresce, losing their electronic energy by light emission. They may revert to the ground state in a radiationless conversion, dissipating their energy as heat, or they may react chemically either intramolecularly or bimolecularly.

The energy relationship between electronic states, and some of the primary processes that can occur, can be represented conveniently on a diagram of the type first used by Jablonski.[2,4] (fig. 1).

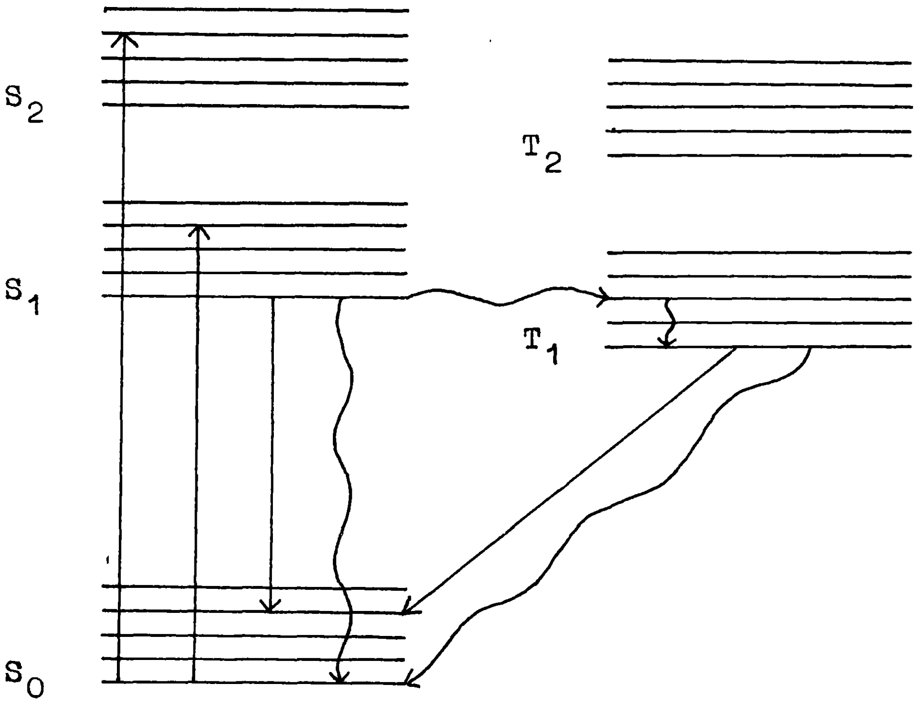


Figure 1. Typical energy level diagram for an aliphatic carbonyl compound. Wavy lines indicate radiationless processes; straight lines indicate radiative processes.

Little information is available on the radiationless transition $S_1 \longrightarrow S_0$. There is some evidence that this process is unimportant for aromatic hydrocarbons,[5] but this is probably not true for many other classes of compound.[6,7]

Intersystem crossing is thought to be an isothermal process, promoted by strong coupling between the lowest vibrational levels of the singlet state and the iso-energetic vibrational levels of a triplet state. Fluorescence is not observed from aromatic carbonyl compounds such as benzophenone. However, the quantum yield of phosphorescence from benzophenone is close to unity, so intersystem crossing must be extremely efficient. In carbonyl compounds, the energy separation between the first excited singlet and triplet states is small,[2] and intersystem crossing is enhanced by the strong vibrational coupling that results from this small energy difference. For compounds where the π,π^* triplet lies below the n,π^* singlet, another factor is important. El-Sayed has shown that the vibrational overlap integrals for non-radiative transitions between states of different electronic origin are an order of magnitude greater than for transitions between states of the same electronic origin. The rate of intersystem crossing from $S_1(n,\pi^*)$ to $T(\pi,\pi^*)$ is therefore a factor of 10^3 greater than the rate of crossing from $S_1(n,\pi^*)$ to $T(n,\pi^*)$.[8]

For the analogous radiationless conversion of T_1 to S_0, the large energy difference between the states precludes strong vibrational coupling and this process is very slow.[9] Radiative deactivation of the triplet state is also slow because of the barrier imposed by the necessity for an electron spin inversion. The inefficiency of modes of deactivation of triplet states means that the lifetimes of these states are generally much longer than those of singlet states. Triplet states of typical organic molecules have lifetimes in the range 10^{-6}-1 sec.. Triplet states are therefore extremely important in photochemistry because their long lifetimes enable them to take part in bimolecular chemical reactions.

1.2. PHOTOSENSITISATION.

The irradiation of a solution containing stilbene and a photosensitiser such as benzophenone, 1,2-benzanthrone, or eosin under conditions such that only the sensitiser absorbs the incident light, results in the cis-trans isomerisation of the stilbene.[10] The photosensitiser is recovered quantitatively. Photosensitisers can be seen to behave somewhat like catalysts: they undergo no permanent chemical change, but are excited by photon absorption and enter a sequence of processes which result in their regeneration at the end of the cycle.

There are two mechanisms of photosensitisation:

1. The excited state of the sensitiser may transfer its electronic energy to an acceptor molecule. The excited state of the acceptor so formed can then undergo the usual deactivation processes.
2. The excited state of the sensitiser may interact with the substrate to form radicals.

The photosensitised isomerisation of stilbenes is considered to occur by an energy transfer mechanism,[10] though the intermediacy of biradical species has been implicated in some cases where the energy of the sensitiser is below that required for energy transfer to the stilbene.[11]

Sensitisation by Energy Transfer.

A general condition for efficient energy transfer is that the energy of the excited state of the acceptor is below that of the sensitiser. When the energy levels of sensitiser and acceptor are close, transfer becomes inefficient, probably because of reverse energy transfer from the acceptor to the sensitiser.[12,13]

Energy transfer can occur between two molecules in molecular contact, where, because of overlap of the electron clouds of the two molecules, an electron exchange may occur: the electron in a high energy orbital in the sensitiser may find itself in a high energy orbital associated with the acceptor. This exchange mechanism of energy transfer has been treated theoretically by Dexter.[14] Singlet-singlet and triplet-triplet energy transfer can occur by this mechanism. For example, the irradiation of a solution of a suitable sensitiser (diethyl ketone, phenanthrene, naphthalene) and biacetyl, under conditions where only the sensitiser absorbs the incident light, results in quenching of the sensitiser fluorescence, accompanied by the sensitisation of biacetyl fluorescence.[15,16] The Stern-Volmer constants[a] for sensitisation and quenching are found to be comparable. Triplet-triplet energy transfer can be detected by the sensitisation and quenching of biacetyl phosphorescence.[12,13] Flash photolysis has also been used to detect triplet-triplet energy transfer[17] and the isomerisation of stilbenes mentioned above is a particularly interesting example of a photosensitised reaction involving triplet-triplet energy transfer.

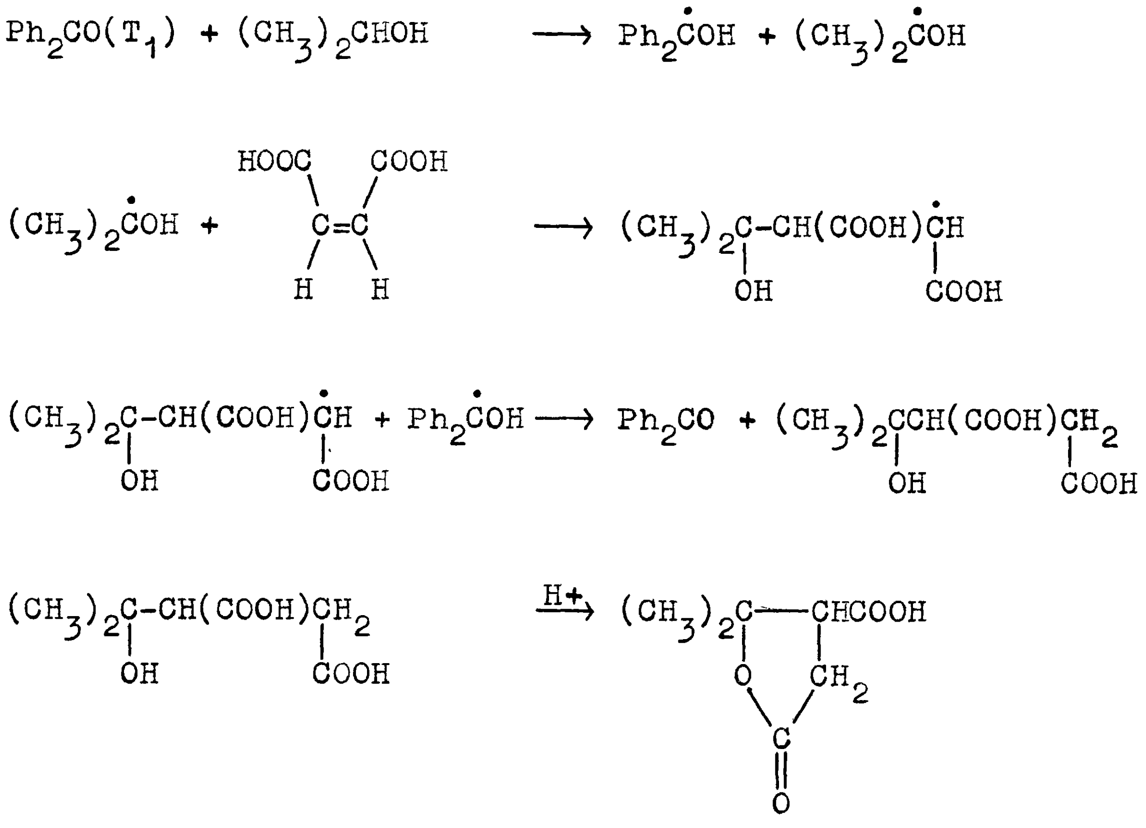
Since the efficiency of exchange energy transfer depends on bimolecular contact, it will obviously be effected by solvent viscosity. In a rigid glass, molecular diffusion

[a] See appendix 1.

should be particularly inhibited, yet singlet-singlet energy transfer has been detected in glasses[18] from low concentrations of sensitisers and acceptors, where nearest neighbour interactions are minimal. The theoretical treatment of a mechanism which allows energy transfer to occur over large distances has been presented by Forster.[19] The treatment that he presents predicts the occurrence of singlet-singlet and triplet-singlet energy transfer by this resonance mechanism. Triplet-singlet energy transfer has recently been postulated in some systems following chemiluminescent reactions.[20]

Sensitisation by Radical Formation.

Photosensitisation via radical formation is known in a number of systems. One example is the formation of terebic acid, by the benzophenone sensitised addition of isopropanol to maleic acid.[21,22] This involves hydrogen abstraction from isopropanol, by triplet benzophenone, to give a radical ($(CH_3)_2\dot{C}OH$) which adds to the double bond of maleic acid. The monoradical formed in this step abstracts a hydrogen atom from the hydroxydiphenylmethyl radical ($Ph_2\dot{C}OH$), thus regenerating the sensitiser, and the adduct loses water to give terebic acid (I). These steps are outlined in scheme 1. Schenck refers to this type of mechanism, involving only monoradicals in the propagation and termination steps, as a 'Type 1' process.[23,24] In contrast, he denotes as 'Type 2' processes mechanisms which involve biradicals. For example, Schenck proposes that the benzophenone photosensitised dimerisation



$$Ph_2CO(T_1) + (CH_3)_2CHOH \longrightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

$$(CH_3)_2\dot{C}OH + HOOC\text{-}CH{=}CH\text{-}COOH \longrightarrow (CH_3)_2C(OH)\text{-}CH(COOH)\dot{C}H(COOH)$$

$$(CH_3)_2C(OH)\text{-}CH(COOH)\dot{C}H(COOH) + Ph_2\dot{C}OH \longrightarrow Ph_2CO + (CH_3)_2C(OH)CH(COOH)CH_2(COOH)$$

$$(CH_3)_2C(OH)\text{-}CH(COOH)CH_2(COOH) \xrightarrow{H+} \text{I}$$

I

Scheme 1. The benzophenone sensitised addition of isopropanol to maleic acid. (Type 1 process).

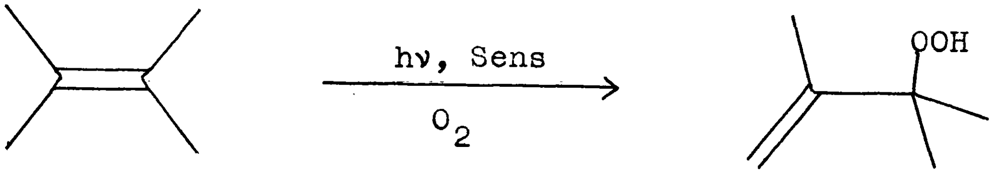
of maleic anhydride is a 'Type 2' process. The mechanism of Schenck's 'Type 2' process is essentially the same as that originally proposed by Schonberg.[25]

Sensitiser ⟶ •Sens• (biradical)
•Sens• + Acceptor (A) ⟶ (•Sens---A•) (biradical)
(•Sens---A•) + A ⟶ A-A + Sensitiser

Excimers and exciplexes[26] which are currently so popular in photochemical mechanisms have some similarity with Schenck's sensitiser-acceptor complex above.

1.3. PHOTOSENSITISED OXIDATION REACTIONS.

Molecular oxygen has a profound effect on a photochemical reaction. For example, irradiation of an anaerobic solution of benzophenone in isopropanol yields benzpinacol and acetone,[22,27] but in oxygenated solution, isopropanol hydroperoxide, hydrogen peroxide and acetone are obtained and the benzophenone is recovered.[27,28] Irradiation of oxygenated solutions of an olefin (with allylic hydrogen atoms) and a dye such as eosin, rose bengal, or methylene blue, results in the conversion of the olefin into an allylic hydroperoxide. For example, under these conditions, 2,3-dimethylbut-2-ene reacts to give 2,3-dimethyl-3-hydroperoxybut-1-ene:[29]

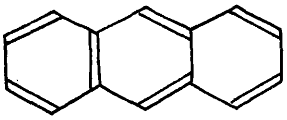
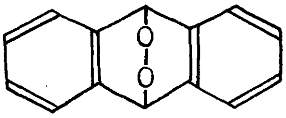
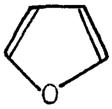
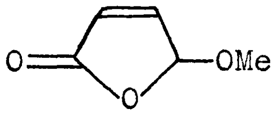
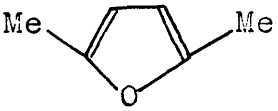
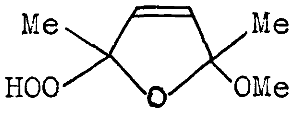
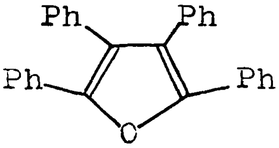
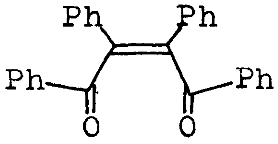
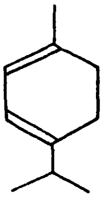
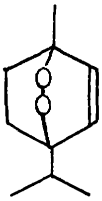
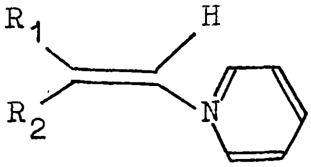
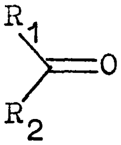
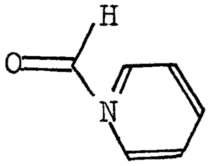
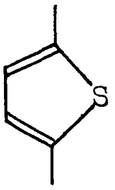
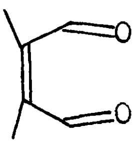
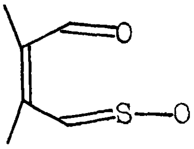


In the absence of oxygen no reaction is observed. Products formed by the photosensitised oxidation of other compounds are shown in table 1. Several useful reviews are available covering the photosensitised oxidation of these and other compounds.[39-45]

Mechanisms of Photosensitised Oxidation.

Benzophenone is photoreduced efficiently by alcohols in anaerobic solution.[22] The primary process in this reaction is the abstraction, by the benzophenone triplet state, of a hydrogen atom from the alcohol. Consequently Gollnick and

Table 1. Products from the photosensitised oxidation of various compounds.

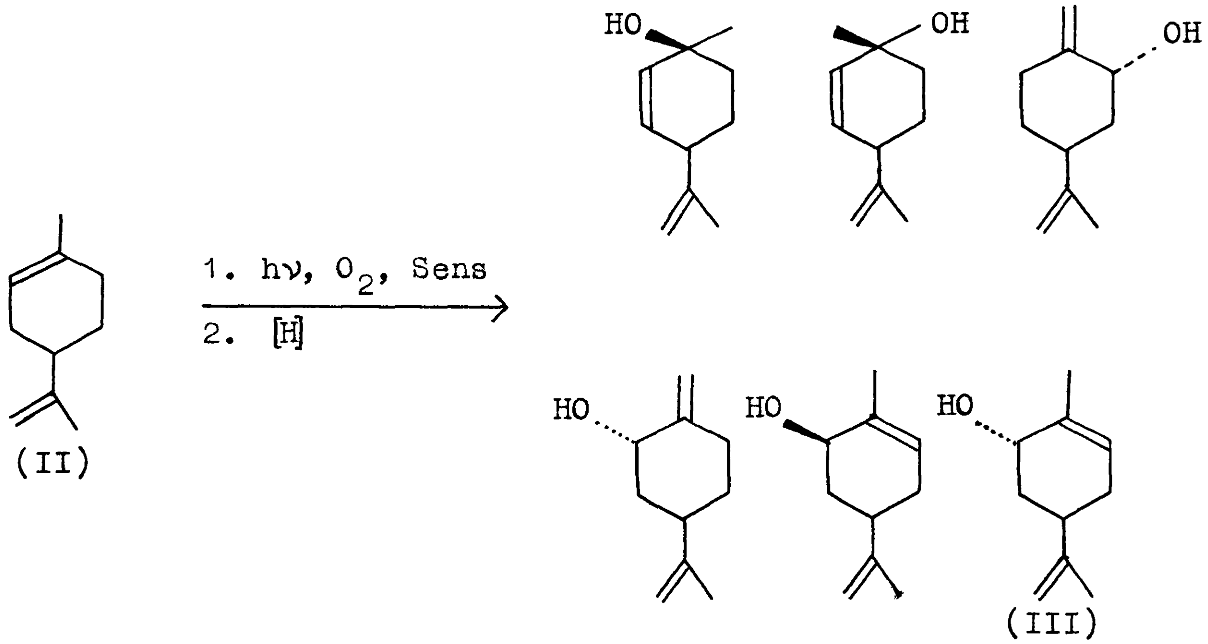
Ref.	Compound		Product
30-32			
34		Methanol adducts of initial peroxide.	
34			
35			
33	 α terpinene		 ascaridole
36			 
37			 
38	CH_3CH_2OH		CH_3CHO CH_3COOH H_2O_2

Schenck suggested that the primary process in the benzophenone photosensitised oxidation of isopropanol was also hydrogen abstraction,[23,24] and that the oxidation was a 'Type 1' process. Their mechanism is as follows.

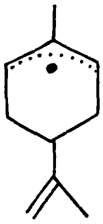
$$
\begin{array}{llll}
B(T_1) & + AH & \longrightarrow \dot{B}H & + \dot{A} \\
\dot{A} & + O_2 & \longrightarrow AOO^{\bullet} & \\
AOO^{\bullet} & + AH & \longrightarrow AOOH & + \dot{A} \\
AOO^{\bullet} & + \dot{B}H & \longrightarrow AOOH & + B
\end{array}
$$

An essential feature of this mechanism is that the excited sensitiser reacts with the alcohol to produce radicals which subsequently react with oxygen to give, ultimately, the observed products.

A completely different type of mechanism operates in the photo-oxidation of olefins sensitised by dyes. A particularly interesting example of this reaction is the photosensitised oxidation of limonene (II). Six products are obtained.[46]



The alcohol (III) is consistently optically pure with all sensitisers used. This stereospecificity rules out the intermediacy of allylic free radicals, because the allylic radical (IV), which would be the precursor of (III), is optically inactive and would lead to racemic products.



(IV)

Schenck, who has made a vast contribution to this field, advocated the view that these reactions were analogous to the 'Type 2' processes discussed earlier:[23] the formation of a biradical addition complex between the sensitiser and oxygen was proposed. This adduct, or 'moloxide', would transfer oxygen to a substrate molecule (A) via a collision complex which would then collapse to ground-state sensitiser and AO_2.

$$\mathrm{Sens} + h\nu \longrightarrow {}^{\bullet}\mathrm{Sens}^{\bullet}$$
$${}^{\bullet}\mathrm{Sens}^{\bullet} + O_2 \longrightarrow {}^{\bullet}\mathrm{Sens{-}O_2}^{\bullet}$$
$${}^{\bullet}\mathrm{Sens{-}O_2}^{\bullet} + A \longrightarrow AO_2 + \mathrm{Sens}$$

The stereospecificity of the reaction was assumed to result from the steric requirements of the sensitiser-oxygen complex.

This mechanism however, does not explain Kautsky's results.[47] He showed that when the sensitiser and substrate molecules were fixed some distance away from each other, by absorbing each separately on silica or alumina, the active species in the photo-oxidation was able to diffuse between them. He proposed that this active species was molecular oxygen in an excited singlet state (see figure 2.) formed by energy transfer from the excited sensitiser. The Kautsky energy transfer mechanism was finally established by the work of Foote and Wexler[48] and Corey and Taylor.[49]

Foote and Wexler showed that singlet oxygen, produced by the action of sodium hypochlorite on hydrogen peroxide, reacts with olefins to give the same products as obtained in the dye-photosensitised oxidation.[48] Moreover, in the case of limonene, where several products are formed in the photo-oxidation reaction, the same product distribution and stereospecificity is obtained in the hydrogen peroxide/sodium hypochlorite reaction.[50]

Corey and Taylor[49] showed that a series of anthracenes could be converted into the corresponding 9,10-endoperoxides by reaction with singlet oxygen produced by an electrodeless discharge.

Since this work was published, the 'e.s.r.' spectrum has been recorded, of singlet oxygen ($^1\Delta_g$) produced by the irradiation of a mixture of oxygen and naphthalene vapour,[52,53] thus showing conclusively that singlet oxygen can be produced by transfer of electronic energy from an excited sensitiser molecule to ground state oxygen. Evidence has also been presented showing that the excited state of the sensitiser involved in the transfer process, is the triplet.[54]

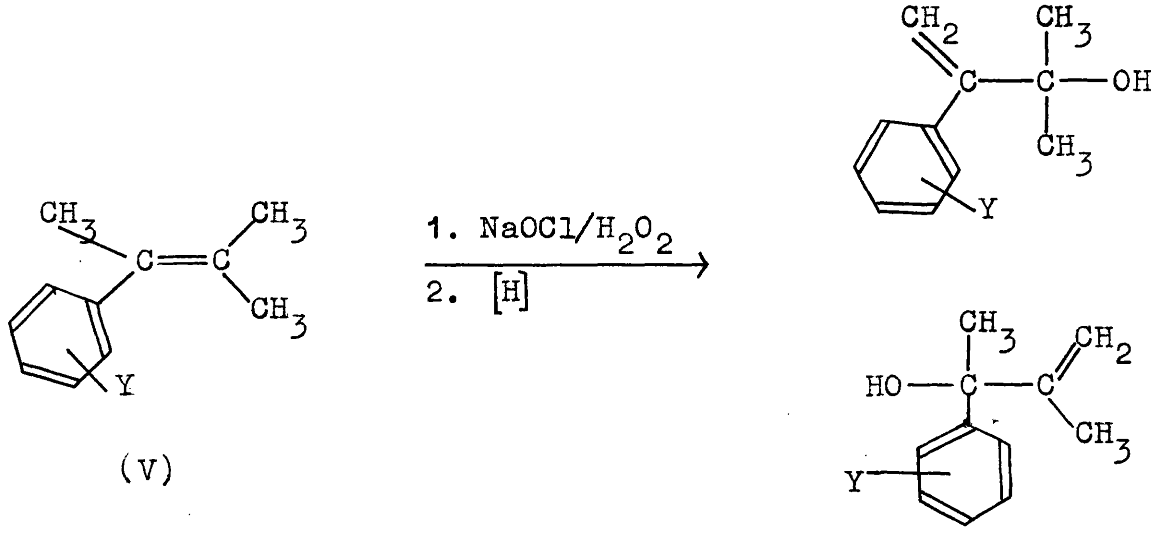
State	Energy	Configuration
$^1\Sigma_g^+$	1.60eV (38k.cal)	$(\ )(\pi_{g2p})^{\uparrow}(\pi_{g2p})^{\downarrow}$
$^1\Delta_g$	0.98eV (22k.cal)	$(\ )(\pi_{g2p})^{\downarrow\uparrow}(\pi_{g2p})$
$^3\Sigma_g^+$	Ground State	$((\text{Inner Shell})(\sigma_{g2p})^2(\pi_{u2p})^4)(\pi_{g2p})^{\uparrow}(\pi_{g2p})^{\uparrow}$

Figure 2. The electronic states of oxygen.[51]

The Chemistry of Singlet Oxygen.

The reaction of chemically generated singlet oxygen with trimethylstyrene (V) has been examined.[43] The effect on the reaction rate and product distribution, of a variety of meta and para substituents was determined. The product distribution was uneffected by substituents, but electron donating substituents appeared to increase the rate of reaction.

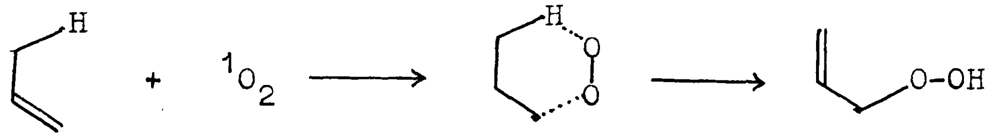
The effect of different solvents on the photosensitised oxidation of 2-methylpent-2-ene was minimal.[43] These results are difficult to interpret quantitatively, but they suggest that singlet oxygen is a somewhat electrophilic reagent.



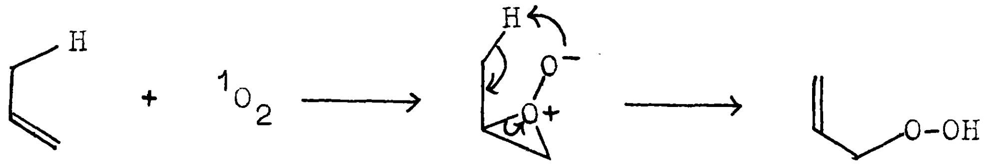
(V)

Three mechanisms have been proposed for the addition of singlet oxygen to olefins:

1. Formation of a cyclic transition state in a type of 'ene' reaction.[55]

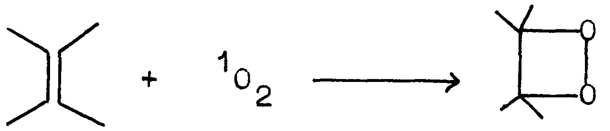


2. Formation of a perepoxide (VI) was suggested by Kopecky.[56]

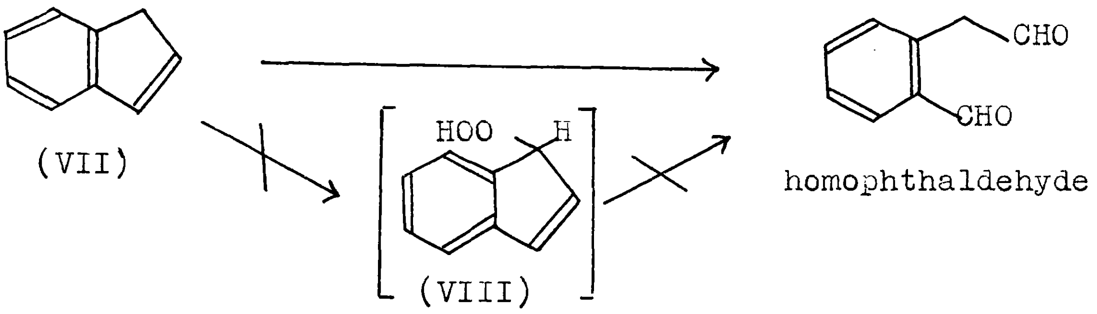


(VI)

3. 1,2 cycloaddition to form a dioxetane.[43]



Indene (VII) is a compound which yields exclusively carbonyl compounds on photo-oxygenation.



It was assumed that an intermediate in this reaction would be the corresponding allylic hydroperoxide (VIII). However, this hydroperoxide was shown to be stable under the reaction conditions and to revert slowly, on heating, to 1-indanone.[57] So the fact that the hydroperoxide (VIII) is not the precursor of homophthaldehyde, rules out the 'ene' mechanism for attack of singlet oxygen on these compounds.

The observation that it is possible to trap intermediates in these reactions using azide ion[58] shows that the reactions must involve intermediates susceptible to attack by nucleophiles. Moreover, dioxetanes of alkyl substituted olefins have been prepared and are known to decompose thermally to yield only carbonyl fragments.[59] It is therefore suggested by Kearns,[58] that in the reaction of singlet oxygen with olefins, carbonyl products arise from dioxetane intermediates and hydroperoxides from perepoxide intermediates.

The role of singlet oxygen in biological systems is being investigated in a number of laboratories. Singlet oxygen has been implicated in the photodynamic action[60] of several substrates. In particular, the photosensitised oxidation of several purine bases has been shown to involve singlet oxygen.[61] Carotenoids have been shown to quench singlet oxygen effectively.[62] Carotenoids are also known to protect living organisms against photodynamic damage[63,64] and it has been found that the efficiency of singlet oxygen quenching by carotenoids parallels the efficiency of the carotenoids for biological protection.[65] This aspect of singlet oxygen chemistry will probably attract considerable attention in the future.

Photo-oxidation involving Radical Formation.

The mechanism of the benzophenone photosensitised oxidation of isopropanol has already been discussed. This mechanism is very similar to the one proposed in Bolland and Cooper's classic study of the photo-oxidation of ethanol sensitised by anthraquinone 2,6-disodium sulphonate.[38] The products of this reaction were found to be acetaldehyde, acetic acid and hydrogen peroxide, and it was suggested that the mechanism must explain three basic observations:

1. The reaction is a non-chain process. This was based on the observations that the quantum efficiency of oxygen uptake is unity and those of product formation are fractional. Furthermore, the rate of oxygen uptake was found to be insensitive to temperature variations and reactant concentrations.
2. Acetic acid and acetaldehyde are formed directly from the alcohol.
3. The photosensitiser operates by cyclic mechanism enabling large numbers of oxygen molecules to take part in photo-oxidation without concomitant destruction of the sensitiser.

The mechanism that they proposed is as follows:

$$\begin{aligned}
&A^{*} + RH \longrightarrow AH\cdot + R\cdot \\
&R\cdot + O_2 \longrightarrow R\dot{O}_2 \\
&\dot{A}H + O_2 \longrightarrow A + H\dot{O}_2 \\
&R\cdot + A \longrightarrow \dot{A}H + \text{aldehyde.}
\end{aligned}$$

$$\left.\begin{array}{l} 2R\dot{O}_2 \\ 2H\dot{O}_2 \\ R\dot{O}_2 + H\dot{O}_2 \end{array}\right] \longrightarrow \text{Products.}$$

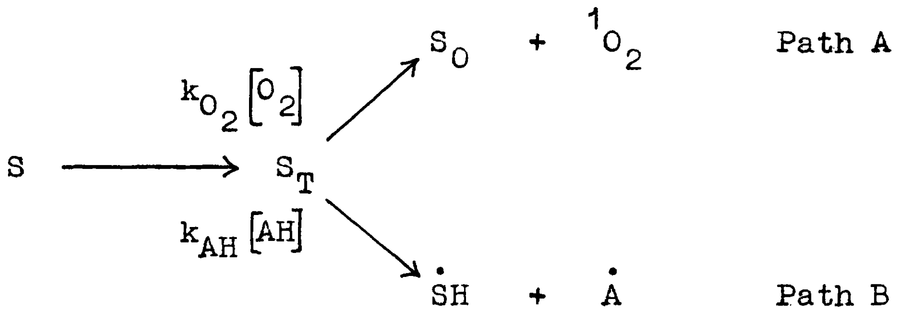
The isolation of isopropanol hydroperoxide in the benzophenone photosensitised oxidation of isopropanol,[27,28] points to the intermediacy of a hydroperoxide in the photo-oxidation of ethanol. However, the primary process in Bolland and Cooper's mechanism, and in the one proposed by Schenck for the photo-oxidation of isopropanol, is hydrogen abstraction from the alcohol by the sensitiser. Both mechanisms also include the subsequent reaction of the alcohol radicals with oxygen. The reaction of radicals with oxygen is an extremely well documented process in thermal autoxidations,[66] and in the photo-oxidation of aldehydes[67] and amides,[68] where the operation of a chain mechanism of the type shown in scheme 2 is well known.

$$\begin{aligned}
&\rightarrow R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \\
&\quad RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}
\end{aligned}$$

Scheme 2. Propagation steps in a chain mechanism of oxidation.

Although the nature of the excited state of the sensitiser involved in the photosensitised oxidation of ethanol was not discussed by Bolland and Cooper, it is reasonable to assume that it is the triplet.[69]

A clear difference is therefore discernible between photosensitised oxidation reactions involving radicals, and those involving singlet oxygen. In singlet oxygen reactions, the primary process involves the interaction of the triplet sensitiser with oxygen, (path A) whereas the primary process in radical reactions is the interaction of excited sensitiser with the substrate (path B).



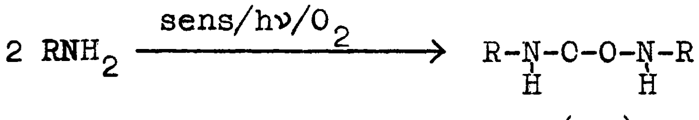
Alcohols do not react with singlet oxygen,[42] nevertheless in the photosensitised oxidation of alcohols, the competition between paths A and B will still occur; reaction of the sensitiser with oxygen will merely quench the oxidation of the alcohol. Obviously the relative efficiencies of each path will depend on the rate constants k_{O_2}, k_{AH}, and on the concentration of oxygen and substrate.

Bolland and Cooper omitted an oxygen-quenching step in their kinetic scheme. It is now known that anthraquinone triplet is quenched by oxygen to give singlet oxygen.[52] However, under the conditions of high alcohol concentration and low oxygen pressures used by Bolland and Cooper for much of their work, the rate of oxygen quenching would probably be small compared to the rate of hydrogen abstraction.

In the photo-oxidation of ethanol sensitised by benzophenone, the yield of acetaldehyde decreases as the oxygen concentration is increased.[27,39] This result is readily explained in terms of the increased importance of path A, oxygen quenching, compared to path B, at high oxygen concentrations.

1.4. THE PHOTOSENSITISED OXIDATION OF AMINES.

Gaffron[70] showed that the irradiation of an oxygenated solution of a sensitiser and amines, led to consumption of oxygen. Oxygen was liberated from the irradiated solution on addition of manganese dioxide. Gaffron suggested that an amine peroxide (IX) was formed.



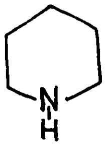
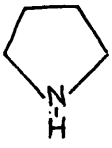
$$2\ RNH_2 \xrightarrow{sens/h\nu/O_2} R\text{-}\underset{H}{N}\text{-}C\text{-}O\text{-}\underset{H}{N}\text{-}R$$

(IX)

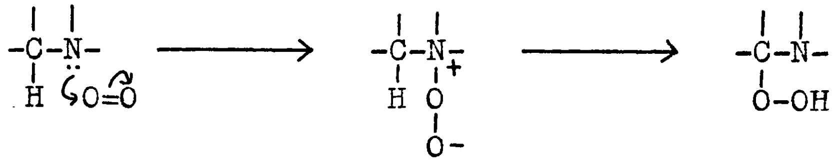
However, Schenck[71] showed that in the photo-oxidation of amines sensitised by rose bengal or haematoporphryn, the amount of oxygen consumed was dependent on the number of α hydrogen atoms that the amine contained. (See table 2) These results indicate that Gaffron's peroxides are probably α-hydroperoxides. It was also found that aldehydes were formed on reduction of the irradiated solutions.[44]

Weil and Mather[72] found that irradiation of oxygenated solutions of amines and methylene blue led to consumption of oxygen, and that the rate of oxygen-uptake was least for primary amines, and increased in the order primary $<$ secondary $<$ tertiary. They also claimed to have isolated a high yield of trimethylamine N-oxide after the irradiation of an oxygenated aqueous solution of methylene blue and trimethylamine.

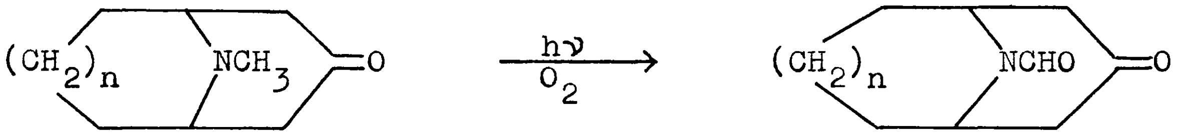
Table 2. Maximum oxygen consumption by amines.[71]

Amine	Oxygen Consumed
CH_3NH_2	1 mole O_2
$CH_3CH_2CH_2NH_2$	
$(CH_3)_2CHNH_2$	
$(CH_3)_2CHCH_2NH_2$	
$C_6H_5CH_2NH_2$	
$(CH_3CH_2)_2NH$	2 moles O_2
 	
$(CH_3CH_2)_3N$	2.6 moles O_2
$(CH_3)_3CNH_2$	no reaction

Gollnick[44] suggested that these reactions involved singlet oxygen. He proposed a mechanism which involved initial electrophilic attack by singlet oxygen on the nitrogen atom of the amine (a step reminiscent of perepoxide formation) followed by a C-H insertion reaction.



Singlet oxygen has been proposed as the active species in the conversion of the N-methyl groups in pseudopelletierine and tropinone to N-formyl groups, by either direct or senstised photo-oxidation.[73]



n=1 pseudopelletierine
n=0 tropinone

This reaction does not occur with singlet oxygen generated by the hypochlorite/hydrogen peroxide method.

Some steroidal tertiary amines have also been shown to give carbonyl compounds on photo-oxidation.[74] The authors of this work were not sure whether singlet oxygen was involved.

The proposition that singlet oxygen is involved in the photo-oxidation of amino compounds must be questioned however, in view of the recent reports that some tertiary amines efficiently quench singlet oxygen, without themselves being consumed.[75] 1,4-Diazabicyclo[2,2,2]octane, N,N'-tetramethylethylenediamine, and N-allylpiperidine were all found to be chemically unreactive towards singlet oxygen, generated by chemical or photochemical means, or by an electrodeless discharge. Yet all these amines were found to retard the photo-oxygenation of typical singlet oxygen acceptors. Other workers[76] examined the interaction between singlet oxygen, generated by a microwave discharge, and primary, secondary, and tertiary methylamines and ethylamines. They confirmed that amines quenched singlet oxygen, and that no oxidation products were formed. The rate constants for the quenching process were found to correlate with the ionisation potentials of the amines. Consequently, it was proposed that quenching involved a reversible electron transfer process.

The Object of this Work.

The object of this work is to determine the mechanism of the photosensitised oxidation of amines; in particular, to discover whether or not singlet oxygen is involved.

Section Two: RESULTS AND DISCUSSION

2.1. THE PHOTO-OXIDATION OF AMINES SENSITISED BY BENZOPHENONE.

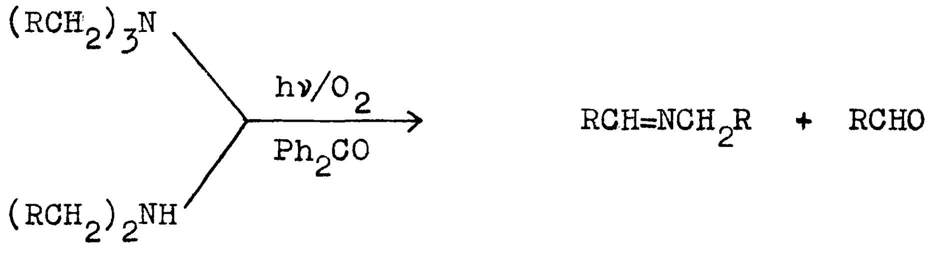
It was mentioned in the previous section that benzophenone sensitises the photo-oxidation of alcohols. Other aspects of the photochemistry of benzophenone have been studied in great detail.[1,2] In anaerobic solution, benzophenone is photoreduced by alcohols,[22,27,77-81] hydrocarbons,[82,83] and amines.[84-88] Photoreduction by primary and secondary amines containing αC-H groups leads to benzpinacol, and imines derived from the corresponding amine. Photoreduction by tertiary amines yields benzpinacol and mixed coupling products. A lot of evidence has been accumulated to show that the photochemically reactive state in these photoreductions is the benzophenone triplet.[77,78,89]

2.1.1. RESULTS.

Product Studies.

Irradiation of oxygenated benzene solutions of amines and benzophenone, produced products formed by oxidation of the amine. These products are shown in table 3.

Aliphatic secondary and tertiary amines gave imines and aldehydes as major products.



For example, both tri-n-propylamine and di-n-propylamine gave propionaldehyde and N-propylpropionaldimine. Tertiary amines also gave small yields of amides. Only aldehydes were isolated from primary aliphatic amines.

Tertiary aromatic amines were dealkylated to give primary and secondary anilines. Aldehydes and amides were also obtained. For example, N,N-dimethylaniline was converted into N-methylformanilide in good yield. Other products were N-methylaniline and aniline. N-methylformanilide was not the precursor of the secondary or primary amines since it was found to be stable under the irradiation conditions. Imines were not isolated from aromatic amines.

The methods used to isolate the products from aromatic amine photo-oxidation included acid extraction and column chromatography. Primary amines were not formed by hydrolysis of imines because imines were not detected by g.l.c. analysis of the solution from the oxidation of N,N-dibenzylaniline directly after photolysis. Moreover, aniline, from the photo-

Table 3. Products from the benzophenone-sensitsed photo-oxidation of amines.

Amine	Initial amount. (m.mol)	Time of irradiation (hours)	Amine consumed (m.mol)	Products	Yield (m.mol)	% Ph_2CO Recovered
Tri-n-propylamine (TNP)	24.0	2	12.0	Propionaldehyde	4.8	80
				$EtCH=NCH_2Et$	2.4	
Di-n-propylamine (DNP)	24.1	2	a	Propionaldehyde	1.9	90
				$EtCH=NCH_2Et$	a	
n-Propylamine (NP)	24.0	2	a	Propionaldehyde	2.0	80
Triethylamine (TEA)	24.0	2	9.7	Acetaldehyde	4.8	70
				$MeCH=NEt$	3.2	
				Diethylacetamide	trace	
Diethylamine (DEA)	24.0	2	1.2	Acetaldehyde	0.5	80

a. Amount produced could not be estimated.

Table 3 continued.

Amine	Initial amount. (m.mol)	Time of irradiation (hours)	Amine consumed (m.mol)	Products	Yield (m.mol)	% Ph_2CO Recovered
Tribenzylamine (TBA)	14.6	7	14.3	Benzaldehyde	13.3	80
				Benzamide	1.0	
				Benzoic acid	1.3	
				$PhCH{=}NCH_2Ph$	5.0	
Dibenzylamine (DBA)	15.4	14	1.5	Benzaldehyde	1.4	95
				$PhCH{=}NCH_2Ph$	0.5	
Benzylamine (BA)	15.8	14	2.8	Benzaldehyde	2.6	95
N-Ethyldi-isopropylamine	24.0	2	14.2	Acetone	6.8	85
				Acetaldehyde	5.1	
				$(Me)_2C{=}NEt$	2.2	
				$MeCH{=}NCH(Me)_2$	1.8	
t-Butylamine	15.2	14	0.8	Unidentified		80

Table 3 continued.

Amine	Initial amount. (m.mol)	Time of irradiation (hours)	Amine consumed (m.mol)	Products	Yield (m.mol)	% Ph_2CO Recovered
N,N-Dimethylaniline	15.1	14	14.8	N-Methylformanilide	7.4	90
				N-Methylaniline	2.9	
				Aniline	0.7	
N-Methylaniline	14.9	14	14.1	Aniline	4.2	90
				Azobenzene	0.7	
N,N-Diethylaniline	15.0	7	12.0	Acetaldehyde	15.5	90
				Aniline	4.0	
				N-Ethylaniline	3.1	
				Acetanilide	0.3	
N,N-Dibenzylaniline	15.4	7	13.3	Benzaldehyde	11.8	80
				Aniline	1.3	

Table 3 continued.

Amine	Initial amount. (m.mol)	Time of irradiation (hours)	Amine consumed (m.mol)	Products	Yield (m.mol)	% Ph_2CO Recovered
N-Benzyl-N-methyl-aniline	15.2	7	14.7	Benzaldehyde	11.0	80
				Benzylaniline	0.1	
				Benzanilide	0.4	
				Aniline	1.0	
				Methylaniline	0.4	
N-Benzyl-N-ethyl-aniline	15.0	7	12.0	N-Ethylaniline	3.2	90
				Acetaldehyde	7.2	
				Benzaldehyde	9.6	
				Acetanilide	0.4	
				Benzanilide	0.4	
1,4-Diazabicyclo-[2,2,2] octane	55.4	14	37.0	1:1 Adduct	6.1	40
				Oxygenated amine derivatives.		

-oxidation of dibenzylaniline, was detected by g.l.c. and the yield, as estimated by this technique, agreed closely with the yield obtained after aqueous work-up and column chromatography.

Products formed by oxidation at the nitrogen atom were not found in these reactions: tertiary amines did not give N-oxides nor secondary amines N-hydroxylamines.

In all cases the solutions were highly coloured after irradiation and in many cases an immiscible aqueous layer was formed. No peroxides were detected by iodometric titration. A balance of material was not obtained in any of the reactions studied though from most of them benzophenone was recovered almost quantitatively.

When oxygenated benzene solutions of amines alone were irradiated, no significant reaction occurred though solutions of aromatic amines were discoloured; presumably by the formation of oxygen-amine contact charge transfer complexes.[90] No reaction was observed in oxygenated benzene solutions of benzophenone and amines in the dark. Irradiation, of benzophenone alone, in oxygenated benzene, produced negligible reaction.

The Rate of Oxygen Uptake.

For a series of tertiary, secondary and primary aliphatic amines, the rate of oxygen uptake was measured. The results are shown in table 4. For all the amines studied, this rate was zero order for at least the first 10% of the reaction. The rates shown in table 4 are initial rates taken over no more than 2% reaction.

Table 4. Rates of oxygen uptake. (ml. per. min.)

Amine	Tribenzyl-	Dibenzyl-	Benzyl-	Triethyl-	Diethyl-
$3\text{x}10^{-2}$M	0.12	-	-	0.11	-
$1\text{x}10^{-1}$M	0.25	0.022	0.050	0.16	0.022
$3\text{x}10^{-1}$	0.34	0.030	0.070	0.23	0.028

Amine	Tri-n-propyl-	Di-n-propyl-	n-Propyl-
$3\text{x}10^{-2}$M	0.14	-	-
$1\text{x}10^{-1}$M	0.17	0.017	0.025
$3\text{x}10^{-1}$M	0.23	0.023	0.050

The rates of oxygen uptake for the primary amines were identical, within experimental error, as were those for the secondary amines. For tribenzylamine, the rate was slightly greater than for the other tertiary amines. The rates of oxygen uptake all increase with increasing amine concentration. Tertiary amines react faster than primary, which react faster than secondary amines.

The Effect of Sensitiser Concentration on the Rate of Oxygen Uptake.

The effect of benzophenone concentration on the photo-oxidation of tribenzylamine was examined. The results are illustrated in figure 3. The variation in the rate of oxygen uptake with sensitiser concentration may be attributed solely to the changes in optical density of the system. When light absorption by the sensitiser is complete, the rate becomes independent of the sensitiser concentration. The slight decrease in rate at high benzophenone concentration is probably a result of low light penetration in the cell at these concentrations.

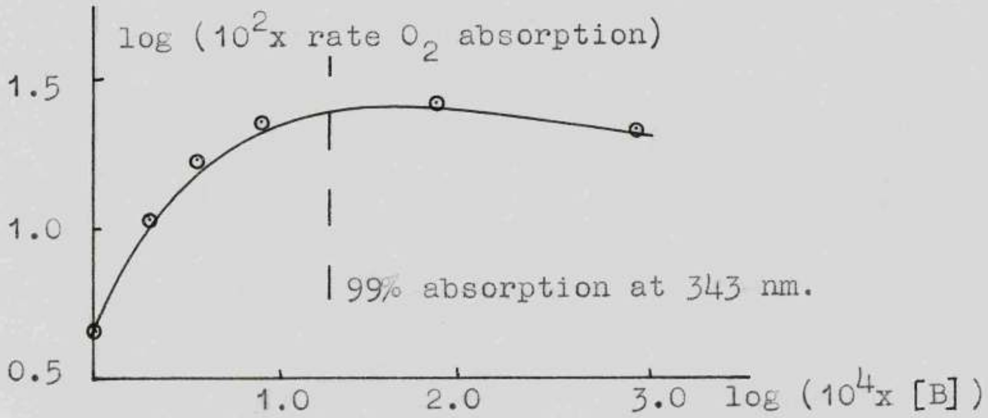


Figure 3. The dependence of the rate of oxygen uptake on benzophenone concentration.

Dependence of the Rate on Light Intensity.

The effect of light intensity on the rate of oxygen uptake by a number of amines is illustrated in table 5.

Table 5. Dependence of rate on light intensity.

Relative	Rate/Relative Intensity				
Intensity	TNP	DNP	NP	TEA	TBA
1.00	4.2	5.2	1.0	4.1	2.5
0.48	4.4	4.7	1.0	4.4	3.1
0.25	4.3	4.5	1.1	4.5	2.9
0.11	4.2	4.6	1.0	4.4	3.1

Clearly the rate is directly proportional to the incident light intensity.

Solvent Effects.

The results recorded so far were obtained from reactions run in benzene. The rate of oxygen uptake by primary, secondary and tertiary propylamines in acetonitrile solution was also measured. The rates in acetonitrile were the same as those in benzene. Obviously solvent polarity has no significant effect on the rate of oxygen uptake.

Quantum Efficiency of Oxygen Uptake.

The rates of oxygen uptake in table 4 were converted to quantum efficiencies by measuring the incident light intensity after successive rate determinations. The potassium ferrioxalate method of Hatchard and Parker[91] was used. These results are shown in table 6. For tertiary amines, these quantum efficiencies exceed unity at amine concentrations greater than 10^{-2}M.

Table 6. Quantum Efficiencies of Oxygen Uptake.

Amine	TBA	DBA	BA	TEA	DEA	TNP	DNP	NP
3×10^{-2}M	2.2	-	-	2.0	-	2.5	-	-
1×10^{-1}M	4.5	0.40	0.90	2.9	0.40	3.1	0.31	0.45
3×10^{-1}M	6.2	0.55	1.30	4.2	0.50	4.2	0.41	0.91

Table 7. Quantum yields of product formation and amine disappearance.

Tri-n-propylamine

Amine		Imine		Propionaldehyde		Time
m.mol. reacted	Φ	m.mol. formed	Φ	m.mol. formed	Φ	(min.)
6.0	4.8	3.0	2.4	2.9	2.3	30
9.0	3.6	1.9	0.8	3.2	1.3	60
11.0	2.9	2.2	0.6	4.1	0.9	90
12.0	2.4	2.4	0.4	4.3	0.8	120

Di-n-propylamine

Time	Propionaldehyde	
(min.)	m.mol. formed	Φ
30	0.6	0.5
60	1.1	0.4
120	1.9	0.4

n-Propylamine

Time	Propionaldehyde	
(min.)	m.mol. formed	Φ
30	0.9	0.7
60	1.4	0.5
120	1.9	0.4

Triethylamine

Time	Amine		Acetaldehyde	
	m.mol. reacted	Φ	m.mol. formed	Φ
30	2.1	1.6	3.8	3.0
60	6.2	2.4	4.8	1.9
90	9.3	2.4	7.0	1.6
120	11.1	2.2	7.7	1.5

Quantum Yields of Product Formation and Amine Disappearance.

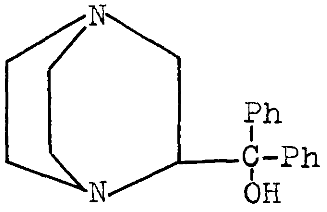
These results are shown in table 7. For the tertiary amines studied, product quantum yields and quantum efficiencies of amine disappearance exceed unity. The quantum yields of product formation decrease with extent of reaction. This may be attributed to two factors: concomitant photo-oxidation of the products and inhibition of the reaction by other light absorbing species. The quantum yield of amine disappearance shows that the reaction is inhibited at long reaction times. The quantum yields of aldehyde formation confirm that tertiary amines are oxidised more efficiently than secondary amines.

2.1.2. DISCUSSION.

Reaction of Singlet Oxygen Quenchers.

N-Ethyldi-isopropylamine and triethylamine are known to quench singlet oxygen generated by a microwave discharge, and to remain chemically unchanged;[75,76] yet benzophenone sensitises the photo-oxidation of these amines. Triethylamine is photo-oxidised to acetaldehyde and the quantum yield for acetaldehyde formation is found to be greater than one. N-Ethyldi-isopropylamine is also oxidised efficiently to acetaldehyde, acetone, and a mixture of imines.

1,4-Diazabicyclo[2,2,2]octane (DABCO) is also an efficient quencher of singlet oxygen. Although the major product from the irradiation of an oxygenated solution of benzophenone and DABCO, was the 1:1 adduct (X), some amine oxidation products were obtained.



(X)

(The formation of coupled products in oxygenated solution is one of the peculiarities of DABCO which will be discussed in detail later).

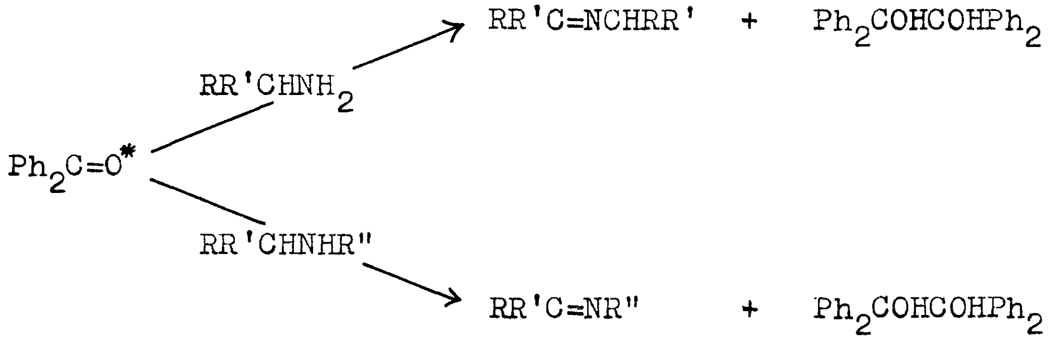
In view of the efficiency with which these amines act as physical quenchers for singlet oxygen, it is unlikely that the oxidations are initiated by the attack of singlet oxygen on the amine.

Quantum Yields.

The discovery that, for tertiary amines, the quantum yields of product formation, amine disappearance, and oxygen uptake exceed one means that more than one oxygen-reactive centre is produced by each quantum of light absorbed. This fact must be accounted for in the oxidation mechanism and is clearly incompatible with a mechanism in which attack by singlet oxygen on an amine molecule is the sole oxygen consuming step.

Correlation with Reduction.

It was reported by Cohen[87] that benzophenone is photoreduced by aliphatic amines containing α C-H groups. The products of the reactions were benzpinacol and imines.



Davidson[85] found that tertiary aromatic amines also photoreduce benzophenone to give benzpinacol and mixed coupling products.

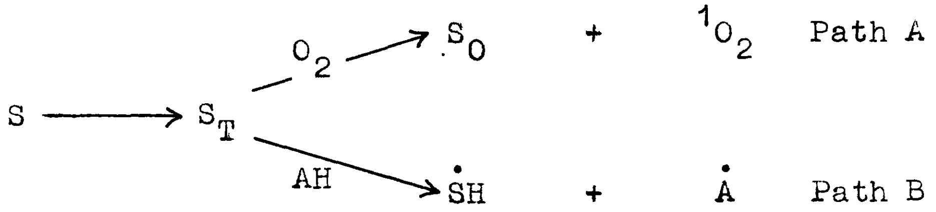
In the photo-oxidations studied, only those amines with α C-Hgroups were oxidised efficiently. t-Butylamine was not efficiently oxidised. This is good evidence that the photo-oxidations, like the photoreductions, involve hydrogen abstraction by triplet benzophenone. In this context, the photo-oxidation of N-benzyl-N-ethylaniline is particularly interesting. If the primary process is hydrogen abstraction, the ratio of acetaldehyde to benzaldehyde formed, indicates that the abstracting species shows little preference for the benzylic C-H bond over the alkyl C-H bond. Such behaviour is typical of reactions of triplet ketones with amines.[86]

Competition between Hydrogen Abstraction and Oxygen Quenching.

It is proposed that the primary process in the benzophenone-sensitised photo-oxidation of amines is hydrogen abstraction from the amine by triplet ketone and that the reactions do not involve singlet oxygen. This is based on:

1. The oxidation of singlet oxygen quenchers.
2. The high quantum yields for tertiary amines.
3. The correlation of oxidation with reduction.

It was explained in the introduction that in oxygenated solution the excited sensitiser may react with oxygen (path A) or with the substrate (path B). The outcome of this competition depends on the concentration of oxygen and substrate and the magnitude of the appropriate rate constants.



The concentration of oxygen in benzene would be between 10^{-3}M and 10^{-2}M, and the rate constant for quenching of triplet benzophenone by oxygen, k_{O_2}, is around $10^9 M^{-1}s^{-1}$. If the rate constant for hydrogen abstraction from the amines, k_{AH}, is taken as $10^8 M^{-1}s^{-1}$ and with an amine concentration of 10^{-1}M, then hydrogen abstraction would be at least as efficient as oxygen quenching. The initiation of these reactions by hydrogen abstraction, even in competition with oxygen quenching, is therefore quite feasible.

It is proposed that the mechanism of photo-oxidation involves hydrogen abstraction to give an α-amino radical, which can then react with oxygen, or other species, to give products.

Relative Rates of Photo-oxidation.

Cohen proposed that the photoreduction of benzophenone by amines involved electron transfer from the amine to triplet benzophenone, followed by proton transfer, the overall process being equivalent to a hydrogen atom abstraction.

$$Ph_2CO(T) + RCH_2NH(CH_2)R \longrightarrow Ph_2\dot{C}-\bar{O} + RCH_2\overset{+\cdot}{N}HCH_2R$$

$$Ph_2\dot{C}-\bar{O} + RCH_2\overset{+\cdot}{N}CH_2R \longrightarrow Ph_2\dot{C}-OH + R\dot{C}HNHCH_2R$$

Because of experimental difficulties, rate constants for the interaction of triplet benzophenone with secondary and tertiary amines, could not be determined by quenching studies. However, rate constants have been reported for photoreduction of the 4-benzoyl benzoate anion by primary, secondary, and tertiary amines.[92] These values, which were obtained by standard quenching methods,[77,93] are shown in table 8.

Table 8. Rate constants for the photoreduction of the 4-benzoylbenzoate anion by amines (from ref. 92).

Amine	$\frac{k_d}{k_r}$ M	$\frac{k_q}{k_r}$	$k_r^{\dagger} M^{-1} s^{-1}$	$k_d s^{-1}$
2-$BuNH_2$	0.103	44	6.3×10^7	6.4×10^6
2-BuNHMe	0.030	16	1.6×10^8	4.8×10^6
2-$BuNMe_2$	0.011	2.7	9.4×10^8	10.2×10^6
Et_3N	0.021	4.2	6.0×10^8	12.7×10^6

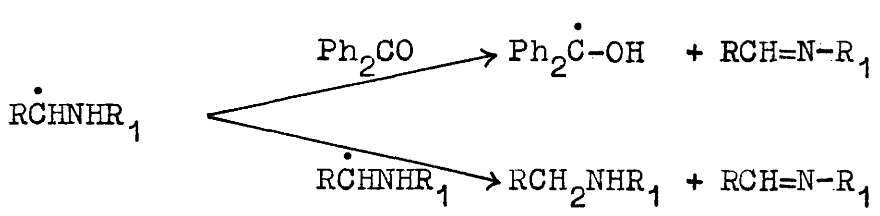
† values of k_r were calculated from $\frac{k_q}{k_r}$ assuming k_q to be diffusion controlled.

The values of k_r rise from primary to secondary to tertiary amine; while this order could merely reflect the number of available α hydrogens, it also correlates with ionisation potential. The relative rates of quenching of benzophenone phosphorescence by amines also follow this order.[94]

It might therefore be expected that, initially, tertiary amines would be photo-oxidised faster than secondary amines which would be faster than primary, if the primary process in photo-oxidation is the same as in photoreduction. The relative rates of oxygen uptake show however, that primary amines react faster than secondary amines.

This example illustrates that it is generally imprudent to relate empirically, overall rates of photochemical reactions with rate constants for the primary process.[95] The subsequent steps in the reaction mechanism must also be considered. The difference between the order of relative rates of photo-oxidation and that of the rate constants for ketone/amine interaction may be rationalised by an examination of the oxygen consuming steps in the reaction mechanism.

It is proposed that reaction is propogated by reaction of an α-amino radical with oxygen. The α-amino radicals from primary and secondary amines can also disproportionate or possibly react with ground state benzophenone.[88]



$$R\dot{C}HNHR_1 \xrightarrow{Ph_2CO} Ph_2\dot{C}\text{-}OH + RCH{=}N\text{-}R_1$$

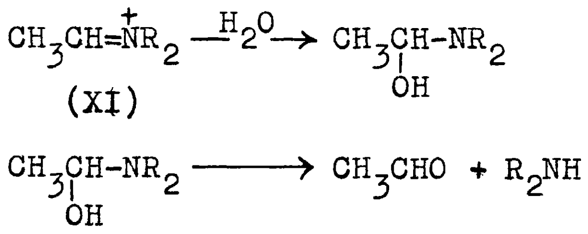
$$R\dot{C}HNHR_1 \xrightarrow{R\dot{C}HNHR_1} RCH_2NHR_1 + RCH{=}N\text{-}R_1$$

These reactions will deplete the number of radical centres available to react with oxygen. The rate of these reactions will depend on the strength of the N-H bond being broken. These bonds in primary amines are stronger than those in secondary amines.[2] These reactions will therefore be more favourable for secondary amines than for primary amines. Consequently the reactions with oxygen, of amino radicals from primary amines will be more efficient than the reaction of the corresponding radicals from secondary amines.

The Formation of Products.

Irradiation of benzophenone and secondary amines in anaerobic benzene solution produces imines.[87] It was suggested by Cohen that these imines could arise by reaction of the initially formed α-amino radical with ground state benzophenone, by analogy with the photoreduction by isopropanol.[79] The formation of these compounds in the photo-oxidation reactions could occur by the same process. They could also be formed by the disproportionation reaction discussed in the previous paragraph.

Irradiation of benzophenone and tertiary amines in anaerobic aqueous solution leads to the formation of aldehydes and secondary amines.[96] It was proposed that products arose by hydrolysis of an iminium ion (XI).



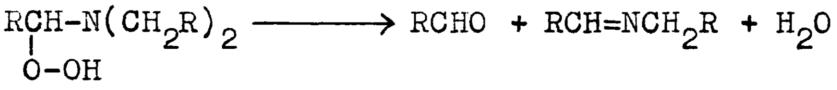
$$\underset{(XI)}{CH_3CH{=}\overset{+}{N}R_2} \xrightarrow{H_2O} CH_3\underset{OH}{\underset{|}{C}}H{-}NR_2$$

$$CH_3\underset{OH}{\underset{|}{C}}H{-}NR_2 \longrightarrow CH_3CHO + R_2NH$$

The hypothesis that aldehydes are formed by the hydrolysis of an iminium ion in the photo-oxidations carried in anhydrous benzene, is rejected for two reasons:

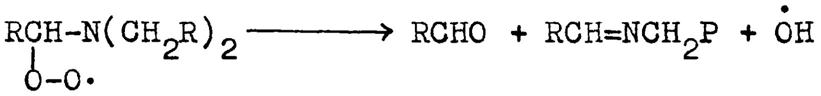
1. The formation of a charged species, in a non-polar solvent such as benzene, seems unlikely.
2. Secondary amines, which should also be formed by such a hydrolysis, were not detected in the photo-oxidation studies, using tertiary aliphatic amines.

It is proposed that imines and aldehydes are formed from tertiary amines in the photo-oxidation reactions, by decomposition of an amine hydroperoxide:



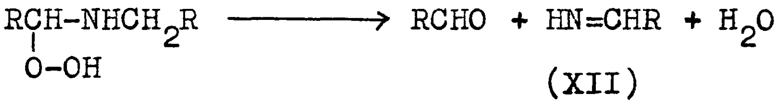
$$\mathrm{R}\underset{\substack{\mid \\ \mathrm{O{-}OH}}}{\mathrm{C}}\mathrm{H{-}N(CH_2R)_2} \longrightarrow \mathrm{RCHO} + \mathrm{RCH{=}NCH_2R} + \mathrm{H_2O}$$

or by decomposition of an amine peroxy radical:



$$\mathrm{R}\underset{\substack{\mid \\ \mathrm{O{-}O\cdot}}}{\mathrm{C}}\mathrm{H{-}N(CH_2R)_2} \longrightarrow \mathrm{RCHO} + \mathrm{RCH{=}NCH_2P} + \overset{\bullet}{\mathrm{O}}\mathrm{H}$$

Aldehydes could be formed from secondary amines by a similar mechanism. This should produce an unsubstituted imine (XII):



$$\mathrm{R}\underset{\substack{\mid \\ \mathrm{O{-}OH}}}{\mathrm{C}}\mathrm{H{-}NHCH_2R} \longrightarrow \mathrm{RCHO} + \underset{\mathrm{(XII)}}{\mathrm{HN{=}CHR}} + \mathrm{H_2O}$$

Unsubstituted imines were not detected in the photo-oxidations, but they are known to be less stable than N-substituted imines and to polymerise readily.[97]

It is unlikely that aldehydes were formed by the photochemical hydrolysis of imines,[98] because primary amines were not detected from tertiary aliphatic amines. However, some imine did react during the later stages of the reaction. This is illustrated in figure 4.

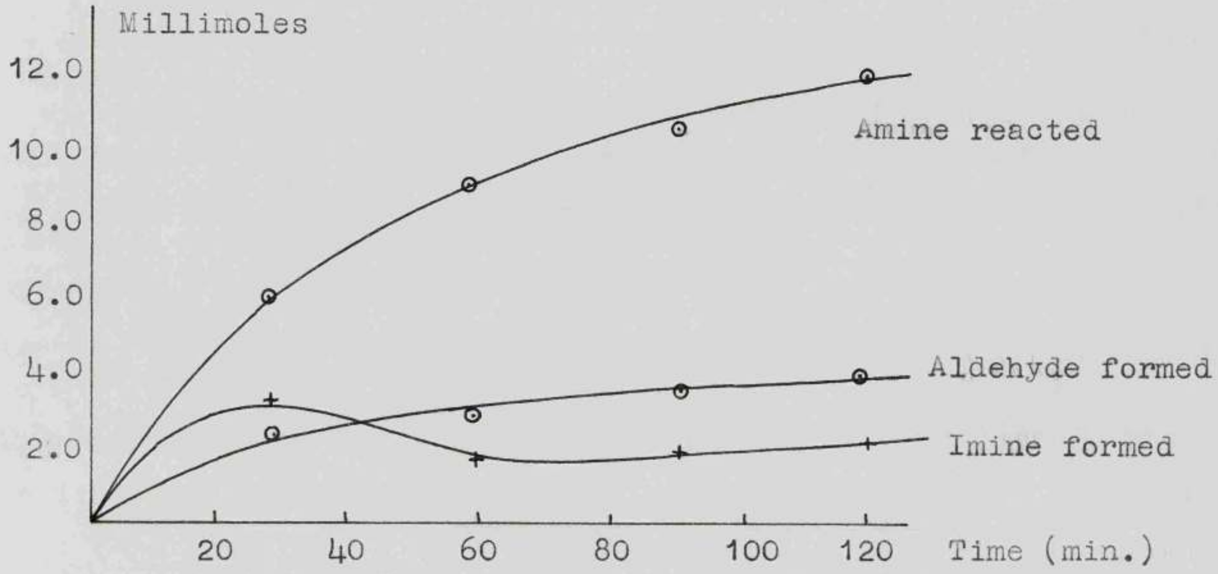


Figure 4. Product yield against time for the photo-oxidation of tri-n-propylamine.

The Cyclic Action of the Sensitiser.

To explain the quantitative recovery of benzophenone from the reaction mixture, a mechanism is required that allows benzophenone to initiate the photo-oxidation, and be regenerated at the end of the cycle. Hydrogen abstaction from amines, by benzophenone triplet, gives ketyl radicals,[99] which, under anaerobic conditions, undergo rapid recombination to give benzpinacol. Oxygen reacts rapidly with ketyl radical ions;[100] so reaction with the protonated radical is also likely to be efficient:

$$Ph_2\dot{C}\text{-}OH + O_2 \longrightarrow Ph_2C{=}O + H\dot{O}_2$$

It is probable because of the relatively high oxygen concentration, that reaction with oxygen is far more efficient than reaction involving two radicals e.g.

$$Ph_2\dot{C}\text{-}OH \quad + \quad R\dot{C}HNR_2 \longrightarrow Ph_2C{=}O \quad + \quad RCH_2NR_2$$

It is therefore assumed that reaction with oxygen is the dominant mode of sensitiser regeneration.

The Mechanism.

The most important steps in a mechanism which is compatible with all the experimental data, are shown below.

Initiation:

$$B_T \quad + \quad AH \longrightarrow \dot{A} \quad + \quad \dot{B}H \tag*{a}$$

Propagation:

$$\dot{A} \quad + \quad O_2 \longrightarrow A\dot{O}_2 \tag*{b}$$

$$A\dot{O}_2 \quad + \quad AH \longrightarrow \dot{A} \quad + \quad AO_2H \tag*{c}$$

$$H\dot{O}_2 \quad + \quad AH \longrightarrow H_2O_2 \quad + \quad \dot{A} \tag*{d}$$

Product Formation:

$$\left.\begin{array}{ll} A\dot{O}_2 & \text{e} \\ AO_2H & \text{f} \end{array}\right] \longrightarrow \text{products}$$

Sensitiser Regeneration:

$$\dot{B}H \quad + \quad O_2 \longrightarrow H\dot{O}_2 \quad + \quad B \tag*{g}$$

Chain Termination:

$$\dot{A} \quad + \quad \dot{A} \longrightarrow \text{Imine} + \text{Amine} \tag*{h}$$

$$\dot{A} \quad + \quad H\dot{O}_2 \longrightarrow AO_2H \tag*{i}$$

$$H\dot{O}_2 \quad + \quad H\dot{O}_2 \longrightarrow H_2O_2 \quad + \quad O_2 \tag*{j}$$

Together with other radical recombination reactions.

$AH = RCH_2NR'R''$ $\qquad \dot{B}H = Ph_2\dot{C}-OH$

B = Benzophenone $\qquad \dot{A} = R\dot{C}HNR'R''$

$\dot{A}O_2 = R\underset{\overset{|}{O-\dot{O}}}{C}HNR'R'' \qquad AO_2H = R\underset{\overset{|}{O-OH}}{C}HNR'R''$

Reaction (h) applies in the case of secondary and primary amines.

Comment.

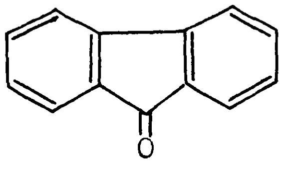
The mechanism of the benzophenone-sensitised photo-oxidation of amines has been shown to involve radicals and not singlet oxygen. Unfortunately little evidence is available to show whether or not benzophenone is an efficient sensitiser of singlet oxygen production. Other sensitisers, including ketones such as fluorenone, dyes such as methylene blue and the fluoresceins, and hydrocarbons, are known to produce singlet oxygen efficiently. The behaviour of these compounds as sensitisers for the photo-oxidation of amines, will be examined in the following sections.

2.2. THE USE OF OTHER KETONES AS SENSITISERS FOR THE PHOTO-OXIDATION OF AMINES.

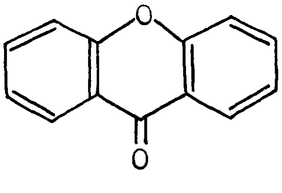
The sensitisation of singlet oxygen formation by oxygen-quenching of triplet benzophenone is not well documented, but benzophenone is known to interact rapidly with amines. Other ketones were sought which are known to sensitise singlet oxygen formation and which are inefficiently photoreduced by amines. Under these conditions, oxygen should compete effectively for the triplet sensitiser and singlet oxygen formation should be efficient; consequently reactions involving singlet should be enhanced.

Fluorenone (XIII) is an efficient sensitiser of singlet oxygen formation.[101] It is photoreduced by aromatic amines,[86] and by primary, secondary and tertiary aliphatic amines in both benzene and acetonitrile solution,[102] but the photoreduction of fluorenone is less efficient than the photoreduction of benzophenone. Kearns argues convincingly that the lowest triplet state of fluorenone is a π,π^* state,[103] and it is generally true that π,π^* states are reduced less efficiently than n,π^* states.[104,105]

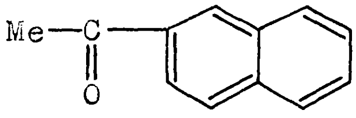
Other ketones; p-aminobenzophenone, xanthone (XIV), and and β-naphthyl methyl ketone (XV), which are assumed to have low π,π^* triplet states, were also used as sensitisers. Unfortunately, data is not available on the efficiency of singlet oxygen formation by these ketones.



(XIII)



(XIV)



(XV)

The ketones were used to sensitise the photo-oxidation of triethylamine, di-n-propylamine, and n-propylamine.

2.2.1. RESULTS.

Oxygenated benzene solutions of the three amines, containing the ketone sensitiser, were irradiated, and the products analysed by g.l.c. The results are shown in table 9.

With all the sensitisers, triethylamine was converted into N-ethylacetaldimine, diethylamine and acetaldehyde. The primary and secondary propylamines gave propionaldehyde.

After irradiation of anaerobic solutions of the ketones and amines, a decrease in the intensity of the carbonyl absorption in the infra-red spectrum was observed, indicating that reduction had occurred. Photoreduction of all the ketones was very much less efficient than the corresponding photoreduction of benzophenone. The ketones were also less efficient than benzophenone in sensitising the photo-oxidation of the amines. p-Amino-benzophenone was slightly more reactive than the others.

2.2.2. DISCUSSION.

Triplets with the π,π^* configuration are known to be less reactive in hydrogen abstraction reactions than n,π^* triplets.[104,105] In the π,π^* configuration the half vacant bonding orbital is spread over the entire π system rather than being localised at the oxygen atom in the n,π^* case. Hydrogen abstraction by such a species might be expected to require extensive electronic reorganisation to localise the radical centre, and therefore be subject to a large activation energy. This activation energy would be reflected in a low rate constant for hydrogen abstraction.

There is some doubt about the nature of the triplet state of p-aminobenzophenone which undergoes photoreduction. Early

Table 9. Products from the photo-oxidation of amines sensitised by ketones.

Amine	Initial amount. (m.mol.)	Time of irradiation (min.)	Amine consumed (m.mol.)	Products	Yield (m.mol.)	Reduction under N_2
1. Sensitiser = p-aminobenzophenone.						
Triethylamine	12.5	180	4.2	Acetaldehyde	1.2	yes
				$EtN=CHCH_3$	0.9	
				Diethylamine	1.1	
Di-n-propylamine	12.5	60	a	Propionaldehyde	0.6	yes[b]
n-Propylamine	12.5	60	a	Propionaldehyde	0.3	yes[b]
2. Sensitiser = fluorenone.						
Triethylamine	12.5	120	2.8	Acetaldehyde	0.6	yes
				$EtN=CHCH_3$	0.5	
				Diethylamine	0.1	
Di-n-propylamine	12.5	60	a	Propionaldehyde	0.5	yes[b]
				One other unidentified component.		
n-Propylamine	12.5	30	a	Propionaldehyde	0.6	yes[b]

a. Amount produced could not be estimated.

Table 9 continued.

Amine	Initial amount. (m.mol.)	Time of irradiation (min.)	Amine consumed (m.mol.)	Products	Yield (m.mol.)	Reduction under N_2
3. Sensitiser = β-naphthyl methyl ketone.						
Triethylamine	12.5	1000	6.8	Acetaldehyde	0.7	yes
				$EtN{=}CHCH_3$	0.3	
				Diethylamine	1.2	
Di-n-propylamine	12.5	60	a	Propionaldehyde	1.0	yes[b]
n-Propylamine	12.5	60	a	Propionaldehyde	trace	yes[b]
4. Sensitiser = xanthone.						
Triethylamine	12.5	90	2.0	Acetaldehyde	0.6	yes
				$EtN{=}CHCH_3$	0.2	
				Diethylamine	0.3	
Di-n-propylamine	12.5	70	a	Propionaldehyde	0.8	yes
				Two other unidentified components.		
n-Propylamine	12.5	60	a	Propionaldehyde	0.3	yes

b. Increase in U.V.absorption but decrease in I.R. absorption.

work indicated that it was an n,π^* state,[106] but later work on the emission from p-aminobenzophenone indicates that it may be a π,π^* state.[107] However the rate constant for hydrogen abstraction from triethylamine by this species is reported to be between $5x10^6$ and $1.2x10^7$ $M^{-1}s^{-1}$. This is considerably lower than the rate constant for interaction of triethylamine with triplet benzophenone.[94]

If the photosensitised oxidation of amines involves singlet oxygen, efficient oxidation would be expected under conditions where, because of low rate constants for hydrogen abstraction, singlet oxygen formation is the dominant mode of deactivation of the triplet sensitiser. The reactions of the four ketones studied provide just these conditions of inefficient hydrogen abstraction, nevertheless photo-oxidation is inefficient. It is therefore suggested that these photosensitised oxidations, like those sensitised by benzophenone, are initiated by hydrogen abstraction from the amine, by triplet ketone.

In view of the inefficiency of the photoreduction of these ketones under anaerobic conditions, it is perhaps surprising that photo-oxidation, initiated by hydrogen abstraction, occurs at all. However, the photo-oxidation mechanism proposed is a chain mechanism, and even though the number of radicals produced by initial hydrogen atom abstraction may be small, a large number of radicals may be produced by subsequent reactions.

Although a major factor contributing to the inefficiency of photoreduction is the low rate constant for hydrogen abstraction, another factor may also be important. Benzophenone is not photoreduced by aniline.[109] Flash photolysis of anaerobic solutions of aniline and benzophenone in a variety of solvents shows clearly the presence of the ketyl radical ($Ph_2\dot{C}OH$) and the anilino radical ($Ph\dot{N}H$). Irradiation of an oxygenated solution of benzophenone and aniline leads to oxidation of the aniline to give azobenzene.[109] Similarly, benzophenone is not photoreduced efficiently by diphenylamine, yet the radicals $Ph_2\dot{C}OH$ and $Ph_2\dot{N}$ were observed on flash photolysis of an anaerobic solution. Irradiation of an oxygenated solution of diphenylamine and benzophenone leads to the formation of diphenylnitroxide.[110] An explanation for these results is that the initial hydrogen abstraction is reversible.

$$
\begin{array}{lllll}
R_2NH & + & Ph_2CO(T) \longrightarrow & R_2\dot{N} & + \; Ph_2\dot{C}OH \\
Ph_2\dot{C}OH & + & R_2\dot{N} \longrightarrow & R_2NH & + \; Ph_2CO
\end{array}
$$

Hydrogen abstraction from amines containing α C-H groups may also be reversible.

$$
\begin{array}{lllll}
R'_2CO(T) & + & RNHCH_2R \longrightarrow & R'_2\dot{C}OH & + \; RNH\dot{C}HR \\
R'_2\dot{C}OH & + & RNH\dot{C}HR \longrightarrow & R'_2CO & + \; RNHCH_2R
\end{array}
$$

Studies using benzophenone with optically active amines,[88] and other ketones with optically active alcohols,[105] appear to rule out this reversibility, but recent work by Davidson and Steiner[111] indicates that such reversibility is not impossible. It was found that irradiation of an anaerobic solution of N-phenylglycine and benzophenone led to a good yield of N-methylaniline; benzophenone was recovered. Their mechanism is shown below:

$$\begin{aligned}
&Ph_2CO(T) + PhNHCH_2COOH \longrightarrow PhNHCH_2CO\dot{O} + Ph_2\dot{C}OH\\
&PhNHCH_2CO\dot{O} \longrightarrow PhNH\dot{C}H_2 + CO_2\\
&PhNH\dot{C}H_2 + Ph_2\dot{C}OH \longrightarrow PhNHMe + Ph_2CO
\end{aligned}$$

The last step is the same as the back reaction discussed in the context of hydrogen abstraction from amines. If hydrogen abstraction from amines is reversible, in the presence of oxygen, reaction of the ketyl radical and the amine radical with oxygen would reduce the efficiency of the reverse reaction, and significant oxidation could occur, as in the case of aniline and diphenylamine.

2.3. THE DYE-SENSITISED PHOTO-OXIDATION OF AMINES.

Early work by Schenck and Gaffron on the dye-sensitised photo-oxidation of amines was described in the introduction. The mechanism by which dyes such as rose bengal, eosin, and methylene blue sensitise the photo-oxidation of various types of compound have been widely studied,[39,44] and it has been shown that these dyes efficiently sensitise the formation of singlet oxygen.[35,112] The photo-oxidation of amines sensitised by these dyes was therefore examined to discover whether singlet oxygen is involved in this reaction, or whether photo-oxidation occurs by a radical mechanism similar to that operating in the reactions sensitised by ketones.

2.3.1. RESULTS.

Product Studies.

The products obtained from the methylene blue-sensitised photo-oxidation of various amines are shown in table 10. Methanol was used as solvent for most of the reactions and the solutions were flushed continuously with pure oxygen during irradiation. Under these conditions aliphatic tertiary amines were found to react efficiently to give carbonyl compounds and imines. Secondary and primary aliphatic amines were found to be relatively unreactive, as were N-alkylated anilines and aniline. Prolonged irradiation of oxygenated aqueous solutions of methylene blue and triethylamine or trimethylamine, with light of low intensity, gave a trace of the corresponding N-oxides.

With rose bengal and eosin as sensitisers, tertiary aliphatic amines reacted efficiently in oxygen-flushed solutions to give carbonyl compounds and imines, while primary and secondary amines again appeared relatively unreactive. The products from these reactions are shown in table 11.

In anaerobic solution, the dyes were all photobleached efficiently by tertiary aliphatic amines. Primary and secondary aliphatic amines were much less efficient photobleaching agents. Aniline, N,N-dimethylaniline, N,N-diethylaniline and 1,4-diazabicyclo[2,2,2]octane (DABCO) did not bleach methylene blue efficiently.

The photo-oxidation of primary, secondary and tertiary aliphatic amines, sensitised by rose bengal, was found to be

Table 10. Products from the methylene blue-sensitised photo-oxidation of amines.

Amine	Initial amount. (m.mol.)	Time of irradiation (hr.)	Amine consumed (m.mol.)	Products	Yield (m.mol.)
Triethylamine	20.0	17	10.0	Acetaldehyde	25.0
Ethyldi-isopropylamine	20.0	17	7.5	Acetone	4.2
				Acetaldehyde	3.1
				Mixture of imines	
Tri-n-propylamine	20.0	17	13.2	Propionaldehyde	11.0
				EtCH=NPr	4.0
Di-n-propylamine	19.7	17	<2.0	None detected	
n-Propylamine	20.0	17	<2.0	None detected	
Trimethylamine	150	26	93.0	N-Oxide	1.2
Triethylamine	150	26	46.0	N-Oxide	0.5
				Acetaldehyde	20.0
Tribenzylamine	18.0	20	5.4	Benzaldehyde	4.0
				$PhCH=NCH_2Ph$	1.0
Aniline	20.0	17	No detectable reaction		
N,N-Dimethylaniline	20.0	16	No detectable reaction		
N,N-Diethylaniline	20.0	17	No detectable reaction		
DABCO	20.0	17	No detectable reaction		

Table 11. Products from the photo-oxidation of amines sensitised by eosin and rose bengal.

Amine	Initial amount. (m.mol.)	Time of irradiation (hr.)	Amine consumed (m.mol.)	Products	Yield (m.mol.)
1. Sensitiser = rose bengal.					
Triethylamine	7.5	20	4.5	Acetaldehyde	8.0
Tribenzylamine	18.0	21	6.3	Benzaldehyde	4.2
				$PhCH=NCH_2Ph$	Trace
Ethyldi-isopropylamine	7.5	20	4.2	Acetaldehyde	1.5
				Acetone	2.3
Tri-n-propylamine	7.5	20	5.0	Propionaldehyde	4.8
				EtCH=NPr	2.1
Di-n-propylamine	7.5	20	<0.5	None detected.	
n-Propylamine	7.5	20	<0.5	None detected.	
2. Sensitiser = eosin.					
Triethylamine	7.5	19	4.0	Acetaldehyde	6.3
Tri-n-propylamine	7.5	20	4.2	Propionaldehyde	3.6
				EtCH=NPr	1.5
Tribenzylamine	17.5	22	6.4	Benzaldehyde	3.2
				$PhCH=NCH_2Ph$	1.0

more efficient in air-saturated rather than oxygen-saturated solution. Relative efficiencies are shown in table 12.

Table 12. A comparison of the amount of amine oxidised in reactions run under oxygen and air.

Amine	Time of irradiation	Percentage amine reacted	
		Air	Oxygen
Triethylamine	9 hr	35	25
Tri-n-propylamine	16 hr	58	50
Di-n-propylamine	16 hr	37	10
n-propylamine	17 hr	28	7

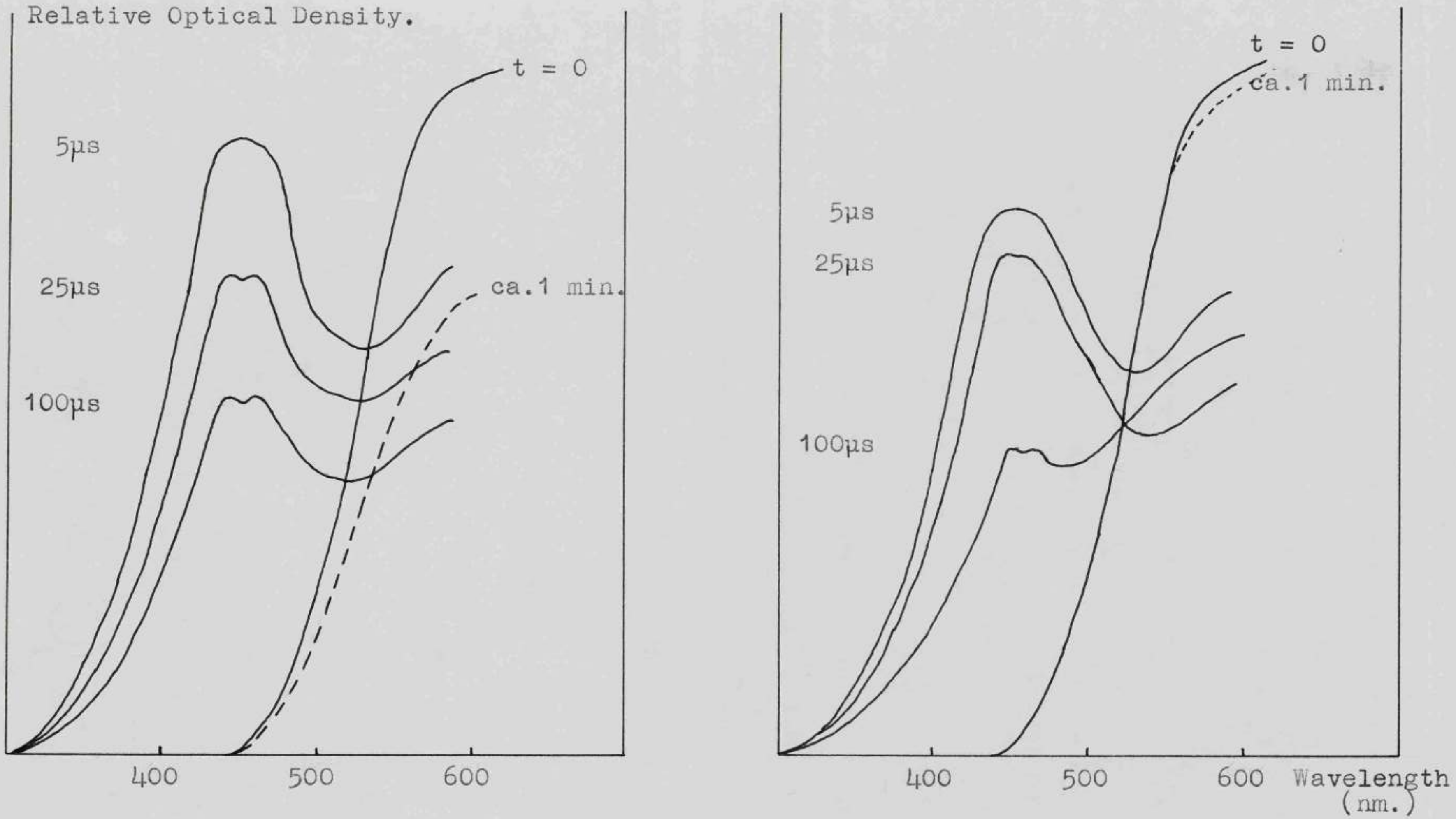
Flash Photolysis Studies.

The reactions were also studied by flash photolysis, and the results of experiments with methylene blue as sensitiser are shown in table 13. Spectral changes that occur after the flash photolysis of methanol solutions of methylene blue with aliphatic tertiary amines and with aromatic amines, are shown in figures 5a-d. The illustrations show the results obtained with triethylamine and with N,N-dimethylaniline. Tri-n-propylamine and N-ethyl-N,N-di-isopropylamine gave a similar result to triethylamine. N,N-Diethylaniline, aniline and DABCO behaved, qualitatively, in the same way as N,N-dimethylaniline.

Air saturated solutions of methylene blue alone in methanol solution showed no transient species or photobleaching on flash photolysis. No transient species were detected after the flash photolysis of any of the amines alone in methanol solution.

Table 13. Results of the flash photolysis of solutions of amines and methylene blue.

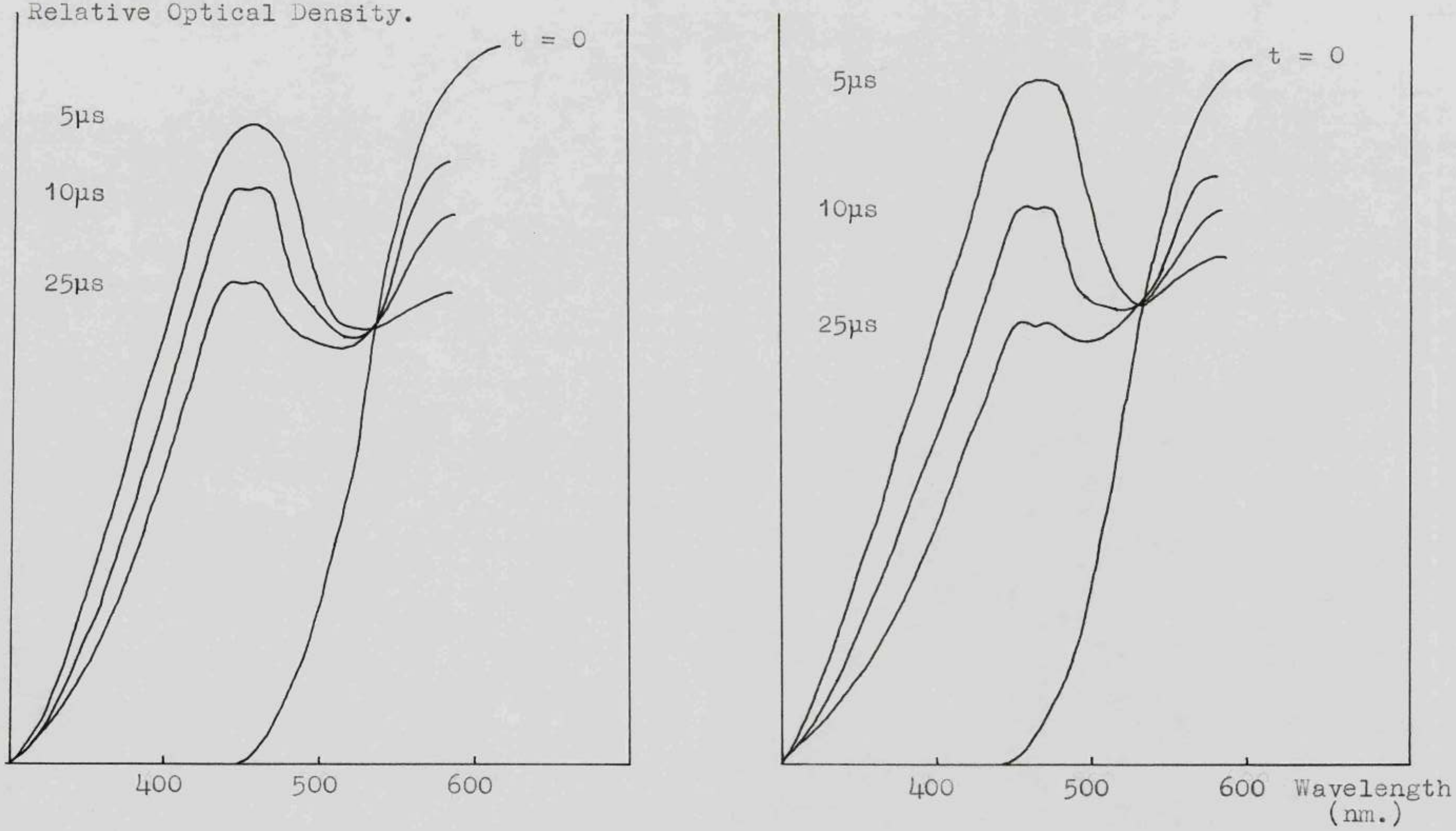
Amine	Concentration (M)	Conditions	Formation of a transient species (λ_{max}410,430nm)	Photobleaching
Tri-n-propylamine	ca. 5×10^{-3}	N_2	yes	Mainly permanent bleaching
	ca. 5×10^{-3}	Air	yes	Reversible bleaching
Triethylamine	ca. 5×10^{-3}	N_2	yes	Mainly permanent bleaching
	ca. 5×10^{-3}	Air	yes	Reversible bleaching
Di-n-propylamine	ca. 5×10^{-3}	N_2	yes	Mainly permanent bleaching
	ca. 5×10^{-3}	Air	no	None
	$> 5 \times 10^{-1}$	Air	yes	Reversible bleaching
n-Propylamine	ca. 5×10^{-3}	N_2	yes	Mainly permanent bleaching
	ca. 5×10^{-3}	Air	no	None
DABCO, Aniline, Dimethylaniline, and Diethylaniline.	ca. 5×10^{-3}	N_2	yes	Fast reversible bleaching
	ca. 5×10^{-3}	Air	yes	Fast reversible bleaching



(b) Anaerobic solution.

(a) Aerobic solution.

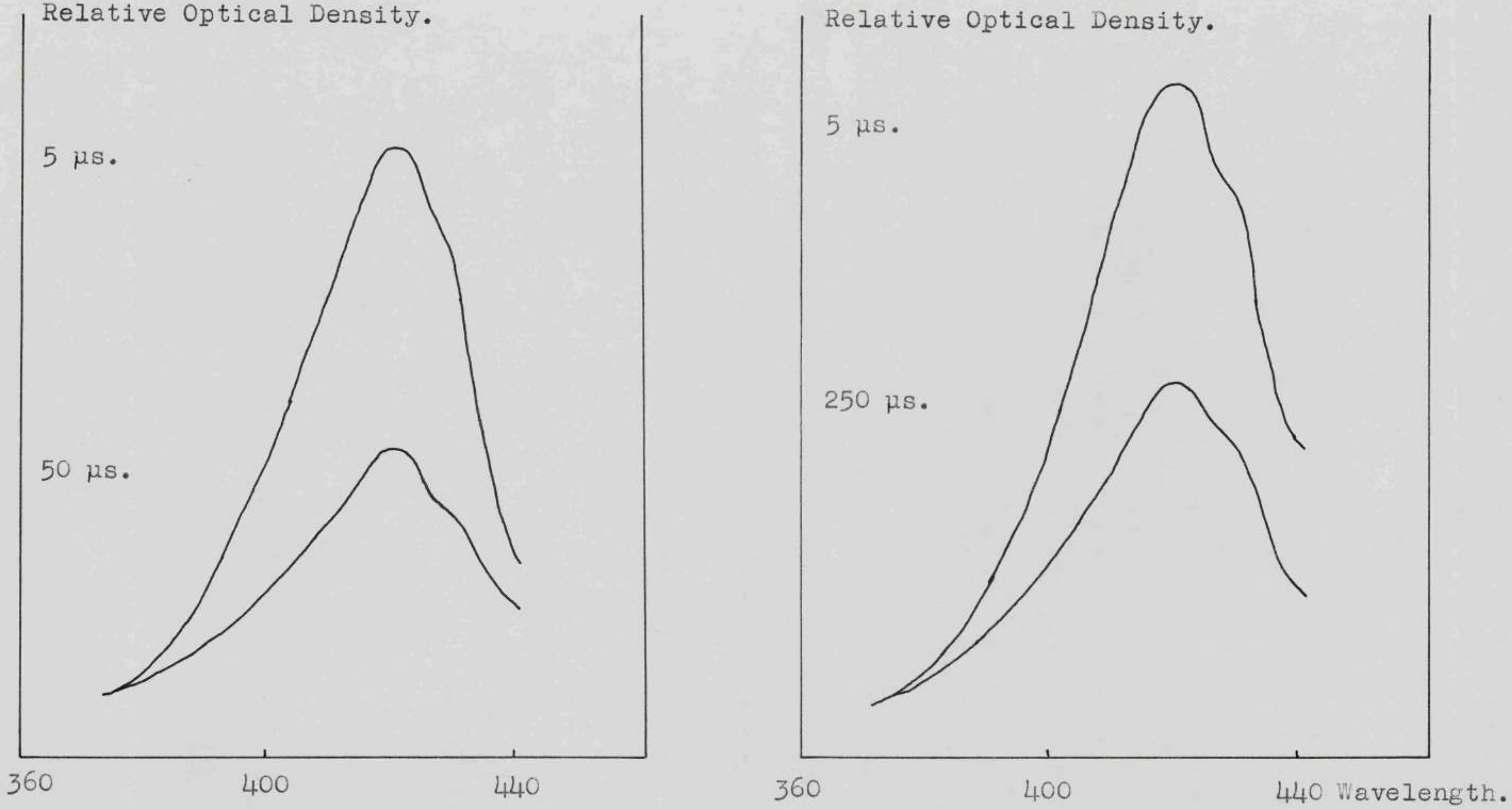
Figure 5. a,b. Spectral changes following the flash photolysis of solutions of methylene blue and triethylamine.



(c) Anaerobic solution.

(d) Aerobic solution.

Figure 5. c,d. Spectral changes following the flash photolysis of solutions of methylene blue and N,N-dimethylaniline.



(a) Aerobic Solution.

(b) Anaerobic Solution.

Figures 6a, 6b. Spectral changes after the flash photolysis of solutions of triethylamine and rose bengal.

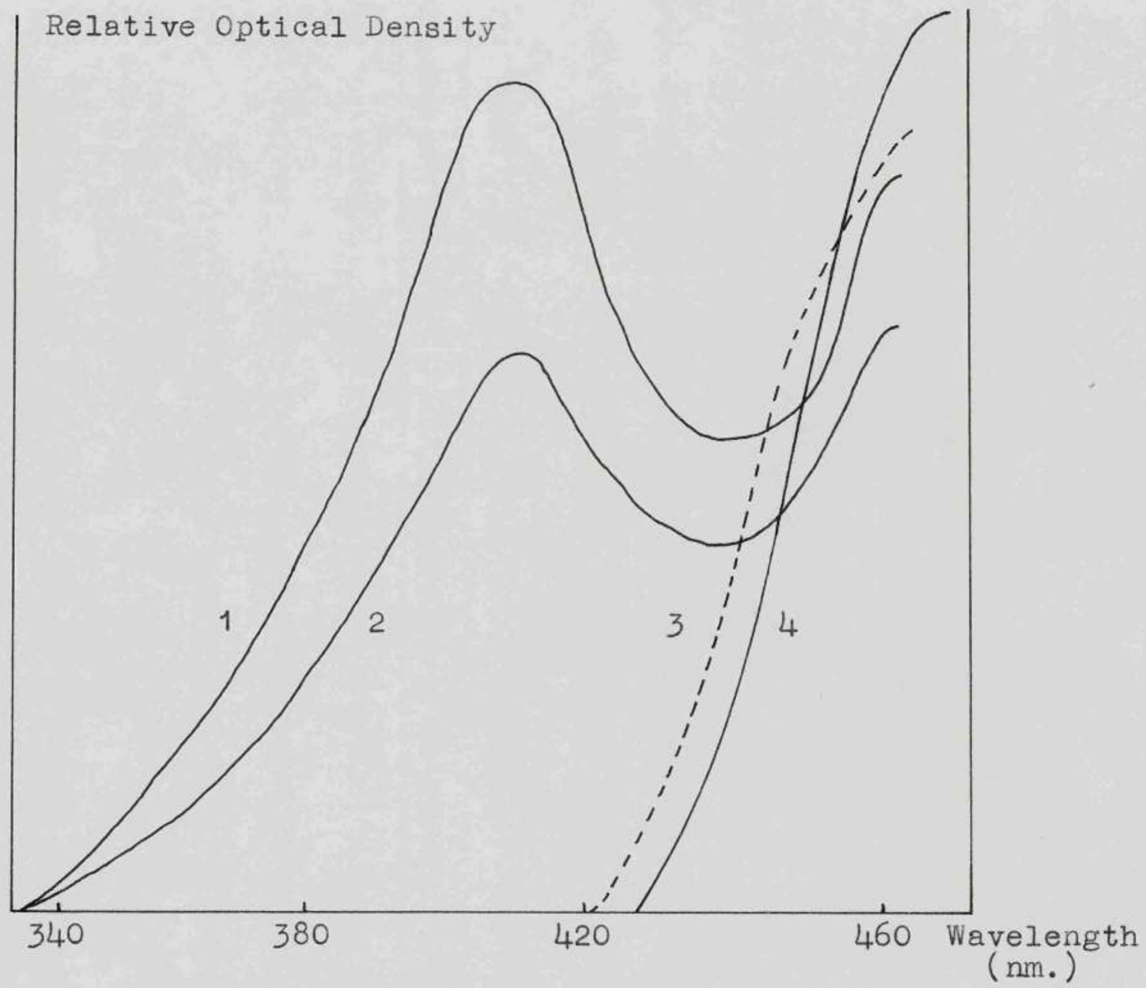


Figure 6c. Spectral changes after the flash photolysis of an anaerobic solution of eosin and triethylamine. 1. t = 5µs., 2. t = 200µs., 3. t = 1min. after three consecutive flashes, 4. t = 0.

Flash photolysis of oxygen-free solutions of rose bengal and high concentrations of tertiary aliphatic amines showed a transient species (λ_{max} 420 nm.) with a lifetime of around 500μs. After the flash, the absorption maximum of the dye was shifted to shorter wavelengths. Similar experiments with eosin showed a transient species (λ_{max} 410 nm.) again with a lifetime of around 500μs. (see figures 6a-c). The formation of transient species from both rose bengal and eosin was accompanied by weak reversible photobleaching. In air saturated solution the lifetimes of the transient species were much shorter (approximately 100μs.). Transient species were not observed with aliphatic primary or secondary amines, nor with aniline, N-alkylated anilines, or DABCO.

2.3.2. DISCUSSION.

Product Studies.

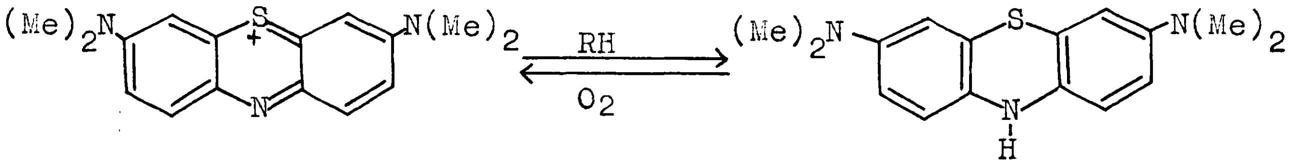
The products obtained from the dye-sensitised photo-oxidation of tertiary aliphatic amines were imines and carbonyl compounds, the same as those obtained from the benzophenone-sensitised reactions. This implies that ketones and dyes sensitise the photo-oxidation of amines by a common mechanism.

Reaction of Singlet Oxygen Quenchers.

Methylene blue and rose bengal sensitise the photo-oxidation of triethylamine and ethyldi-isopropylamine. As in the benzophenone sensitised reactions, these amines, both physical quenchers of singlet oxygen, were oxidised to carbonyl compounds and imines. In view of the efficiency with which these amines quench singlet oxygen without undergoing any permanent chemical reaction[75,76] it is unlikely that singlet oxygen is the active species in these photo-oxidations.

Correlation with Reduction.

The amines that are efficiently oxidised are those which photobleach the dyes in anaerobic solution. Tertiary aliphatic amines photobleach methylene blue efficiently, whereas with primary and secondary aliphatic amines, photobleaching is very slow. Photobleaching of methylene blue is thought to be a photoreduction process[113-117] in which methylene blue (XVI) is converted to the leuco form (XVII).



(XVI) (XVII)

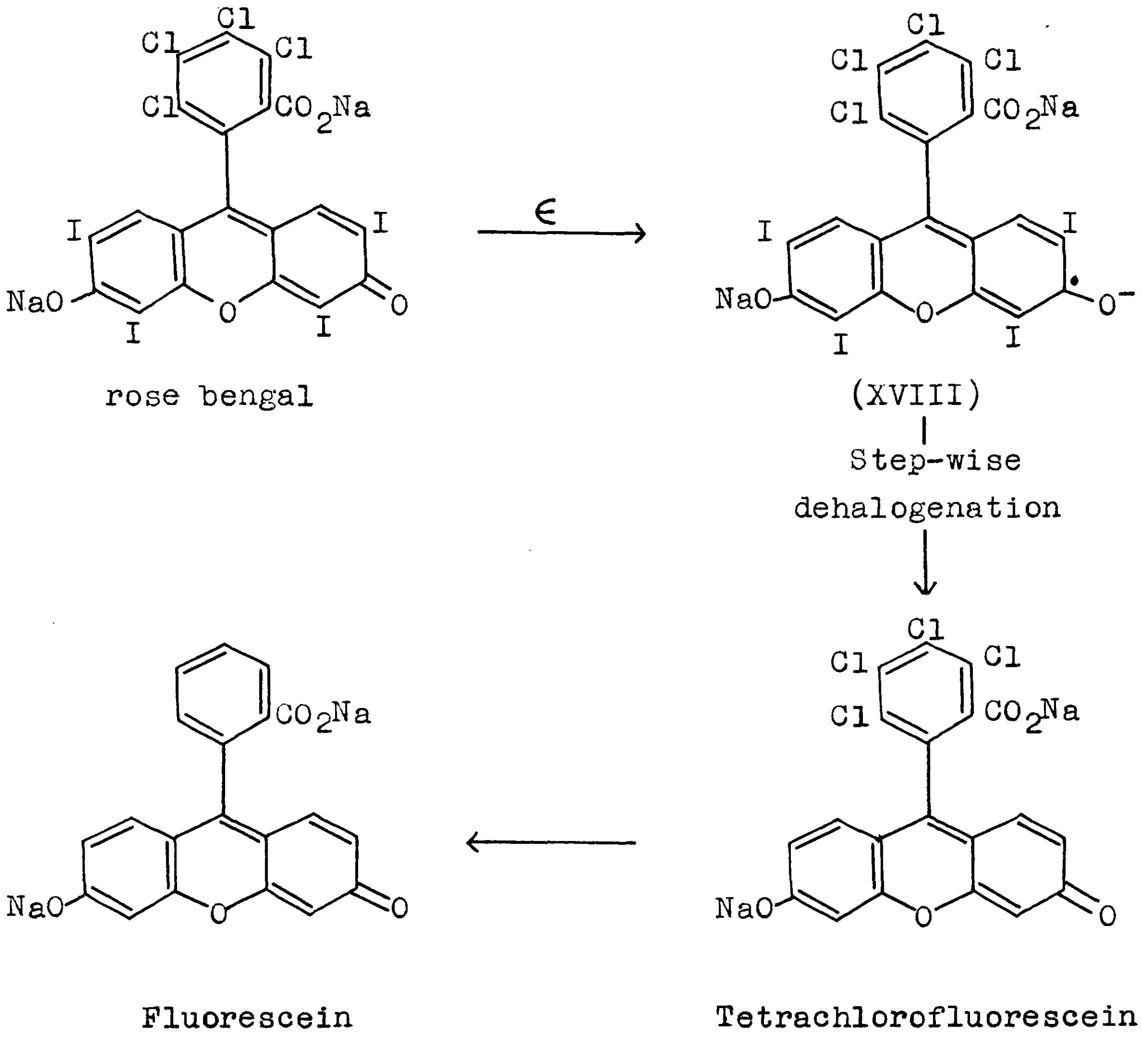
The leuco form reacts with oxygen to regenerate methylene blue.[114,116]

Methylene blue does not photosensitise the oxidation of DABCO, which is a physical quencher of singlet oxygen. However, DABCO does not photoreduce methylene blue in anaerobic solution. Aniline, N,N-dimethylaniline, and N,N-diethylaniline do not photoreduce methylene blue, and methylene blue does not sensitise the photo-oxidation of these compounds.

It is significant that methylene blue, a good sensitiser of singlet oxygen formation, does not sensitise the photo-oxidation of aromatic amines such as dimethylaniline and diethy-aniline, or DABCO, the photo-oxidation of which is sensitised by benzophenone and other compounds. If the photo-oxidation is initiated by attack of singlet oxygen on the amines, it is difficult to see why methylene blue does not sensitise the photo-oxidation of these amines. Whereas this fact is consistent with a mechanism in which the primary process in photo-oxidation is the same as in photoreduction.

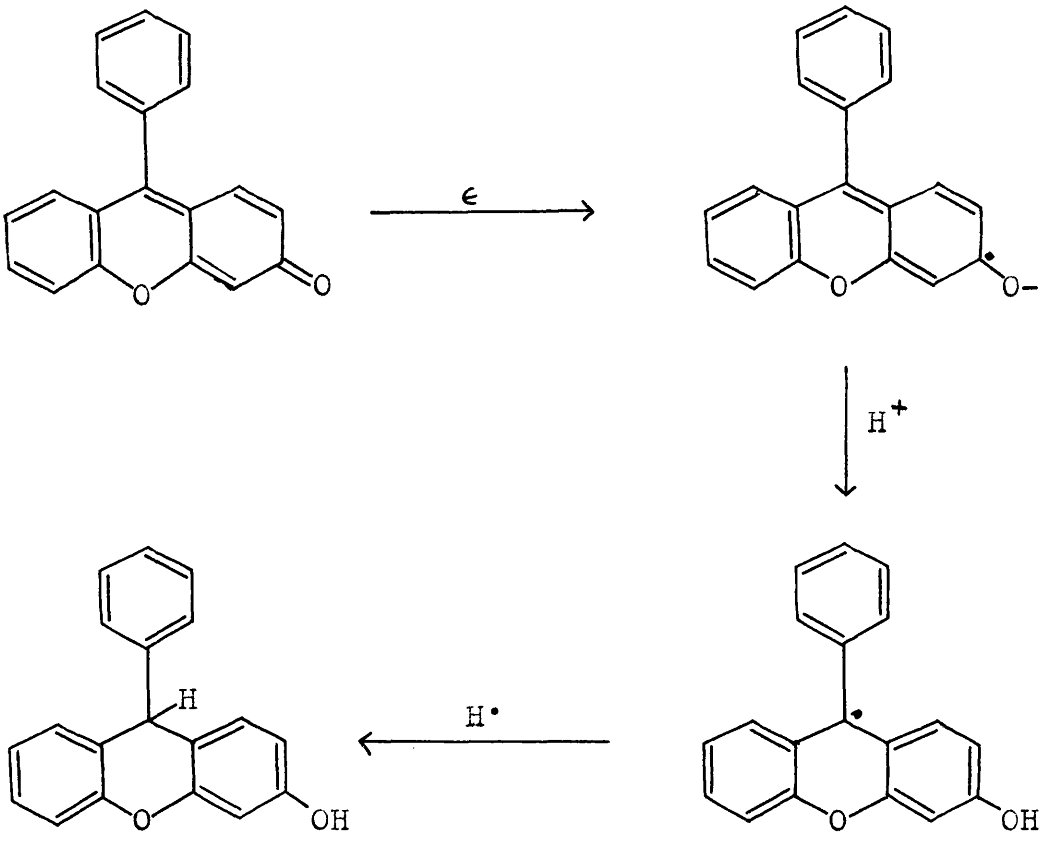
Eosin and rose bengal are both photobleached by tertiary aliphatic amines in anaerobic solution, and both dyes sensitise the photo-oxidation of these amines. The dyes are not photobleached efficiently by primary or secondary aliphatic amines, and the photo-oxidation of these amines, sensitised by these dyes is inefficient.

Photobleaching of eosin and rose bengal is accompanied by a shift of the dye absorption maxima to shorter wavelengths. This wavelength shift has been reported previously by Oster and co-workers.[118] They irradiated anaerobic solutions of fluorescein dyes and tertiary amines such as triethanolamine or tetramethylethylenediamine, and detected photobleaching accompanied by a short wavelength shift of the dye absorption maximum. Oster suggests that irradiation of the dye / amine solution causes electron transfer from the amine to the dye. The electron-rich semi-quinone, formed by electron transfer, can then stabilise itself by dehalogenation. Thus, by successive dehalogenation, rose bengal is converted into 3,4,5,6-tetrachlorofluorescein and thence to fluorescein by prolonged irradiation of an oxygen-free aqueous solution of rose bengal and tetramethylethylenediamine (scheme 3).



Scheme 3.

Some of the rose bengal is converted to a colourless species which is assumed to be a dihydro compound (scheme 4). The formation of this colourless species would explain the observed photobleaching. Photobleaching does not occur in oxygenated solution because both the dihydro compound, and particularly the semi-quinone, will react rapidly with oxygen to regenerate the original dye. Eosin is believed to behave in a similar manner to rose bengal.



Scheme 4. Formation of the dihydro compound.

The correlation between oxidation and reduction has been noted by Oster, who stated;

> 'Only those dyes which are capable of being photoreduced can act as sensitisers for photo-oxidation.'

While this is not true in a general sense (for example, oxygenation of olefins by singlet oxygen), it appears to be true in the case of amines.

Oster suggested that dyes sensitise the photo-oxidation of amines to give N-oxides or N-hydroxylamines.[114] This suggestion was probably prompted by Weil and Mather's results,[72] but no further evidence of N-oxidation has been presented. It has been pointed out that oxidation of amines at α-carbon atoms is more reasonable.[120]

Flash Photolysis Studies.

The most important fact revealed by the investigation of these reactions by flash photolysis, is that excited dye molecules can interact with amines, even in the presence of dissolved oxygen.

On flash photolysis of air saturated methanol solutions of methylene blue and tertiary aliphatic amines, a transient species was detected (λ_{max} 410,430 nm.). Transient species were not observed on flashing solutions of methylene blue, or the amines, separately. Therefore the transient species produced in the amine / dye solution could only have been formed by the interaction of excited dye molecules with amine. Formation of the transient species was accompanied by photobleaching of the ground-state dye absorption band. In oxygenated solution this photobleaching was completely reversible, complete recovery taking about one minute, see figure 5a. In deoxygenated solution (figure 5b), photobleaching is also reversible to some extent, but complete recovery does not occur.

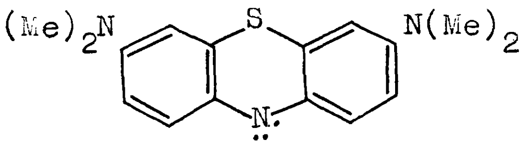
Anaerobic solutions of secondary aliphatic amines and methylene blue on flash photolysis showed the formation of a transient species, accompanied by photobleaching. The photobleaching was reversible to a certain extent, though full recovery did not occur. However, in air-saturated solution, transient species were only observed when very high concentrations of amine were used. This can reasonably be interpreted to mean that the rate constant for the interaction of excited dye with secondary amines is less than the rate constant for the reaction of the dye with tertiary amines. With low concentrations of secondary amines, oxygen-quenching of the excited dye dominates, but by increasing the amine concentration amine molecules can compete effectively with oxygen for the excited dye.

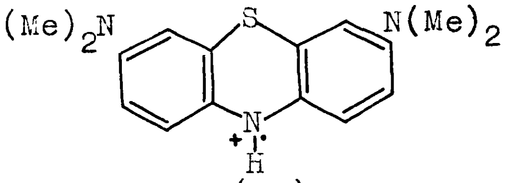
Transient species are not observed after the flash photolysis of air-saturated solutions of methylene blue and low concentrations of primary amines. Again, the rate constant for interaction of the excited dye with primary amines is probably small. Attempts to detect intermediates using high concentrations of primary amines met with the difficulty that with such high concentrations of these amines, methylene blue is converted, by a dark reaction, into an unidentified red compound. In deoxygenated solution, primary amines behaved as secondary or tertiary amines.

The reason for the inactivity in dye sensitised photo-oxidations, of aromatic amines and DABCO is also revealed by flash photolysis. In both aerobic and anaerobic solution, a transient species is formed (λ_{max}410,430 nm.). This transient species decays rapidly to regenerate methylene blue. The presence of an isobestic point, and the fact that the solution completely recovers its original optical density, suggests that no permanent reaction occurs, the primary process being completely reversible. (See figures 5c,5d.).

The Identity of the Transient Species.

The photochemistry of methylene blue has recieved a lot of attention, notably from Parker,[121] and the Japanese workers Koizumi,[122] and Matsumoto.[123] Parker reported the formation of two transient species, following the flash photolysis of aqueous solutions of methylene blue. Both species absorbed between 350 and 450 nm.,but one was very short-lived, and the other long-lived ($T_{\frac{1}{2}}$ 10µs and 400µs respectively). He suggested that the short-lived species was the methylene blue triplet state, and that the long-lived one was the semi-quinone of methylene blue (XIX), formed by electron transfer from water to methylene blue. In the presence of good electron donors (e.g.ferrous ions), only the long lived intermediate was observed.

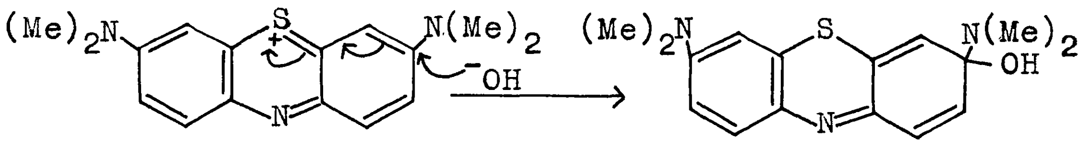

(XIX)


(XX)

The protonated form (XX) of this semi-quinone had previously been generated by potentiometric titration, and its absorption spectrum measured.[124] It was found to have a strong band at 440 nm.. Koizumi and co-workers[122] found that a transient species was produced (λ_{max} approximately 420 nm.) following the flash photolysis of solutions of methylene blue and reducing agents such as E.D.T.A., allylthiourea, and trimethylamine. It was proposed that this intermediate was also the semi-quinone (XIX) formed by electron transfer from the reducing agent to methylene blue triplet. Further work by Matsumoto supports that proposal.[123]

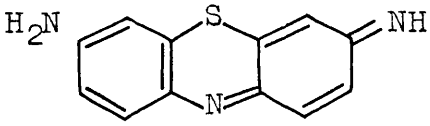
The transient species observed with all the amines in this present work is therefore identified as a semi-quinone of methylene blue. It is not certain whether this species is the unprotonated semi-quinone obtained by electron transfer, or whether it is the protonated form which can be generated either by electron transfer followed by proton transfer, or by hydrogen atom abstraction. However, since the absorption maximum of the species detected in this work is at a slightly lower wavelength than that of the protonated form, generated by potentiometric titration,[124] it is thought that it is probably the unprotonated form. It is still difficult to say whether this form is produced first, by electron transfer, or whether production of the protonated form occurs first, followed by loss of a proton.

Attempts to measure the effect of pH on the absorption spectrum of the transient species were unsuccessful, because in basic solution, methylene blue is converted into an ether-soluble red compound, possibly by nucleophilic attack on the dye molecule.



(XXI)

7-Amino-3-phenothiazime (XXII), with a conjugated structure similar to (XXI) has been made, and is red.[125]

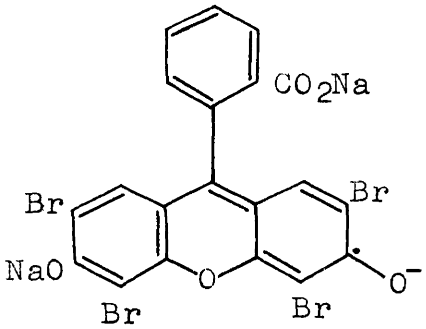


(XXII)

The flash photolysis of methylene blue and DABCO in acetonitrile solution reveals the same transient absorption as is observed when methanol is used as solvent. Protonation of a species formed by initial electron transfer is unlikely in an aprotic medium such as acetonitrile, and hydrogen atom abstraction from DABCO is unfavourable.[120] It is therefore probable that the primary process with all the amines is electron transfer from the amine to the excited dye.

Oxygen appears to have little effect on the lifetime of the transient species. Diarylamino radicals are reputed to be stable to oxygen,[126] so the insensitivity of the transient species towards oxygen is compatible with its identification as the semi-quinone (XIX).

Flash photolysis studies of eosin have been reported by Zwicker and Grossweiner,[127] and later by Koizumi and co-workers. Zwicker and Grossweiner studied the photo-oxidation of phenol, sensitised by eosin. They obtained a transient absorption spectrum (λ_{max} 410 nm.), which they assigned to a semi-reduced form of eosin (XXIII), which is produced by electron transfer from phenol to triplet eosin. Again, whether the absorption spectrum is that of the protonated form, or that of the unprotonated form (XXIII) is uncertain. These workers favour the view that the species is the unprotonated radical-ion and that the primary process with fluorescein dyes is indeed electron transfer. Koizumi with his group[128] studied the photoreduction of eosin by allylthiourea and E.D.T.A.. These workers detected a transient absorption spectrum (λ_{max} 408 nm.), which they also assigned to the semi-reduced form of eosin.



(XXIII)

It is therefore proposed that the transient species detected following the flash photolysis of eosin and tertiary amines is also the semi-reduced form of eosin (XXIII), produced by electron transfer from the amine to an excited eosin molecule.

The transient absorption spectrum produced by the flash photolysis of solutions of rose bengal and amines is assigned to the semi-reduced form of rose bengal (XVIII), by analogy with eosin.

The reason that the transient species have shorter lifetimes in aerobic solution is probably because semi-reduced fluoresceins, like other ketyl radical-anions, would react rapidly with oxygen, to generate the superoxide ion ($\dot{O}_2^-$).[100]

The Mechanism of the Reaction.

It is believed that the dye-sensitised photo-oxidation of amines involves a radical mechanism, similar to that operating in the photo-oxidations sensitised by ketones. This belief is based on the following evidence.

1. The nature of the products from the dye-sensitised photo-oxidations, which are the same as those obtained from the photo-oxidations sensitised by ketones.
2. The efficient oxidation of physical quenchers of singlet oxygen.
3. The correlation of oxidation with reduction.
4. The flash photolysis results, which show that amines can compete effectively with oxygen in reacting with the excited dye.

A reaction scheme that takes into account all the experimental observations is as follows.

$$\begin{array}{lclcccl}
D_T & + & AH & \xrightarrow{k_r} & \dot{D}^- & + & \overset{\bullet +}{AH} \\
D_T & + & O_2 & \xrightarrow{k_q} & D_0 & + & {}^1O_2 \\
\dot{D}^- & + & \overset{\bullet +}{AH} & \xrightarrow{k_{-r}} & D_0 & + & AH \\
\dot{D}^- & + & \overset{\bullet +}{AH} & \xrightarrow{k_{H^+}} & \dot{DH} & + & \dot{A} \\
\dot{DH} & + & O_2 & \longrightarrow & D_0 & + & HO_2^\bullet \\
\dot{A} & + & O_2 & \longrightarrow & AO_2^\bullet & & \\
AO_2^\bullet & + & AH & \longrightarrow & AOOH & + & \dot{A}
\end{array}$$

$$\left.\begin{array}{l} AO_2^\bullet \\ AOOH \end{array}\right] \longrightarrow \text{Products}$$

$$\text{Radicals} \longrightarrow \text{Chain Termination}$$

D = Dye; AH = Amine; $\dot{A}$ = α amino radical

In the reactions sensitised by rose bengal and eosin, other steps may be included. These are the interaction of oxygen with the dye radical-anion to give the superoxide ion, and the subsequent reactions of the superoxide ion.

From this mechanism, two effects, which would decrease the efficiency of photo-oxidation, are discernible. If k_r is small, then the initial reaction between triplet sensitiser and amine would be inefficient, and oxygen quenching would predominate. Reaction between sensitiser and amine would be favoured by increasing the amine concentration. Such an effect is observed in the flash photolysis of methylene blue and secondary amines, and with the fluoresceins and tertiary amines. Thus the photo-oxidation of secondary amines (and presumably primary amines), sensitised by methylene blue, is inefficient because k_r is small. Secondly, if the rate constant for the reverse electron transfer reaction, k_{-r}, is much greater than that for proton transfer, k_{H^+}, then photo-oxidation will not proceed efficiently. With all the dyes and all the amines used, the observed photobleaching was reversible to some extent. With tertiary aromatic amines and DABCO, photobleaching was completely reversible. This ready reversibility of the primary process compared to proton transfer is undoubtedly the reason for the stablity of these amines towards photo-oxidation sensitised by dyes such as methylene blue. It is not clear however, why this reverse process should be so favoured for these amines.

The Work of Schaeffer and Zimmerman.

Recently, results of an investigation of the dye-sensitised photochemical oxidation of primary, secondary, and tertiary butylamines have been published by Schaeffer and Zimmerman.[129] They performed a very thorough product study in an attempt to elucidate the mechanism of the reaction. They proposed that the initial reaction of primary and secondary butylamines was dehydrogenation to form imines.

$$CH_3CH_2CH_2CH_2NH_2 \longrightarrow CH_3CH_2CH_2CH{=}NH$$

$$(CH_3CH_2CH_2CH_2)_2NH \longrightarrow BuN{=}CHCH_2CH_2CH_3$$

In the case of the primary amine, they suggested that the initially formed butyraldimine reacts with excess amine to give N-butylbutyraldimine. The host of products they detected from both primary and secondary amines, arise, they suggested, from subsequent reactions of N-butylbutyraldimine.

In the ketone-sensitised photo-oxidations described in sections 2.1 and 2.2, it was suggested that dehydrogenation of primary and secondary amines by disproportionation of the corresponding α-amino radical was a reaction which actually inhibited photo-oxidation. It was proposed that photo-oxidation products were formed by reaction of the α-amino radicals with oxygen, and by the subsequent reactions of the resulting hydroperoxy radical. Schaeffer and Zimmerman do not favour this route to oxidation products though they do not present any evidence against it.

The observation that fluorescein dyes do in fact sensitise the photo-oxidation of primary and secondary amines is in contrast to the observations recorded in table 10, that primary and secondary aliphatic amines are unreactive in these reactions. Schaeffer and Zimmerman's results were obtained from solutions which were continuously flushed with air during irradiation. The results quoted in table 10 were obtained from solutions which were flushed continuously with pure oxygen during irradiation. The photo-oxidation of the propylamines was repeated in air saturated solution. The results, in table 12, show that aliphatic amines react more efficiently in air saturated than oxygen saturated solution. That is, the extent of oxidation decreases with increasing oxygen concentration. This is further evidence that singlet oxygen is not involved, since at high oxygen concentrations, quenching of the sensitiser triplet is enhanced, thus depleting the number of triplet dye molecules available to react with the amine. A similar phenomenon was observed in the benzophenone-sensitised photo--oxidation of ethanol.[27,39]

Schaeffer and Zimmerman found that the major products from the photo-oxidation of tributylamine were N,N-dibutylformamide, dibutylamine, and butyraldehyde, together with small amounts of N-butylbutyraldimine. The major products from the photo-oxidation of tripropylamine, reported in tables 10 and 11, were propionaldehyde and N-propylpropionaldimine. The reasons for this difference in products are uncertain. Schaeffer and Zimmerman suggest that the precursor of the products from tributylamine is the enamine 2-ethylvinyldibutylamine (XXIV).

$(Bu)_2NCH{=}CHEt$

(XXIV)

If this is so, it is possible that the initially formed α-amino radical from tributylamine disproportionates or reacts with oxygen, to give the enamine, more readily than the radical from tripropylamine.

$$RCH_2\dot{C}HNR'_2 \longrightarrow RCH{=}CHNR'_2$$

Why this pathway should be more favourable for tributylamine is unknown.

Despite these differences between the products obtained from tributylamine and tripropylamine, the types of products obtained from both studies are compatible with a radical mechanism.

The Excited State of the Sensitiser.

It has been assumed that the excited state of the dye which interacts with the amines is the triplet state. This assumption was also made by other workers who studied the photoreduction of methylene blue,[121,123] and the fluoresceins.[127] To provide further justification for this assumption, the effect of amines on the intensity of fluorescence from these dyes was examined, to ensure that under the conditions used for the photo-oxidation studies, reaction was not occurring via the singlet state of the dyes.

The intensity of fluorescence from methylene blue was unaffected by the presence of primary, secondary, or tertiary amines. Fluorescence from rose bengal and eosin was not quenched by primary or secondary amines, but was quenched slightly by tertiary aliphatic amines. The Stern-Volmer constants for the quenching of rose bengal and eosin fluorescence by tri-n-propylamine, in both acetonitrile and methanol solution, were 5.2 and 4.9 respectively. These values are much smaller than those obtained by quenching of hydrocarbon fluorescence (see table 14, section 2.4), where amines are known to interact with hydrocarbon singlet states at a diffusion controlled rate,[130] and where solvent polarity has a dramatic effect on quenching efficiency. Although the concentration of dye used in the fluorescence quenching experiments was a factor of 10 lower than that used in the photo-oxidation studies, it is probably safe to conclude that interaction of amines with these dyes occurs predominantly through the triplet state of the dye.

2.4. HYDROCARBONS AS SENSITISERS.

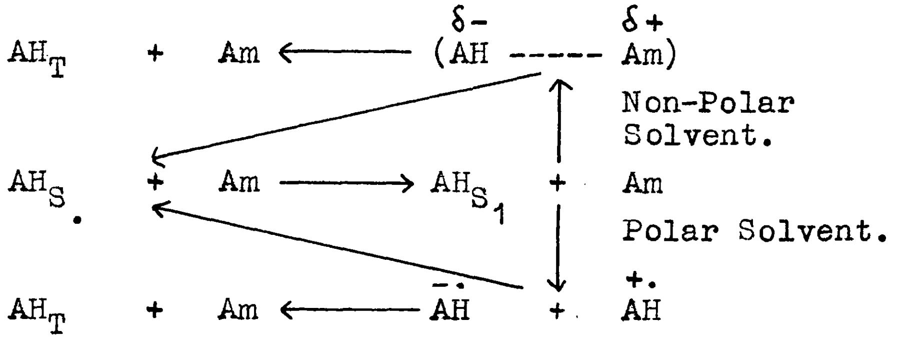
Weller[130-132] and other workers[133-135] have shown that amines of low ionisation potential quench the fluorescence of a number of aromatic hydrocarbons. Typical Stern-Volmer constants for this quenching are shown in table 14. It has been suggested that the quenching involves the formation of an exciplex between the amine and the aromatic hydrocarbon. (The term exciplex is used to mean a charge transfer complex in an excited state, the ground state of which is dissociative.)

Table 14. Stern-Volmer constants for the quenching of perylene fluorescence by amines.[130]

Amine	Solvent	k ($l.mol^{-1}$)
Diethylaniline	Acetonitrile	102.0
	Benzene	7.5
Dimethylaniline	Acetonitrile	106.0
	Benzene	8.8
Aniline	Acetonitrile	47.0
	Benzene	0.1
Triethylamine	Acetonitrile	23.5
	Dimethylformamide	10.3

The quenching of perylene fluorescence by amines has been studied extensively. Leonhardt and Weller[130,131] have examined this system by flash photolysis and by conventional fluorescence techniques. Their observations may be summarised as follows. In solvents of high dielectric constant, quenching appeared to be diffusion controlled. By flash photolysis, the perylene radical-anion, the perylene triplet, and with aromatic amines, the amine radical cation were observed by absorption spectroscopy following the photolysis flash. In solvents of low dielectric constant, the quenching efficiency was lower by one or two orders of magnitude, and only triplet-triplet absorption was observed following flash photolysis. In low dielectric solvents, a broad, structureless emission to the red of the normal fluorescence was found, and assigned to the exciplex between the amine and hydrocarbon. This emission was not observed with solvents of high dielectric constant, in which the exciplex is presumably completely dissociated into radical ions.

The essentials of the mechanism of the quenching process proposed by Leonhardt and Weller, on the basis of their results, are shown in scheme 5.



AH = aromatic hydrocarbon.

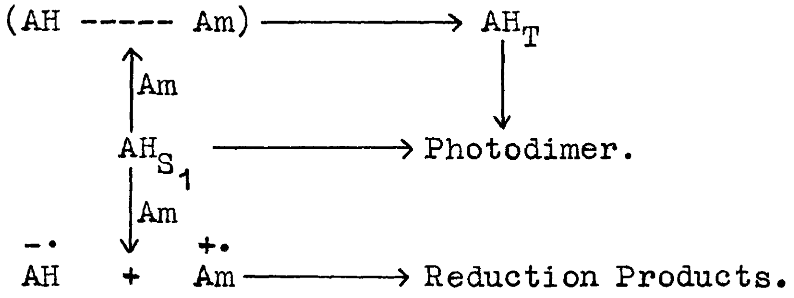
Am = Amine.

Scheme 5. Mechanism of the quenching of perylene fluorescence by aromatic amines.

Most steps in this scheme have been verified by the kinetic studies of Ware and Richter.[135]

Aliphatic tertiary amines have also been found to quench aromatic hydrocarbon fluorescence, and emission from exciplexes has been detected in non-polar solvents.[133,134]

The discovery that amines add photochemically to styrenes,[136] prompted investigations of the products of photolysis of aromatic hydrocarbons with amines. Davidson[137] found that irradiation of benzene solutions of anthracene and acenaphthylene, containing tertiary amines, gave photodimers, whereas photoreduction occurred in acetonitrile solution. Using the fact that acenaphthylene produces cis and trans photodimers from the singlet and triplet state respectively, he was able to determine the origin of the photodimers obtained. The discovery that only the cis photodimer was formed under conditions where radical ion formation predominated, showed that in this case radical ions do not decay via the triplet state of the hydrocarbon, presumably because proton transfer, leading to reduction, is extremely efficient; and that some dimerisation occurs directly from the singlet state. The interpretation of these results in terms of Weller's mechanism requires that reduction occurs via radical ions, and that trans photodimers are produced from the triplet state of the hydrocarbon formed by the break up of the exciplex: scheme 6.



Scheme 6. Product formation from solutions of amines and aromatic hydrocarbons.

Similar results were obtained by other workers studying the photochemical reactions of anthracene and N,N-dimethylaniline,[138] and this work was also extended by Barltrop[139] who examined some naphthalenes with triethylamine.

It seemed therefore, that these reactions of aromatic hydrocarbons with amines were analogous to the reactions of ketones and dyes already discussed. An important difference is that interaction between hydrocarbons and amines involves the hydrocarbon singlet state, whereas the other compounds reacted via their triplet states.

Aromatic hydrocarbons are also good sensitisers of singlet oxygen formation,[54] though it has been proposed that singlet oxygen is only formed by oxygen quenching of the hydrocarbon triplet and not by quenching of the singlet. However, oxygen does quench aromatic hydrocarbon singlet states at a diffusion controlled rate,[140,141] possibly by a charge transfer mechanism similar to that proposed by Weller for quenching by amines.

So as with ketones and dyes, there will be a competition between oxygen and amine, for the singlet hydrocarbon. This competition may be disturbed by the formation of a contact charge transfer complex between the aromatic hydrocarbon in its ground state, and oxygen, such as is observed with toluene,[143] and other aromatic compounds.[90,142]

2.4.1. RESULTS.

Product Studies.

Anthracene, naphthalene, perylene, and phenanthrene were found to sensitise the photo-oxidation of triethylamine, tri-n-propylamine, and N,N-dimethylaniline in oxygenated acetonitrile solution. The products from these reactions are

Table 15. Products from the photo-oxidation of amines sensitised by aromatic hydrocarbons.

Amine	Initial amount. (m.mol)	Final amount. (m.mol)	Products	Yield (m.mol)
1. Sensitiser = Naphthalene.				
Tripropylamine	15.0	7.0	Propionaldehyde	3.1
			EtCH=NPr	2.3
Triethylamine	15.0	7.8	Acetaldehyde	1.2
2. Sensitiser = Anthracene.				
Tripropylamine	12.5	6.2	Propionaldehyde	2.6
			EtCH=NPr	1.5
Triethylamine	12.5	3.2	Acetaldehyde	2.0
			MeCH=NEt	3.0
Diethylaniline	2.5 7	2.1	Acetaldehyde	Trace
			Ethylaniline	Trace

Table 15. continued.

Amine	Initial amount. (m.mol)	Final amount. (m.mol)	Products	Yield (m.mol)
3. Sensitiser = Phenanthrene				
Tripropylamine	12.5	8.7	Propionaldehyde	1.0
			EtCH=NPr	0.8
Triethylamine	12.5	2.5	Acetaldehyde	2.5
			MeCH=NEt	1.8
4. Sensitiser = Perylene				
Tripropylamine	30.0	18.2	Propionaldehyde	3.5
			Di-n-propylamine	1.0
			EtCH=NPr	4.0
Triethylamine	30.0	15.0	Acetaldehyde	5.0
			Diethylamine	1.0
Diethylaniline	2.5	0.4	Acetaldehyde	Trace
			Ethylaniline	1.0

shown in table 15. Primary and secondary aliphatic amines were found to be unreactive.

The hydrocarbons were all photoreduced by tertiary amines in deoxygenated acetonitrile solution. Quantum yields[a] for these reactions are shown in table 16.

Table 16. Quantum yields for the photoreduction of aromatic hydrocarbons by triethylamine and dimethylaniline.

Hydrocarbon	Concentration	Wavelength of irradiation	TEA	DMA
Anthracene	5×10^{-4} M	352 nm.	0.15	0.95
1,2-Benzanthracene	5×10^{-4} M	360 nm.	0.18	0.71
Naphthalene	3×10^{-3} M	313 nm.	0.14	-
Perylene	8×10^{-4} M	430 nm.	0.013	1.0
Phenanthrene	3×10^{-3} M	338 nm.	0.16	-

Naphthalene, perylene, and phenanthrene did not sensitise the photo-oxidation of amines in oxygenated benzene solution, nor were these hydrocarbons photoreduced by amines in deoxygenated benzene solution. Some photo-oxidation did occur in benzene solution with anthracene as sensitiser, though less than 10% of the amine reacted and no products could be separated by g.l.c. The solution was intensely coloured however, after irradiation and the anthracene was consumed.

From the photo-oxidations using hydrocarbons other than anthracene, the sensitiser was recovered quantitatively. In anthracene sensitised oxidations in acetonitrile, some

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[a] These values were obtained by Mr. D. Brimage.

anthracene was consumed. However, the initial amount of anthracene in solution was only 2.5×10^{-2} millimoles, and this amount led to the oxidation of 6.3 millimoles of tripropylamine, 9.3 millimoles of triethylamine, and 0.4 millimoles of dimethylaniline. Obviously anthracene is acting as a photosensitiser for amine oxidation, but it is also being used up in competing reactions, possibly the formation of the 9,10-endoperoxide.

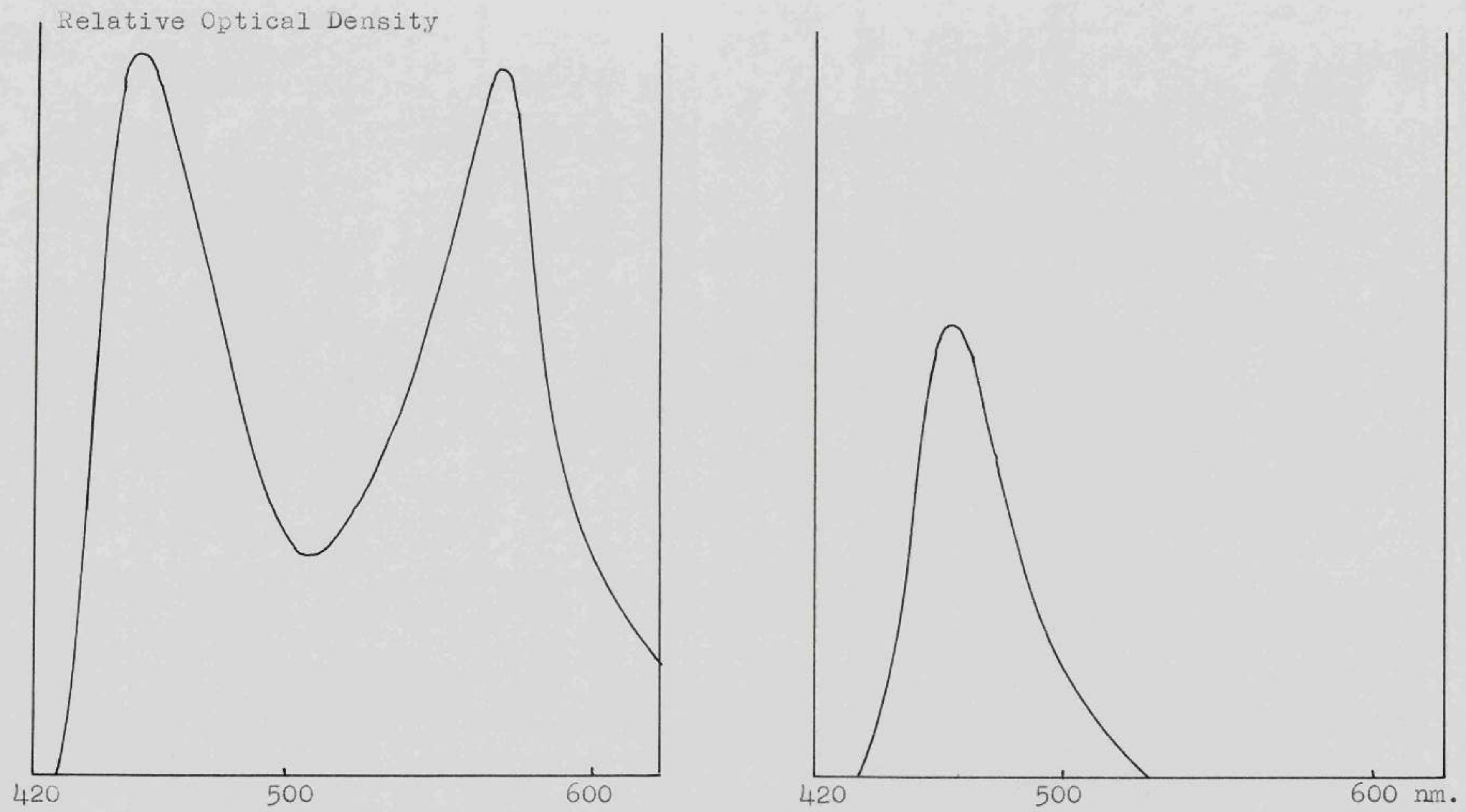
Triphenylene was not photoreduced by the amines studied, either in benzene or acetonitrile solution, nor did this hydrocarbon sensitise the photo-oxidation of amines.

Flash Photolysis Studies.

Flash photolysis of anaerobic acetonitrile solutions of perylene with N,N-dimethylaniline and N,N-diethylaniline, showed the formation of the perylene radical anion and the amine radical cation. In aerobic solution, only the amine radical cation was observed. These results are illustrated in figures 7a and 7b. The amine radical cation was not observed on flash photolysis of amine alone in oxygenated solution.

Initial studies on the kinetics of decay of the perylene radical anion generated in anaerobic acetonitrile solution containing dimethylaniline, showed the decay to be first order (see figure 8).

The perylene radical anion was also observed on flash photolysis of anaerobic solutions of perylene and triethyamine in acetonitrile. The anion was not observed in air saturated solution.



(a) Anaerobic solution, (t = 5μs.)

(b) Aerobic solution, (t = 5μs.)

Figure 7, Spectra of transient species produced by the flash photolysis of solutions of perylene and N,N-diethylaniline in acetonitrile.

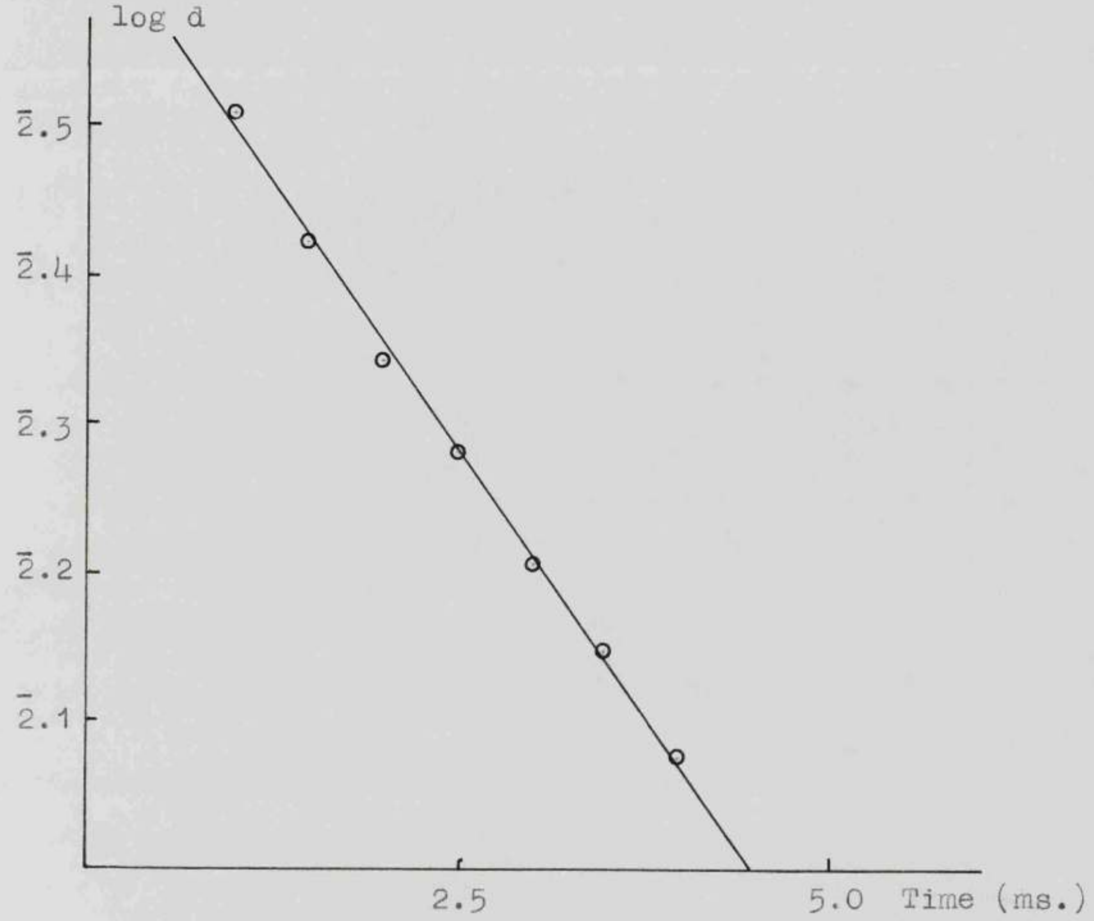


Figure 8. The decay of the perylene radical anion in anaerobic acetonitrile solution containing dimethylaniline.

Flash photolysis of acetonitrile solutions of anthracene and dimethylaniline produced the dimethylaniline radical cation in both aerobic and anaerobic solution. The anthracene radical anion, λmax 714 nm,[144] was not observed. Attempts to observe the naphthalene radical anion, λmax 813 nm,[145] by flash photolysis of solutions of naphthalene and triethylamine, were unsuccessful.

2.4.2. DISCUSSION.

Product Studies.

The major products from the photo-oxidations of aliphatic amines were aldehydes and imines, the same products as obtained when benzophenone, other ketones, and dyes were used as photosensitisers. Diethylaniline gave acetaldehyde and ethylaniline, which again were among the products obtained when benzophenone was used as a sensitiser. It is therefore probable that these products are formed by a common mechanism.

In all these reactions, the products isolated represented only a small part of the total amount of amine consumed. All the solutions were intensely coloured after irradiation, particularly solutions of diethylaniline. Solutions of aliphatic amines deposited a red solid around the lamp during irradiation. This would account for some of the amine which reacted. Unfortunately the red solid was not identified.

Ramakrishnan[146] has isolated compounds formed by the oxidative coupling of dimethylaniline radical-cations, from among the products of the photo-oxidation of dimethylaniline sensitised by anthracene. The presence of products such as these would explain the intense colour of the solutions of diethylaniline after irradiation. These types of products have been obtained from amine radical-cations generated by direct photolysis of aromatic amines,[147,148] and by polarographic studies.[149]

Solvent Effect.

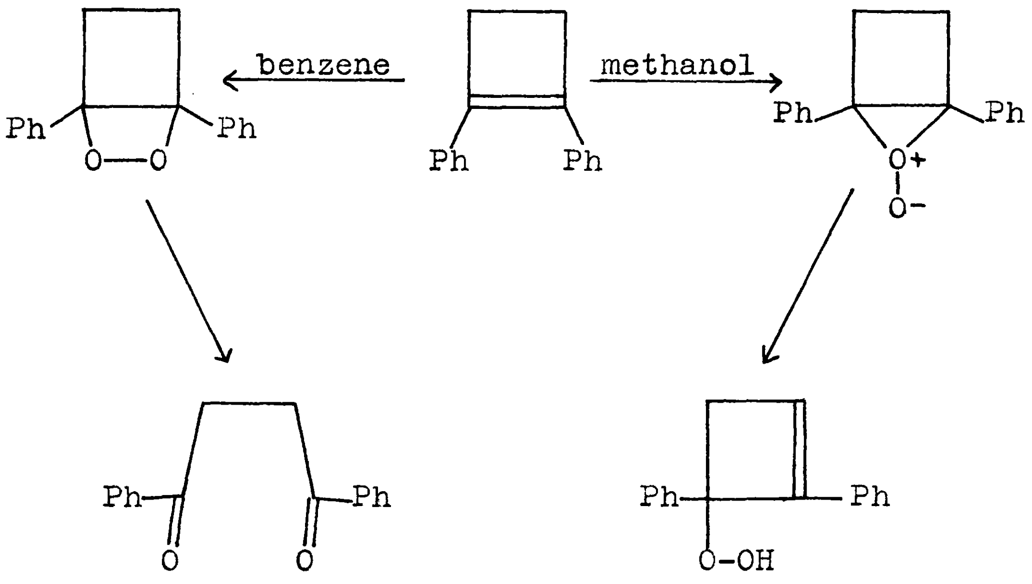
Solvent polarity has a dramatic effect on these reactions. With hydrocarbons other than anthracene, no detectable reaction occurred in benzene solution; yet irradiation of acetonitrile solutions under the same conditions led to reaction of around 50% of the amine. Photoreduction of the hydrocarbons exhibited this same solvent effect, a report of which has already been published.[137]

Oxidations of other organic compounds, involving singlet oxygen, do not in general show such a solvent effect. Foote[43] measured the effect of solvent on the ratio of the rate constant for the deactivation of singlet oxygen (k_d), to the rate constant for the reaction of singlet oxygen with 2-methylpent-2-ene, (k_r).

$$^1O_2 \longrightarrow {}^3O_2 \qquad k_d$$

$$^1O_2 + A \longrightarrow AO_2 \qquad k_r$$

Some of these ratios for solvents of different dielectric constant are given in table 17. No correlation of reactivity with solvent polarity is observed: solvents as different as benzene and methanol give $^{k}d/k_r$ values which differ only slightly. Solvent polarity has been found to effect the nature of the products from the photo-oxygenation of 1,2-diphenylcyclobutene.[101] In methanol, reaction of 1,2-diphenylcyclobutene with singlet oxygen gave predominantly the hydroperoxide (XXV), whereas in benzene the major product was the diketone (XXVI).



(XXVI) (XXV)

Scheme 7. Photo-oxygenation of 1,2-diphenylcyclobutene.[101]

The authors of this work proposed that formation of the hydroperoxide involved a perepoxide intermediate, whereas formation of the diketone involved a dioxetane (scheme 7).

Table 17. Values of k_d/k_r for the sensitised photo-oxygenation of 2-methylpent-2-ene.

Solvent	Dielectric[150] constant	k_d/k_r
Benzene	2.2	0.10
Acetone	20.7	0.08
Methanol	32.6	0.17

If the photosensitised oxidation of amines is initiated by attack of singlet oxygen, and if a perepoxide-type intermediate proposed by Gollnick[44] is involved, reaction might be expected to be more favourable in polar solvents. However, no comparable solvent effect was observed when benzophenone or other ketones were used to sensitise amine photo-oxidation.

Significantly, solvent has a pronounced effect on the photoreduction of hydrocarbons by amines. Photoreduction of perylene, phenanthrene, and naphthalene by the amines only occurs in deoxygenated acetonitrile solution; not in benzene. These hydrocarbons do not sensitise the photo-oxidation of amines in benzene solution, but oxidation is efficient in acetonitrile. This correlation of photo-oxidation with photoreduction was observed with other sensitisers. It is evidence that the same primary process operates in photo-oxidation as operates in photoreduction, and that this primary process is the interaction of the excited sensitiser with amine.

Flash Photolysis.

Radical-ions are observed after the flash photolysis of perylene and amines in acetonitrile solution, but not in benzene solution. Presumably therefore, the primary process in the photoreduction of hydrocarbons by amines is electron transfer from the amine to the hydrocarbon.

In air-saturated solution only the amine radical cation is observed. This is not formed by direct electron transfer from amine to oxygen, since the cation is not observed in the absence of sensitiser, and the energy levels of the amine excited states are too high for energy transfer to precede electron transfer. It is thought that the primary process in air-saturated solution is electron transfer from amine to the hydrocarbon singlet state, and that this is followed by electron transfer from the hydrocarbon radical-anion to oxygen.

$$\overset{-\bullet}{ArH} + O_2 \longrightarrow ArH + \overset{-\bullet}{O_2}$$

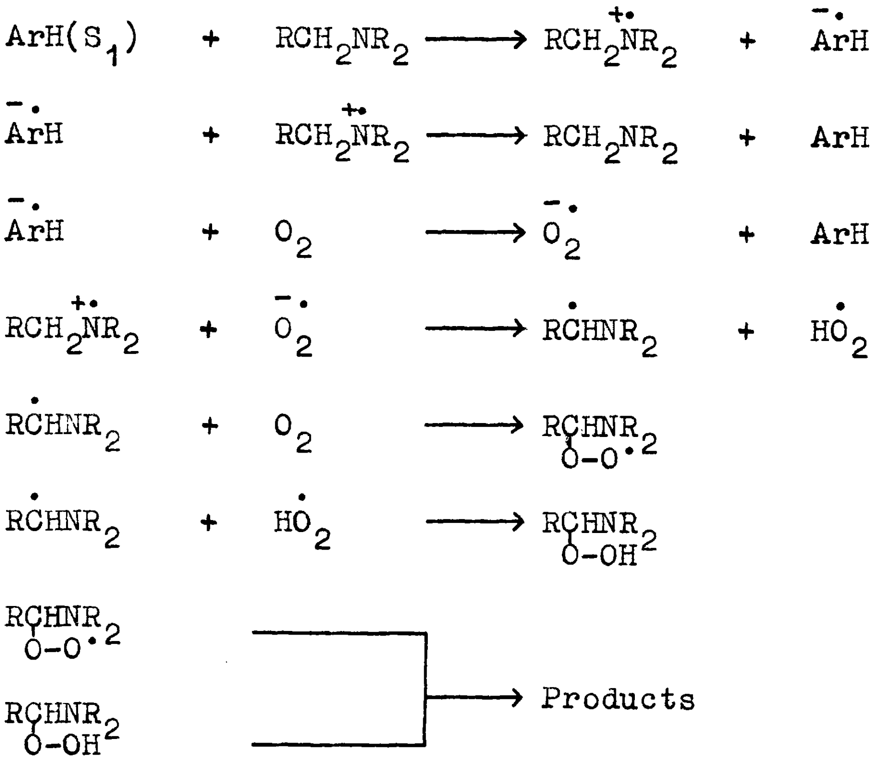
The reason that the naphthalene and anthracene radical ions are not observed is probably that the photographic plate and the photo-electric detector are insensitive in the absorption region of these species.

The Mechanism.

It is proposed that a radical mechanism operates in the photo-oxidation of amines sensitised by aromatic hydrocarbons.
Three main pieces of evidence have been presented to support this.

1. The products, which are the same as those obtained with other sensitisers, are compatible with a radical mechanism.
2. Photo-oxidation correlates with photoreduction in which the primary process is electron transfer.
3. The photo-oxidation of triethylamine, a physical quencher of singlet oxygen, is sensitised by hydrocarbons.

A mechanism which is compatible with the experimental evidence is shown on the following page.



$$ArH(S_1) + RCH_2NR_2 \longrightarrow RCH_2\overset{+\bullet}{N}R_2 + \overset{-\bullet}{ArH}$$

$$\overset{-\bullet}{ArH} + RCH_2\overset{+\bullet}{N}R_2 \longrightarrow RCH_2NR_2 + ArH$$

$$\overset{-\bullet}{ArH} + O_2 \longrightarrow \overset{-\bullet}{O_2} + ArH$$

$$RCH_2\overset{+\bullet}{N}R_2 + \overset{-\bullet}{O_2} \longrightarrow R\overset{\bullet}{C}HNR_2 + H\overset{\bullet}{O}_2$$

$$R\overset{\bullet}{C}HNR_2 + O_2 \longrightarrow R\underset{O-O\bullet}{C}HNR_2$$

$$R\overset{\bullet}{C}HNR_2 + H\overset{\bullet}{O}_2 \longrightarrow R\underset{O-OH}{C}HNR_2$$

$$\left.\begin{array}{l} R\underset{O-O\bullet}{C}HNR_2 \\ R\underset{O-OH}{C}HNR_2 \end{array}\right] \longrightarrow \text{Products}$$

This mechanism differs from those proposed for the photo-oxidations sensitised by ketones and dyes in that in this case, it is thought that a proton is transferred to the superoxide ion, rather than to the radical-anion of the hydrocarbon. With all the sensitisers however, the reaction sequence is considered to be initiated by interaction of the excited sensitiser with amine rather than by formation of singlet oxygen.

Tropinone and Pseudopelletierine.

The report[73] that singlet oxygen is involved in the direct photo-oxidation of tropinone and pseudopelletierine, and in the photo-oxidation of these compounds sensitised by triphenylene, naphthalene, and rose bengal, is clearly incompatible with the conclusions reached so far. When the photo-oxidation of tropinone was carefully re-examined, it was found that the photo-oxidation of this compound was not sensitised by naphthalene or triphenylene in benzene solution. When benzene solutions of tropinone and naphthalene or triphenylene were irradiated under conditions such that only the 'sensitiser' absorbed light, no detectable reaction occurred. When two solutions, one containing tropinone alone, the other containing tropinone and naphthalene or triphenylene, were irradiated simultaneously with light of mainly 310 nm. wavelength, it was found that the amount of reaction that occurred in the presence of naphthalene or triphenylene, was proportional to the amount of light absorbed directly by tropinone at 310 nm.. Naphthalene and triphenylene merely acted as light filters and reduced the amount of reaction occurring compared to that in the solution containing tropinone alone. It was found however, that rose bengal did sensitise the photo-oxidation of tropinone but it was also noted that rose bengal was photoreduced efficiently by tropinone in oxygen-free methanol solution. When tropinone alone was irradiated in anaerobic solution, a decrease in the intensity of the carbonyl absorption in the I.R. spectrum was noted.

It is proposed therefore, that the photo-oxidation of tropinone and pseudopelletierine sensitised by rose bengal involves initial interaction between excited dye and amine molecules; and further, that the direct photo-oxidation involves intermolecular interaction between an amino group and an excited carbonyl group.

The authors of the original work have since questioned this interpretation[73a] and have presented further evidence in favour of their original interpretation. Their evidence is as follows.

1. Kinetic studies are briefly reported which imply that hydrocarbons do in fact sensitise the reaction.
2. The reaction is quenched by DABCO, without concomitant oxidation of this species. DABCO is a known physical quencher of singlet oxygen, and is also believed by these authors to be destroyed in typical ketone/amine radical reactions.
3. The photo-oxidation of N-methyl granatanine, obtained by reduction of the carbonyl group of pseudopelletierine, is sensitised by rose bengal and naphthalene.

The fact that the kinetic studies revealed that the initial rate of reaction obtained by direct irradiation was identical to those with naphthalene and triphenylene as sensitisers is in direct contrast to the results reported above on the photo-oxidation of tropinone.

The quenching effect of DABCO does not indicate necessarily that singlet oxygen is involved in the photo-oxidation. DABCO also quenches excited carbonyl compounds[151] and singlet states of aromatic hydrocarbons,[a] without itself being consumed. Quenching by DABCO of the photo-oxidation of pseudopelletierine would therefore be expected even if a radical mechanism is involved.

Rose bengal sensitises the photo-oxidation of tertiary aliphatic amines, and evidence to show that this reaction did not involve singlet oxygen was presented in section 2.3. Thus,

[a] See appendix 2.

the sensitisation by rose bengal, of the photo-oxidation of the tertiary aliphatic amine N-methyl granatanine, does not imply that the photo-oxidation involves singlet oxygen.

In view of the results reported in section 2.4 on the sensitisation of amine photo-oxidation by hydrocarbons, it is surprising that naphthalene sensitises the photo-oxidation of N-methyl granatanine in benzene solution. The results in section 2.4 show that usually a polar solvent is necessary for such a reaction to occur. Possibly these workers did not use anhydrous benzene. A trace of water in the solvent may increase polarity sufficiently to stabilise the radical ions, and to allow photo-oxidation to occur by a radical pathway. Further work is necessary to resolve this question conclusively. It is interesting however, that these authors did not report the use of triphenylene as a sensitiser for the photo-oxidation of N-methyl granatanine, since triphenylene is not reduced by amines in either polar or non-polar solvents, and it does not sensitise the photo-oxidation of other tertiary amines.

2.5. THE PRIMARY PROCESS IN THE PHOTOREACTIONS OF KETONES WITH AMINES.

A discussion of the nature of the primary process in the photoreduction of ketones by amines, and in the photo-oxidation of amines sensitised by ketones was deliberately avoided in earlier sections. This has been the subject of controversy for a number of years.

Cohen suggested that the primary process in the photoreduction of ketones by amines was electron transfer from amine to the triplet carbonyl group, followed by rapid proton transfer from the α C-H group.[88] This suggestion was based on the following evidence.

1. The primary process is insensitive to physical quenchers such as naphthalene or ferrocene.
2. The deuterium isotope effect for photoreduction of benzophenone by cyclohexylamine-1-d is smaller than would be expected if direct hydrogen abstraction occurs.
3. The rate constants for interaction of amine with the ketone triplet increase in the order primary $<$ secondary $<$ tertiary amine; which correlates with ionisation potential of the amines.[92,94]

Davidson and Lambeth found that the photoreduction of benzophenone by benzhydrol was quenched by triphenylamine and tri-p-tolylamine. Quenching by tri-p-tolylamine was more efficient than quenching by triphenylamine, and the quenching of triphenylamine was greater in acetonitrile than in benzene solution. They suggested that these results were consistent with a quenching mechanism involving electron transfer from amine to triplet benzophenone.[152] Initial results of a flash photolysis study indicated that the tri-p-tolylamine radical-cation was indeed formed in this system.[99]

A comparison of the emission properties and photoreactions of γ-dimethylaminobutyrophenone with those of valerophenone and amines, led Wagner[153] to conclude that the primary process between amines and ketone triplets was not simple hydrogen abstraction. Yet his results were seemingly inconsistent with an actual electron transfer process. However, he concluded that some sort of charge-transfer complex between tertiary amines and ketones must occur. Wagner, in common with previous workers,[88,154] could not find any evidence by I.R., U.V., or N.M.R. spectroscopy, of interactions between tertiary amines and aromatic ketones. He did find however, that emission from γ-dimethylaminobutyrophenone was much longer lived than that from valerophenone, showing that interactions between amines and excited ketones may in fact occur.

It is a widely held opinion that some type of complex is formed between amines and excited carbonyl compounds. Hammond has proposed the intermediacy of a triplet exciplex in the photoreaction of Michler's ketone (4,4'-bis-(dimethylamino)-benzophenone) with benzophenone.[155]

These results all show that the primary process between amines and excited ketones is not direct hydrogen abstraction and that some charge-transfer, or exciplex formation may occur.

Results of further work by Cohen on this problem, indicate that other factors may be involved. Cohen found[151] that aniline, diphenylamine, and DABCO (ionisation potentials 7.7, 7.4, and 7.2 eV respectively) retard the photoreduction of fluorenone by triethylamine, and that the efficiency of quenching by anilines is increased by electron donating, and decreased by electron withdrawing para substituents. The results are claimed to support the hypothesis that quenching involves charge-transfer interactions between the ketone triplet and amine. However, triphenylamine (I.P. 6.9 eV.) does

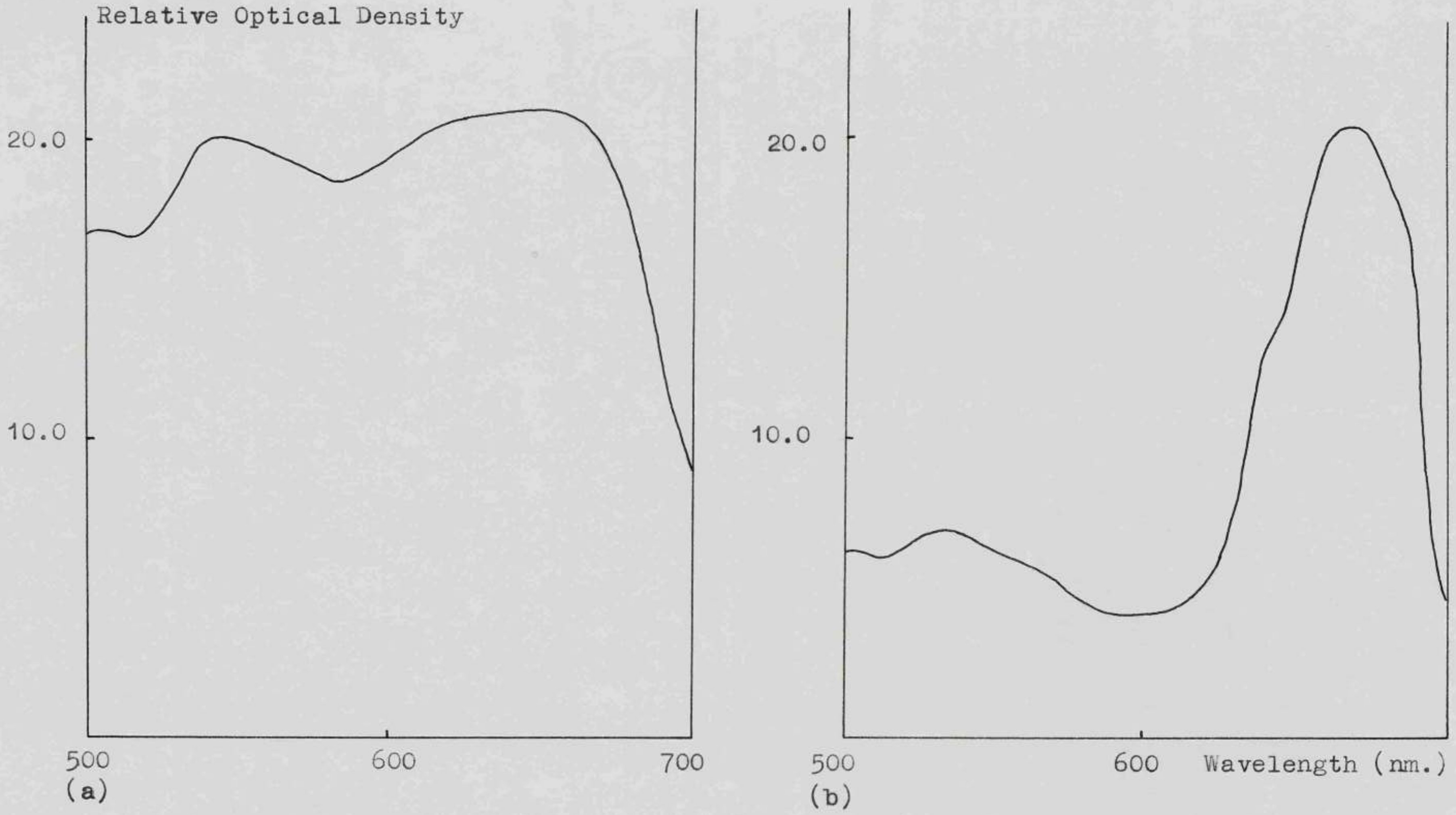


Figure 9. Spectra of transient species produced by the flash photolysis of acetonitrile solutions of tri-p-tolylamine and benzophenone in (a) nitrogen flushed solution, and (b) air-saturated solution.

not quench the photoreduction efficiently, and the efficiency of the other amines as quenchers does not correlate well with ionisation potential. For example diphenylamine quenches five times more effectively than DABCO, though their ionisation potentials are comparable. Moreover, a higher concentration of triethylamine than quencher is used in these reactions; if photoreduction is held to proceed by initial electron transfer, and if quenching is also an electron transfer process, it is surprising that these amines should quench the photoreduction by triethylamine (I.P. 7.8 eV.[156]) at all. Clearly factors other than ionisation potential are involved.

The object of the following work is to explore the interactions between amines and excited aromatic carbonyl compounds, in an attempt to elucidate the mechanism of the primary process in photoreductions and photo-oxidations.

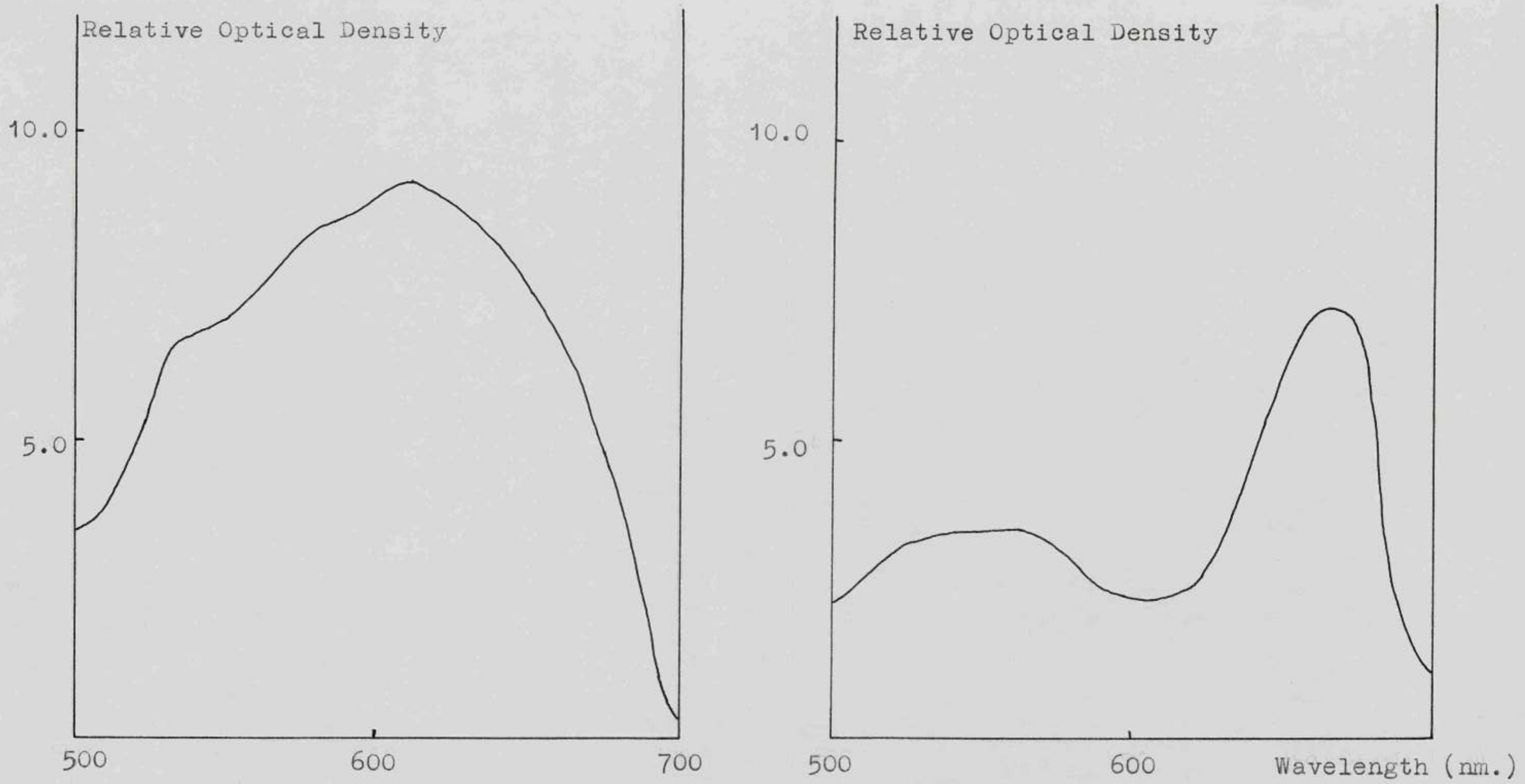
2.5.1. RESULTS.

The Interaction of Amines with Benzophenone.

The formation of the tri-p-tolylamine radical-cation following the flash photolysis of solutions of tri-p-tolylamine and benzophenone was re-examined.

1. Photographic Work.

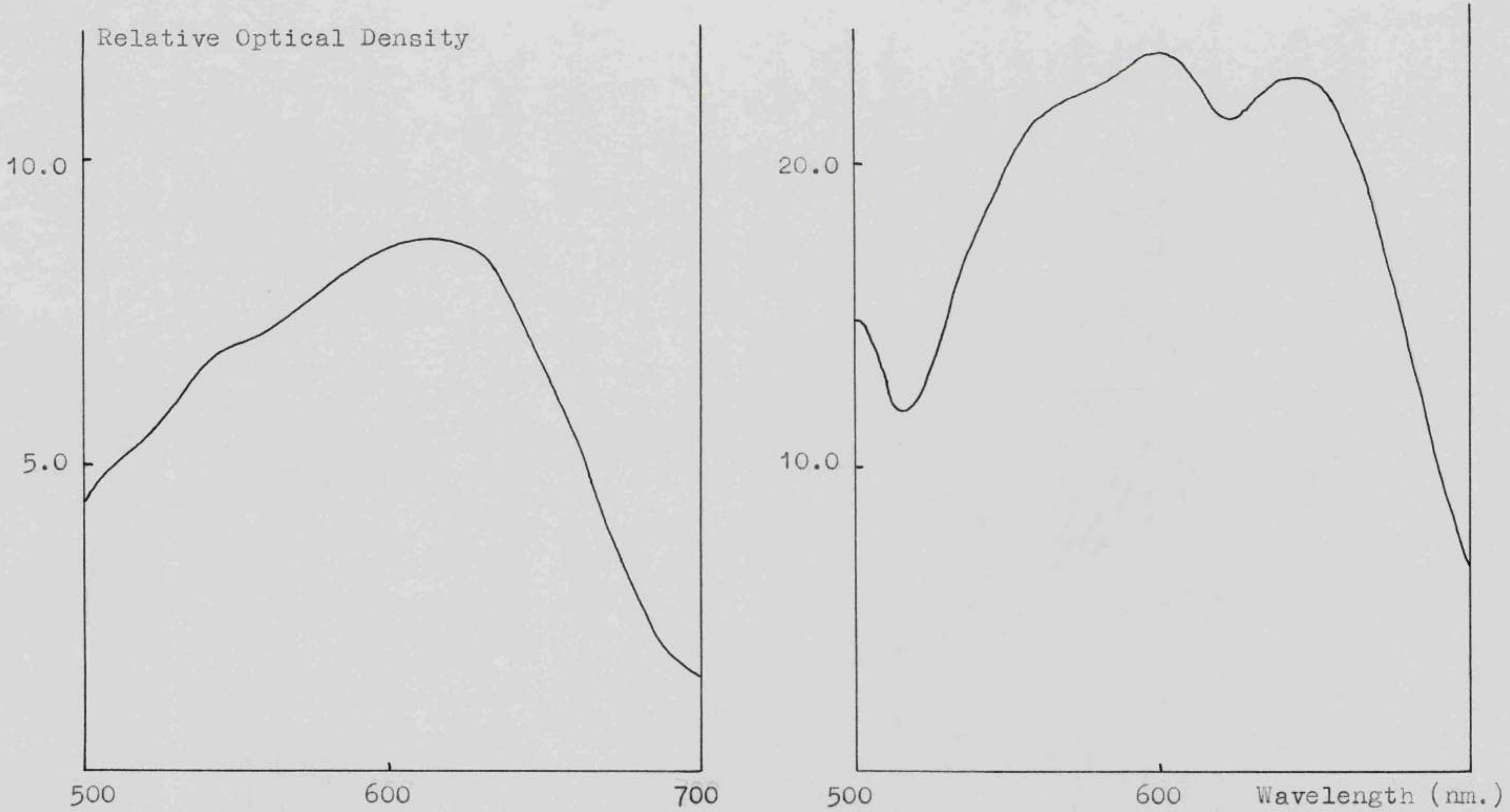
Flash photolysis of acetonitrile solution of tri-p-tolylamine and benzophenone in a pyrex cell produced a transient absorption spectrum extending from 500 to 700 nm., (figure 9a). Flash photolysis of an air saturated solution gave a transient absorption spectrum, λ_{max}670 nm., (figure 9b). Flash photolysis



(a) Anaerobic solution.

(b) Aerobic solution.

Figure 10. Spectra of transient species obtained by flash photolysis of acetonitrile solutions of tri-p-tolylamine. (t = 25µs)



(a) Triphenylamine alone.

(b) Triphenylamine plus benzophenone.

Figure 11. Spectra of transient species produced by the flash photolysis of nitrogen-flushed acetonitrile solutions of triphenylamine.

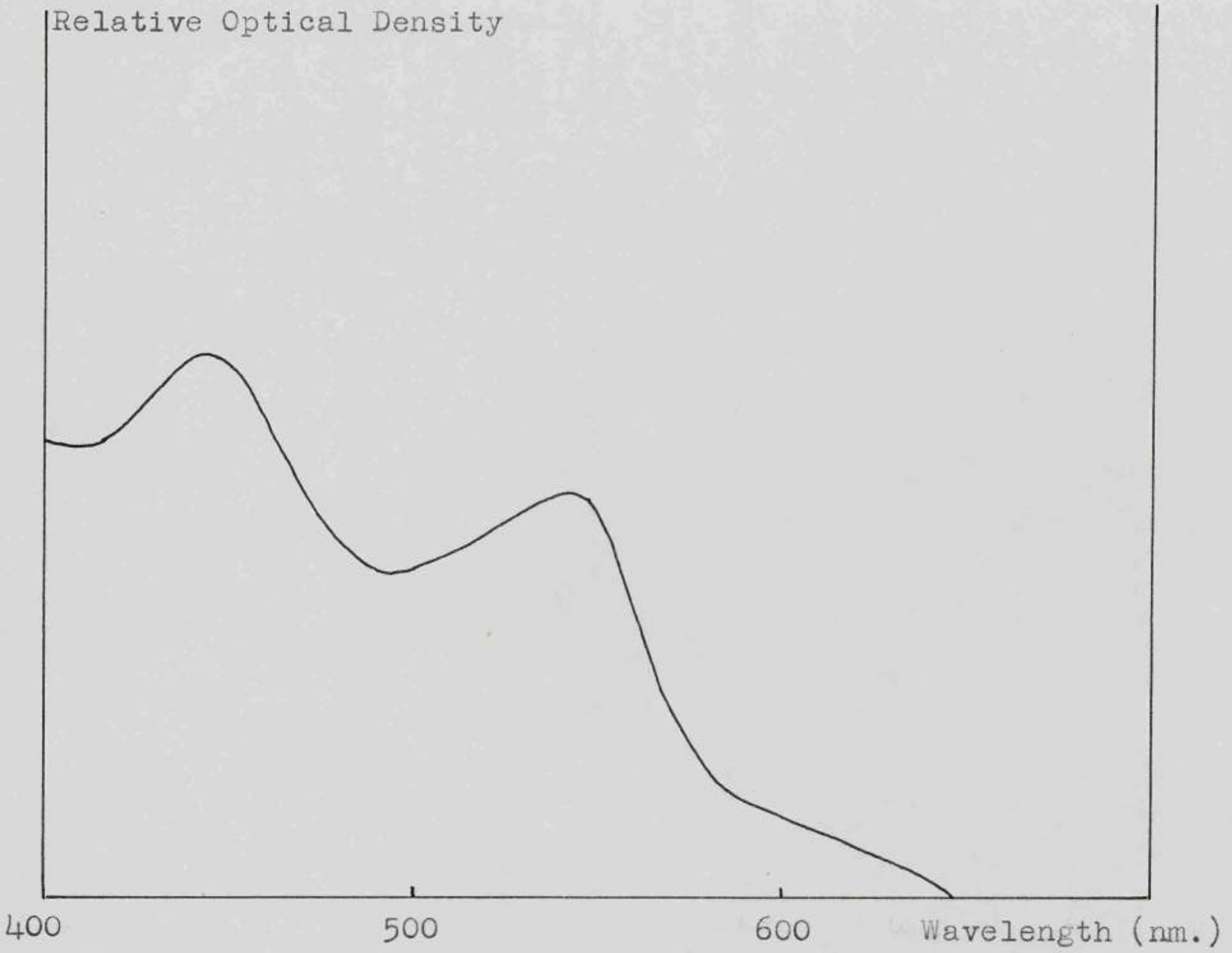


Figure 12. **Transient absorption spectrum obtained following the flash photolysis of an anaerobic acetonitrile solution of aniline and benzophenone.** (t = 5μs)

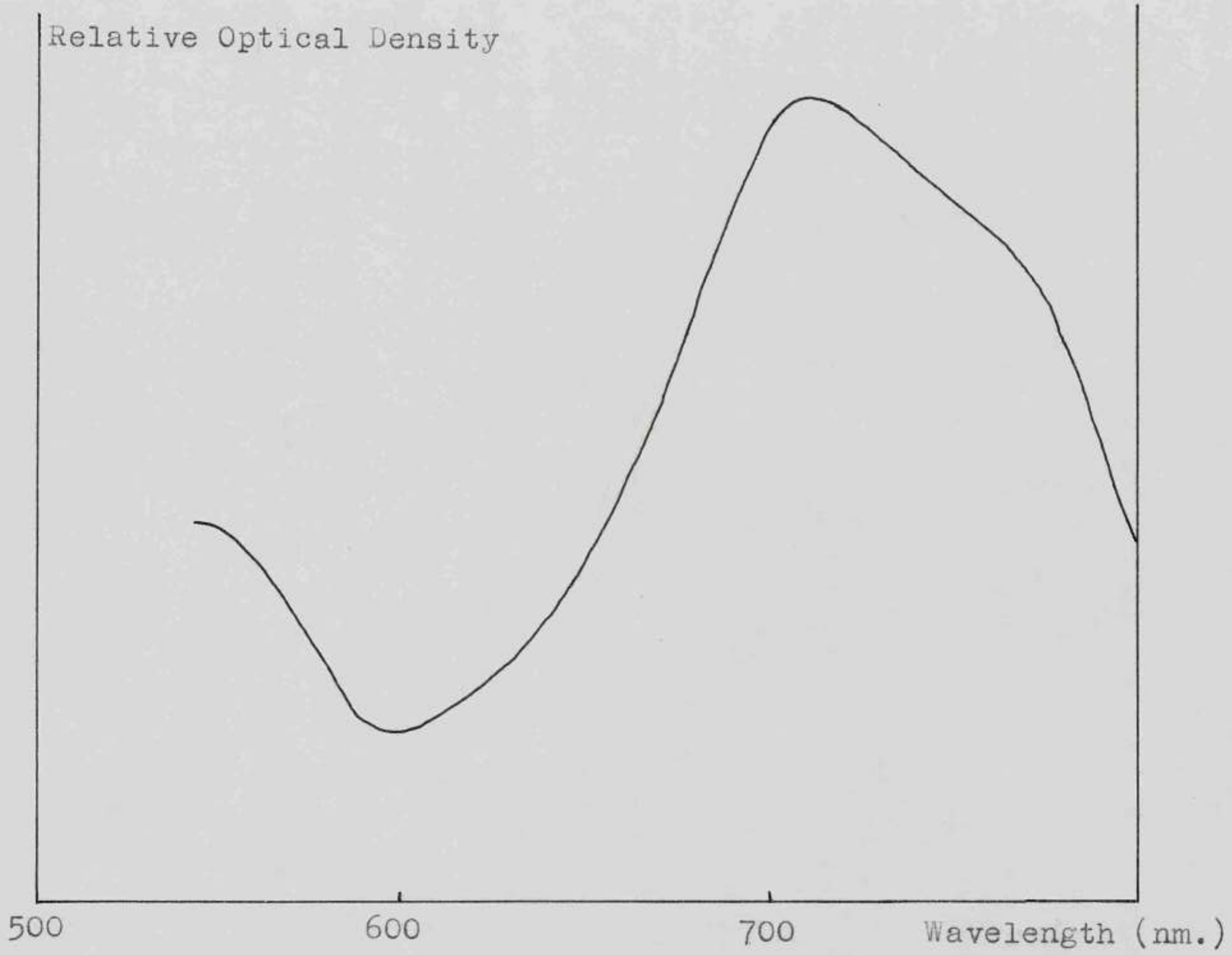


Figure 13. Absorption spectrum of transient species formed by flash photolysis of an anaerobic solution of benzophenone and diphenylamine in acetonitrile. (t = 25μs)

of the amine alone in anaerobic solution gave a different transient spectrum, λ_{max} 610 nm. (figure 10a), whereas the amine alone in air saturated solution showed the formation of the transient species with absorption maximum 670 nm. but with a smaller intensity than that obtained from solutions of the amine and benzophenone, (figure 10b).

When the experiments were repeated using a quartz cell, the appearance of the spectra was the same but their intensity was greater in every case.

The same experiments were performed using triphenylamine, diphenylamine, and aniline. In air saturated solutions of these amines in acetonitrile, with or without benzophenone, no transient species were detected by flash photolysis. Flash photolysis of diphenylamine or aniline alone in deoxygenated acetonitrile in a pyrex vessel produced no transient species, but flash photolysis of triphenylamine in deoxygenated solution produced the transient spectrum, λ_{max} 610 nm., shown in figure 11a. Flash photolysis of solutions of the amines and benzophenone in deoxygenated acetonitrile, produced transient species, the absorption spectra of which are shown in figures 11b, 12, and 13.

2. Kinetic Studies on the Tri-p-tolylamine Radical-Cation.

The decay of the tri-p-tolylamine radical-cation, formed by the flash photolysis of acetonitrile solutions of tri-p-tolylamine, under various conditions, was examined using the flash photolysis photo-electric technique.[157] The change in optical density of the solution at 670 nm. was monitored. A quartz vessel was used for this work. The results are summarised in table 18. The effect of benzophenone and oxygen on the decay of the radical-cation is illustrated in plate 1.

The Interaction of Amines with Fluorenone.

The transient absorption spectrum produced by the flash photolysis of solutions of fluorenone and triethylamine is shown in figure 14. The spectrum of species produced by the flash photolysis of a solution of fluorenone and diphenylamine is shown in figure 15a. Flash photolysis of a solution containing fluorenone, triethylamine, and diphenylamine produced a weak transient absorption spectrum, which is shown in figure 15b.

2.5.2. DISCUSSION.

The Interaction of Amines with Benzophenone.

Transient species that might be expected to be produced by the flash photolysis of solutions of benzophenone and tri-arylamines are the amine radical-cation, the ketyl radical-anion, and possibly the neutral ketyl radical. The radical-cation of triphenylamine absorbs at 655 nm.[158] and that of tri-p-tolylamine at 670 nm..[159] The ketyl radical-anion absorbs at 620 nm.[78] and the protonated neutral radical at 545 nm..[78] Consequently it is difficult to see which of these species is produced by the flash photolysis of solutions of benzophenone and tri-arylamines under anaerobic conditions, (figures 9a, 11b). Flash photolysis of air-saturated solutions of benzophenone and tri-p-tolylamine produces a transient species with absorption maximum 670 nm.

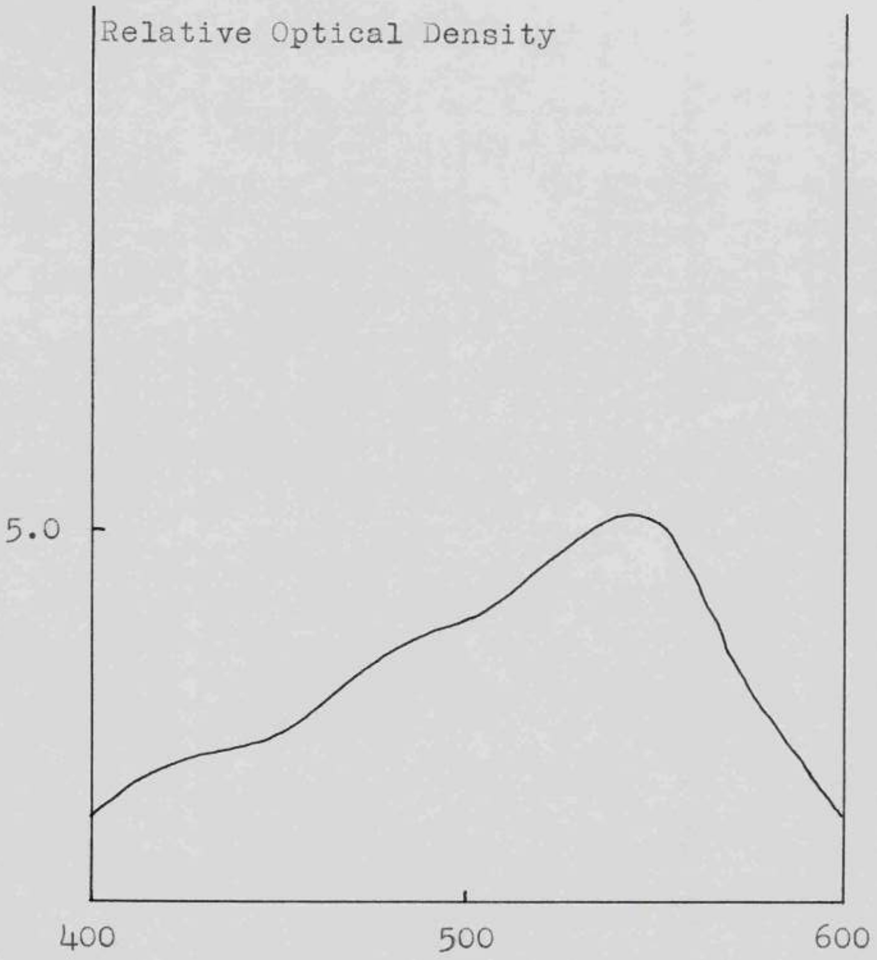


Figure 14. Transient absorption following flash photolysis of a solution of triethylamine and fluorenone.

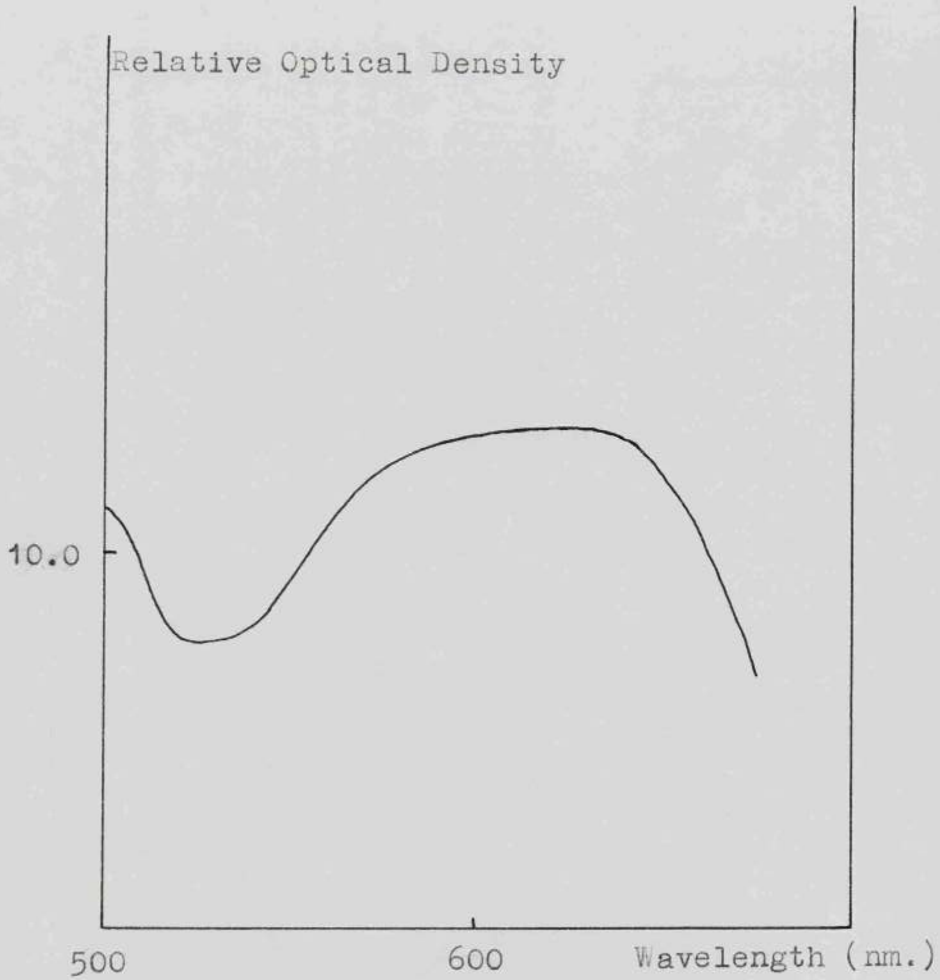


Figure 16. Absorption spectrum obtained by subtracting the spectrum in fig. 9b from that in fig. 9a.

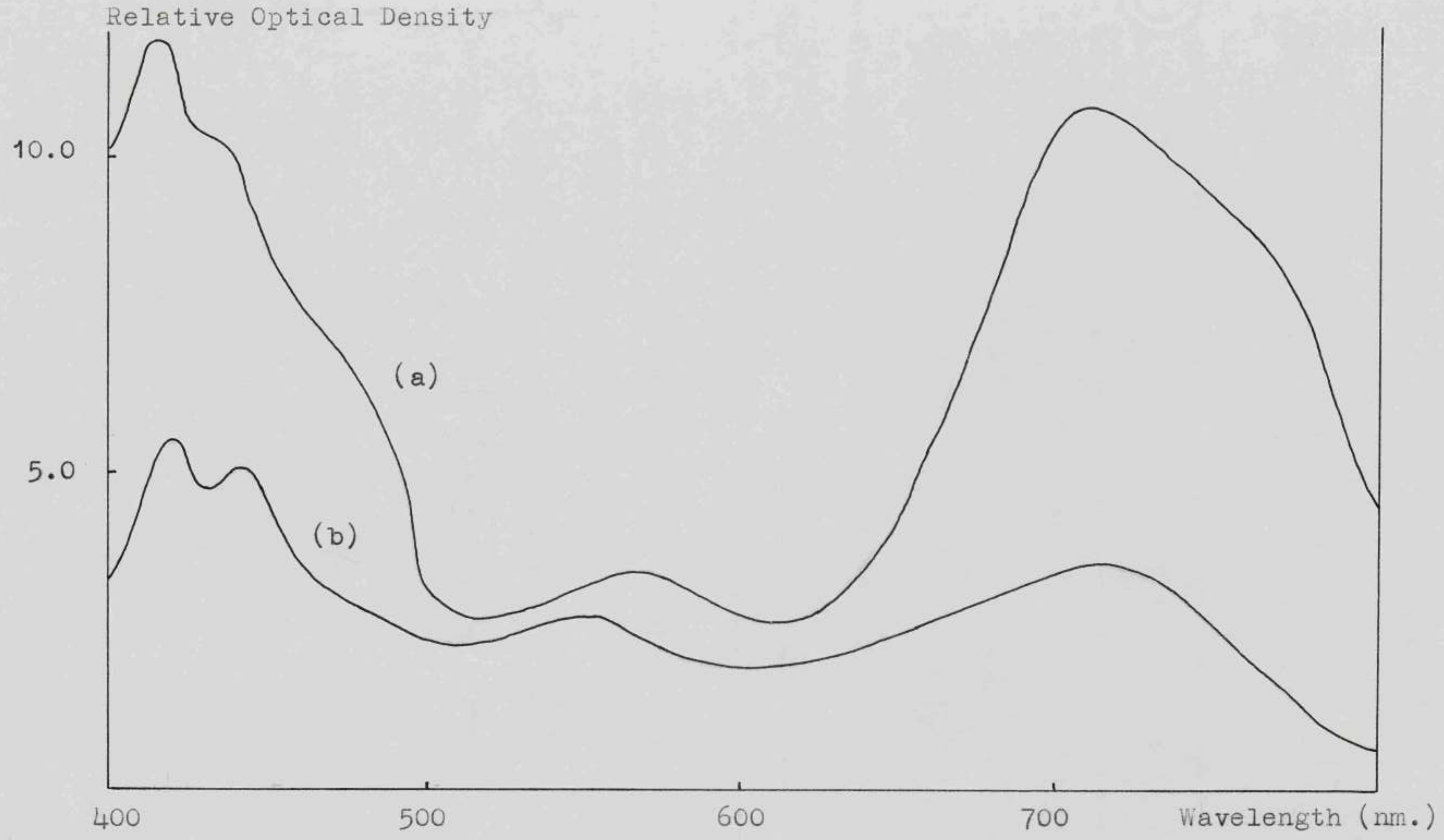


Figure 15. Spectra of transient species produced by flash photolysis of (a) a solution of fluorenone and diphenylamine, and (b) a solution of fluorenone, diphenylamine and triethylamine, both in nitrogen-flushed acetonitrile. (t=5μs)

Table 18. The decay of the tri-p-tolylamine radical-cation.

Benzophenone concentration	Amine concentration	Air/O_2	Kinetics	Half-life (μs.)	D
	6×10^{-4} M	air	complex	570	0.3
	1×10^{-3}	air	complex	510	0.5
	3×10^{-3}	air	complex	940	0.5
	1×10^{-2}	air	complex	670	0.6
1×10^{-4} M	1×10^{-4} M	air	complex	237	0.8
1×10^{-4}	3×10^{-4}	air	complex	420	1.0
1×10^{-4}	1×10^{-3}	air	complex	775	1.3
1×10^{-4}	3×10^{-3}	air	complex	800	1.6
3×10^{-4} M	1×10^{-4} M	air	complex	316	0.5
3×10^{-4}	3×10^{-4}	air	complex	712	1.0
3×10^{-4}	1×10^{-3}	air	complex	750	1.4
3×10^{-4}	3×10^{-3}	air	complex	850	1.8
1×10^{-3} M	1×10^{-4} M	air	complex	750	1.0
1×10^{-3}	3×10^{-4}	air	complex	3750	1.9
1×10^{-3}	1×10^{-3}	air	1st order	170000	>2
1×10^{-3}	3×10^{-3}	air	1st order	76000	>2
3×10^{-3} M	1×10^{-4} M	air	complex	900	0.9
3×10^{-3}	3×10^{-4}	air	complex	5000	1.9
3×10^{-3}	1×10^{-3}	air	1st order	160000	>2
3×10^{-3}	3×10^{-3}	air	1st order	230000	>2
	1×10^{-3} M	O_2	complex	2250	1.1
	1×10^{-2}	O_2	complex	2500	1.1

(figure 9b). This absorption is assigned to the radical-cation of tri-p-tolylamine.[159] In contrast, no transient species are detected from triphenylamine under these conditions.

It is proposed that the tri-p-tolylamine radical-cation is formed by electron transfer from the amine to triplet benzophenone. In air-saturated solution, oxygen reacts with the ketyl radical-ion to give the superoxide ion ($O_2^{\cdot -}$), by electron transfer.[100] Consequently, the spectrum of the ketyl radical-anion is not obtained following flash photolysis of air-saturated solutions. Evidence that the ketyl radical-anion is indeed formed in the absence of oxygen is shown in figure 16. Figure 16 shows the absorption spectrum obtained by subtracting the spectrum of the tri-p-tolylamine radical-cation (figure 9b) from the spectrum in figure 9a. The spectrum obtained is a good representation of the spectrum of the ketyl radical-anion published by Porter.[78]

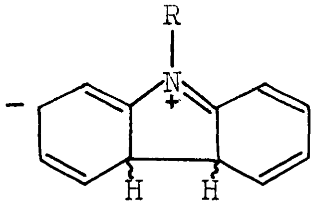
Some radical-cation is formed when oxygenated solutions of tri-p-tolylamine alone are flashed, (figure 10b). In pyrex apparatus, the amount of cation formed in solutions not containing benzophenone is small. The amount increases considerably when quartz apparatus is used. When most of the incident light is absorbed by benzophenone, it is thought that the major pathway for amine radical-cation formation is interaction of the amine with triplet benzophenone. In polar solvents the triplet level of tri-p-tolylamine (67.1 k.cal.) is just below that of benzophenone (68.9 k.cal.). There is therefore a possibility that the interaction of amine with triplet benzophenone is triplet-triplet energy transfer from benzophenone to amine, followed by electron ejection from amine to benzophenone ground-state. However, because of the small difference between the energy levels of the two species, energy transfer is likely to be inefficient; so the major pathway for cation formation is thought to be electron transfer from amine to triplet benzophenone. When the amine is flashed in the absence of benzophenone, the cation is presumably formed by direct electron ejection from excited amine to oxygen.

$$\mathrm{TPTA}^{*} + \mathrm{O_2} \longrightarrow \mathrm{TPTA}^{+\cdot} + \mathrm{O_2^{-\cdot}}$$

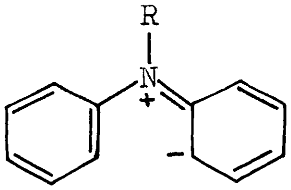
Such direct electron transfer has been postulated before.[160,161] It was first thought that photo-ionisation of amines was a biphotonic process,[161] like photo-ionisation of aromatic hydrocarbons.[162] However, evidence has been presented[160] showing that electron transfer from amines to oxygen occurs by single photon absorption by a ground-state contact charge transfer complex,[90,160] or by the interaction of the singlet excited state of the amine with ground-state oxygen.[160]

The radical-cation of tri-p-tolylamine is considerably more stable than the radical-cation of triphenylamine.[163] This could be the reason for the fact that no radical-cation is detected by flash photolysis of solutions of triphenylamine. Alternatively, the ionisation potential of triphenylamine, which is higher than that of tri-p-tolylamine, may be too high for complete electron transfer to occur.

The identity of the intermediate (λ_{max} 610 nm.), which is formed by flash photolysis of both triphenylamine and tri-p-tolylamine alone in anaerobic solution (figures 10a, 11a), has intrigued several workers. Kemp obtained a similar spectrum following the pulse radiolysis of triphenylamine.[164] and he assigned this absorption to the triplet state of the amine. Linschitz[165,166] proposed however, that this '610' intermediate was in fact some other species, formed from the amine triplet. Irradiation of diphenylamine and N-substituted diphenylamines in aerobic solution yields carbazoles,[167] and the '610' absorption observed on flash photolysis was assigned[165] to an ionic species (XXVII) which may possibly cyclise (XXVIII).



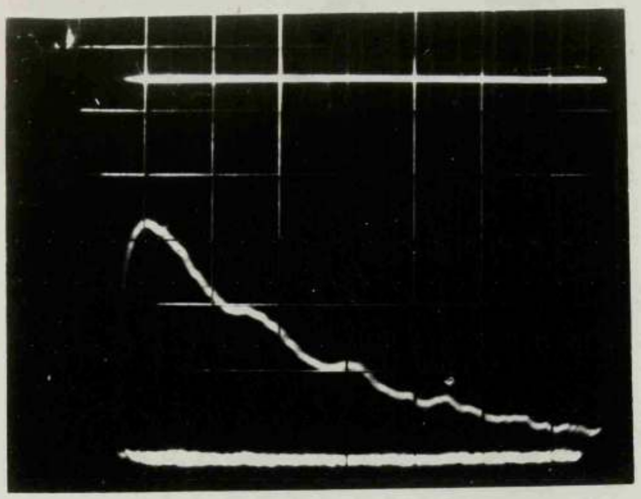
(XXVIII)



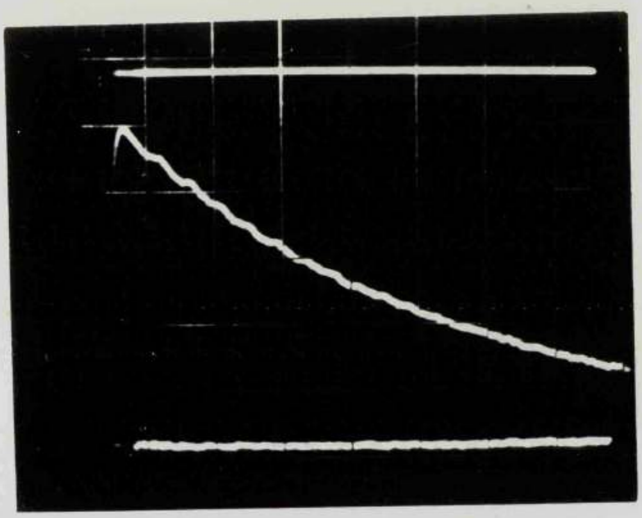
(XXVII)

This '610' species is thought to be an intermediate in carbazole formation. The triplet of triphenylamine has subsequently been detected,[168] and was found to absorb at 531 nm.

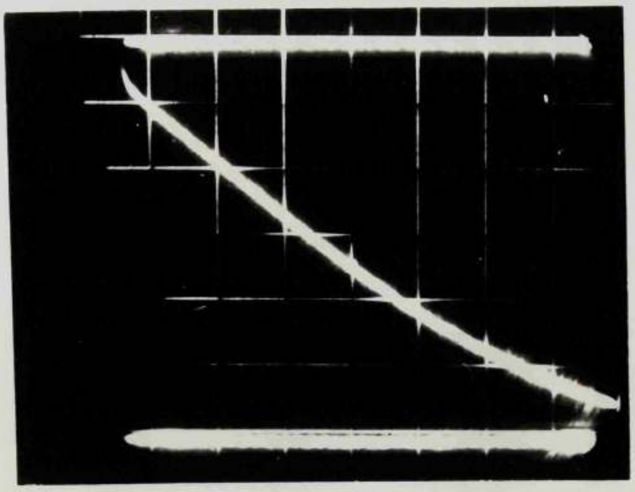
The transient species absorbing at 700 nm., obtained by flash photolysis of solutions of benzophenone and diphenylamine, is assigned to the radical $Ph_2\dot{N}$;[170] that absorbing at 550 nm. is assigned to the ketyl radical.[78] The radical cation of the amine (λ_{max} 620 nm.[158]) was not observed. (See figure 13). If the primary process in this system is electron transfer, it must be followed by an extremely rapid proton transfer. It is possible that an exciplex is formed between the amine and triplet ketone, and that proton transfer occurs with-



(a) 1 x 10^{-3}M amine in air-saturated solution. (300 µs. per division)



(b) 1 x 10^{-3}M amine in oxygen-saturated solution. (1 ms. per division)



(c) 1 x 10^{-3}M amine, 1 x 10^{-3} M benzophenone in air-saturated solution. (100 ms. per division)

Plate 1. The decay of the tri-p-tolylamine radical- cation, in acetonitrile solution under various conditions.

in the lifetime of this exciplex.

One of the transient species obtained by flash photolysis of solutions of aniline and benzophenone is thought to be the ketyl radical (λ_{max} 545 nm.). It is not possible to say conclusively whether the other is the amine radical cation, or the anilino radical.[171] (See figure 12).

The Decay of TPTA$^{+\cdot}$.

The photo-electric experiments on the decay of the tri-p-tolylamine radical cation were performed in quartz apparatus, therefore with solutions of amine and benzophenone, the amine itself absorbed a proportion of the incident light.

In plate 1. the effect of oxygen and benzophenone on the production and decay of the radical cation is illustrated..

The amount of cation produced increases with increasing oxygen concentration. This implies that the cation is formed by a mechanism involving some bimolecular interaction between the excited amine and oxygen, and not photo-ionisation of an isolated amine molecule. The presence of benzophenone in solution also increases the amount of cation produced. In this case, two factors are involved. First, as with oxygen, electron transfer to benzophenone probably involves bimolecular interaction between amine and ketone, an interaction which is favoured by high concentrations of both species. Second, the results of the experiments using the photographic technique indicate that in solutions of benzophenone and amine, formation of the cation will occur to a large extent by the interaction of amine with triplet benzophenone, as well as by interaction of the ketone with excited amine. This would also be expected to increase the amount of cation formed. Unfortunately, an estimate of the relative importance of these two pathways for cation formation is not possible from these results.

From the decays reproduced in plate 1, it is also apparent that the lifetime of the cation increases considerably with an increase in oxygen concentration, and even more so in the presence of benzophenone. With air-saturated solutions of amines and benzophenone, the results of the photographic work indicate that the initially formed radical-anion reacted with oxygen to give the superoxide ion, and to regenerate benzophenone. If this is so, it is difficult to see why the lifetime of the cation should be so enormously increased in the presence of benzophenone. It is therefore suggested that this increase in lifetime is predominantly a consequence of the large amount of ionic species produced initially in the presence of benzophenone. The production of a large amount of radical-cation implies the production of a corresponding large amount of anionic species. Under these conditions, when the radical-cation diffuses away from the site of its initial production, it will soon encounter another anion. It is therefore probable that the increase in lifetime results from the stabilising effect of the presence of a 'coordination sphere' of anions around the cation.

The results summarised in table 18 confirm that the amount of cation produced increases with increasing benzophenone concentration, and with increasing amine concentration.

They also show that the lifetime of the cation increases dramatically when the optical density of solution at 670 nm., immediatly after the flash, is greater than 2.

At high amine and high benzophenone concentrations, the decay becomes first order. Thus the rate of decay under these conditions is directly proportional to the cation concentration, and the rate law is of the form:

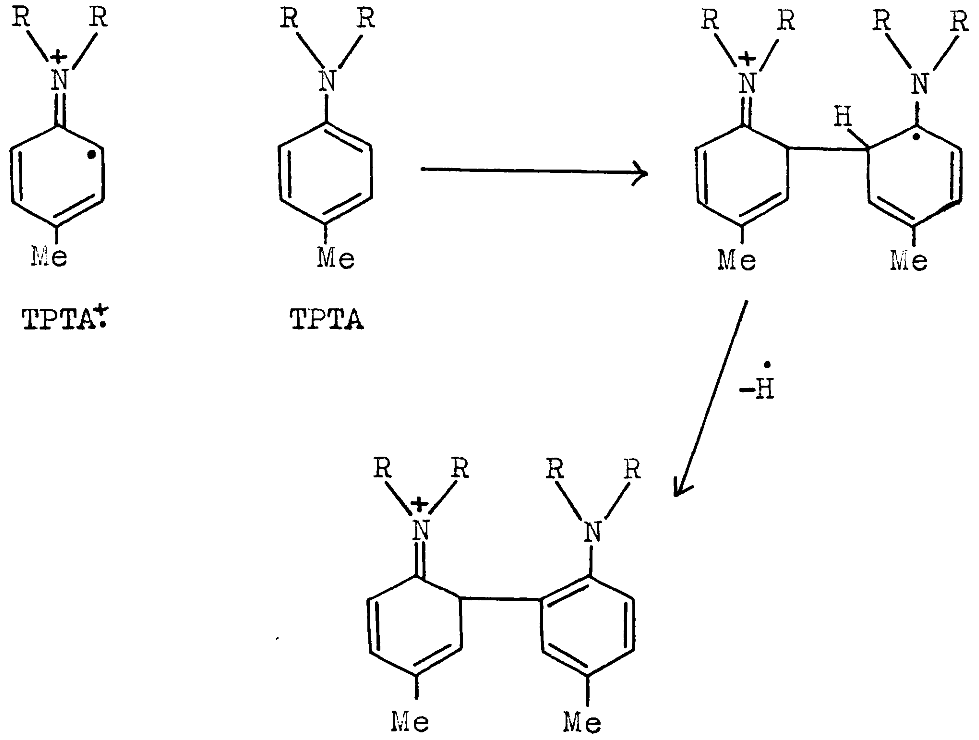
$$\text{Rate} = k' [\text{TPTA}^{+\cdot}] .$$

The 'rate constant' in this expression is a composite rate constant, which includes a concentration term which is effectively constant. With a benzophenone concentration of 1×10^{-3} M and an amine concentration of 1×10^{-3} M, the composite rate constant is $4.0\ s^{-1}$. When the amine concentration is increased by a factor of 3, the rate constant increases to $9.1\ s^{-1}$. This indicates that the composite rate constant includes an amine-concentration term and the rate law is of the form:

$$\text{Rate} = k[\text{Amine}]\ [\text{TPTA}^{+\cdot}] .$$

This implies that the radical-cation decays by reacting with ground-state amine. It has been proposed by McKellar that amines react with amine radical-cations to give coupled products.[147,148] In this case, coupling could occur at the ortho position, the species reacting via their resonance forms. If this is so, the bimolecular rate constant for the reaction is approximately 3.5×10^{3} l.mol.$^{-1}$s.$^{-1}$. The rate constant for a similar coupling reaction, though this time involving the para positions of an amine, where the para positions were not blocked by substituents, was found by McKellar[147] to be

1.4×10^{6} l.mol.$^{-1}$s.$^{-1}$, and the rate constant for the coupling of the triphenylamine radical-cation, generated by polarographic methods,[149] was found to be 2.4×10^{3} l.mol.$^{-1}$s.$^{-1}$.

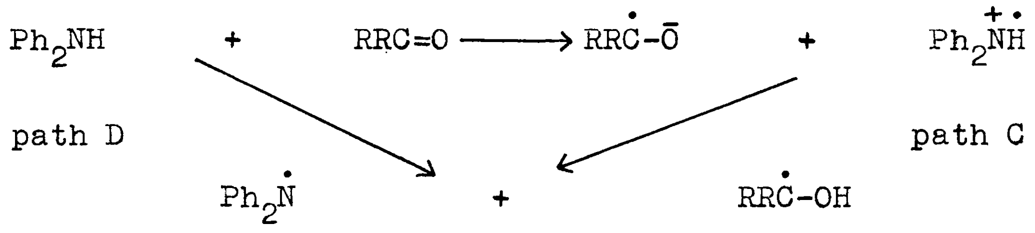


The Interaction of Amines with Fluorenone.

Fluorenone is photoreduced by triethylamine,[102,151] and an intermediate in this reaction is the 9-hydroxyfluorenyl radical.[169] The U.V. spectrum of this species has not been reported. Flash photolysis of an anaerobic solution of fluorenone and triethylamine produces a weak absorption spectrum (figure 14a). This is tentatively assigned to the 9-hydroxyfluorenyl radical.

The photoreduction of fluorenone by triethylamine is quenched by diphenylamine.[151] No products are observed following the irradiation of anaerobic solutions of fluorenone and diphenylamine, yet flash photolysis of such solutions shows the production of the diphenylamino radical, λ_{max} 700 nm.[170] The corresponding cation ($Ph_2\overset{\bullet+}{N}H$ λ_{max} 620 nm.[158]) was not observed. (See figure 15a.)

This is evidence that diphenylamine quenches the photoreduction of fluorenone with triethylamine, by competing for excited ketone. The absence of products indicates that the primary process between fluorenone and diphenylamine is reversible. However from these results, it is still impossible to say whether the primary process is electron transfer followed by an extremely rapid proton transfer (path C), or whether the primary process is direct hydrogen abstraction (path D).

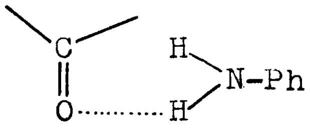


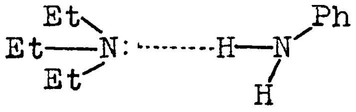
The absorption spectrum obtained following the flash photolysis of an anaerobic solution of fluorenone, triethylamine, and diphenylamine is very weak. (See figure 15b). Quenching is therefore not entirely due to the preferential reaction of excited fluorenone with diphenylamine.

Cohen's results[151] show that the efficiency with which amines quench the photoreduction of fluorenone by triethylamine is not directly related to ionisation potential. Diphenylamine quenches the reaction more efficiently than DABCO although the ionisation potentials of the two amines are comparable. This leads to the supposition that the presence of an N-H group may influence quenching.

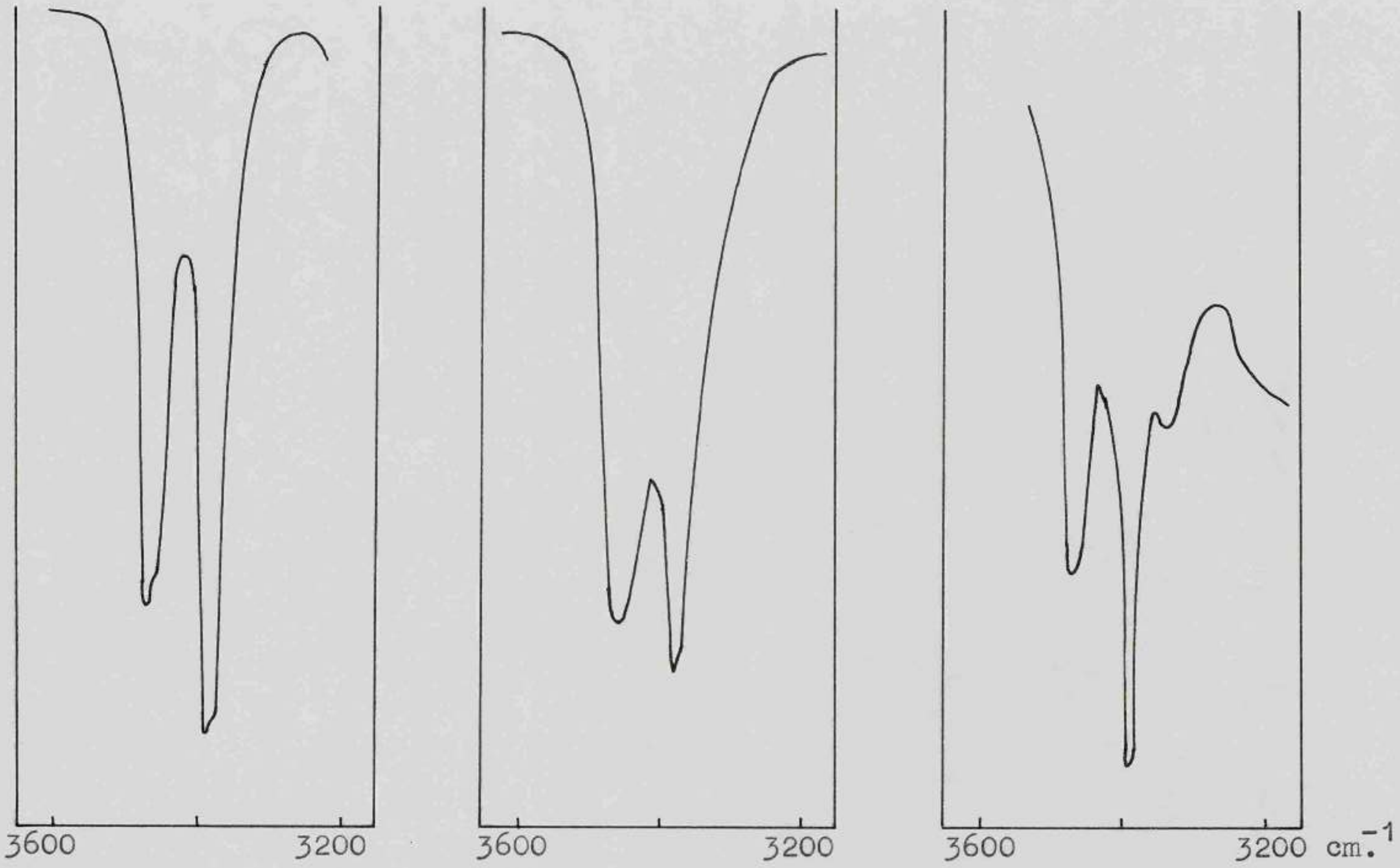
It was mentioned earlier that many workers were unable to detect any ground-state association between aromatic carbonyl compounds and amines. Amines do not appear to effect the I.R. and U.V. absorption of aromatic carbonyl compounds in any way. However, fluorenone has an effect on the N-H absorption of aniline in the I.R. region. Fluorenone appears to broaden this N-H absorption. Triethylamine also alters the aniline N-H absorption slightly. These effects are illustrated in figure 17.

This effect on the N-H absorption is only slight and it is difficult to interpret quantitatively. It could well imply that some ground state interaction takes place between aniline and fluorenone, and also between aniline and triethylamine. This interaction could be some form of hydrogen bonding.





It is possible that primary and secondary amines quench the photoreduction of fluorenone by competing efficiently for the excited ketone, to which they may be hydrogen bonded, and also by hydrogen bonding to triethylamine and thus effectively reducing the amount of free amine available to react with the ketone.



a. Aniline alone.

b. Aniline/fluorenone.

c. Aniline/triethylamine.

Figure 17. N-H absorption from the infra-red spectrum of aniline in benzene solution.

Conclusions.

Definite evidence for electron transfer from amines to excited carbonyl compounds has only been obtained with tri-p-tolylamine and benzophenone. This amine has a low ionisation potential and an extremely stable radical-cation which cannot easily lose its charge by proton transfer. Because the cation is so stable, it is relatively long-lived.

It is proposed that the interaction of excited ketones with other amines also involves some degree of electron transfer, but complete charge separation may not occur because of the instability of the resulting radical-ions, and the rapidity of the subsequent proton transfer reaction.

With primary and secondary amines, it is thought that hydrogen bonding between the hydrogen atom of the amine and the oxygen of the carbonyl group may be an important factor in the reactivity of amines with carbonyl compounds.

2.6. SUMMARY.

The photo-oxidation of amines sensitised by benzophenone and other ketones, fluorescein and thiazine dyes, and aromatic hydrocarbons has been examined. The major products obtained from the sensitised photo-oxidation of aliphatic amines were aldehydes and imines. The benzophenone-sensitised photo-oxidation of N-alkylated anilines gave de-alkylated amines, amides and aldehydes.

It is proposed that the primary process in all these reactions is the interaction of the amine with excited sensitiser, and that the products are formed by subsequent radical reactions. The reactions are not initiated by attack of singlet oxygen on the amine.

The most important evidence presented in favour of a radical mechanism is as follows.

1. The types of products formed are compatible with the operation of a radical mechanism. The same types of products are obtained with all the sensitisers used, which implies that all the sensitisers act by a common mechanism.
2. Only those compounds which are photoreduced by amines in deoxygenated solution act as sensitisers for the photo-oxidation of these amines. The implication of this is that the primary process involved in photo-oxidation is the same as is involved in photoreduction, namely the interaction of amine with the excited sensitiser.
3. Flash photolysis of aerobic solutions of dyes or aromatic hydocarbons with amines produced transient species which could only have been formed by the interaction of amine with the excited sensitiser. This is direct evidence that amines can react efficiently with the excited sensitiser, even in the presence of oxygen, and that the primary process which initiates these reactions is not the formation of singlet oxygen.
4. Amines such as triethylamine and ethyldi-isopropylamine, which are efficient physical quenchers of singlet oxygen, are photo-oxidised efficiently using ketones, dyes, or aromatic hydrocarbons as sensitisers. This is strong

evidence that singlet oxygen is not the active species in these photo-oxidations.

The primary process with all the sensitisers used appears to involve electron transfer or exciplex formation. the fact that amines can compete effectively with oxygen for the excited sensitiser is due to the rapidity of such charge transfer processes.

Section Three: EXPERIMENTAL

Instrumentation.

Routine infra-red spectra were recorded on a Perkin--Elmer 237 or 257 grating spectrophotometer. Ultra violet and visible spectra were obtained using a Unicam S.P. 800 recording spectrophotometer, the wavelength accuracy of which was checked periodically with holmium or didymium filters, and the absorbance accuracy with a standard solution of potassium dichromate in sulphuric acid. Mass spectra were obtained from an A.E.I. M.S. 9 mass spectrometer, and n.m.r. spectra were run on a Varian T 60 machine. Melting points were determined on a Kofler Block, and were uncorrected . Elemental analyses were carried out by Rapid Elemental Analyses, Beaconsfield.

G.L.C. analysis was performed with a Perkin-Elmer F 11 unit, with flame ionisation detector. The column packings used for aldehyde analysis were 10% Apiezon L on Chromosorb P, and 20% di-isodecylphthalate on Chromosorb P. The packings used for amine and imine analysis were 8% Carbowax 20 M with 2% potassium hydroxide on Chromosorb W, and Penwalt 223 plus 4% potassium hydroxide.

3.1. Benzophenone-Sensitised Photo-oxidations.

Materials.

Most amines were obtained commercially from either Hopkin and Williams Ltd., or Koch-Light Ltd. They were all either distilled under dry nitrogen or recrystallised from appropriate solvents before use. Benzophenone, from B.D.H. Ltd., was used without further purification. Benzene was analytical grade, previously dried over sodium wire, and distilled under dry nitrogen before use.

N-Benzyl-N-methylaniline and N-benzyl-N-ethylaniline were both obtained by reduction of the benzoyl derivative of the corresponding secondary amine with lithium aluminium hydride. N-Ethyldi-isopropylamine was obtained by lithium aluminium hydride reduction of the acetyl derivative of di-isopropylamine. The usual procedure is described below.

Preparation of N-methyl benzanilide. Benzoyl chloride (1 mole) was placed in a dropping funnel attached to a 2 l. three necked flask. The flask was fitted with an efficient mechanical stirrer and a drying tube and was immersed in an ice bath. A solution of anhydrous methyl aniline (3 moles) in anhydrous benzene (150 ml.) was introduced into the flask. The acid chloride was added very slowly from the dropping funnel to the vigorously stirred solution, the addition taking about two hours. The mixture was stirred at room temperature overnight. Water (200 ml.) was added, the layers were separated, and the aqueous phase was extracted with two 100 ml. portions of ether. The extracts were combined with the benzene layer, washed with saturated sodium chloride solution, and dried over anhydrous magnesium sulphate (100g.). Most of the benzene was removed on the evaporator, petrol was added, and a portion of the product was induced to crystallise by immersing in an acetone/cardice mixture and scratching with a glass rod. The remainder of the product was seeded with the crystals obtained, and the whole of the product was recrystallised from ligroin to give white crystals (yield 0.79moles, 70%) m.p. 57-59°C.

Preparation of N-Benzyl-N-methylaniline. In a 1 l. three necked flask equipped with a reflux condenser and dropping funnel, both protected by drying tubes, was placed a suspension of lithium aluminium hydride (0.17 moles) in anhydrous ether (150 ml.). The mixture was stirred with a magnetic stirrer. A solution of amide (0.17 mole) in anhydrous ether (100 ml.) was added at such a rate as to maintain gentle reflux. The flask was then left at room temperature with the mixture stirring, for 12 hours. The solution was then refluxed in a heating mantel for 6 hours, with stirring. The heating mantel was replaced by an ice bath, and water (70 ml.) was added slowly with vigorous stirring. After the addition of water, a cold solution of sodium hydroxide (40g.) in water (100 ml.) was added at once. The liquid was decanted from the hydroxides, and was washed with water. The ether layer was then extracted with 2N hydrochloric acid. The extract was made basic and was extracted with ether. The ether was removed, and the resulting amine was chromatographed on alumina, eluting with petrol, then distilled under nitrogen, b.p. 220°C. (4 mm.Hg), yield

0.06 moles (34%).

Product Studies.

Two methods of irradiation were used for product studies.

Irradiation Method A. The solution of amine and benzophenone in benzene was irradiated with a Hanovia medium-pressure, immersion, mercury lamp (125 W.) contained in a water-cooled Pyrex jacket. Oxygen was continuously bubbled through the solution during irradiation. The following experiments were carried out using this method.

Photo-oxidation of N,N-dimethylaniline. A solution of dimethylaniline (1.83g.) and benzophenone (1.63g.) in benzene (150 ml.) was irradiated for 14 hours. After irradiation, the solution was extracted with 2N hydrochloric acid. The aqueous extract was made basic with aqueous sodium hydroxide solution, and extracted with ether. The ether was removed on a rotary evaporator and the residue adsorbed onto an alumina column. Elution with petrol yielded dimethylaniline (36mg.), N-methylaniline (0.31g.). Elution with 50% ether/petrol gave aniline (65mg.). The solution left after acid extraction was evaporated and the residue also chromatographed on alumina. Elution with ether gave benzophenone (1.25g.) and N-methylformanilide (1.0g.). The identity of the products was established by comparing their I.R. and n.m.r. spectra and behaviour on both alumina and silica T.L.C. plates, with authentic samples.

Photo-oxidation of N,N-diethylaniline. A solution of diethylaniline (2.23g.) and benzophenone (1.36g.) in benzene (150 ml.) was irradiated for 7 hours. G.L.C. analysis of a portion of the solution showed the presence of acetaldehyde (0.68g.). The bulk of the solution was extracted with 2N hydrochloric acid. Chromatography of the acid extract on alumina gave diethylaniline (0.45g.) and N-ethylaniline (0.37g.), by elution with petrol. Elution with 50% ether/petrol yielded aniline (0.37g.). Chromatography on alumina of the residue after acid extraction, yielded benzophenone (1.3g.) and acetanilide (40mg.) m.p. and mixed m.p. 114-116°C (from ether).

Photo-oxidation of Tribenzylamine. A solution of tribenzylamine (4.19g.) and benzophenone (1.38g.) in benzene (150ml.) was irradiated for 7 hours. The solution was extracted with 2N sodium hydroxide solution and then with 2N hydrochloric acid. The base extract was chromatographed on silica to yield benzamide (0.12g.) m.p. and mixed m.p. 127-128°C (from ethanol), and benzoic acid (0.16g.) m.p. and mixed m.p. 121-122°C (from water), after elution with ether and 10% methanol/ether respectively. The acid extract was chromatographed on alumina to yield tribenzylamine (0.086g.) and benzaldehyde (0.045g.) by elution with petrol. The residue after acid and base extraction was chromatographed on alumina to yield benzaldehyde (1.26g.) and benzophenone (1.11g.) by elution with 10% ether/petrol. G.L.C. analysis of the original solution showed the presence of N-benzylbenzaldimine (0.97g.).

Photo-oxidation of Dibenzylamine. A solution of dibenzylamine (3.04g.) and benzophenone (1.35g.) in benzene (150ml.) was irradiated for 14 hours. G.L.C. analysis of the solution after irradiation showed dibenzylamine (1.0g.), benzaldehyde (0.15g.) and N-benzylbenzaldimine (0.098g.). Less than 5%

benzophenone had reacted, as determined by G.L.C.

Photo-oxidation of Benzylamine. A solution of benzylamine (1.69g.) and benzophenone (1.40g.) in benzene (150ml.) was irradiated under oxygen for 14 hours. G.L.C. analysis showed 0.30g. amine had reacted to yield benzaldehyde (0.28g.). Less than 5% benzophenone was used as estimated by G.L.C.

Photo-oxidation of N-methylaniline. A solution of N-methyaniline (1.60g.) and benzophenone (1.34g.) in benzene (150ml.) was irradiated under oxygen for 14 hours. The solvent was removed and the residue chromatographed on alumina to yield azobenzene (0.14g.) m.p. and mixed m.p. 66-68°C from ethanol by elution with petrol, methylaniline (0.086g.) and aniline (0.39g.) by elution with 50% ether in petrol.

Photo-oxidation of Dibenzylaniline. A solution of dibenzylaniline (4.2g.) and benzophenone (1.36g.) in benzene (150ml.) was irradiated under oxygen for 7 hours. The solvent was removed and chromatography of the residue on alumina yielded dibenzylaniline (0.055g.), benzophenone (1.10g.) by elution with petrol, benzaldehyde (1.25g.) and aniline (0.12g.) by elution with 50% ether /petrol.

Photo-oxidation of N-Benzyl-N-Methylaniline. A solution of benzylmethylaniline (2.97g.) and benzophenone (1.36g.) in benzene (150ml.) was irradiated under oxygen for 7 hours. The solution was evaporated and the residue chromatographed on alumina. Elution with 5% ether/petrol gave benzaldehyde (1.2g.), N-benzylaniline (0.015g.) and N-methylaniline (0.043g.). Elution with ether yielded aniline (0.093g.) and benzanilide (0.079g.) m.p. and mixed m.p. 160-162°C (from ether).

Photo-oxidation of N-Benzyl-N-Ethylaniline. A solution of amine (3.16g.) and benzophenone (1.36g.) in benzene (150ml.) was irradiated for 7 hours. G.L.C. analysis after irradiation showed benzylethylaniline (0.64g.), N-ethylaniline (0.39g.), acetaldehyde (0.32g.), benzaldehyde (1.02g.), acetanilide (0.054g.), and benzanilide (0.079g.). More than 90% benzophenone was unchanged.

Photo-oxidation of 1,4-Diazabicyclo[2,2,2]octane. A solution of the amine (6.2g.) and benzophenone (1.36g.) in benzene (150ml.) was irradiated for 14 hours. The solvent was removed and the residue was chromatographed on silica. Elution with benzene gave a yellow oil which crystallised to yield 1,4-diaza-2-(hydroxydiphenylmethyl)-bicyclo[2,2,2]octane (1.8g.) m.p. (from benzene) 218-219°C (sublimes); ν_{max} 3300cm^{-1}(br.); τ 2.6 br. (10H), 6.4 (1H,triplet), and 6.8-7.6 (11H,complex); $^m/e$ 294, 277, 183, and 111; found: C, 77.3; H, 7.5; N, 9.6. $C_{19}H_{22}N_2O$ requires C, 77.9; H, 7.5; N, 9.6%. Elution with 10% ether/benzene gave benzophenone (0.92g.). Further elution gave oxygen containing fragments whose structures have not been unambiguously assigned.

Irradiation Method B. A solution of amine and benzophenone in benzene was irradiated using a Rayonet photochemical reactor equipped with 12 75W. incandescent tubes emitting light of mainly 350nm. wavelength. The solution was contained in 1cm. diameter quartz tubes and oxygen was continually bubbled through the solution during irradiation via a capillary tube. The remainder of the product studies were carried out using this method.

Photo-oxidation of Triethylamine. A solution of triethylamine (2.4g.) and benzophenone (0.14g.) in benzene (25ml.) was irradiated for 2 hours. G.L.C. analysis after irradiation showed triethylamine (1.6g.) and acetaldehyde (0.2g.). A trace of diethylacetamide was also detected. The solvent was removed from the bulk of the solution and the residue was chromatographed on alumina. By elution with ether, benzophenone (1.0g.) was recovered.

Photo-oxidation of Tri-n-propylamine. A solution of tripropylamine (3.43g) and benzophenone (0.14g.) in benzene (150ml.) was irradiated for 2 hours. G.L.C. analysis of the resulting solution showed tripropylamine (1.7g.), propionaldehyde (0.28g.), and N-propylpropionaldimine (0.24g.). Analysis for benzophenone showed more than 80% remaining.

Photo-oxidation of Di-n-propylamine. A solution of dipropylamine (2.42g.) and benzophenone (0.13g.) in benzene (25ml.) was irradiated for 2 hours. G.L.C. analysis after irradiation showed propionaldehyde (0.11g.) and N-propylpropionaldimine. The imine and amine were not sufficiently resolvable on the column used to permit accurate quantitative analysis. Analysis for benzophenone showed more than 90% remaining.

Photo-oxidation of n-Propylamine. A solution of amine (1.37g.) and benzophenone (0.13g.) in benzene (25ml.) was irradiated for 2 hours. G.L.C. analysis showed propionaldehyde (0.12g.). The amine was not resolvable from the solvent peak so no estimate of the amount of amine used could be made. Analysis for benzophenone showed more than 80% remaining.

Photo-oxidation of Diethylamine. A solution of diethylamine (1.7g.) and benzophenone (0.13g.) in benzene (25ml.) was irradiated for 2 hours. G.L.C. analysis of the resulting solution showed diethylamine (1.6g.) and acetaldehyde (0.02g.).

Photo-oxidation of N-Ethyl-N,N-di-isopropylamine. A solution of amine (3.1g.) and benzophenone (0.14g.) in benzene (25ml.) was irradiated for 2 hours. G.L.C. analysis of the resulting solution showed ethyldi-isopropylamine (1.3g.), acetaldehyde (0.2g.), acetone (0.4g.), N-ethyldimethylketimine (0.2g.), and N-isopropylacetaldimine (0.1g.).

Preparation of Authentic Imine Samples.[172] The general procedure used is as follows. The aldehyde or ketone (0.1mole) was added drop-wise to the primary amine (0.1mole) at 0°C with stirring. The stirring was continued for 1 hour after the addition was complete. The solution was allowed to reach room temperature, and anhydrous potassium carbonate was added to break up the intermediate carbinolamine, and to remove water. The mixture was stirred for 24 hours; the liquid was decanted, and the imine was distilled through a fractionating column under a stream of dry nitrogen.

The method for preparing N-ethyldimethylketimine and N-phenylbenzaldimine was similar to that described above except that after the addition of potassium carbonate the mixture was refluxed under nitrogen for 2 hours.

Rates and Quantum Yields of Oxygen Uptake. The rate of the benzophenone-sensitised photo-oxidation of aliphatic amines was studied by examining the rate of absorption of oxygen into the solution at constant pressure. The rate of dissolution of oxygen is governed by the rate of the chemical reaction and not by physical diffusion provided the two following conditions are fulfilled.[67]

1. The vapour pressure of the amine solution must be negligible in comparison with the oxygen pressure to ensure that contact of oxygen with the liquid is not hindered.
2. There must be sufficiently efficient stirring of the liquid phase to ensure that the rate of dissolution of oxygen is independent of the rate of stirring and thus, the rate of oxygen-uptake is not distorted by the rate of diffusion of oxygen in the liquid phase.

The rates of oxygen-uptake were measured by use of a constant pressure gas burette coupled to the reaction cell. The reaction cell was a T-shaped cylindrical vessel of 80ml. capacity, with flat Pyrex windows, equipped with a hollow glass stirrer which was rotated at high speed by an external magnet to aerate the solution by centrifugal force. The cell, stirrer, and constant pressure gas burette have been described in detail elsewhere.[173] The rate of oxygen uptake was independent of stirrer speed when speeds greater than 1000rev.min.$^{-1}$ were used. All experiments were therefore carried out with a stirrer speed of 1500rev.min.$^{-1}$ and condition 2. above was satisfied.

A typical procedure is as follows. A solution of amine (for concentrations see table 4.) and benzophenone (1 x 10^{-2}M) in benzene was made from stock solutions by dilution, and kept in the dark until required. The reaction vessel was filled with solution, and the whole apparatus was immersed in a water bath maintained at 25±5°C. (The vapour pressure of benzene at this temperature is approximately 90 mm Hg,[150] which is sufficiently low to satisfy condition 1. above.) The apparatus was purged with oxygen for 15min. prior to irradiation. The solution was irradiated with a Hanovia medium pressure mercury arc (125W), equipped with a Pyrex sleeve and water cooling jacket. The light from the lamp was passed through a condensing lens and a Chance O.X.1 filter, to give a beam of mainly 350nm. radiation. The initial rate of oxygen-uptake was measured with a 10ml gas burette. Readings were usually taken at 1min. intervals.

The light intensity was measured by the potassium ferrioxalate method of Hatchard and Parker.[91] The optical density of the phenanthroline/ferrous complex was measured on a Hilger-Watts single beam visible and ultraviolet spectrometer, which was previously calibrated with standard solutions of this complex. The variation in light intensity between experiments was less than 15%. The average light intensity was $2.3 \pm 0.3 \times 10^{16}$ quanta s^{-1}.

Quantum Yields of Amine Disappearance and Product Formation.

The general procedure was as follows. A solution of amine (24 m.mol.) and benzophenone (0.75 m.mol.) in benzene (25ml.) was irradiated in a Rayonet reactor equipped with lamps emitting mainly 350nm. radiation. Oxygen was bubbled through the solutions continuously during photolysis. Samples were withdrawn at intervals and analysed by G.L.C..

The light intensity was again determined by the potassium ferrioxalate method. Variation in light intensity between experiments was less than 25%. The average light intensity was 4.71×10^{17} quanta s^{-1}. The results are shown in table 7.

3.2. Photo-oxidations Sensitised by Other Ketones.

Materials.

The ketones were all obtained commercially, and were recrystallised from appropriate solvents before use. The amines, from Hopkin and Williams Ltd., were distilled under dry nitrogen before use. Authentic imines were prepared by the method described earlier.

Irradiation Procedure. A solution of amine (5×10^{-1}M) and ketone (5×10^{-2}M) in benzene (50ml.) was divided between two quartz tubes, each holding 25ml.. Nitrogen was flushed through one of these solutions, and oxygen or air through the other, via glass cinters immersed in each solution. The two solutions were irradiated simultaneously using a Rayonet reactor which could be equipped with fluorescent tubes emitting light of 310nm. or 350nm. wavelength. The tubes used depended on the absorption maximum of the ketone. After irradiation, the solution irradiated under oxygen was examined by G.L.C. for product formation. The results are shown in table 9. The solution irradiated under nitrogen was examined by U.V. and I.R. spectroscopy for evidence of carbonyl group reduction. These results are also shown in table 9.

3.3. Dye-sensitised Photo-oxidations.

Materials.

Most amines were obtained commercially. All liquid amines were distilled under dry nitrogen before use. Tribenzylamine was recystallised twice from ether. N-Ethyl-N,N-di-isopropylamine was obtained by lithium aluminium hydride reduction of the acetyl derivative of N,N-di-isopropylamine using the method described earlier. Methylene blue, obtained from the Aldrich Chemical Co. Ltd. as the iodide, was used without further purification. Rose bengal and eosin were obtained from B.D.H. Ltd., and were also used without further purification. Methanol was dried over magnesium and was distilled before use.

Irradiation Procedures. Two methods of irradiation were used. The first method was used to study the products of the methylene blue-sensitised photo-oxidation of triethylamine, N-ethyl-N,N-di-isopropylamine, tri-n-propylamine, di-n-propylamine, n-propylamine, N,N-dimethylaniline, N,N-diethylaniline, aniline, and 1,4-diazabicyclo[2,2,2]octane. The procedure was as follows. A solution of amine (0.2M) and methylene blue (3×10^{-4}M) in methanol (100ml) was irradiated for ca.17 hours with eight 20W fluorescent daylight tubes. The solution was contained in a Pyrex tube equipped with a glass cinter. Oxygen was bubbled through the solution continuously during the irradiation, via the cinter. After photolysis the solution was analysed for product formation using G.L.C.. The products are shown in table 10.

This procedure was also used to study products formed in the rose bengal-sensitised photo-oxidation of triethylamine, N-ethyl-N,N-di-isopropylamine, and the propylamines; and to determine the products formed in the photo-oxidation of triethylamine and the propylamines sensitised by eosin. These products are shown in table 11.

The second method of irradiation was used in a study of the products formed in the photo-oxidation of tribenzylamine sensitised by methylene blue, rose bengal, and eosin. A solution of tribenzylamine (0.09M) and sensitiser (ca.10^{-4}M) in methanol (200ml) was irradiated for ca.20 hours with a 150W tungsten lamp. Oxygen was bubbled through the solution continuously during photolysis. After photolysis the product mixture was analysed by G.L.C.. These results are shown in tables 10 and 11.

Photoreduction Studies. A methanolic solution of amine (1×10^{-1}M) and sensitiser (sufficient to give an optical density of ca.1.5 at the wavelength of maximum absorption of visible light), was contained in a bulb attached to a circular cell of path length 5mm. The solution was outgassed in a minimum of four freeze-thaw cycles. The solution was poured into the cell by inverting the bulb, and the solution was irradiated with a 750W tungsten lamp. The decrease in optical density was measured at suitable intervals with a Unicam S.P.800 recording spectrophotometer with a suitably adapted cell holder.

All the tertiary aliphatic amines examined photoreduced methylene blue, eosin, and rose bengal efficiently. Primary and secondary amines were less efficient photobleaching agents. Reproducible initial rates of photobleaching were not obtained however. Aromatic amines such as aniline or dimethylaniline did not photobleach these dyes efficiently, nor did 1,4-diazabicyclo[2,2,2] octane.

The Effect of Oxygen Concentration on the Extent of Reaction. A solution of amine (0.5M) and rose bengal (10^{-4}M) in methanol (50ml) was divided equally between two Pyrex tubes. These tubes were immersed in a soda-glass tank through which tap water was passed to act as a heat filter. Oxygen was bubbled through one solution and air through the other at approximately the same rate. Both tubes were irradiated simultaneously with a 750W tunsten projector lamp. After irradiation the solutions were analysed for residual amine by G.L.C. using n-hexane as internal standard. The results in table 12. show the mean value of two successive runs. (Air is approximately 21.0% oxygen by volume.)[174]

Flash Photolysis Studies. The flash photolysis apparatus was basically an F.P.1 unit from the Northern Precision Co. Ltd., comprising a vertical cell compartment with two vertical quartz flash lamps. These lamps were attached to a bank of condensers of 10µf capacity. The spectral flash source was a 'Garton Type' flash tube operated from a 10µf rapid discharge condenser. The photolysis and spectroscopic lamps were discharged at 15 and 8kV, and the lifetimes of the flashes at half peak intensity were ca. 5µs and 2µs respectively. The reaction vessel was a Pyrex tube 20cm long and 1.8cm in diameter. Absorption spectra of transient species were obtained on a Hilger medium quartz spectrograph, and recorded on Ilford H.P.3 photographic plates.

Solutions were deoxygenated by flushing with nitrogen overnight, or by a minimum of four freeze-thaw cycles using a high-vacuum line incorporating a mercury diffusion pump.

Plate photometry was carried out on a Joyce-Loebl double beam recording microdensitometer. The spectrum recorded on the photographic plate before the photolysis flash, was scanned; then spectra recorded at various time intervals after the photolysis flash were monitored. The difference between the density of the photographic plate before the photolysis flash, and that recorded at intervals after the photolysis flash, was plotted, in arbitrary units, at 10nm. intervals across the spectral range.

Fluorescence Quenching Studies. These were carried out using a Baird-Atomic spectrofluorimeter coupled to a Varian x/y recorder. Solutions of dyes (1×10^{-5}M) in methanol and in acetonitrile were used. Various concentrations of tri-n-propylamine, di-n-propylamine, and n-propylamine were added, and the ratio of fluorescence intensity in the absence of amine to that in the presence of amine was plotted for each amine concentration. The Stern-Volmer quenching constants obtained from the slopes of these linear plots are quoted on p.79.

3.4. Hydrocarbon-sensitised Photo-oxidations.

Materials.

All amines and sensitisers were obtained commercially. The amines were distilled under nitrogen before use. Phenanthrene was found to contain anthracene in small amounts. This was removed by irradiation of an anaerobic solution of phenanthrene in benzene since under these conditions, anthracene forms an insoluble dimer. The solution was filtered, and the phenanthrene recovered. It was then recrystallised twice before use. Anthracene and perylene were used without further purification. Benzene, previously dried over sodium wire, was distilled under dry nitrogen before use. The method used for purifying acetonitrile is shown below.

Purification of Acetonitrile.[175] Acetonitrile (800ml) and benzoyl chloride (10ml) were refluxed in a 1 l. round bottomed flask for 1 hour. The acetonitrile was then distilled into a receiver containing water (10ml). Anhydrous sodium carbonate was added (20g.), and the mixture was refluxed for 2 hours. The acetonitrile was distilled into a receiver fitted with a drying tube. Anhydrous sodium carbonate (10g.) and potassium permanganate (15g.) were added and the mixture was again distilled. The distillate was made slightly acidic with concentrated sulphuric acid, and the liquid was decanted from the precipitated ammonium sulphate. The acetonitrile was then distilled through a fractionating column with a reflux ratio of 20:1. A small forecut was discarded.

G.L.C. Analysis and Flash Photolysis. The procedure followed was the same as described earlier.

Photo-oxidations Sensitised by Naphthalene or Phenanthrene.

A solution of sensitiser (10^{-3}M) and amine (concentration as in table 15.) in acetonitrile (25ml), contained in a quartz tube

1.5cm in diameter, equipped with a glass cinter, was irradiated for 16 hours. Irradiation was carried out using a Rayonet reactor fitted with fluorescent tubes emitting light of 310nm. wavelength. Oxygen was bubbled through the solution during irradiation, via the cinter. After irradiation, the solution was examined for product formation using G.L.C..

Photo-oxidations Sensitised by Anthracene. The same procedure as above was followed, but fluorescent tubes emitting light of 350nm. wavelength were used.

Photo-oxidations Sensitised by Perylene. A solution of perylene (5×10^{-3}M) and amine (concentration as in table 15) in acetonitrile (125ml) was irradiated for 20 hours, using an Hanovia medium pressure mercury arc (125W). The lamp, surrounded by a Pyrex water-cooling jacket, was immersed in the solution. Oxygen was bubbled through the solution continuously during irradiation. After irradiation, the solution was examined for product formation using G.L.C..

Reactions using Benzene as Solvent. The experiments described above were repeated with benzene as solvent. With sensitisers other than anthracene no reaction occurred. With anthracene as sensitiser the solution was highly coloured after irradiation. By T.L.C. it was discovered that the anthracene had been consumed. No products from the amines were detected by G.L.C., and less than 10% of the amine reacted.

The Photo-oxidation of Tropinone. A solution of tropinone (1×10^{-2}M) and naphthalene (1×10^{-1}M) in benzene (25ml), and a solution of tropinone (1×10^{-2}M) alone in benzene (25ml) were irradiated simultaneously in a Rayonet reactor equipped with lamps emitting 310nm. radiation. Oxygen was bubbled through both solutions during photolysis. After irradiation for 9 hours, G.L.C. analysis with n-hexane as internal standard showed that no tropinone had reacted in either solution. The experiment was repeated under conditions such that tropinone would absorb some incident light directly, that is, the tropinone concentration was increased to 3×10^{-1}M in each solution. (ϵ for tropinone at 310nm. is 23). Analysis of these solutions by G.L.C. after irradiation showed that less reaction had occurred in the presence of naphthalene. The ratio of the amount of tropinone that reacted in the presence of naphthalene, to that which reacted in the absence of naphthalene was 0.19. This ratio was determined by G.L.C. analysis for residual tropinone, and by I.R. analysis for the amount of amide formed in each solution. The ratio expected on the basis of naphthalene merely acting as a light filter was 0.22.

The experiment was repeated with triphenylene as sensitiser. A solution of tropinone (3×10^{-1}M) and triphenylene (1×10^{-1}M) in benzene (25ml) was irradiated simultaneously with a solution containing tropinone (3×10^{-1}M) alone. Oxygen was bubbled through the solution continuously during photolysis. After irradiation, G.L.C. analysis of the solution showed that less reaction had occurred in the presence of triphenylene.

3.5. The Primary Process in the Photoreactions of Ketones with Amines.

Materials.

The amines and ketones were purified as previously described. Acetonitrile was purified as outlined in the previous section. p-Iodotoluene, required for the preparation of tri-p-tolylamine, was prepared using the method described by Vogel.[176] Copper powder, also required for the preparation of tri-p-tolylamine, was prepared by the method of Brewster and Groening.[177]

Preparation of Tri-p-tolylamine.[178] The method of Walter was used, but the work-up procedure was modified. p-Toluidine (22.5g.), p-iodotoluene (98.5g.), anhydrous potassium carbonate (32.5g), and copper powder (1.15g.) in nitobenzene (50ml) were refluxed for 48 hours. The nitrobenzene was removed by steam distillation to leave a black crystalline cake in the aqueous layer. This was dissolved in benzene (1 l.) and adsorbed on basic alumina (Spence type H, 200g.). The benzene was removed on a rotary evaporator, and the alumina was washed with petrol (500ml). The petrol solution was evaporated to leave crude tri-p-tolylamine (13.6g.). The amine was then chromatographed on an alumina column, eluting with petrol. The product was recrystallised twice from glacial acetic acid to give white needles (11.5g., 14%), m.p.114-117°C. (Reported[178] m.p.115-117°C).

Flash Photolysis Studies. Flash photolysis of fluorenone systems was carried out using the Northern Precision F.P.1

instrument already described. The diphenylamino radical (λ_{max} 700nm.) was detected on Kodak I.R. E.R. photographic plates. Because of the insensitivity of these plates, four consecutive exposures were made, using a fresh solution each time. The slit widths on the spectrograph were the largest that could be used without interference from scattered light from the photolysis flash becoming significant.

The flash photolysis apparatus used for the work on benzophenone and tri-arylamines was made by I.C.I. Ltd. (Dyestuffs Division). It was of conventional design and included both photographic and photoelectric attachments for detection of transient species. Both Pyrex and quartz reaction vessels were used. These were 22cm long and 1.5cm in diameter. The photolysis and spectroscopic lamps were constructed of quartz, and were attached to banks of condensers of capacity 10µf. and 2µf. respectively. The photolysis and spectroscopic lamps were discharged at 9kV and 10kV, and the lifetimes of the flashes at half peak intensity were approximately 45µs and 50µs respectively.

For the photographic technique, the spectra were obtained on a Hilger medium quartz spectrograph, and were recorded on Kodak I.R. E.R. photographic plates, using four exposures. Plate photometry was again carried out on a Joyce-Loebl double beam recording microdensitometer.

A Hilger photo-electric scanning unit (type E720) incorporating an R.C.A. I.P.28 photomultiplier was used for the photo-electric measurements. The signal from the photomultiplier was directly coupled to an oscilloscope and photographed with an oscilloscope camera using Polaroid film. The monitoring light source was a d.c. operated xenon lamp (150W). The vertical linearity of the oscilloscope response was checked using neutral density filters, which were calibrated on a Unicam S.P.800 spectrophotometer.

A typical oscilloscope trace is shown in figure 18.

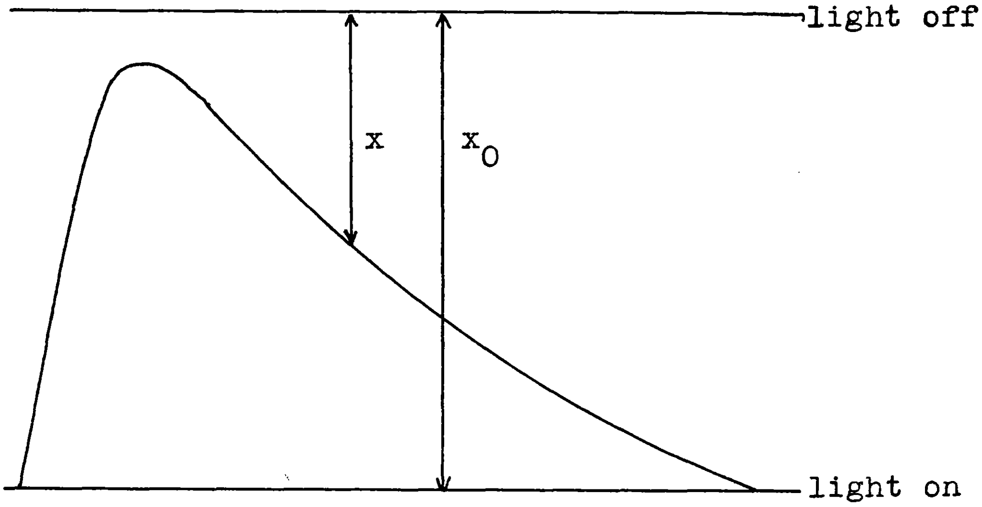


Figure 18. A typical oscilloscope trace showing the decay of a transient species with time.

If the oscilloscope response is proportional to light intensity:

I_0 = k('light on' deflection - 'light off' deflection) = kx_0

I = k('transient' deflection - 'light off' deflection) = kx

where k is a constant which depends on detector sensitivity and which need not be determined. Since $\log {}^{I_0}/_{I} = \log {}^{x_0}/_{x} = \epsilon cl$, relative or absolute concentrations can be determined as a function of time, and the order and rate of transient reactions determined. If the decay of the transient species is zero order, a plot of $\log {}^{x_0}/_{x}$ against time will be linear. If the decay is first order, a plot of $\ln(\log^{x}0/_{x})$ against time will be linear, slope k (the rate constant for the reaction). A plot of $(\log^{x}0/_{x})^{-1}$ against time will be linear if the decay is second order, and the slope of this plot will be $^{k}/_{\epsilon}$ where k is the rate constant for the reaction and ϵ is the extinction coefficient for the transient species.

<u>I.R. Studies of Aniline.</u> The effect of fluorenone and triethylamine on the N-H absorption of aniline was studied using a Perkin-Elmer 225 grating infrared spectrophotometer. The spectra were run in anhydrous benzene solution using sodium chloride solution cells. The concentrations used were; aniline (0.5M), fluorenone (0.5M), and triethylamine (1.0M).

Appendix 1. The Stern-Volmer Equation.

Consider the following simple scheme for the formation and decay of an excited state.

$$X + h\nu \longrightarrow X^{*} \qquad \text{Excitation}$$

$$X^{*} \xrightarrow{k_f} X + h\nu \qquad \text{Emission}$$

$$X^{*} \xrightarrow{k_i} X \qquad \text{Internal quenching}$$

$$X^{*} + Q \xrightarrow{k_q} X + Q \qquad \text{External quenching}$$

Under steady state conditions: $\frac{d[X^{*}]}{dt} = -\frac{d[X^{*}]}{dt} = 0$

i.e. $-\frac{d[X^{*}]}{dt} = k_f[X^{*}] + k_i[X^{*}] + k_q[Q][X^{*}] = I_{abs.}$

The quantum yield of fluorescence (F) is given by:

$$F = \frac{k_f[X^{*}]}{I_{abs.}}$$

so in the presence of quencher,

$$F = \frac{k_f[X^{*}]}{[X^{*}](k_f + k_i + k_q[Q])}$$

$$= \frac{k_f}{k_f + k_i + k_q[Q]}$$

and in the absence of quencher,

$$F_0 = \frac{k_f}{k_f + k_i}$$

The intensity of fluorescence is proportional to the quantum yield, therefore:

$$\frac{F_0}{F} = 1 + \frac{k_q[Q]}{k_f + k_i} = \frac{I_0}{I}$$

The mean lifetime of the excited state in the absence of quencher is given by the reciprocal of the sum of the rate constants for unimolecular deactivation processes:

$$\tau = \frac{1}{k_f + k_i}$$

so writing $\frac{k_q}{k_f + k_i} = k_q\tau$

$$\frac{I_0}{I} = k_q\tau_x[Q]$$

The Stern-Volmer quenching constant is the quantity $k_q\tau$. From a knowledge of this constant, and the lifetime τ, the rate constant k_q may be evaluated.

If the species Q quenches by energy transfer, and if the emission from Q^* is detectable, then the relative change in the intensity of the emission from Q^* on addition of X may be measured. From such measurements the quantity $k_q\tau_x$ may be evaluated, and $k_q\tau_x$ is then called the Stern-Volmer sensitisation constant. For details of this method and for a rigorous kinetic treatment, see ref. 16 and ref. 179.

Appendix 2. The Photoreactions of DABCO.

Fisch and co-workers[73] suggest that the quenching by DABCO of the direct or sensitised photo-oxidation of pseudopelletierine and tropinone is good evidence for the involvement of singlet oxygen in these oxidations. They say 'diazabicyclo-octane is rapidly destroyed by radical reactions initiated by carbonyl sensitisers, e.g. benzophenone.' [73a]

Fluorenone is photoreduced by triethylamine,[102,180] and an intermediate in this reaction is the 9-hydroxyfluorenyl radical, which has been detected in this system by e.s.r. spectroscopy.[99,169] This reaction is therefore a typical radical reaction initiated by a carbonyl sensitiser. It was shown by Cohen in 1970 that DABCO is an efficient quencher of this photoreduction.[151]

The fact that DABCO quenches the direct photo-oxidation of pseudopelletierine and tropinone does not therefore necessarily imply that the oxidations involve singlet oxygen.

Work carried out in these laboratories indicates that the behaviour of DABCO is difficult to predict. Overall this work is inconclusive, but it is worth reporting in view of the emphasis placed by Fisch on the quenching of photo-oxidations by DABCO.

It was confirmed that DABCO quenches the photoreduction of fluorenone by triethylamine, and G.L.C. analysis revealed that DABCO was not consumed in this reaction. Furthermore, DABCO did not photoreduce fluorenone, xanthone, benzalacetophenone, or acetophenone, in deoxygenated benzene solution, nor did it photoreduce methylene blue or rose bengal in deoxygenated methanol solution. Naphthalene and perylene were also not photoreduced by DABCO in deoxygenated acetonitrile solution. DABCO was not photo-oxidised by any of these sensitisers in oxygenated solution.

Benzophenone (1.82g) was photoreduced by DABCO (6.2g) in deoxygenated benzene solution (200ml) to yield the coupled product (X), (yield 2.2g, 75% based on ketone) and benzpinacol (0.25g, 15%). The coupled product (95%) was also formed in oxygenated solution (see section 2.1.1.).

p-Aminobenzophenone (2.14g) was also photoreduced by DABCO (6.2g) in deoxygenated benzene solution (200ml) to give the pinacol (0.75g, 35%), and a compound which was probably the corresponding coupled product.

The formation of such a large proportion of coupled product in the reaction with benzophenone in both oxygenated and deoxygenated solution, implies that once radicals are formed by initial hydrogen abstraction, they do not diffuse apart, but recombine rapidly.

It is apparent, from the results with all the sensitisers examined, that the reactions of DABCO do not depend on the energy of the triplet state of the sensitisers: benzophenone (E_T68.5k.cal.mole^{-1})^2 is photoreduced whereas xanthone (E_T74.2 k.cal.mole^{-1})^2 and acetophenone (E_T73.6k.cal.mole^{-1})^2 are not.

In view of the efficiency with which other amines of low ionisation potential quench the fluorescence of aromatic hydrocarbons,[130-135] it was expected that DABCO would also be an efficient quencher of hydrocarbon singlet states. The effect of DABCO on the fluorescence of a number of aromatic hydrocarbons was therefore examined. DABCO was found to quench the fluorescence of naphthalene, anthracene, perylene and chrysene. The Stern-Volmer quenching constants are shown in the table. The rate constants for the quenching process were evaluated using the mean lifetimes also shown in the table.

Hydrocarbon	K $l.mole^{-1}$	$\tau(x10^9)$sec	k_q $l.mole^{-1}$ s^{-1}
Naphthalene	85.2	8.3^a	1.2×10^{10}
Chrysene	81.4	20.0^a	0.4×10^{10}
Anthracene	78.6	6.5^b	1.2×10^{10}
Perylene	79.5	6.2^c	1.3×10^{10}

(a). From ref. 179. (b). From ref. 181.

(c). Calculated from the data in ref. 130.

The results in the table show that DABCO quenches aromatic hydrocarbons singlet states at a rate which approaches the diffusion controlled limit. DABCO would therefore be expected to quench the photo-oxidation of amines sensitised by hydrocarbons. Such quenching would not imply the involvement of singlet oxygen.

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The Photosensitised Oxidation of Amines.

Abstract of a thesis presented for the degree of Doctor of Philosophy in the Faculty of Science of the University of Leicester, by R.F.Bartholomew.

The Photosensitised Oxidation of Amines.- Abstract.

The photo-oxidation of amines sensitised by benzophenone and other ketones, fluorescein and thiazine dyes, and aromatic hydrocarbons has been examined. The major products obtained from the sensitised photo-oxidation of aliphatic secondary and tertiary amines were aldehydes and imines. Only aldehydes were obtained from aliphatic primary amines. The benzophenone sensitised photo-oxidation of N-alkylated anilines gave de-alkylated amines, amides and aldehydes.

It is proposed that the primary process in all these reactions is the interaction of the amine with excited sensitiser, and that the products are formed by subsequent radical reactions. The reactions are not initiated by attack of singlet oxygen on the amine.

The most important evidence presented in favour of a radical mechanism is as follows.

1. The types of products formed are compatible with a radical mechanism. The same types of products are obtained with all the sensitisers used, which implies that the sensitisers act by a common mechanism.
2. Only those compounds which are photoreduced by amines in deoxygenated solution act as sensitisers for the photo-oxidation of these amines. This implies that the primary process in photo-oxidation is the same as in photoreduction, namely the interaction of amine with excited sensitiser.
3. Flash photolysis of aerobic solutions of dyes or aromatic

hydrocarbons with amines produced transient species which could only have been formed by the interaction of amine with the excited sensitiser.

4. Amines such as triethylamine and ethyldi-isopropylamine, which are efficient physical quenchers of singlet oxygen, are photo-oxidised efficiently with all the sensitisers used. This is evidence that singlet oxygen is not the active species in these photo-oxidations.

Evidence from flash photolysis studies is also presented, which implies that the primary process with all the sensitisers involves electron transfer or exciplex formation. The fact that amines can compete effectively with oxygen for the excited sensitiser is due to the rapidity of such electron transfer processes.