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THE REACTIONS OF ELECTRONICALLY EXCITED MOLECULES IN SOLUTION

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REACTIONS which require the absorption of light by one of the chemical species present may be termed photosensitised reactions. The excited molecule may (i) transfer some or all of the energy it has acquired through absorption of a quantum of light, to other molecules present; (ii) become an ion through some electron-transfer process; (iii) split into two fragments or radicals, in which the total electron spin momentum is not zero, but the total charge is; (iv) react in its excited state with another molecule; or (v) re-emit the absorbed quantum as fluorescence or phosphorescence.

Photosensitisation can then occur either through an *induced* dissociation or reaction of an *acceptor* molecule, caused by energy acquired from the sensitiser molecule, or through reaction of the ions, radicals, or excited molecules formed in the first stage; *i.e.*, through either an energy transfer or an immediate chemical reaction.

In order to describe fully the mechanism of a photosensitised chemical reaction, it is necessary to know the initial effect of the absorption of a quantum of light on the sensitiser molecule, the subsequent fate of the excited absorber molecule, the nature of the unstable intermediate or intermediates responsible for the actual sensitisation, and, finally, the sequence of molecular rearrangements caused by chemically reactive collisions of the unstable intermediates.

The first half of this Review is devoted to a discussion of the processes involved in the formation and decay of electronically excited molecules, and of the quenching processes which lead to chemical reaction in solution

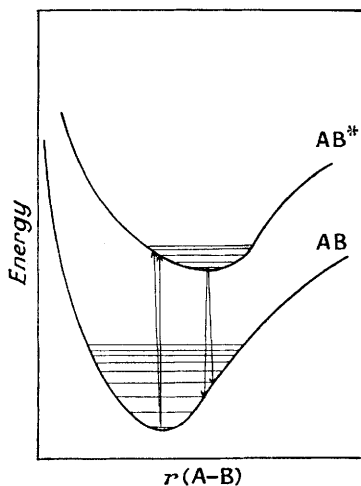## Formation and decay of electronically excited molecules.

Absorption of Light.—The interaction of light with matter is governed by quantum-mechanical laws. The light is quantised into photons of energy $h\nu$, where h is Planck's constant and ν is the frequency of the light; whether or not a molecule will absorb a quantum of energy $h\nu$ depends on whether there is an energy difference between two energy levels in the molecule equal to $h\nu$ and whether a transition between these two states is allowed by symmetry and momentum-conservation rules, etc. The energy in the molecule can be divided into kinetic (translational, vibrational, and rotational) and electronic contributions: electronic transitions require the greatest energies. With each electronic level there are associated vibrational levels, and with each vibrational level, rotational levels. A photon of light in the visible or ultraviolet range of the spectrum is sufficiently energetic to effect an electronic transition in the absorbing molecule. The excited

1*   3

molecule might then react with another, since its reactivity is greatly increased, or it might possibly dissociate or cause another molecule to dissociate into radicals, which subsequently react in divers ways. It is because photons in this range are capable of rupturing the molecule that visible and ultraviolet light are of chemical importance.

During an electronic transition the nuclei of the molecule can be considered to be stationary, since the transition occurs within about 10^{-15} sec. Thus a transition on an energy-level diagram is approximately vertical; this is known as the Franck–Condon principle. Other transitions near the vertical can also occur, but with a smaller probability, since the principle is not entirely rigid.

The majority of the unexcited molecules will be in the ground electronic and vibrational states. A typical transition on an energy-level diagram is shown in Fig. 1, in which the molecule is initially excited into upper

FIG. 1. *Potential energy diagram for a ground and an excited state.*

r (A–B)

vibrational levels of the excited state. (Diatomic molecules are considered for simplicity, since an *n*-atomic molecule would require an *n*-dimensional diagram.)

The Decay Processes of Electronically Excited Molecules.—*Fluorescence.* The vibrational quanta possessed by the electronically excited molecule will be quickly degraded into thermal energy, through intermolecular collisions, especially in solution. Since the undisturbed lifetime of the excited state is of the order of 10^{-8} sec., it being assumed that the transition back to the ground state is allowed, emission of the absorbed quantum as *fluorescence* will occur from the lowest vibrational level of the upper state

to upper levels of the ground state, *i.e.*, the fluorescence emission spectrum will be of longer wavelength than the absorption spectrum and will bear an approximately "mirror-image" relationship to the absorption. This is shown diagrammatically in Fig. 1.

Internal conversion. In many cases, the electronically excited state of the molecule, although potentially fluorescent, is deactivated before it can re-emit its energy as fluorescence. This can occur, amongst other ways, when there is a crossing of potential-energy surfaces of the excited and the ground electronic states. A radiationless transition can then occur from the excited state to high vibrational levels in the ground state. The vibrational energy is then quickly degraded into thermal energy through intermolecular collisions.

One of the most striking effects exhibited by solutions of condensed-ring aromatic hydrocarbons is the strong fluorescence observed when the solutions are irradiated with visible or ultraviolet light. Since there are so many atoms in these molecules the number of potential-energy surfaces in an energy diagram is large, and the possibility of crossing of such surfaces is correspondingly large. Yet the strong fluorescence indicates that internal conversion does not take place as often as would be expected. Now all these molecules possess ring systems of conjugated π-orbitals. If, on excitation by an absorbed quantum, the electronic transition occurs in these orbitals, then the atomic framework of the molecules will be little disturbed: the potential-energy surfaces will be almost parallel, and the chance of their crossing will be small. The possibility of internal conversion will therefore be small, and the molecules will show a strong fluorescence in an inert solvent.

Energy transfer through collision. Two kinds of collision can be visual-ised, "elastic" collisions in which there is no transfer of energy from the excited to the unexcited molecule, and "inelastic" collisions in which there is an energy transfer. These collisions are sometimes called "collisions of the second kind". The most likely conditions for an energy transfer obtain when there is resonance between corresponding energy levels, *i.e.*, elec-tronic, vibrational, or rotational. The smaller the amount of energy which appears as kinetic energy in a transfer, the more likely it is that the transfer will occur. Electronic energy transfer may lead to the phenomenon of sensitised fluorescence, as well as the possibility of a dissociation of the acceptor molecule. Collision with solvent molecules may so perturb the electronic energy levels of a molecule as to facilitate the internal conversion of the excited state of the molecule, in which case the fluorescence efficiency will vary from one solvent to another.

Dissociation. As was mentioned earlier, the absorption of a photon of visible or ultraviolet light by a molecule can, in some instances, lead to its rupture. This can occur either through the excited molecule's being in a repulsive state, or through its having sufficient vibrational energy in either its upper or lower state to cause it to dissociate. Generally the bond broken

is the same one as was responsible for the light absorption (*e.g.*, disulphides, azo-compounds, etc.). Sometimes, however, when the bond energies in the chromophoric group are greater than that of the absorbed quantum, the energy may find its way to another weaker bond in the molecule through resonance-energy transfer and *this* bond is broken. For example, the irradiation of acetone leads to the production of a methyl and an acetyl radical, although the light is absorbed by the carbonyl group. This process can be thought of as an internal energy transfer.

Chemical quenching. The excited state can lose its energy, not only through a physical energy transfer on collision, but also through chemical reaction with the quencher molecule. In many cases *self-quenching* of the excited state may occur, either as a physical effect analogous to solvent quenching, or else through dimerisation. Examples of these processes will be discussed later.

The triplet state[1,2]

In small molecules electronic transitions involving changes in the multiplicity of the molecule (*i.e.*, the total spin momentum of the electrons) are forbidden, by spin-momentum conservation rules. However, in the case of large molecules, perturbation of the energy levels leads to a partial breakdown of this selection rule, and the transition can occur. In 1941 Lewis and his co-workers[3] suggested that the metastable phosphorescent state of fluorescein might be the triplet state, and three years later Lewis and Kasha[4] definitely identified the phosphorescence of a large range of aromatic molecules with a first triplet–ground singlet transition. This was experimentally proved for fluorescein in the following year by Lewis and Calvin through measurements of its paramagnetic susceptibility in the phosphorescent state.[5]

The lifetime of the triplet state may be of the order of seconds in the glassy state,[4] in which deactivating collisions do not occur, and of the order 10^{-4} sec. in solution in the liquid phase.[6] Since a system in which the electron spins are parallel has a lower energy than one in which the spins are all coupled (Hund's rule), the first triplet level lies below the first excited singlet level.

Phosphorescence and Slow Fluorescence.—If a transition from the triplet state to the ground singlet state occurs, with the emission of a photon, the light emitted is of considerably longer wavelength than the fluorescence emission, since the first triplet level is lower than the first excited singlet state. This emission is known as *phosphorescence*. However, there may also be a transition from the triplet state back to the first excited singlet state,

[1] C. Reid, *Quart. Rev.*, 1958, **12**, 205.
[2] M. Kasha, *Chem. Rev.*, 1947, **41**, 401.
[3] G. N. Lewis, D. Lipkin, and T. Magel, *J. Amer. Chem. Soc.*, 1941, **63**, 3005.
[4] G. N. Lewis and M. Kasha, *ibid.*, 1944, **66**, 2100.
[5] G. N. Lewis and M. Calvin, *ibid.*, 1945, **67**, 1232.
[6] G. Porter and M. W. Windsor, *Discuss. Faraday Soc.*, 1954, **17**, 178.

owing to chance thermal excitation. A fluorescent singlet–singlet transition can then occur. This differs from ordinary fluorescence in involving a delay of the order of a second in the glassy state, and it is known as *slow fluorescence*. (There is some ambiguity in the "labelling" of these two emissions in the literature, but in this Review phosphorescence will always be taken as referring to a triplet state-to-ground singlet state emission, *i.e.*, a "forbidden" transition.) Phosphorescence is independent of temperature, whereas slow fluorescence is not. The increase in the lifetime of the triplet state in passing from liquid to solid solutions is related to the viscosity of the solvent, although this effect is not fully understood.[6,7] In liquid solution, phosphorescence is not observed, the triplet state being deactivated in a radiationless process through interaction between the triplet state and the solvent. This interaction becomes increasingly less important as the viscosity of the solvent increases. The triplet's lifetime also depends on the actual nature of the solvent in some cases, and the triplet states of anthracene and naphthalene do not show the same viscosity-dependence in the same series of solvents. It is apparent that the nature of solvent deactivation of the triplet state is as yet unexplained.

Energy transfer. Triplet–triplet energy transfer has recently been shown to occur in the glassy state,[8] leading to sensitised phosphorescence. The acceptor molecule must have a lower triplet energy than the donor.

Absorption in the triplet state. Just as absorption of light can lead to transitions between singlet states, so also can absorption lead to transitions between triplet states. Providing the population of the first triplet level is sufficient, this absorption can be seen in the glassy state by means of intense cross-irradiation,[9] and in the liquid state by means of synchronised flash techniques.[6]

Singlet–triplet absorption. Snow and Allsopp were the first to assign a weak transition in ethylene to a singlet–triplet absorption.[10] They were thus the first to postulate such a transition in a complex polyatomic molecule. The transition is the reciprocal of phosphorescence, and can be observed most strongly when there is strong perturbation of the electronic energy levels in the absorber molecule. The presence of heavy atoms, either in the solvent[11] or in the absorbing molecule itself,[12,13] and the effect of high pressures of oxygen on the liquid solution,[14] can cause strong perturbations which break down the spin-momentum conservation rules.

Jablonski diagram. The energy-level diagram first advanced by Jablonski[15] (except that he did not identify the metastable phosphorescent state with

[7] G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, 1958, *A*, **245**, 238.
[8] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, 1956, **52**, 1042.
[9] G. N. Lewis and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2424.
[10] C. P. Snow and C. B. Allsopp, *Trans. Faraday Soc.*, 1934, **30**, 93.
[11] M. Kasha, *J. Chem. Phys.*, 1952, **20**, 71.
[12] D. S. McClure, *ibid.*, 1949, **17**, 905; 1951, **19**, 670; 1952, **20**, 682.
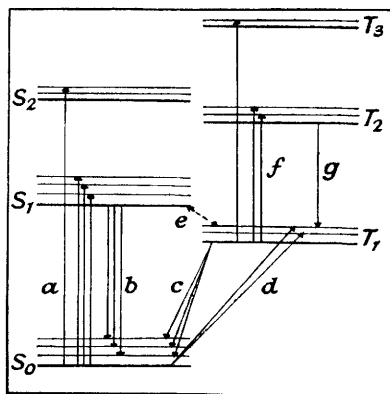[13] M. Mizushima and S. Koide, *ibid.*, 1952, **20**, 765.
[14] D. F. Evans, *J.*, 1957, 1351.
[15] A. Jablonski, *Z. Physik*, 1935, **94**, 38.

the triplet state) summarises the electronic transitions described, which are relevant to condensed-ring aromatic hydrocarbons, dyes, etc., in solution.

FIG. 2.   *Jablonski diagram.*

a, Singlet–singlet absorption; b, fluorescence (normal and slow), internal conversion, solvent quenching; c, phosphorescence, internal conversion, solvent quenching; d, singlet–triplet absorption; e, excited singlet–triplet transitions; f, triplet–triplet absorptions; g, internal conversion.

Chemical consequences of the quenching of electronically excited molecules

If we ignore the possibility of dissociation of the excited molecule, then chemical reaction can be either a primary or a secondary effect of the quenching of the excited state by a foreign molecule. If reaction is the primary effect, then reaction between the excited molecule and the quencher molecule is the cause of the quenching; the electronic energy of the excited molecule is transformed into chemical energy of the products. If reaction is a secondary effect, then quenching is through a collision of the second kind, and the energy which the quencher molecule has acquired is sufficient to cause it to react: this photosensitisation is through an energy transfer. Let us consider these two types of photoreaction in turn.
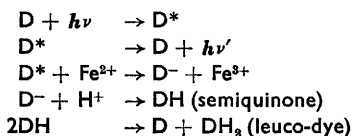
Chemical Reaction of Excited Molecules.—Many examples of such reactions have been investigated and these may be classified into electron transfers, abstractions, or addition reactions.

Electron transfer. When a polyatomic molecule is excited to the first excited singlet state (from a singlet ground state), one of the electrons in the molecule vacates its orbital for the next higher one, although the total spin remains zero. If the excited molecule captured an electron through

collision with a quencher molecule, this electron would occupy the vacated orbital and the transition of the excited electron back to the ground state would be blocked; fluorescence would then be impossible. The resultant species would be both an ion (by virtue of the negative charge it would have acquired) and a radical (by virtue of the odd electron in the molecule).

An example of fluorescence quenching which is believed to proceed through such a mechanism is given by the quenching of Methylene Blue by ferrous ions in aqueous solution. The following steps may be visualised:[16,17]

$$D + h\nu \rightarrow D^*$$
$$D^* \rightarrow D + h\nu'$$
$$D^* + Fe^{2+} \rightarrow D^- + Fe^{3+}$$
$$D^- + H^+ \rightarrow DH \text{ (semiquinone)}$$
$$2DH \rightarrow D + DH_2 \text{ (leuco-dye)}$$

The chemical effect of the electron transfer is the eventual reduction of the dye to the leuco-form. A reverse transfer is exhibited in the quenching of fluorescence by ceric ions, which are reduced to cerous. In this case, the excited electron is transferred to the quenching ion.

Abstraction reactions. These reactions generally involve the reduction of the excited molecule through abstraction of a hydrogen atom from the quencher molecule. For example, Bridge and Porter[18] have investigated the reactions of excited quinones in alcoholic solutions, and have been able to observe the transient absorption spectra of the reduced quinone intermediates in a duroquinone solution. They were: the semiquinone radical QH·, appearing in solvents containing abstractable hydrogen at pH $\leqslant$ 7, and the radical ion ·Q⁻, appearing in solutions of pH $\geqslant$ 7. They also observed the absorption of the triplet excited quinone in viscous paraffin solutions, but were able to show that it was the singlet excited state rather than the triplet state which was responsible for the abstraction.

To digress, it may be remarked that this work is of very considerable importance in that the intermediates have been identified unequivocally by means of synchronised flash techniques,[19] and not by inference alone. In the past, the investigation of a photosensitised chemical reaction was always limited by the fact that, although the variation of the concentrations of stable products and reactants could be followed analytically, not only the concentration, but even the *nature* of the unstable intermediates could only be inferred or guessed. However, with the advent of flash photolytic techniques, the characteristic electronic absorption (or emission) spectra of intermediates with lifetimes as short as twenty or thirty microseconds can be detected, if their concentrations and extinction coefficients are sufficiently large. (The technique has recently been extended to infrared

[16] E. Gaviola, *ibid.*, 1927, **42**, 853; 1927, **48**, 397.
[17] W. Kirchhoff, *ibid.*, 1940, **116**, 115.
[18] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259.
[19] G. Porter, *ibid.*, 1950, *A*, **200**, 284.

absorption wavelengths.[20]) The time resolution is governed by the duration of the photolytic and spectroscopic flashes, the former generally having by far the greater duration. If it is possible to identify the absorption spectra of the intermediates, their nature is known: further, if the lifetime of the intermediates is sufficiently long, photometry of the transient absorption spectra can be used to follow the way in which the concentrations of the unstable intermediates vary with time, and the rate constants of very fast reactions can be determined.

Data obtained from these techniques, when coupled with those obtained from conventional kinetic techniques, give a far less ambiguous description of the photosensitised reaction than was possible by means of kinetic techniques alone. The subject has been reviewed fairly recently,[21] but a considerable volume of new work has been published since then dealing with reactions both in the gas phase and in solution. Where relevant, this later work is discussed in this review.

Addition reactions. Many of the addition reactions of electronically excited molecules in solution appear to involve the triplet state rather than the excited singlet state. This justifies the suggestion that the triplet state of a polyatomic molecule can be considered as a diradical. However, it is the *localisation* of the electrons rather than their uncoupling which leads to the consideration of the triplet state as a diradical state. A diradical might conceivably be in a singlet state, and oxygen has a ground triplet state. Since the triplet states of many polyatomic molecules are postulated to enter into reactions analogous to radical reactions, there must be some localisation of electrons in the triplet state which does not occur in the singlet state.

The formation of the transannular peroxides of polynuclear aromatic hydrocarbons such as anthracene[22] and rubrene[23] provides a good example of an addition reaction involving electronically excited molecules. The triplet state of the hydrocarbon is involved, but the exact mechanism of the reaction is still not agreed upon, and will be more fully discussed later.

Photosensitisation through Energy Transfer—In a strict definition, it is only these reactions which are true sensitisations, in the sense that the absorbing molecule acts as a catalyst and does not enter into the chemical reaction. Examples of such reactions in solution are not very common.

Pruckner and Weigert in 1931[24] found that acetone sensitised the photoisomerisation of nitrobenzaldehyde to nitrosobenzoic acid, and concluded that the sensitisation must proceed through an energy transfer from the acetone solvent to the aldehyde. Further, this transfer must occur before the acetone itself has had time to dissociate, since no dissociation of the acetone was observed. Presumably this is due to the delay during which

[20] K. N. Tanner and R. L. King, *Nature*, 1958, **181**, 963.
[21] R. G. W. Norrish and B. A. Thrush, *Quart. Rev.*, 1956, **10**, 149.
[22] C. Dufraisse and G. Gerard, *Compt. rend.*, 1935, **201**, 428.
[23] C. Moureu, C. Dufraisse, and P. M. Dean, *ibid.*, 1926, **182**, 1440.
[24] F. Pruckner and F. Weigert, *Z. phys. Chem., Bodenstein Festband*, 1931, 775.

the energy which the acetone has acquired finds its way to the weakest bond in the molecule. Similar results have been obtained for ethyl iodide dissolved in benzene.[25]

In 1940 West and Miller published work on the photolysis of alkyl iodides in hexane solution, sensitised by aromatic hydrocarbons such as benzene and naphthalene.[26] They concluded that singlet excited naphthalene molecules sensitised the rupture of the carbon–iodine bond through a resonative transfer of vibrational energy on collision. The quantum efficiency of the sensitisation was found to be greater than that of the fluorescence, so it was postulated that a second non-fluorescent species could also sensitise the photolysis. Since the optical densities of the iodide and sensitiser were additive they discounted the formation of an intermediate complex between the sensitiser and the quencher.

In contrast to this sensitisation, examples are known of sensitised photolyses in which the sensitising species need not be capable of fluorescence at all, and in which a complex between the sensitiser and the quencher is involved in the photolysis. For example, the Eder reaction between mercuric chloride and ammonium oxalate is sensitised by ferric ions, which do not fluoresce, and in the photolysis of oxalic acid sensitised by the excited uranyl ion there is an energy transfer from the uranyl ion to the acid in a complex during the lifetime of the excited uranyl ion. The fluorescence of the uranyl ions is weakened by oxalate ions, and simultaneously the oxalic acid disappears.[27,28]

All the examples of sensitisation through energy transfer seem to involve the excited singlet state rather than the triplet state. This could be due to the fact that, if quenching occurs, it will occur before the transition from the excited singlet state to the triplet state has been made.

Some General Aspects of Quenching—It is of interest to distinguish between the quenching of excited states by molecules which are permanently in contact with the fluorescent molecule, *i.e.*, solvent quenching, and quenching by a third molecule present in low concentrations in a solution of the absorbing species. In the case of solvent quenching, the quenching process need not be particularly efficient, since the collision frequency will be high. In the case of quenching by a third molecule present in very low concentrations the quenching process must be very efficient, occurring at almost every collision, since the collisions between the excited molecules and the quencher molecules are so rare. The longer the lifetime of the excited molecule, the more likely it is that it will be quenched. Thus Boudin[29] and Kautsky and Hirsch[30] were able to show that the phosphorescence of dyes such as eosin, erythrosin, and phloxin was completely quenched by small

[25] W. West and B. Paul, *Trans. Faraday Soc.*, 1932, **28**, 788.
[26] W. West and W. E. Miller, *J. Chem. Phys.*, 1940, **8**, 849.
[27] P. Pringsheim, *Physica*, 1937, **4**, 733.
[28] A. H. Carter and J. Weiss, *Proc. Roy. Soc.*, 1940, *A*, **174**, 351.
[29] S. Boudin, *J. Chim. phys.*, 1930, **27**, 285.
[30] H. Kautsky and A. Hirsch, *Chem. Ber.*, 1931, **64**, 2677.

traces of dissolved oxygen, although the quenching of the fluorescence was undetectable.

The efficiency with which a third molecule quenches fluorescence generally varies with the dielectric constant (polarity) of the solvent, and the temperature. The variations can be either positive or negative in both cases. If the temperature-dependence is positive then the quenching is a "collisional" process, depending on the rates at which the molecules diffuse together. If, however, the temperature-dependence is negative, then the quenching process must involve some kind of intermediate complex, i.e., the potential-energy curve for the approach of the two molecules is not entirely repulsive but has a small trough. The heats of formation of such complexes are of the order of 1—3 kcal./mole; thus the forces between the molecules causing this potential minimum must be either "dispersion forces" or "dipole interactions". Dipole interactions will be favoured in polar solvents and dispersion forces in non-polar solvents. It is probably only a matter of degree whether the complex formation is "real", since the temperature-dependence is governed by the shape of the potential-energy curve for the molecular encounter. If the curve happens to show a minimum then a complex is postulated; this situation could be regarded as a "sticky collision".

This concludes the discussion of the processes involved in the quenching of electronically excited molecules, which lead to chemical reaction in solution. The remainder of the Review is devoted to a survey, illustrative rather than comprehensive, of published work. References to more comprehensive reviews of specialised topics are also given.

The photoreactions are classified under a series of main headings, and the similarities which exist between particular reactions are emphasised. Although a wide diversity are described, the primary processes are all restricted to those mentioned previously.

(A.) **Self-quenching and Dimerisation.**—The phenomenon of self-quenching of fluorescence in solution leading to the formation of dimers or even polymers is an example of an addition reaction between an electronically excited molecule and a quencher molecule. For example, in benzene solutions of anthracene increasing concentration leads to strong quenching of the fluorescence,[31] and dianthracene is formed in solution more than 10^{-2}M. The dimer has been shown to have a "bridge" structure across the 9 and the 10 position of the anthracene ring system.[32] It has often been suggested that the reaction proceeds through the collision of singlet excited and unexcited anthracene molecules, followed by the formation of a triplet diradical intermediate (e.g., Bowen and Tanner[33]). However, in view of the fact that self-quenching of triplet anthracene in hexane

[31] E. J. Bowen and A. Norton, Trans. Faraday Soc., 1939, **35**, 44.

[32] F. D. Greene, S. L. Misrock, and J. R. Wolfe, jun., J. Amer. Chem. Soc., 1955, **77**, 3852.

[33] E. J. Bowen and D. W. Tanner, Trans. Faraday Soc., 1955, **51**, 475.

solutions is undetectable up to 10^{-3}M,[6,7,34] it may be concluded that the dimerisation proceeds exclusively through the singlet state.

Dammers-de Klerk has recently investigated the dependence of the efficiency of fluorescence on concentration for benzene, naphthalene, and anthracene.[35] With benzene and anthracene the fluorescence intensity vanishes at high concentrations, but it does not disappear for naphthalene. He has proposed a scheme in which these effects can be interpreted in terms of the stability of an intermediate complex between the excited and unexcited molecules.

With anthracene a stable dimer is formed; the excited dimer does not fluoresce because of strong intramolecular quenching in the complex:

$$A + {}^1A^* \rightarrow AA^* \rightarrow AA$$
$$\downarrow$$
$$h\nu$$
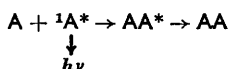
In the case of naphthalene, the fluorescence wavelength does not vary with concentration; accordingly it is suggested that there is a small interaction leading to the formation of an unstable complex which has a lifetime long enough to allow for its fluorescing, but that the interaction in the complex is not sufficient to change the fluorescent wavelength from that of the monomer:

$$A + {}^1A^* \rightarrow AA^* \rightarrow A + A$$
$$\downarrow \qquad \downarrow$$
$$h\nu \qquad h\nu + A + A$$
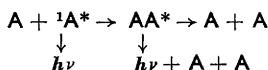
With benzene, if any complex is formed it dissociates before fluorescing and the quenching is of a collisional nature:

$$A + {}^1A^* \rightarrow A + A$$
$$\downarrow$$
$$h\nu$$
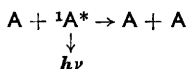
Förster and Kasper in 1955[36] proposed a similar scheme to account for the concentration-dependence of the fluorescence of pyrene. They found that at low concentrations the fluorescence was violet, and at high concentrations it was blue; they attributed the former to the fluorescence of the excited monomer, and the latter to a metastable excited dimer. The stability of this dimer would lie between that of naphthalene and anthracene:

$$A + {}^1A^* \rightarrow AA^* \rightarrow AA \rightarrow A + A$$
$$\downarrow \qquad \searrow \qquad \nearrow$$
$$h\nu \qquad h\nu' + AA$$
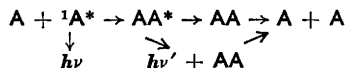
A large number of photodimerisations, either in solution or in suspension in the solid phase, have been reported, and these have been reviewed by Mustafa.[37] Amongst the classes of compound which undergo this

[34] R. Livingston and D. W. Tanner, *ibid.*, 1958, **54**, 765.
[35] A. Dammers-de Klerk, *Molecular Physics*, 1958, **1**, 141.
[36] T. Förster and K. Kasper, *Z. Elektrochem.*, 1955, **59**, 976.
[37] A. Mustafa, *Chem. Rev.*, 1952, **51**, 1.

reaction are substituted anthracenes, nitrogen analogues of anthracene (*e.g.*, 1-aza-anthracene[38]), and some phenyl-substituted ethylenes (*e.g.*, cinnamic acid, stilbene, acenaphthene, benzylideneacetophenone, etc.). The latter form cyclobutane derivatives, as

$$2\text{Ph·CH:CH·COPh} \rightarrow \begin{array}{c} \text{Ph·CH·CH·COPh} \\ | \quad\quad | \\ \text{PH·CH·CH·COPh} \end{array}$$
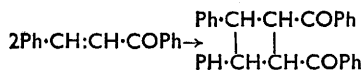
Cinnamic acid will only dimerise in the solid phase, yielding α-truxillic acid. Finally, it may be remarked that most of these photo-dimerisations are reversible, and many of the dimers dissociate in the dark.

Although the self-quenching of triplet anthracene is undetectable up to concentrations of the order of 10^{-3}M, the self-quenching of triplet eosin and fluorescein has been detected at concentrations as low as 10^{-6}M.[39] The fact that the self-quenching could be observed at such dilutions excluded the possibility of its being the singlet state which was being quenched, since the lifetime of the triplet is so much greater than that of the singlet excited state. The self-quenching of metastable (triplet?) chlorophyll has been observed by Livingston,[40] who suggested that the metastable chlorophyll was quenched solely by metastable and unexcited chlorophyll molecules, and not by the solvent. More recently, Linschitz and Sarkanen have investigated the formation and decay of metastable chlorophylls a and b in solution,[41] using a photolytic flash of under 5 μ sec. duration, together with photoelectric techniques to follow the decay of the absorption of the metastable chlorophyll. The very short flash gives a very much better time resolution than that obtained in earlier investigations, and the photoelectric technique is far more accurate than the flash photolytic–flash photographic methods at first employed.[6] They established that there is only one metastable state of chlorophyll, and that its decay involves both first- and second-order processes, together with a certain amount of self-quenching. All the relevant rate constants have been measured. A small second-order contribution to the decay of the triplet state of a large number of polynuclear aromatic hydrocarbons has been detected recently by Porter and his co-workers,[42] also by photoelectric techniques; the plate photometry used in earlier work was not sensitive enough to detect the second-order decay.

All these triplet self-quenching processes appear to be physical rather than chemical, and no dimers are formed.

(B.) **Quenching by Oxygen.**—Dissolved oxygen very often quenches fluorescence, especially of aromatic molecules. Sometimes this quenching

[38] A. Etienne, *Ann. Chim. (France)*, 1946, **12**, 1; A. Etienne and J. Robert, *Compt. rend.*, 1946, **223**, 331.

[39] A. H. Adelman and G. Oster, *J. Amer. Chem. Soc.*, 1956, **78**, 913.

[40] R. Livingston, *ibid.*, 1955, **77**, 2179.

[41] H. Linschitz and K. Sarkanen, *ibid.*, 1958, **80**, 4826.

[42] G. Porter, personal communication.

is accompanied by the oxidation of the fluorescent molecule, but this is not always the case. For example, as Bowen pointed out,[43] the fluorescence of naphthalene is very strongly quenched by oxygen, but peroxide is not detected. Thus the quenching is due to a mechanism such as
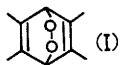
$$^1A^* + X \rightarrow (AX)^* \rightarrow A + X + \text{kinetic energy}$$

where X is the quencher, rather than

$$^1A^* + O_2 \rightarrow AO_2$$
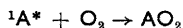
As early as 1930, Boudin was able to separate a short and a long-lived fluorescence of eosin.[29] Potassium iodide reduced both the fluorescence and the phosphorescence, but the phosphorescence curve showed the closest resemblance to the inhibiting effect of potassium iodide on the photo-oxidation. It was concluded that the photo-oxidation of eosin proceeded through a metastable state. That this conclusion is generally applicable is supported by the observation that the ease with which the photo-oxide is formed bears a close relationship to the triplet-energy level of the excited species. For example, all linear polyacenes except naphthalene form photo-oxides (pentacene > naphthacene > anthracene), whereas the non-linear condensed ring aromatic hydrocarbons either do not react with oxygen at all, or else less readily than do the linear polyacenes.

Clar and John in 1930 were the first to show that the photo-oxide of pentacene had a transannular structure[44] (I) across the *meso*-positions, and it has since been shown that this is a general structure of photo-oxides. The subject of photo-oxidation has been reviewed by Bergmann and McLean,[45] and by Etienne.[46]

The mechanism of the photo-oxidation of condensed-ring aromatic hydrocarbons is still a subject of some controversy. Let us consider first the quenching of the excited singlet state by oxygen. It is well established that this is of a purely physical nature, but, since oxygen is paramagnetic, it has been suggested by Terenin[47] that it could effect a spin reversal in the singlet excited state, to yield the triplet state. (Terenin, who was the first to suggest this in 1944, also stressed the probable importance of the triplet state of eosin in its photoreactions). However, Porter and Windsor have shown that although oxygen quenches triplet anthracene very strongly in hexane solution, the *initial* yield is independent of the oxygen concentration, within the experimental error.[7] Thus the importance of "paramagnetic quenching" in the formation of the triplet state can be questioned, although the induced ground singlet–triplet *absorptions* of aromatic molecules in solution under high pressures of oxygen have been observed

[43] E. J. Bowen, *Nature*, 1942, **149**, 528.
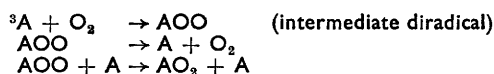[44] E. Clar and F. John, *Ber.*, 1930, **63**, 2967.
[45] W. Bergmann and M. J. McLean, *Chem. Rev.*, 1941, **28**, 367.
[46] A. Etienne, "Traité de Chimie Organique", Masson, Paris, Vol. 17, 1944, p. 1299.
[47] A. Terenin, *Acta Physicochim. U.R.S.S.*, 1943, **18**, 210.

recently by Evans.[14] In view of Porter and Windsor's results, it seems probable that the triplet state of anthracene is formed directly through a unimolecular process from the excited singlet state, under the small pressures of oxygen which would be employed in the experimental study of the photo-oxidation.

For the actual reaction of triplet molecules with oxygen, two mechanisms may be considered. Bowen and Tanner have advanced the following mechanism for the photo-oxidation of anthracene, substituted anthracenes, and rubrene in carbon disulphide solution:[33]

$$^3A + O_2 \quad \rightarrow AOO \qquad \text{(intermediate diradical)}$$
$$AOO \quad \rightarrow A + O_2$$
$$AOO + A \rightarrow AO_2 + A$$

An intermediate diradical is formed which can either dissociate, or cyclise to yield the transannular peroxide. An unexcited anthracene molecule is postulated to enter into the cyclisation step in order to explain the experimental expression for the quantum yield of peroxide formation

$$\text{Quantum yield} = \frac{k_1 [A]}{1 + k_2 [A]}$$

where k_1 and k_2 are constants. The suggestion that an intermediate complex was involved in these reactions was first postulated by Koblitz and Schumacher.[48] Both these workers and Bowen and Tanner found a rather curious dependence of the quantum yield of photo-oxidation on the presence of small amounts of other solvents in the carbon disulphide solution. The relative rates of photo-oxidation of anthracene in carbon disulphide solutions containing 0·03 mole % of another solvent are shown in the Table (Bowen and Tanner's results being used).

Additive	Rate	Density	Additive	Rate	Density
None	100	1.63	Toluene	32	0.87
Chloroform	85	1.5	Thiophen	30	1.06
Bromobenzene	46	1.5	Naphthalene	28	solid
Chlorobenzene	37	1.11	Benzene	27	0.88
Pyridine	35	0.98	α - Bromo-		
α - Chloro-			naphthalene	26	1.49
naphthalene	33	solid	Hexane	19	0.66

The reduction in the rate of photo-oxidation cannot be due entirely to reaction with the added solvent (*e.g.*, hydrogen abstraction), since in the case of added solvents which contain abstractable hydrogen it is not those

[48] W. Koblitz and H. J. Schumacher, *Z. phys. Chem.*, 1937, **35**, *B*, 11.

solvents which most easily lose a hydrogen atom[49] that are the most effect-ive. It is suggested by the Reviewer that the effect is mainly a physical one, and can be readily explained in terms of a solvent cage. Lampe and Noyes showed that the quantum efficiency of photolytic reactions is greater in the gas phase than in solution,[50] and they suggest that this is due to the greater probability of the recombination of the initial photolysis products in a solvent cage. To support this suggestion, they investigated the photolysis of iodine in solvents of increasing density, and found that the quantum efficiency of the photolysis decreased as the solvent density increased. In the Table it can be seen that the rate of the photo-oxidation increases with density (except with α-bromonaphthalene); if it is postulated that the intermediate diradical dissociates less easily in a solvent of high density, owing to a cage effect, then the results in the Table are easily explained. The anomalous behaviour of α-bromonaphthalene might be due to the fact that the macroscopic density is not the best measure of the "cage density".

Porter and Windsor[6,7] found that if dissolved oxygen were present in a solution of anthracene in hexane, then repeated flashing removed the oxygen (the triplet lifetime increased to a constant value), but no depletion of the total anthracene concentration was detected. The only conclusion that can be drawn from these observations is that in this particular case the oxygen is removed through reaction with hexane. Livingston and Tanner have recently reported that repeated flashing of anthracene in a bromobenzene solution containing dissolved oxygen did *not* remove the oxygen, although the bimolecular rate constant for the quenching of triplet anthracene by oxygen was almost the same in the two solvents.[34]

The second reaction scheme which has been suggested to account for the photo-oxidation of anthracene, etc., is that advanced by Porter and Windsor involving the formation of metastable singlet excited oxygen,[7] through an energy transfer from the triplet anthracene. The excited oxygen molecule can then decay, add on to an unexcited anthracene molecule, or abstract a hydrogen atom from a hexane solvent molecule; a solvent cage would not affect a reaction proceeding by this mechanism.

To summarise, it seems probable that the added solvent effect is due both to a cage effect and, in at least one case, to a reaction with the solvent; however, since the solvent-cage explanation is inconsistent with an energy-transfer mechanism, the Reviewer favours the reaction scheme involving the formation of an intermediate complex.

Livingston and Ryan have explained the photo-oxidation of chlorophyll in methanol solution in terms of an analogous intermediate complex.[51] The system is complicated by the occurrence of a reversible photobleaching of the solution in the *absence* of oxygen, which has been interpreted as due

[49] R. A. Gregg and F. R. Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328.
[50] F. W. Lampe and R. M. Noyes, *J. Amer. Chem. Soc.*, 1954, **76**, 2140.
[51] R. Livingston and V. Ryan, *ibid*,. 1953, **75**, 2176.

to reversible oxidation of metastable triplet (?) chlorophyll by the solvent.[52]

Transannular compounds analogous to the photo-oxides are also formed by nitric oxide and anthracene and some of its derivatives on irradiation,[53] and Porter and Windsor have shown that nitric oxide, like oxygen, quenches the triplet state of anthracene very efficiently.[7]

(C.) **Sensitised Photo-oxidations.**—Schenk and his co-workers have developed a general synthetic technique for the production of trans-annular peroxides of cyclic dienes, and the hydroperoxides of a large range of mono-olefins.[54,55] Dyes such as eosin, Methylene Blue, and chlorophyll (to quote only a few examples) are found to photosensitise the oxidations, often in cases where there is no direct photo-oxidation. Some examples of sensitised diene oxidations are the production of ascaridole (II) from α-terpinene, the peroxide of cyclohexadiene, and the peroxides of substituted furans (III).
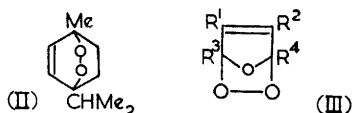

Mono-olefins which have been oxidised through this technique to yield hydroperoxides include cyclohexene, 1-methylcyclohexene and a range of terpenes. It is interesting to note that very often the hydroperoxide formed is an isomer of that formed through the more usual autoxidation process, and although cumene is very easily autoxidised, it does not undergo sensitised photo-oxidation. Since autoxidations are known to proceed through radical-chain mechanisms, a different process must be involved in the sensitised oxidations.

Schenk has suggested a general reaction scheme involving the formation of an intermediate diradical peroxide complex formed from the triplet sensitiser:

$$^3S + O_2 \rightarrow SO_2 \qquad \text{(Intermediate diradical)}$$
$$SO_2 + A \rightarrow S + AO_2$$
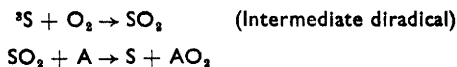
where S is the sensitiser and A is the acceptor. He has also suggested that the direct photo-oxidation of compounds such as anthracene, naphthacene, and rubrene is a special case of a general sensitisation where the sensitiser itself acts as its own acceptor.[56]

$$SO_2 + S \rightarrow S + SO_2$$
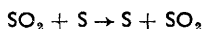
[52] R. Livingston and J. Knight, *J. Phys. Chem.*, 1950, **54**, 703.
[53] H. Weil-Malherbe and J. Weiss, *J.*, 1944, 541.
[54] G. O. Schenk, *Angew. Chem.*, 1952, **64**, 12.
[55] G. O. Schenk, K. G. Kinkel, and H.-J. Mertens, *Annalen*, 1953, **584**, 125.
[56] G. O. Schenk, *Naturwiss.*, 1954, **41**, 452.

This is consistent with the reaction scheme which was favoured in the previous section. Schenk has also listed sensitisers which do not act as acceptors,[56] amongst them chlorophyll; however, as was mentioned earlier, Livingston and Ryan showed that chlorophyll *is* oxidised according to the above mechanism,[51] whence the results quoted by Schenk in this case appear to be incorrect.

A particularly interesting sensitiser investigated by Schenk and his co-workers is 1,4-diphenylcyclopentadiene (IV), which acts as a sensitiser and as an acceptor, and can be photo-oxidised directly.[57] For example, it
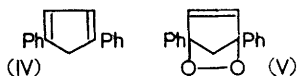

will photosensitise the peroxidation of α-terpinene to ascaridole, Methylene Blue will photosensitise its peroxidation to give the transannular peroxide (V), and the same peroxide can be formed directly when the light is absorbed by the diene itself.

Seeley and Calvin[58] have found that benzoin will act as a photosensitiser in the oxidation of zinc, copper, and nickel porphins, and that only the light absorbed by the benzoin is effective. The quantum yield is independent of both the benzoin and the porphin concentrations, and it is suggested that the rate of the reaction depends only on the rate of formation of triplet benzoin. Several other aromatic ketones were found to act as sensitisers, as well as anthracene and anthraquinone.

(D.) **General Photochemical Additions.**—In the same way as the direct photoaddition of oxygen to unsaturated substrates in solution could be described as a special case of a general sensitised oxidation, so also may photo-oxidation be considered as a special case of a general photoaddition reaction.

The addition of olefins and aldehydes to 1,2-diketones and *ortho*-quinones such as phenanthraquinone have been investigated by Mustafa, Schönberg, and others.[59,60] For example, stilbene will form a cyclic compound with phenanthraquinone when irradiated in solution.[59] Whether it is the quinone and/or the stilbene which is excited is uncertain,
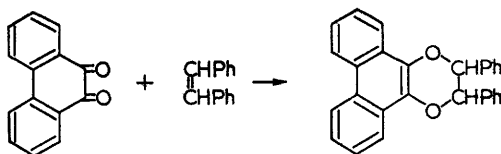
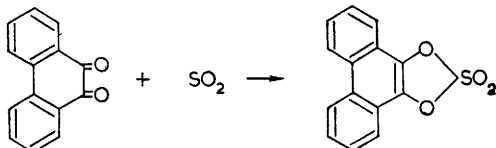[57] G. O. Schenk, W. Müller, and H. Pfennig, *ibid.*, p. 374.
[58] G. R. Seeley and M. Calvin, *J. Chem. Phys.*, 1955, **23**, 1068.
[59] A. Schönberg and A. Mustafa, *J.*, 1944, 387; 1948, 2126.
[60] A. Mustafa, *Chem. Rev.*, 1947, **40**, 181.

since both will undergo photochemical reactions (*e.g.*, stilbene will dimerise in sunlight[61]):

Sulphur dioxide will also react in analogous way:

and more recently the addition of some aldehydes and stilbene to 4-cyano-1,2-naphthaquinone in sunlight has been investigated. Aldehydes form either ring compounds or addition compounds, so that in this case the reaction is not a simple addition:
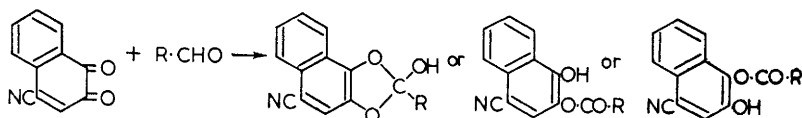

Reactions which are believed to involve the initial addition of excited ketones to unsaturated substrates have been described by Büchi and others. For example, benzaldehyde will add to the double bond in 2-methylbut-2-ene on irradiation,[62] and it has been suggested that the first step in the reaction is the excitation of the benzaldehyde to a diradical (triplet ?) state:[63]
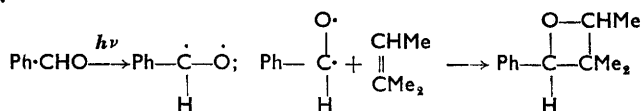
Of course, if the aldehyde or ketone dissociates, the addition follows the normal chain mechanism, and the two types of reaction will be competitive.

The addition of benzaldehyde to dibutylacetylene is believed to involve a cyclic intermediate,[64] which in this case is unstable and rearranges:
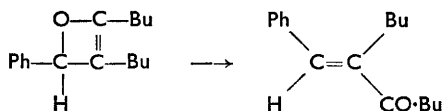
A similar reaction has also been proposed to explain the photochemical reaction between 2-methylbut-2-ene and nitrobenzene.[65]

[61] A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Amer. Chem. Soc.*, 1955, **77**, 3850.
[62] E. Paterno and G. Chieffi, *Gazzetta*, 1909, **39**, 341.
[63] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, 1954, **76**, 4327.
[64] G. Büchi, J. T. Koffron, E. Koller, and D. Rosenthal, *ibid.*, 1956, **78**, 876.
[65] G. Büchi and D. E. Ayer, *ibid.*, p. 689.

The photochemical formation of polysulphones and sulphinic acids has been investigated by Dainton and Ivin.[66] Photoexcited sulphur dioxide will react with paraffins and olefins in both the gas and the liquid phase. From paraffins, sulphinic acids are formed, apparently through a direct addition of excited sulphur dioxide:

$$SO_2{}^* + RH \rightarrow R \cdot SO_2H$$

In the case of the olefins, if reaction is in the gas phase sulphinic acids are produced through the enolisation of the primary addition product, but in the liquid phase polysulphones are formed. It was suggested that this could be explained either by a ceiling-temperature effect or by a delay in the enolisation of the intermediate. The reaction scheme suggested is as follows:
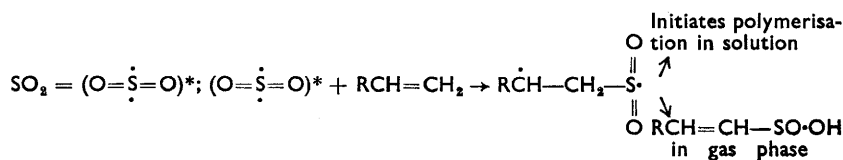
The reactivity of dienes to Diels–Alder addition, like their reactivity to photo-oxidation, appears to be a function of their triplet excitation energies, and it has been shown recently by Litherland[67] that maleic anhydride will form an adduct with anthracene at room temperature, when the latter is irradiated in an outgassed benzene solution. The reaction must involve excited anthracene since the rate of the thermal addition at room temperature was negligible in comparison with the photochemical addition. If, as seems likely, the excited anthracene is in the triplet state, this reaction provides another example of an addition reaction involving a molecule in the triplet state.

This concludes the survey of the addition reactions of electronically excited molecules in solution. We next deal with photochemical oxidation–reduction and abstraction reactions.

(E.)   **Oxidation–Reduction and Abstraction Reactions.**—These reactions are of considerable practical importance since the fading and tendering of dyes absorbed on cellulosic fibres is believed to proceed through such processes. It also appears likely that the initial step in the photosynthetic reaction is an oxidation–reduction process involving metastable excited chlorophyll.

The possible primary processes in the fading and tendering of dyes have been mentioned in earlier sections of this Review, and have been discussed
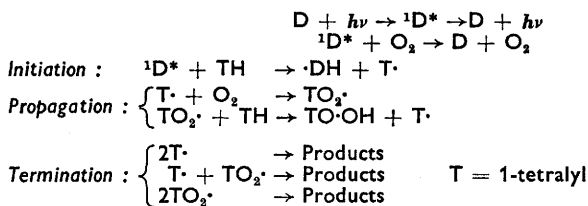
[66] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, 1950, **46**, 374, 382.
[67] K. L. Litherland, personal communication.

very lucidly by Bridge and Porter.[18] There could be reaction of either the excited singlet or triplet state of the dye with the substrate, in which there is either an electron transfer (yielding a radical-ion) or a hydrogen abstraction (yielding a semiquinone radical). As was also mentioned earlier, Bridge and Porter have been able to identify the intermediates involved in the photolysis of quinones in solvents containing abstractable hydrogen and, in particular, they have investigated the aqueous alcohol–duroquinone system. This system is very much more simplified than the practical system, by the exclusion of oxygen, which would certainly enter into the reactions involving the fading and tendering of dyes. However, it would probably only enter into the scheme in secondary reactions (except for the possibility of inducing singlet–triplet conversions). Its presence could complicate the system from the spectroscopic point of view, since the absorption spectra of products formed might well mask those of the intermediates.

It was found, rather surprisingly, that it was the singlet rather than the long-lived triplet which was the intermediate excited state. The primary step is the abstraction of a hydrogen atom from the solvent by the singlet excited dye; the quinone radical-ion absorption spectrum was also observed, but this was formed through the dissociation of the semiquinone radical, not through an electron transfer, and it did not enter the reduction mechanism. The equilibrium $\cdot QH \rightleftharpoons \cdot Q^- + H^+$ lies to the right or left depending on the pH of the solution.

Bamford and Dewar have studied the autoxidation of tetralin photosensitised by vat dyes,[68] and found that the following kinetic scheme fitted the results they obtained:

$$D + h\nu \rightarrow {}^1D^* \rightarrow D + h\nu$$
$$^1D^* + O_2 \rightarrow D + O_2$$

Initiation : $^1D^* + TH \rightarrow \cdot DH + T\cdot$

Propagation : $\begin{cases} T\cdot + O_2 \rightarrow TO_2\cdot \\ TO_2\cdot + TH \rightarrow TO\cdot OH + T\cdot \end{cases}$

Termination : $\begin{cases} 2T\cdot \rightarrow \text{Products} \\ T\cdot + TO_2\cdot \rightarrow \text{Products} \quad T = \text{1-tetralyl} \\ 2TO_2\cdot \rightarrow \text{Products} \end{cases}$

The singlet excited dye abstracts hydrogen from the tetralin, and a chain reaction is initiated yielding the peroxide of tetralin as the main product. In this investigation, the emphasis is laid on the mechanism and kinetics of the radical chain rather than on that of the sensitisation, and the fate of the radical DH· is not mentioned.

Bolland and Cooper[69] have made a particularly complete investigation of the oxidation of ethanol in non-alkaline aqueous solution, photosensitised by disodium anthraquinone-2,6-disulphonate, and in this work the mechanism of the sensitisation has been discussed at length. An efficient

[68] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1949, *A*, **198**, 252.
[69] J. W. Bolland and H. R. Cooper, *ibid.*, 1954, *A*, **225**, 405.

cyclic process is postulated involving the singlet excited dye both in the presence and in the absence of oxygen. In the absence of oxygen, the process is as follows:

$$^1A^* + RH \rightarrow \cdot AH + R\cdot$$
$$R\cdot + A \rightarrow Aldehyde + \cdot AH$$
$$2AH\cdot \rightarrow A + AH_2$$
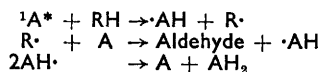
The ethanol is oxidised to acetaldehyde, and the two semiquinone radicals react together, to yield the leuco-dye and regenerate a molecule of the quinone. In the presence of oxygen, the semiquinone radical is oxidised, and the following reaction steps take place:

$$\cdot AH + O_2 \rightarrow HO_2\cdot + A$$
$$R\cdot + O_2 \rightarrow RO_2\cdot$$
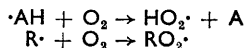
These two peroxidic radicals then react together to yield hydrogen peroxide, acetaldehyde, and acetic acid, and the radicals $R\cdot$ are removed in similar bimolecular termination steps. The reaction of the semiquinone radical with the radicals $R\cdot$, $RO_2\cdot$, and $HO_2\cdot$ is neglected in view of the rapidity of its reaction with oxygen. In the overall reaction scheme, then, the quinone is being constantly regenerated in a cyclic process, and simultaneously the ethanol is oxidised to acetaldehyde and acetic acid. The scheme proposed by Bamford and Dewar appears to be an over-simplification in the light of this later work.

These reactions are of practical importance in their analogy to the tendering of dyes adsorbed on cellulosic materials, i.e., the light-induced reaction of the dye with the fibre. The initial step in all these reactions appears to be the abstraction of a hydrogen atom from the substrate by the excited dye, rather than an electron transfer: the excited state might be either the singlet or the triplet,[70] although recent work favours the reaction of the excited singlet state. The field has been thoroughly reviewed in a symposium on "Photochemistry in Relation to Textiles".[70]

The study of oxidation–reduction processes photosensitised by chlorophyll and related substances has received a great deal of study in connection with the primary reactions in photosynthesis. For example, the autoxidation of allylthiourea, photosensitised by ethyl chlorophyllide, was investigated by Gaffron in 1933[71] and the kinetic data which he obtained have been shown to be consistent with the participation of a long-lived excited state of the sensitiser by Weiss.[72] Livingston has pointed out that most reactions sensitised by chlorophyll involve the metastable state of the dye,[73] and that this state is generally assumed to be identical with the triplet state. Only when the reactant is present in high concentrations, as in liquid solutions, or in a thermally stable complex with the chlorophyll, can

[70] E. J. Bowen (Symposium, "Photochemistry in Relation to Textiles"), J. Soc. Dyers and Colourists, 1949, 65, 613.
[71] H. Gaffron, Biochem. Z., 1933, 264, 251.
[72] J. Weiss (Symposium), J. Soc. Dyers and Colourists, 1949, 65, 135.
[73] R. Livingston, "Research in Photosynthesis", Interscience, New York, 1957, p. 3.

the excited state of chlorophyll be involved. It has also been suggested that the photochemical reactions of chlorophyll *in vivo* involve the triplet *excited* level,[74] in which the metastable chlorophyll in the first triplet level is excited to a *higher* triplet level, through an energy transfer from a singlet excited chlorophyll molecule. By this means 60 to 70 kcal./mole become available for a hydrogen-abstraction reaction, instead of the 33 kcal./mole of the first triplet level.

The subject of photosynthesis has been comprehensively reviewed by Rabinowitch,[75] and a review of the physicochemical aspects of photo-synthesis is being prepared by Livingston.[76] Consequently, a detailed dis-cussion of the photochemistry of chlorophyll would be out of place here. However, for the sake of completeness, a brief mention will be made of some ideas which are generally accepted in connection with the primary photosynthetic reaction.

It seems well established that, in the primary photochemical process, chlorophyll is excited to the triplet state and in this state undergoes an oxidation–reduction reaction. Whether this reaction involves a hydrogen transfer to or from the chlorophyll, or whether it involves an electron transfer is not clear. The theories which have been advanced for the mechanism of the primary photosynthetic reaction are based mainly on observations of the photochemistry of chlorophyll solutions *in vitro*: however, it must be remembered that the photochemical reactions of chlorophyll *in vivo* may not be strictly comparable, owing to the changed environment of the molecule.

Calvin and Dorough[77] have investigated the photochemical reactions of molecules similar to chlorophyll.* For example, the photo-oxidation of zinc chlorin (VI) by naphtha-1,2-quinone, in which there is a hydrogen transfer from the dihydropyrrole ring to yield the corresponding porphin, has been found to occur with a low quantum efficiency (of the order of a few per cent.).
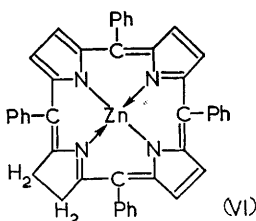
A mechanism involving the oxidation of the triplet excited chlorin by the quinone is postulated from the kinetic data. The work has been extended

* Only a brief discussion is given here; the work has recently been reviewed by Reid.[1]

[74] J. Franck, *ibid.*, p. 19.
[75] E. Rabinowitch, "Photosynthesis", Interscience, New York, Vol. 1, 1945; Vol. II, Part 1, 1951; Vol. II, Part 2, 1956.
[76] R. Livingston, *Quart. Rev.*, in the course of preparation.
[77] M. Calvin and G. D. Dorough, *J. Amer. Chem. Soc.*, 1948, **70**, 699.

to other quinones,[78] and a relationship between the oxidation potential and the quantum efficiency of the photo-oxidation was found for the *ortho*- and *para*-series of quinones, severally. The *ortho*-quinones were the more effective, presumably for steric reasons.

The photoreduction of the porphin back to the chlorin is effected by benzoin.[58] The mechanism postulated (again from the kinetic data) involves reaction between triplet benzoin, and both triplet and unexcited singlet porphin.

The photoreduction of eosin Y by allylthiourea (acting as a hydrogen donor) in aqueous solution has been investigated by Adelman and Oster.[39] Observations on the fluorescence efficiency, the quenching of excited eosin, and the kinetic results lead to the postulate of a metastable state of the dye as the sensitising intermediate in the reaction. In a later paper[79] on the photoreduction of fluorescein and its halogenated derivatives by allylthiourea, a similar mechanism was postulated. Increasing halogenation did not alter the quantum yields of production of metastable states, or their lifetimes very much, although the internal reversion of the excited singlet to the ground singlet state did increase. A comparison between the phosphorescence quenching and the retardation of the photoreduction in a viscous medium demonstrated the equivalence of the metastable state and the triplet state.

When dyes are added to solutions of high-polymeric materials with which they can bind, it has been shown that their chemical properties can be altered quite remarkably. For example, when triphenylmethane dyes are bound to polymeric acids, a strong reducing agent will reduce the free dye only in the dark, whereas in the light, only the bound dye is reduced.[80]

It has been found by Evans, Uri, and others [81,82] that when certain ion pairs are irradiated in solution, they will initiate the polymerisation of vinyl monomers. For example, if a ferric ion complex $Fe^{3+}X^-$ is irradiated, where X^- could be OH^-, F^-, N_3^-, or $C_2O_4^-$, the light absorption is said to be due to a transition involving a charge transfer within the complex, as

$$Fe^{3+}X^- \rightleftharpoons Fe^{2+}X$$
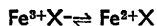
and this species can then dissociate to yield a free radical and a ferrous ion. Naturally, if a vinyl monomer is present, the free radicals produced will attack the monomer, and a polymerisation will be initiated. In support of this, it has been found that in the case of chloride and fluoride complexes the polymer has chlorine and fluorine end-groups. Radicals produced in this way will also attack a benzene nucleus ; [83] for example, hydroxyl radicals from a ferric complex will substitute in the ring system in benzoic

[78] F. M. Huennikins and M. Calvin, *ibid.*, 1949, **71**, 4024.

[79] A. H. Adelman and G. Oster, *ibid.*, 1956, **78**, 3977.

[80] G. Oster and J. Bellin, *ibid.*, 1957, **79**, 294, and earlier publications.

[81] M. G. Evans and N. Uri, *Nature*, 1949, **164**, 404: M. G. Evans, M. Santappa, and N. Uri, *J. Polymer Sci.*, 1951, **7**, 243.

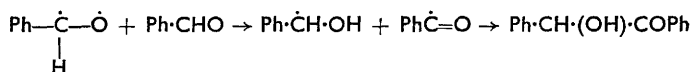[82] T. B. Copestake and N. Uri, *Proc. Roy. Soc.*, 1955, *A* **228**, 252.

[83] H. G. C. Bates, M. G. Evans, and N. Uri, *Nature*, 1950, **166**, 869.

acid. These electron-transfer processes have been reviewed by Uri.[84]

To complete this particular section, a few miscellaneous examples of photochemical reactions in solution will be discussed in which the primary process is believed to involve an abstraction reaction.

Bowen and Rohatgi have investigated the quenching of the fluorescence of anthracene in carbon tetrachloride solution,[85] and postulate a quenching mechanism involving the abstraction of a chlorine atom from the solvent by the singlet excited anthracene. The trichloromethyl and 9-chloroanthryl radicals so formed then react in divers ways. A similar reaction between excited anthracene and cumene and 9,10-dihydroanthracene, involving a hydrogen abstraction, has recently been shown to occur, although it is suggested that in these reactions it is the triplet state of anthracene which is involved.[86]

Bäckström, as far back as 1934,[87] suggested that the polymerisation of benzaldehyde on irradiation proceeded through the opening of the carbonyl group, and the reaction proceeded as follows:

$$Ph\!-\!\overset{|}{\underset{H}{\overset{\cdot}{C}}}\!-\!\dot{O} + Ph\!\cdot\!CHO \rightarrow Ph\!\cdot\!\dot{C}H\!\cdot\!OH + Ph\dot{C}\!\!=\!\!O \rightarrow Ph\!\cdot\!CH\!\cdot\!(OH)\!\cdot\!COPh$$

Finally, it has been postulated that the photochemical addition of cyclohexanone and oct-1-ene proceeds through the initial transfer of a hydrogen atom from the ketone to the olefin, followed by a radical chain process.[88] A similar mechanism will explain the reaction between carbonyl compounds and alcohols on irradiation in solution.[89]

(F.) **Sensitised Photopolymerisations.**—(Only direct sensitisations in the absence of oxygen will be reviewed here, since sensitised oxidations are well-known to involve radical intermediates in many cases, which would initiate polymerisation indirectly.)

Bamford and Dewar in 1949 investigated the photosensitisation of styrene polymerisation by vat dyes.[90] They suggested that this sensitisation had a common origin to the tetralin autoxidation (see previous section) in the initial formation of radicals through the abstraction of hydrogen from the substrate (either tetralin or styrene) by the excited dye. The activity of the dyes in the autoxidation is closely similar to the tendering activities of the dyes on cellulosic materials, but their activities in the photopolymerisation are quite different. Presumably, a different mechanism is involved in the two sensitisations. Bamford and Dewar suggest an energy transfer,[91]

[84] N. Uri, *Chem. Rev.*, 1952, **50**, 414.
[85] E. J. Bowen and K. K. Rohatgi, *Discuss. Faraday Soc.*, 1953, **14**, 143.
[86] R. G. W. Norrish and J. P. Simons, *Proc. Roy. Soc.*, in the press
[87] H. C. J. Bäckström, *Z. phys. Chem.*, 1934, **25**, *B*, 99.
[88] M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, 1953, **18**, 1225.
[89] Ch. Weizmann, E. Bergmann, and Y. Hirshberg, *J. Amer. Chem. Soc*, 1938, **60**, 1530.
[90] C. H. Bamford and M. J. S. Dewar (Symposium), *J. Soc. Dyers and Colourists*, 1949, **65**, 680.
[91] C. H. Bamford and M. J. S. Dewar, *Nature*, 1949, **163**, 214.

but it is equally possible that it is the triplet state of the dye, rather than the excited singlet state, which is reacting in the polymerisation.

Melville and Whyte in the same year, rather qualitatively investigated the dye-sensitised photopolymerisation of vinyl acetate.[92] The majority of the sensitisers used were ineffective, e.g., fluorescein and anthracene had no effect. However, some diketones and benzoin were effective. The polymerisations all had an induction period which was regarded as "real" and not due to impurities in the monomer. Koizumi and his co-workers found that fluorescein, trypaflavin, eosin, and other dyes were effective in photosensitising the polymerisation of styrene. It is noteworthy that fluorescein will sensitise the polymerisation of styrene,[93,94] but not that of vinyl acetate. Zinc chlorin was found to inhibit the polymerisation, although it has a long-lived triplet state (this does not necessarily mean that it does not initiate, since it might also retard in the chain propagation). The sensitising effect was greatly dependent on temperature.

Uri, in 1952, used a mixture of chlorophyll a and b to sensitise the photopolymerisation of methyl methacrylate.[95] In the presence of oxygen there was no polymerisation. The sensitisation had a low quantum efficiency; in the presence of reducing substances such as ascorbic acid and allylthiourea the rate of polymerisation was greatly increased. (This could be explained in terms of a hydrogen abstraction leading to the formation of radicals which can initiate.)

Benzoin and its carbon-14 labelled methyl ether have been used to sensitise the photopolymerisation of methyl methacrylate by Mochel, Crandall, and Peterson.[96] Between twelve and fifteen sensitiser units were found to be incorporated in the polymer chain in the light, and none in the dark, by means of a radioactive assay. This could be explained either by diradical initiation and termination by combination, or by copolymerisation with excited benzoin. However, neither of these explanations was satisfactory. The molecular weights measured agreed with those found for monoradical initiation, and the rates of polymerisation were proportional to the square-root of the initiator concentration (indicating bimolecular termination). The quantum yield was of the order of 1250 methyl methacrylate units polymerised per quantum absorbed at 3660 Å, which appeared to be too high to be consistent with copolymerisation of excited benzoin and methyl methacrylate.

Luner and Szwarc have shown that benzene, anthracene, and naphthacene sensitise the photolysis of acetyl peroxide in 2,2,4-trimethylpentane solution.[97] They appear to believe that the sensitisation follows the same

[92] H. W. Melville and R. B. White (Symposium), *J. Soc. Dyers and Colourists*, 1949, **65**, 703.

[93] M. Koizumi, Z. Watanabe, and A. Kuroda, *J. Inst. Polytech., Osaka City Univ.*, 1951, C, No. 1, 1; *Chem. Abs.*, 1953, **46**, 4915.

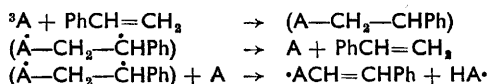[94] M. Koizumi, Z. Watanabe, and A. Kuroda, *Nature*, 1955, **175**, 770.

[95] N. Uri, *J. Amer. Chem. Soc.*, 1952, **74**, 5808.

[96] W. E. Mochel, J. L. Crandall, and J. H. Peterson, *ibid.*, 1955, **77**, 494.

[97] C. Luner and M. Szwarc, *J. Chem. Phys.*, 1955, **23**, 1978.

mechanism as the naphthalene-sensitised photolysis of ethyl iodide.

Anderson and Norrish have reported that anthracene will photosensitise the polymerisation of styrene, the anthracene being used up in the course of the reaction.[98] More anthracene was removed than could be accounted for by the removal of anthracene in the initiating steps alone. Norrish and Simons have investigated the kinetics and mechanism of this reaction in detail[86] and have established that the triplet state of anthracene was involved in the initiation, and that both triplet and unexcited singlet anthracene copolymerised with the styrene. Pyrene and chrysene were found to react with styrene in an analogous way, although in their cases the rate of copolymerisation was negligible, owing to the smaller reactivity of the unexcited sensitisers and to the considerably smaller population of their triplet states as compared with anthracene. The initiation mechanism which is proposed is analogous to the mechanism of the photo-oxidation of anthracene, involving the formation of a triplet sensitiser-monomer complex which either dissociates or reacts with an unexcited sensitiser molecule. A hydrogen transfer leads to the formation of two monoradicals which initiate the polymerisation:

$$
\begin{aligned}
^3A + PhCH=CH_2 &\rightarrow (A—CH_2—CHPh) \\
(\dot{A}—CH_2—\dot{C}HPh) &\rightarrow A + PhCH=CH_2 \\
(\dot{A}—CH_2—\dot{C}HPh) + A &\rightarrow \cdot ACH=CHPh + HA\cdot
\end{aligned}
$$

Reaction of the complex with a monomer molecule was neglected, since at very low sensitiser concentrations the initiation efficiency tended almost to zero in every case. This is probably due to the greater resonance stabilisation in the radical HA· than in the styrene radical.

It was also shown that the concentration-dependence of the unsensitised photopolymerisation of styrene was consistent with a similar initiation mechanism, where triplet monomer replaces triplet sensitiser; *i.e.*, a triplet monomer–unexcited monomer complex is formed which can transfer a hydrogen atom to a third monomer molecule, yielding two monoradicals.

Finally, it is noteworthy that the rate constant of the reaction between triplet anthracene and the polystyryl radical was found to be of the order of 10^{11} l.mole^{-1} sec.$^{-1}$ and, as would be expected, to have a zero energy of activation. This is consistent with the theory, advanced by Levy and Szwarc,[99] that the reactivity of polynuclear aromatic hydrocarbons to radical addition depends only on their ground singlet–triplet energy differences. If the molecule which was being attacked were *already in* the triplet state, then the radical addition should have a zero energy of activation, and a very high rate constant.

The reaction between triplet anthracene and styrene has been utilised in a method for preparing block and graft copolymers.[100] In the normal

[98] V. Sten Anderson and R. G. W. Norrish, *Proc. Roy. Soc.*, in the press.
[99] M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, 1955, 77, 1949.
[100] K. L. Litherland and R. G. W. Norrish, unpublished work.

reaction, the aromatic character of the anthracene is partially lost in the copolymerisation. However, if 9-vinylanthracene or anthrylacrylic ester is copolymerised with styrene, anthracene molecules are incorporated in a polymer chain with their aromatic character intact. Radical copolymerisation was found to be impossible since the vinylanthryl radical was too unreactive, and so styrene and vinylanthracene were copolymerised ionically, with stannic chloride as catalyst. When the resultant copolymer was irradiated in methyl methacrylate solution, block and graft copolymers were produced on the anthracene–styrene backbone. The detailed mechanism of the reaction was not investigated.

This concludes the survey of photochemical reactions relevant to this Review. Although the number of photosensitised reactions in solution which have been studied is large, a considerable number of these reactions are still imperfectly understood: this is probably due in part to the complexity of many of the secondary processes in these reactions. However, as has been mentioned, the application of synchronised flash techniques to this field of research should help to unravel many of the complexities which exist. Although it is tempting to try to fit each reaction into a comprehensive scheme, it is probably wiser to treat each reaction on its own merits in the first instance.