PRIMARY PROCESSES IN PHOTO-OXIDATION

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THIS Review is an interpretation of photochemical primary processes, particularly oxidations by molecular oxygen, in terms of simple molecular spectroscopy. It deals only with the intramolecular (unimolecular) and intermolecular (bimolecular) reactions of the electronically excited molecules formed as a consequence of absorption of radiation in the visible and the ultraviolet region of the spectrum. Secondary reactions, *e.g.*, reactions of free radicals formed by dissociation, are not considered at all.

Photochemistry cannot be divorced from spectroscopy, and particularly not when primary reactions are considered. The sound principles upon which molecular spectroscopy is based provide a good foundation for the interpretation of photochemistry. Absorption and emission spectroscopy establish the nature and properties of electronically excited molecules. Hence, by this method, the photochemist can take a major step toward the interpretation of his results.

It is our purpose, first, to present some basic principles of molecular spectroscopy which pertain to the photochemical primary process in general, and then to discuss examples of photo-oxidations which have been most widely studied in the gaseous, liquid, or solid phase.

Other reviews in this field include the following: Förster[1] has reviewed the primary processes generally, while Noyes, Porter, and Jolley[2] have considered the specific cases of ketones of low molecular weight; Simons[3] has discussed the reactions of electronically excited molecules in solution; and photo-oxidation processes have been reviewed by Etienne[4] and by Bergmann and McLean.[5]

1. The excitation process

The essence of a photochemical reaction is that the activation energy of the reaction is supplied by light energy. If visible light is used this energy corresponds to about 40 kcal./mole. The electronic configuration of the excited species is not in general the same as that of the parent unexcited molecule. Molecules may interact with electromagnetic vibrations of a particular frequency which, varying from substance to substance, depends on the nature of the electronic structure of the molecule. Saturated molecules normally do not interact with visible or near-ultraviolet light. Molecules containing π-electrons, on the other hand, usually absorb throughout this range. Consequently the latter type of molecule, which

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[1] Förster, *Z. Elektrochem.*, 1952, **56**, 716.
[2] Noyes, Porter, and Jolley, *Chem. Rev.*, 1956, **56**, 49.
[3] Simons, *Quart. Rev.*, 1959, **13**, 3.
[4] Etienne, "Traité de Chimie Organique," 1944, Vol. XVII, Masson, Paris, p. 1299.
[5] Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367.

includes aromatic hydrocarbons, their heterocyclic analogues, aldehydes, ketones, etc., is the type most accessible to experimental study.

These molecules have an even number of electrons. All the bonding orbitals are completely filled with electrons according to the Pauli principle when the molecule is in the ground state.* Thus these molecules have no resultant spin angular momentum, s, which is equivalent to all electrons being paired. The multiplicity of a state is given by the rule:

$$\text{Multiplicity} = 2s + 1$$

In the case where $s = 0$, the multiplicity is one, and the state is a singlet state. All the molecules under consideration have singlet ground states. The probability of changing the resultant spin momentum during an electronic transition is zero if spin–orbital interaction is neglected. In discussions of singlet ground states, the only other multiplicity which may arise (through violations of the above rule brought about by spin–orbital perturbations) is three, and the resulting state is a triplet. This is shown in Fig. 1, where (*a*) indicates the unexcited state and (*b*) the excited singlet state. Inversion of the spin of the excited electron results in the formation of a state (*c*) with two unpaired electrons, which is a triplet ($2s + 1 = 3$). The next possible multiplicity, the quintuplet, never arises in practice as the transition probability is prohibitively low, so low in fact that such states have never been observed in emission or absorption for any polyatomic molecules with an even number of electrons.

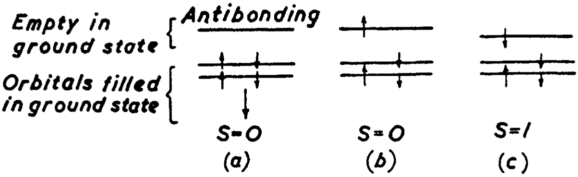

FIG. 1. *Schematic representation of the orbital structure of a molecule: (a) in the ground singlet state, (b) in the first excited singlet state, and (c) in the triplet state. The diagram does not give accurate relative energies. The energy of the first singlet state above ground is not simply the difference in energy between the highest occupied and lowest unoccupied orbitals. The interaction of the excited and unexcited configurations will affect the energy of the state.*

The frequency which excites a molecule to an upper state is predetermined by the relative energy spacings of the occupied and the unoccupied orbitals of the molecule. In all the molecules considered in this Review the lowest unoccupied molecular orbital is an anti-bonding π-orbital. Excitation involves the spontaneous promotion of an electron from an occupied orbital into this anti-bonding orbital. The intensity of the absorption of light by an assemblage of molecules is an experimental measure of the

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* This statement is true only if the highest occupied level is non-degenerate.

probability of the promotion of an electron to any given level. The more intense the absorption the more probable is the transition between the states.

There are three main types of excitation: (i) The excited electron may originate from a bonding π-orbital, in which case the resulting electronic state is designated a $^1(\pi,\pi^*)$ state (read as "singlet pi-pi star"). In this case, the bonding in the upper state will be different from that in the ground state because there is one less bonding electron in the former. The transitions in the ultraviolet and the visible region of the spectrum exhibited by conjugated aromatic hydrocarbons and polyenes involve excitation to states of this type. (ii) The excited electron may originate from a bonding σ-orbital. The resulting state is a $^1(\sigma,\pi^*)$ state (singlet sigma-pi star). Such states are not important in photochemistry as they are seldom the lowest singlet electronic states of molecules which absorb in the visible and near-ultraviolet region. (iii) The excited electron may originate by promotion of an electron from a non-bonding orbital, n, into the π^*-orbital. In molecules which contain oxygen or nitrogen the non-bonding pairs occupy n-orbitals. These n-orbitals often have higher energy than the occupied π-orbitals and consequently the lowest excited singlet states of such molecules are usually $^1(n,\pi^*)$. The lowest excited singlet states[6] of all aldehydes, ketones, quinones, and most *N*-heteroaromatic compounds are $^1(n,\pi^*)$.† Excitation of this type leads to a configuration which has π-bonding properties less removed from those of the ground state than arise from $\pi \rightarrow \pi^*$-excitation; little distortion is then to be expected. This fact and other differences to be discussed in the next section lead to fundamental dissimilarities in the photochemistry of molecules whose lowest excited singlet states are $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$.

It is less convenient to use orbital-energy differences to represent types of excitation than to deal with energy states. The energy of a state above the ground state is essentially the orbital-energy difference. The energy of the electron in the antibonding orbital is lowered by configuration interaction. The latter will, however, not be discussed in detail; the electronic interaction between the excited and the unexcited configuration results in a lowering of the energy of the now occupied antibonding orbital.

2. The properties of (π,π^*) and (n,π^*) states

Associated with each state is a characteristic natural life whose duration is inversely proportional to the strength of the absorption to that state. The strength of absorption is usually measured in terms of the molar extinction coefficient, ϵ, which is defined as $\epsilon = \frac{1}{cl}\log(I_0/I)$, where c is the

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[6] Kasha, *Discuss Faraday Soc.*, 1950, **9**, 14.

† Strictly, an $n \rightarrow \pi^*$ orbital promotion involves the excitation of a non-bonding electron from an orbital which is symmetric to the molecular plane to an antibonding π-orbital which is antisymmetric to this plane. However it is reasonable to extend this useful classification to nearly planar molecules in which the effective skeleton is planar.

concentration in moles/l., l is the length of the absorption path in cm., and $\log (I_0/I)$ is the absorbance of the solution such that (I/I_0) is the fraction of the incident light which is transmitted. In general, the lifetime can be measured experimentally or calculated from the magnitude of the integrated experimental absorption curve. The following approximation is often useful in the near ultraviolet region:

$$\tau_0 \text{ (in sec.)} = 10^{-4}/\epsilon_{\max}.$$

In Fig. 2 typical values of τ_0 are given for both types of transition. The lifetime calculated in this manner is an upper limit since the actual lifetime, which is influenced by the environment, will always be equal to or shorter than the natural radiative lifetime. After the initial excitation to the lowest singlet state, the molecule loses its excitation energy in one or more of the following five ways:*

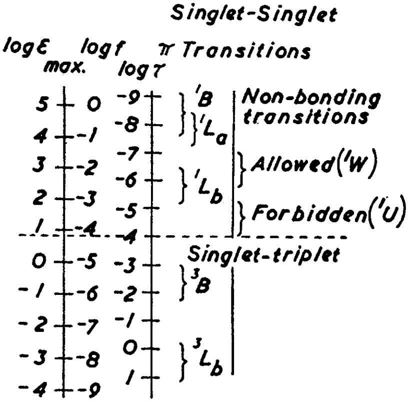

FIG. 2. *The relation between natural (radiative) lifetimes (τ_0), oscillator strengths (f), and extinction coefficients (ϵ) of electronic transitions.*

(i) fluorescence; radiative conversion into the ground state;

(ii) internal conversion; non-radiative conversion into the ground state;

(iii) intersystem crossing; non-radiative transition which involves a spin intercombination to the triplet state;

(iv) photochemical reaction; by unimolecular dissociation or by intermolecular reaction; and

(v) energy transfer non-radiatively to a neighbouring molecule.

The yield of photochemical product depends on the rate of process (iv) in relation to the rates of the other processes. After intersystem crossing, (iii), the molecule, in a triplet state, will follow one of the following courses:

(*a*) phosphorescence; radiative inter-combination with the ground state;†

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* The terms used in this work to describe intramolecular energy conversions are those defined by Kasha.[6]

† A combination is taken to mean a spectroscopic transition between two states of the same multiplicity, while intercombination is reserved for spectroscopic transitions between states of different multiplicity. These terms may be used with respect to radiative and non-radiative transitions.

(*b*) internal conversion; non-radiative inter-combination with the ground state (intersystem crossing is retained for use in spin–orbital dependent processes);

(*c*) photochemical dissociation or reaction; or

(*d*) triplet–triplet energy transfer; non-radiative transfer of electronic energy to a nearby molecule.

There are two other processes to be considered which arise when the molecules are excited to other than the vibrationless level of the first excited state. At a somewhat higher frequency than that of the zero–zero band, the molecules will reach the first excited state with an excess of vibrational energy. In solids, liquids, and gases at high pressures, the perturbing effect of neighbouring molecules rapidly degrades the excess of vibrational energy to thermal energy. Unless there are extremely rapid competing processes, vibrationally excited states rapidly revert to the excited state in vibrational equilibrium with the surrounding medium. Excited molecules are isolated from collisional degradation only in gases at low pressures. Dissociative reactions will be enhanced under these conditions when vibrational energy is required for dissociation.

At still higher frequencies, excitation is into higher electronic states. In most molecules, again in solids, liquids, and gases at high pressure, internal conversion between excited singlet states (or in general between excited states of the same multiplicity) occurs very rapidly. The excess of energy is dissipated as thermal energy in the surroundings. Since internal conversion occurs between isoenergetic states, the process must involve conversion of electronic energy into vibrational energy, followed by rapid degradation of the type discussed in the previous paragraph. Hence, even when a molecule is initially raised to a highly excited electronic state, it rapidly reverts to the vibrationally equilibrated first excited state.*

As a consequence of these rapid radiationless processes, the molecule usually has only one emitting level of a given multiplicity, and that is the lowest excited level of that multiplicity. In the gaseous phase at low pressure, it may not be possible to drain off the excess of vibrational energy and only in this case would vibrational energy be able to influence the rate of a photochemical reaction. One of the fundamental problems in chemical kinetics concerns the degradation of vibrational energy, *i.e.*, the number of gas-phase collisions required to remove a certain quantity of vibrational energy from a vibrationally excited molecule. All that is known is that more than one collision is necessary to degrade such energy completely.

Thus, in solutions, in gases at pressures greater than about 50 mm. of Hg, and in solids and rigid glasses, the quantum yield of the unique emission of a molecule is almost invariably independent of the frequency of the exciting light. This implies that the emitting state is the only one which is important in photochemical reactions in such media.

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* The only confirmed exception is azulene, in which fluorescence occurs only from the second excited state (Viswanath and Kasha, *J. Chem. Phys.*, 1956, **24**, 574).

In Fig. 3, the ground singlet state, first excited state, second excited state, etc., are designated S_0, S_1, S_2, etc. Consider a substance which has a fluorescence yield of 0·5. When x molecules are raised to S_1, $x/2$ of these emit $S_1 \rightarrow S_0$ luminescence. When x molecules are raised to S_2 it is still found that $x/2$ emit $S_1 \rightarrow S_0$ luminescence and that this emission is identical with the first. Within the limits of experimental error all quanta which are lost during the processes of excitation and emission are lost from the lowest state. In other words, the processes responsible for the observation of a luminescence efficiency less than unity occur in times comparable with the fluorescence lifetime, but are very slow compared with the internal conversion and vibrational energy redistributions which occur when the excitation is to a higher electronic state than the first excited state.

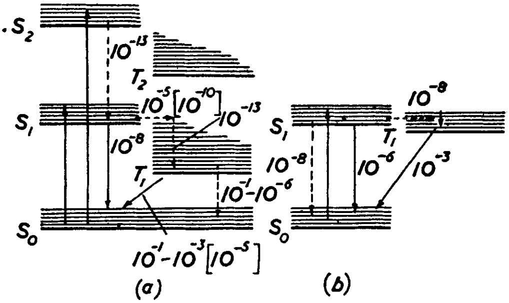

FIG. 3. *Electronic energy state diagram for molecules with:* (*a*) (π,π^*) *states, and* (*b*) (n,π^*) *states. The numbers quoted are unimolecular lifetimes* (*seconds*) *under conditions of thermal quenching at room temperature. Those in parentheses refer to the probable values in the presence of heavy-atom solvents or paramagnetic species. The full lines represent radiative processes and the broken lines non-radiative processes.*

There are a few exceptions to this behaviour. If the molecule contains a group or bond in which the higher excitation energy may be localised and whose absorption is continuous, *e.g.*, the absorption of visible light by a molecule with a C–Br bond, there will be dissociation if there is mixing of the C–Br continuum with the discrete states of the molecule. This is predissociation. The extent of the mixing is likely to be different in each discrete state. Thus the fluorescence yields of such molecules will not be the same when the excitation is into different states. Photodissociation may compete with internal conversion between excited states. Examples which illustrate the influence of photodissociation on luminescence yields are reported in the section on the photo-oxidation of gases.

Recently, Ferguson[7] has discussed the likelihood of intersystem crossing between states other than S_1 and T_1 (the lowest triplet state) (see Fig. 3) in molecules substituted by heavy atoms. Such crossing should result in a variation of the fluorescence yield with excitation energy. A similar variation of the fluorescence yield is observed with some molecules of the

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[7] Ferguson, *J. Mol. Spectroscopy*, 1959, **3**, 177.

ethylenic type. This has been attributed to rapid twisting in the upper states.[8] However, these examples are definitely exceptions to the rule and unless the molecule under study contains one of these features which causes intersystem crossing in upper states *the yield of fluorescence will be independent of the exciting energy* in condensed media. Internal conversion between the emitting singlet level and the ground state is a relatively improbable process, otherwise fluorescence would seldom be observed.

Spin intercombinational processes, such as intersystem crossing, are of particular importance when photo-oxidations are considered. In an isolated molecule, the crossing from one potential-energy surface to another of different multiplicity becomes possible owing to intramolecular perturbation of the electronic state. This involves the interaction of the spin and the orbital motion of the excited electron. The details of spin–orbital interactions will not be dealt with here. There are available non-mathematical discussions by Kasha,[6] by Gilmore, Gibson, and McClure,[9] and by Reid,[10] while more detailed treatments are those of McClure,[11] who deals with aromatic molecules, and Clementi and Kasha,[12] who treat heterocyclic systems. The reader is also referred to Sidman's review[13] where carbonyl compounds are discussed. The rate of intersystem crossing is enhanced by the presence of heavy atoms,[6,14] or of paramagnetic ions[15] or molecules.[16] Oxygen falls in the last class, with the result that most substances have a lower quantum yield of fluorescence in the presence of oxygen than in its absence. The paramagnetism of oxygen appears to be responsible for this luminescence quenching since nitric oxide produces comparable effects in the cases which have been so far examined.[15]

The maximum extinction coefficients for allowed transitions are of the order of 10^4 and may exceed 10^5 for the more intense absorptions. This implies that the radiative lifetimes for $^1(\pi,\pi^*)$ states are 10^{-8} to 10^{-9} second. A photochemical process which involves these radiative states can have an appreciable quantum yield only if the primary process occurs within times of this order of magnitude. For $n \rightarrow \pi^*$ orbital promotions, the maximum extinction coefficients range from 10^1 to 10^3 depending on whether the transition is forbidden or allowed by local symmetry, *i.e.*, the orbital symmetry in the region of the hetero-atom. The radiative lifetimes will range from 10^{-4} to 10^{-7} second. In this case the primary photochemical step can be much slower than that for molecules reacting in $^1(\pi,\pi^*)$ states and yet occur with relatively high yield. Fig. 3 further illustrates these correspondences.

[8] Hochstrasser, *Canad. J. Chem.*, 1959, **37**, 1367.
[9] Gilmore, Gibson, and McClure, *J. Chem. Phys.*, 1952, **20**, 829.
[10] Reid, *Quart. Rev.*, 1958, **12**, 205.
[11] McClure, *J. Chem. Phys.*, 1952, **20**, 682.
[12] Clementi and Kasha, *J. Mol. Spectroscopy*, 1958, **2**, 297.
[13] Sidman, *Chem. Rev.*, 1958, **58**, 689.
[14] McClure, *J. Chem. Phys.*, 1949, **17**, 905.
[15] Clementi and Kasha, *J. Chem. Phys.*, 1957, **26**, 956.
[16] Bowen and Metcalfe, *Proc. Roy. Soc.*, 1951, *A*, **206**, 437.

There are two other differences between (π,π^*) and (n,π^*) states which are important for an understanding of their behaviour in photochemical reactions. First, the energy separation between the $^1(n,\pi^*)$ and the $^3(n,\pi^*)$ states is much less than the corresponding separation for (π,π^*) states.[17] The (n,π^*) triplet should lie fairly close to the (n,π^*) singlet because of the greater distance between the two unpaired electrons in the triplet state. One of these electrons is in an essentially non-localised antibonding π-orbital while the other is at the heteroatom in the localised lone-pair orbital. This means that although the lowest singlet state of a molecule is $^1(n,\pi^*)$, the lowest triplet state may be $^3(\pi,\pi^*)$. This situation probably exists for most nitrogen-containing heteroaromatic compounds.[18] Secondly, the probability of intersystem crossing for molecules whose lowest singlet state is $^1(n,\pi^*)$ is considerably higher than if the lowest state were $^1(\pi,\pi^*)$. This has been shown to be a consequence of the longer radiative lifetime associated with $^1(n,\pi^*)$ states,[12] but may be due partly to the proximity of the singlet and the triplet levels. As a result, fluorescence is either absent or very weak when the lowest excitation energy involves non-bonding electrons. Fig. 3 illustrates these points of difference in terms of the known rate constants for the interstate processes. Although the lowest excited state of a molecule is $^1(n,\pi^*)$, the next higher electronic level may be $^1(\pi,\pi^*)$. Thus, for example, in the vapour-phase photolysis of acetone,[19] the products of primary dissociation are different for excitation into different electronic states where the bonding configurations differ appreciably. Considerations of this nature will not be so important in media where the internal conversion processes are facilitated, *i.e.*, vapours at high pressure, solutions, and solids.

3. Primary reactions

Detailed examination of the nature of luminescence quenching will aid considerably in the elucidation of the course of primary photochemical processes. The quenching of potentially luminescent singlet states can be subdivided according to the products which result from the quenching process: (*a*) the triplet state; from the enhancement of intersystem crossing; (*b*) the ground state; from an increase in the rate of internal conversion; and (*c*) photoproducts; by direct reaction.

Oxygen quenches the fluorescence of most molecules efficiently, and presumably it is mechanism (*a*) that is mainly involved. The efficiency of the radiationless conversion from the lowest triplet state into the ground state is usually higher than that of the radiative process, as is made evident by the absence of phosphorescence from virtually all molecules in the vapour phase or in solution. The internal conversion process is then markedly viscosity-dependent, as illustrated by the appearance, in general, of

[17] Reid, *J. Chem. Phys.*, 1953, **21**, 1906.

[18] Goodman and Harrell, *J. Chem. Phys.*, 1959, **30**, 1131.

[19] Ells and Noyes, *J. Amer. Chem. Soc.*, 1938, **60**, 2031.

phosphorescence in solutions in rigid glasses. The three known exceptions to this are biacetyl, thiobenzophenone,[20] and acetone,[2] which phosphoresce with relatively high quantum yields even in the vapour phase.

Fig. 4 represents the nature of the photochemical primary processes which take place in a system containing oxygen after the absorption of light. The general scheme relates to gas- or liquid-phase oxidations although the values of some of the rate constants differ considerably in the two cases. In the gas phase, the rate of removal of the excess of vibrational energy depends on the collisional frequency and hence on the gas pressure. The absolute rate of a photoreaction such as dissociation may depend on the vibrational-energy content and the nature of the distribution of this energy throughout the many vibrational modes of the molecule. Thus, photochemical reactions in the gas phase have rates which depend on the excitation energy. Unless dissociation occurs, the excess of vibrational energy will be removed after a few collisional periods and the molecule will remain in a nearly vibrationless or thermally equilibrated electronic excited state during the lifetime of that state. Hence, in gas phase systems, steps 1 and 2 of Fig. 4 are essential primary processes. In solutions, the excess of vibrational energy is usually removed by solvent collisions within about 10^{-13} second and the probability of photodissociation does not necessarily vary with the energy of excitation.

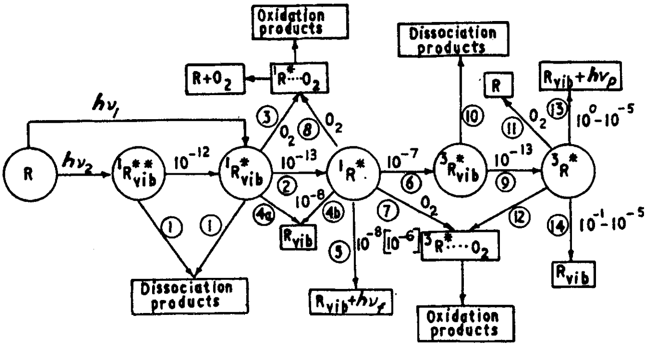

FIG. 4. *Primary photochemical processes. The encircled numbers are reactions referred to in the text.* R *is the molecule in its ground state. Excitation by light of frequency* ν_1 *produces* $^1R_{vib}{}^*$, *the molecule in its lowest excited singlet state with vibrational energy in excess of equilibrium.* $^1R^*$ *is the same state in vibrational equilibrium with the surrounding medium. Light of frequency* ν_2 *excites* R *to* $^1R_{vib}{}^{**}$, *the molecule in a higher singlet electronic state.* $^3R_{vib}{}^*$, *and* $^3R^*$ *represent the molecule in its lowest triplet state with and without excess of vibrational energy, respectively. The values of the lifetimes are in seconds.*

Bimolecular reactions in solution have rates which depend on the number of encounters. The encounter rate is determined by the nature of the Franck–Rabinowitch cage of the solvent and is correspondingly faster than the collision rate between two species at the same temperature and

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[20] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.

concentration in the gaseous phase. A typical upper limit for a bimolecular rate constant in solution is about 10^{10} l. mole^{-1} sec.$^{-1}$. At normal solute concentrations the encounter frequency is at least four orders of magnitude less than 10^{13} sec.$^{-1}$ (*i.e.*, $\not> 10^{9}$ sec.$^{-1}$). The result is that in solutions the rate of a bimolecular photoreaction is seldom determined by the amount of vibrational energy which is initially distributed throughout the molecule. Although step 3 may be important in the gas phase this is not the case in solution. However, the case may arise where the doubly electronically excited molecule $^1R_{\text{vib}}{}^{**}$ dissociates. The actual lifetime of this state is determined mainly by the rate of the non-radiative spectroscopic transition between it and the next singlet state, $^1R_{\text{vib}}{}^{*}$. This lifetime is of the order of 10^{-12} sec. Such a rate constant (10^{12} sec.$^{-1}$) is not necessarily very fast compared with the dissociation rate. Thus one should observe rates of reaction which are constant when the excitation is within any one electronic band system. Steps 4—8 of Fig. 4 cover all the important fates of a singlet excited state. Steps 4, 5, and 6 are the three intramolecular processes of internal conversion, fluorescence, and intersystem crossing, respectively. For $^1(\pi,\pi^*)$ states, these changes occur at approximately the same rate, *ca.* 10^{-8} sec.; for $^1(n,\pi^*)$ states, the fluorescence lifetime is usually much longer, *ca.* 10^{-6} sec. Molecules with a lowest-lying $^1(n,\pi^*)$ state will seldom show other than a weak fluorescence, and the important steps for these molecules are Nos. 4 and 6, internal conversion and intersystem crossing.

The oxygen quenching of a singlet excited state may in theory follow two courses. The first of these involves an enhancement of the rate of intersystem crossing, through steps 7 and 8. In solution, the singlet–triplet crossing rate may be increased by a factor of about a hundred by interaction with oxygen. It is not known what type of collisions are involved in this catalysis. The intermediate state is written as $^3R^* \cdots O_2$ to illustrate the proximity of the two species. It should be possible for this collision complex to give rise to oxidation products. The remaining reaction of the singlet state involves union with oxygen to give instantaneous complexes with the singlet state, $^1R^* \cdots O_2$.

During intersystem crossing, the molecule is expected to remain in the triplet state at an isoenergetic line of the two potential surfaces. After the appropriate collisional processes, this excess of vibrational energy will be removed and the molecule will revert to a nearly vibrationless level (at normal temperature) of the lowest triplet state. These two processes are represented by steps 6 and 9 in Fig. 4. As before, in the gaseous phase, photochemical dissociation (step 10) will usually compete with collisional degradation (step 9) while in solutions the thermal equilibration time will usually be very short compared with the time required for dissociation.

The effect of oxygen on the lowest triplet state of the molecule may be two-fold: (i) photo-oxidation which is chemical union with conservation of spin, step 12; (ii) acceleration of the internal conversion rate into the ground state which would arise because of the paramagnetic influence of oxygen. The latter, which is represented by step 11, arises because the same perturbation which enhances the intersystem crossing probability may enhance the intercombination probability, and hence reduce the lifetime of the triplet state. Internal conversion between the low-lying triplet and the ground state is a particularly difficult process to study experimentally. In order to discover whether this is a true spectroscopic spin-intercombination, and hence sensitive to spin–orbital or paramagnetic perturbation, a complete quantum account is necessary. These perturbations enhance the relative rate of intersystem crossing, and at the same time the natural lifetime of the emitting triplet state is reduced owing to breakdown of the spin selection rules. Recent work by Porter and Wright[21] has indicated that paramagnetic ions and molecules such as oxygen affect the rate of internal conversion into the ground state although the mechanism of this process is not yet clear. Phosphorescence, step 13, usually occurs with a lifetime of 10^{-3} sec. or less in the presence of oxygen or heavy atoms. Internal conversion, step 14, occurs with high relative probability, although the rate is very dependent on the properties of the medium, *e.g.*, the viscosity.

Energy-transfer processes have been omitted from the scheme of Fig. 4. It will be appropriate to discuss them now. This topic has been critically reviewed by Terenin and Ermolaev,[22] although particular reference was not made to photochemical reactions. It has become apparent in recent years that energy of excitation may be non-radiatively transferred from one molecule to another provided the acceptor has energy states lower than the excited state of the donor. Such transfers are known to occur in gaseous, liquid, and crystalline systems. The sensitisation of the β-naphthylamine fluorescence by benzene vapour was originally noted by Neporent,[23] and detailed studies were later made by Dubois.[24] There is little doubt that this system is an example of energy transfer in the vapour phase. Light absorbed by the benzene is emitted as β-naphthylamine fluorescence, and both trivial reabsorption and vibrational stabilisation have been shown not to be responsible for the whole effect.

In dilute solutions, energy transfer from solute to solute and from solvent to solute has been shown to occur. In this respect, aromatic hydrocarbons and quinones have been extensively studied.[22] It has been demonstrated that such transfer of energy can occur over very large distances (compared with molecular dimensions) and that the transfer is non-radiative. These facts suggest that electronic energy transfer may be extremely important in some photochemical systems in the gaseous phase and in solution.

The phenomenon of energy transfer is observed also in crystals. For

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[21] G. Porter and Wright, *Discuss. Faraday Soc.*, 1959, **27**,18.

[22] Terenin and Ermolaev, *Uspekhi Fiz. Nauk*, 1956, **57**, 37.

[23] Neporent. *Zhur. Fiz. Khim.*, 1950, **24**, 1219.

[24] Dubois, *J. Phys. Chem.*, 1959, **63**, 8.

example, light absorbed by an anthracene crystal which contains a small amount of (0·01 mole%) of dissolved tetracene is emitted as tetracene luminescence.[25] Thus the presence of small amounts of impurity in aromatic crystals may radically affect the results of photochemical studies and, in particular, the primary quantum yields. An impressive demonstration of this occurred in studies of the conductivity of anthracene treated with tetracene.[26] It is found that the trapping centres in the anthracene crystal are quenched, *i.e.*, the efficiency of trapping is reduced when the crystal contains dissolved tetracene.

4. Photo-oxidation in the gaseous state

Of the many gas-phase photochemical oxidations which have been studied, most involve primary dissociation into free radicals which subsequently react with oxygen. These reactions are outside the scope of a review on primary processes in photo-oxidation and will not be considered further except to note that the dissociation rate (step 1 of Fig. 4) is much faster than any other reaction which involves $^1R_{vib}{}^*$. The processes to be discussed in this section include all interactions of molecular oxygen with electronically excited species, whether or not such interaction leads directly to chemical reaction.

In only two instances is there unambiguous evidence for direct photo-oxidation of excited molecules in the vapour phase, namely, for biacetyl[27] and keten.[28] Less certain are the cases of acetone,[29] crotonaldehyde,[30] and aniline.[31] Oxygen quenches at least part of the luminescence of biacetyl,[32] acetone,[33,34] aniline,[35] hexafluoroacetone,[36] β-naphthylamine,[37] anthracene,[16] 9-phenylanthracene and 9,10-diphenylanthracene,[38] anthraquinone, anthranol, anthrone, and the 2-amino-, 2-methyl-, 2-ethyl-, and 2-chloro-derivatives of anthraquinone.[39] In general, detailed study of the luminescence and photochemistry of compounds not appreciably volatile at room temperature has been confined to condensed phases, which are discussed in the next sections. Studies of both photochemistry and luminescence are rare, particularly for the vapour phase.

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[25] Bowen, Mickiewitz, and Smith, *Nature*, 1947, **159**, 706.
[26] Bryant, Bree, Fielding, and Schneider, *Discuss. Faraday Soc.*, in the press.
[27] G. B. Porter, *J. Chem. Phys.*, in the press.
[28] G. B. Porter, *J. Amer. Chem. Soc.*, 1957, **79**, 1878.
[29] Marcotte and Noyes, *Discuss. Faraday Soc.*, 1951, **10**, 236; *J. Amer. Chem. Soc.*, 1952, **74**, 783.
[30] Blacet and Volman, *J. Amer. Chem. Soc.*, 1939, **61**, 582.
[31] Vartanyan, *J. Phys. Chem.* (*U.S.S.R.*), 1940, 3, 467.
[32] Groh, *J. Chem. Phys.*, 1953, **21**, 674.
[33] Groh, Luckey, and Noyes, *J. Chem. Phys.*, 1953, **21**, 115.
[34] Heicklen, *J. Amer. Chem. Soc.*, 1959, **81**, 3863.
[35] Vartanyan, *Izvest. Akad. Nauk, S.S.S.R., Ser. Fiz.*, 1938, 3, 341.
[36] Okabe and Steacie, *Canad. J. Chem.*, 1958, **36**, 137.
[37] Dubois, *J. Chem. Phys.*, 1956, **25**, 178.
[38] Stevens, *Trans. Faraday Soc.*, 1955, **51**, 610.
[39] Karyakin *J. Phys. Chem.* (*U.S.S.R.*), 1949, **23**, 1332.

Biacetyl.—Because it exhibits intense phosphorescence, regardless of the state of aggregation, biacetyl has been studied extensively.[27,29,40,41] There are two principal absorption regions in the visible and ultraviolet spectrum, both of which are $n \rightarrow \pi^*$-transitions in which an electron is promoted from a non-bonding orbital on oxygen to a carbonyl antibonding π-orbital.[42] The extinction coefficients are low; the lifetime of the emission from the lowest $^1(n,\pi^*)$ state is about 10^{-5} second; hence the fluorescence yield is small. Photochemical dissociation (step 1 of Fig. 4) occurs provided the exciting light is of wavelength shorter than *ca.* 4000 Å.[40] The photochemical quantum yield, *i.e.*, the yield for the primary dissociation into free radicals, decreases with increasing pressure after excitation to either electronic state. Degradation of vibrational energy increases with increasing pressure; thus fewer molecules can dissociate and more will reach the lower vibrational levels from which fluorescence occurs. The "dissociation" reaction is rupture of one of the carbon–carbon bonds, which in effect gives a mixture of methyl and acetyl radicals and carbon monoxide.

The quantum yield of phosphorescence is quite high, 0·145 at 4358 Å.[43] In this respect, the behaviour of biacetyl is unusual, compared with the majority of molecules which luminesce, in that phosphorescence is observed in gaseous, liquid, and solid phases. The molecule in its triplet state, which is responsible for the phosphorescence, can dissociate if it has vibrational energy equivalent to a temperature well above room temperature. Except at high intensities, where triplet–triplet interaction leads to dissociation, the triplet dissociation only becomes important above about 50°c, and there is at this temperature a corresponding thermal quenching of the phosphorescence.

The luminescence and the photochemical primary reactions of biacetyl in the absence of oxygen can be explained by steps 1, 2, 4, 5, 6, 9, 10, 13, and 14 of Fig. 4. The fluorescence quantum yield is about 0·0024 at 4358 Å, where dissociation is negligible, independent of temperature and pressure.[44] This gives the expected order of magnitude for the apparent lifetime of the singlet state, *i.e.*, *ca.* 10^{-8} second. At 3650 Å and shorter wavelengths, the primary quantum yield for dissociation is small and increases with decreasing pressure and decreasing wavelength of excitation. The data indicate the presence of internal conversion into the ground state from $^1R_{vib}^*$, step 4, Fig. 4, with a relatively high quantum yield, particularly at the longer wavelengths.

In the presence of oxygen, phosphorescence is quenched, but fluorescence is unaffected as shown in Fig, 5. The straight portion of the curve for biacetyl luminescence below 10^{-3} mole l.$^{-1}$ of oxygen, as well as the entire straight line for anthracene luminescence, represents the

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[40] Sheats and Noyes, *J. Amer. Chem. Soc.*, 1955, **77**, 1421, 4532.
[41] Coward and Noyes, *J. Chem. Phys.*, 1954, **22**, 1207.
[42] Sidman and McClure, *J. Amer. Chem. Soc.*, 1955, **77**, 6461.
[43] Almy and Gillette, *J. Chem. Phys.*, 1943, **11**, 188.
[44] Okabe and Noyes, *J. Amer. Chem. Soc.*, 1957, **79**, 801.

quenching effect of oxygen. The luminescence in the second case is fluorescence. The luminescence of biacetyl, in contrast to that of anthracene, does not decrease without limit as the oxygen concentration is increased, but, instead, reaches a small, constant value. This shows that the biacetyl luminescence has two components: phosphorescence, which is quenched by oxygen, and fluorescence, which is unaffected by oxygen. Oxygen does not interact with the singlet state, so that steps 3, 7, and 8 are of negligible importance. Oxygen does interact with the triplet state efficiently.[27] This interaction is chemical, since photo-oxidation is observed in light of wavelength 4358 Å in high yield, while under the same conditions in the absence of oxygen there is no dissociation into free radicals. The quantum yields of products formed in the photo-oxidation are of the order of unity or higher, under conditions such that no radical-chain reaction is likely.[45] The yields are much higher than could be explained on the basis of the phosphorescence yield alone, *i.e.*, there must be internal conversion of the triplet state in the absence of oxygen for which the probability is about six times the probability of phosphorescence. Further, internal conversion of the nearly vibrationless singlet state must be relatively unimportant compared with intersystem crossing. The effect of oxygen cannot be attributed to enhanced intersystem crossing since the fluorescence yield is unaffected by oxygen. With these data, the values for the various specific lifetimes given in the Table can be estimated.

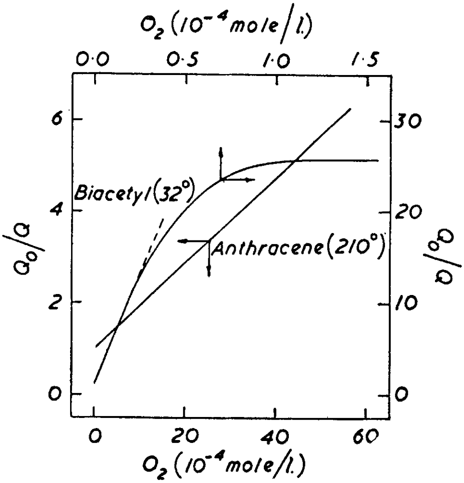

FIG. 5. *Fluorescence quenching by oxygen for anthracene[16] and biacetyl.[32]*

Estimated lifetimes in the biacetyl system

Step (Fig. 4)	4	5	6	12	13	14
Lifetime (sec.$^{-1}$)	10^{-7}	10^{-5}	10^{-8}	2×10^{-9} (O_2)*	10^{-2}	2×10^{-3}

* Oxygen concn. measured in moles/l.

[45] Taylor and Blacet, *Ind. Eng. Chem.*, 1956, **48**, 1505.

Keten.—The interpretation of the photo-oxidation of keten is less certain since no luminescence has been observed.[28,46] The reaction at short wavelengths (*ca.* 2700 Å) is undoubtedly of free-radical nature even in the presence of oxygen, because of the rapid dissociation of excited keten molecules into methylene radicals and carbon monoxide. Near the long-wavelength limit of absorption, excited molecules are both deactivated and oxidised by molecular oxygen. That the deactivation involves the $^1R_{vib}{}^*$ state is demonstrated by the negligible amount of primary dissociation in the presence of oxygen.[28] The short-wavelength photo-oxidation always leads to formation of ethylene with a quantum yield of 0·67, while in light of wavelength 3650 Å this yield is very small above about 50 microns pressure of oxygen. It is possible that the actual reaction of an excited molecule with oxygen which occurs at long wavelengths (and gives carbon monoxide and carbon dioxide among the products, but no ethylene) may involve the triplet state of keten, but, in the absence of luminescence data, it is not possible to determine the nature of the reacting species. This emphasises the tremendous advantage inherent in the study of photochemical reactions of molecules for which luminescence can also be examined. By analogy with biacetyl and other substances, it can be tentatively concluded that this oxidation proceeds *via* the triplet state, and further that the number of excited molecules which reach the triplet state is small, at least in the presence of oxygen.

Acetone.—The phosphorescence of acetone is strongly quenched by oxygen, but fluorescence is unaffected.[33,34,47] Any interaction between oxygen and excited acetone molecules must involve the triplet state, but not the singlet state. The studies of photo-oxidation[29] do not provide unambiguous evidence for direct chemical reaction between the triplet state and oxygen, since the contribution of primary free-radical dissociation cannot be estimated from the available data. Fig. 6 shows that the reaction at room temperature is quite different from that at higher temperatures (where free-radical dissociation is probably complete). A comparison of the photochemical oxidation at long wavelengths with that at short wavelengths is required to assess the extent to which oxidation of the excited molecule contributes to the overall reaction at room temperature. In the interpretation of primary reactions it is desirable in each case to have such photochemical-action spectra, analogous to action spectra of luminescence.

Polyacenes.—In the examples discussed above, optical excitation in the wavelength regions usually studied involves the formation of a $^1(n,\pi^*)$ state. Oxygen has little or no detectable effect on these singlet states (except in the case of keten, where the assignments are not known), but does interact strongly with the triplet. On the other hand, the lowest states of polyacenes (*i.e.*, linear assemblies of fused benzene rings) are (π,π^*). Although most

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[46] Strachan and Noyes, *J. Amer. Chem. Soc.*, 1954, **76**, 3258.
[47] Heicklen and Noyes, *J. Amer. Chem. Soc.*, 1959, **81**, 3858

studies of aromatic hydrocarbons have been limited to the condensed phases, those which have been studied in the vapour phase show strong oxygen-quenching of the fluorescence.[16] As discussed in the previous section, this effect may be attributed to enhanced intersystem crossing brought about by the paramagnetic nature of oxygen. In these systems, phosphorescence is weak, and since the photochemical oxidation has not been studied, the nature of the interaction between $^3(\pi,\pi^*)$ states and molecular oxygen in the vapour is unknown. Even the much studied anthracene–oxygen system, where a transannular peroxide is formed in solution, has not been examined for *photo*-oxidation products in the vapour phase.

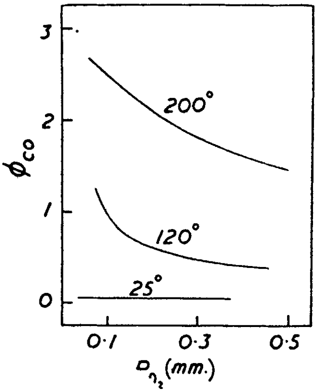

FIG. 6. *The photo-oxidation of acetone at* 3130 Å.[29] Φ_{CO} *is the quantum yield of production of carbon monoxide, one of the products of reaction.*

5. Photo-oxidation in solution

So much work has been published in this field during the past decade that this discussion will be confined to aromatic hydrocarbons and their derivatives in organic solvents and to photosynthetic molecules typified by chlorophyll. The reasons for this restriction are two-fold: a large volume of work has appeared on these topics, whereas other studies have mostly been on isolated topics; and the ultraviolet spectra of these molecules are understood to the extent that we know a considerable amount about the nature of the low-lying energy levels that are important in bimolecular photoreactions.

Anthracene and its Derivatives.—The molecule which has been most widely studied from the point of view of photoreactions in solution is anthracene. The linear polyacenes (anthracene, tetracene, pentacene, etc.) combine with oxygen in the presence of light to form transannular peroxides, the efficiency of this reaction increasing as the conjugated system is extended. The photo-oxides (bridged oxides) are only very weak peroxides and many of them do not liberate iodine from potassium iodide at an appreciable rate. The quantum yields of photo-oxidation and fluorescence are independent of the wavelength of exciting light over the ranges 2600—3650 and 2200—3650 Å, respectively.[7,48] This indicates that rapid collisional degradation and internal conversion always occur until the thermally equilibrated vibrational levels of the lowest excited state are reached. Thus all the photochemical reactions of anthracene originate from this state and the relative quantum yields of each depend on the magnitude of the unimolecular or bimolecular rate constants for the subsequent primary processes. The photoreactions of anthracene that have been studied include fluorescence, photo-oxidation, and dimerisation. Dimerisation gives a compound which consists of two anthracene molecules joined across the 9,10-positions, lacks the typical unsaturation of anthracene, and has an absorption spectrum resembling that of a substituted benzene.

The lowest excited singlet state of anthracene has known symmetry (^1L_a in the Platt notation or $^1B_{2u}$ in group-theoretical notation), and the transition moment dipole is along the short axis of the molecule. The limiting fluorescence yield is 0·24 at very low anthracene concentrations and is not greatly affected by 9- and 10- substituents.[49] The phosphorescence from anthracene is extremely weak and appears in the near-infrared region of the spectrum.[50] In order that the phosphorescence of anthracene dissolved in a rigid glass may be observed a very high light-intensity and a long photographic exposure are necessary. In view of this the postulation of triplet states as reacting species present at appreciable steady-state concentrations also implies that the internal conversion from the lowest triplet ($\tau_0 = 10^{-2}$ second) to the ground state occurs with extremely high efficiency ($k \approx 10^{-6}$ sec.$^{-1}$).

In solvents such as benzene and hexane, anthracene shows fluorescence in dilute solution and dimerises in concentrated solution. Photo-oxidation is very inefficient and is a function of the anthracene concentration but not of the oxygen concentration. The product of the photo-oxidation is a transannular peroxide. The quenching effect of oxygen is not directly related to the oxidation process. In solvents such as carbon disulphide and chloroform, the fluorescence of anthracene is almost completely quenched and photo-oxidation is rapid. When no oxygen is present dimerisation does not readily occur. It has been shown that the results obtained may be fitted to a kinetic scheme in which (i) photodimerisation results from excited singlet molecules, (ii) the photo-oxide is formed from excited molecules in the triplet state, and (iii) concentration quenching is caused by the interaction of singlet excited molecules with unexcited molecules of the substance under consideration, whether this be anthracene or one of its alkyl derivatives.[51]

[48] Hochstrasser, unpublished results.
[49] Popoviko, *Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, 453.
[50] McGlynn, Padhye, and Kasha, *J. Chem. Phys.*, 1955, **23**, 593.
[51] Bowen, *Trans. Faraday Soc.*, 1955, **51**, 475, and earlier references therein.

The participation of a triplet state in this reaction is not an arbitrary postulate. The sum of the quantum yields of fluorescence, of photo-oxidation, and of dimerisation increases with increasing concentration of the solute (except in the case of oxygen-free solutions). At high concentrations, *i.e.*, 2×10^{-2}M, this sum is greater than the limiting quantum yield of fluorescence attained in oxygen-free solutions at low concentrations, *i.e.*, with no concentration quenching or oxygen quenching.[52] The photo-oxidation of anthracene and some of its derivatives in carbon disulphide solution proceeds with a quantum yield close to unity, although the limiting quantum yield for fluorescence in this solvent is very low.[53] Therefore, the processes leading to a low value of the limiting fluorescence yield do not involve direct transition from the excited to the ground state. Instead, the presence of an intermediate active molecule, incapable of fluorescence but able to react with oxygen, is required. Further evidence that this state is in fact a triplet state is found in the flash-photolysis work of Porter and Windsor.[54] Irradiation of anthracene in oxygen-free hexane produced a metastable state (lowest triplet) from which absorption to a higher state (upper triplet) was observed. The half-life of the lower triplet state under these conditions, $5{\cdot}8 \times 10^{-5}$ sec., decreased enormously in the presence of small quantities of oxygen. The triplet–triplet energy separation agrees well with the calculated value for the anthracene molecule.[55] One further instance of diagnostic evidence to support the participation of triplets in these reactions is provided by the nature of the products which arise from the irradiation of anthracene in carbon tetrachloride.[56] The detection of 9-chloro- and 9,10-dichloroanthracene in the products suggests the participation of a diradical which is most likely to be a triplet state. Waters[57] argues that the reactions of anthracene in carbon tetrachloride provide evidence for the diradical nature of the triplet state. It is, however, not true either that a triplet state is a diradical or that a diradical is a molecule in its triplet state in the general case, although in anthracene localisation of electronic charge at positions 9 and 10 satisfactorily accounts for the triplet-state energy derived spectroscopically.

There are two facets of this type of photo-oxidation which still remain difficult to explain. The first is that the quantum yield of photo-oxidation is sensibly independent of the oxygen concentration but does depend on the concentration of anthracene. If the stable peroxide were produced by a bimolecular reaction between oxygen and anthracene in an excited singlet state, the opposite dependence would be expected. This kinetic result is explained by postulating the existence of a reactive "moloxide" of

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[52] Cherkassov and Vember, *Opt. i Spekt.*, 1959, **6**, 503.
[53] Bowen, *Discuss. Faraday Soc.*, 1953, **14**, 143.
[54] G. Porter and Windsor, *J. Chem. Phys.*, 1953, **21**, 2088.
[55] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.
[56] Bowen and Rohatgi, *Discuss. Faraday Soc.*, 1953, **14**, 146.
[57] Waters, *Discuss. Faraday Soc.*, 1953, **14**, 228.

anthracene which may dissociate or form the stable peroxide: other intermediates have indeed been postulated, such as a metastable form of oxygen[58] or a labile anthracene dimer,[59] but the former is physically improbable and the latter may be excluded on the grounds of the small dependence of the triplet-state decay time on anthracene concentration.[60]

The second unexplained factor involves the large dependence of the oxidation rate on the nature of the solvent.[61] In fact the mechanism of the photo-oxidation appears to be different in different solvents. It is likely that these differences are due to three factors: (i) the viscosity, which will determine the rate of bimolecular encounter-controlled reactions as well as influence the rate of internal conversion, (ii) the specific quenching ability of the solvent, which depends on the presence of heavy atoms in the solvent molecules, and (iii) specific solvent–solute interactions, which determine the rate of the radiationless internal conversion into the ground state.

The photo-oxidation of aromatic hydrocarbons is faster in carbon disulphide than in any other solvent. Carbon disulphide appears to have a profound effect on the mechanism of photo-oxidation and for many years preparative chemists have used it as a solvent to obtain high and rapid yields of photo-oxide from literally hundreds of hydrocarbons.[62] One explanation of this phenomenon is concerned with the relative energy spacings of the excited states of the solvent and solute. The mercury 3650 Å lines have been used in nearly all the photochemical studies that have been described; and carbon disulphide has a broad continuum which has an appreciable extinction coefficient at this wavelength. Thus the excited-singlet solute molecule may interact strongly with a carbon disulphide molecule through mixing of the states, and the energy transfer which occurs may accelerate the production of anthracene in its triplet state. It is difficult to decide the mechanism of this energy transfer. First we require to know the nature of the interacting states. It appears reasonably certain that the primary process does not involve the electronically *and* the vibrationally excited molecule. This has been demonstrated by Hochstrasser,[48] who measured the fluorescence yield as a function of the wavelength of the exciting light for anthracene dissolved in solvents such as ethyl iodide and carbon disulphide, both of which exhibit a continuous absorption throughout the region examined. It was found that after correction for solvent absorption the fluorescence yield was constant throughout the range 3000—3800 Å and this implies that the initial vibrational-energy content of the anthracene molecule is not a governing factor and also that the interactions which occur are not dependent on the amount of incident light which is absorbed by the solvent.

With regard to the effect of temperature on the fluorescence yields of

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[58] Kautsky, *Biochem. Z.*, 1937, **291**, 271.
[59] Dufraisse, *Bull. Soc. chim. France*, 1939, **6**, 422.
[60] Linschitz and Sarkanen, *J. Amer. Chem. Soc.*, 1958, **80**, 4826.
[61] Bowen and Tanner, *Trans. Faraday Soc.*, 1955, **51**, 475.
[62] Dufraisse, *Bull. Soc. chim. France*, 1939, **6**, 422.

anthracene derivatives, two distinct types of quenching may occur. In most solvents 9- and 9,10-substituted anthracenes show high fluorescence yields which are strongly temperature- and viscosity-dependent ($E \approx 4$ kcal./mole). Anthracene derivatives having substituents only in the terminal rings show low quantum yields of fluorescence and virtual temperature-independence ($E \approx 0{\cdot}5$ kcal./mole).[63] These results illustrate that there are two types of quenching process. The first involves internal conversion into the ground state, and the second is associated with the enhancement of intersystem crossing. This interpretation is supported by the π-electron nodal distributions in singlet excited anthracene molecules. Substituents in a terminal ring would be expected to affect the inherent intersystem-crossing rate to a greater extent than *peri*-substituents do.

The parallelism between the amount of quenching by oxygen and the amount of photo-oxide formed, which is observed for benzene and some of its methyl derivatives,[64] is not present for the anthracene systems. The sum of the quantum yields of fluorescence and photo-oxidation is *not* equal to the fluorescence quantum yield in oxygen-free solutions at the same concentrations. For example, for 2×10^{-2}M-solutions of 9-methylanthracene, the sum is 0·357, whereas the fluorescence yield in oxygen-free solutions is 0·156. At very low concentrations, 10^{-5}M, the fluorescence yield of an oxygen-free solution is 2·5 times *greater* than for this solution saturated with oxygen.[52] This can only inply that oxygen quenching is considerable although at this concentration the formation of photo-oxide is almost absent.

Studies of the kinetics of dimerisation of anthracene[51, 65, 66] have shown that dimers are formed by reaction of singlet excited molecules with molecules in the ground state, although collisions between these species need not necessarily result in dimer formation.

For anthracene it has been shown that decrease of the fluorescence yield on increase of the anthracene concentration is almost equal to the increased yield of photodimerisation. In this respect, an interesting problem is posed by the recent results of Backström,[67] which involve the continued irradiation of solutions of anthracene and biacetyl with light which is of long enough wavelength (4358 Å) to be absorbed only by the biacetyl. After some time, a precipitate of dianthracene appears. The assumption made in this case is that energy is transferred non-radiatively from triplet biacetyl to populate the triplet level of anthracene and that collision of triplet anthracene with ground-state anthracene molecules then results in the formation of the photo-dimer. However, all the other studies of photodimerisation have indicated that only singlet excited anthracene molecules give rise to dimers and that dimerisation is not in competition with photo-

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[63] Bowen and Sahu, *J. Phys. Chem.*, 1959, **63**, 4.
[64] Bowen and Williams, *Trans. Faraday Soc.*, 1939, **35**, 765.
[65] Weigert, *Naturwiss.*, 1927, **15**, 124.
[66] Cherkassov and Vember, *Opt. i Spekt.*, 1958, **4**, 203.
[67] Backström, *Acta Chem. Scand.*, 1958, **12**, 823.

oxidation. Since the extinction coefficient of anthracene at 4358 Å is less than 10^{-3}, the maximum amount of dimer formed from anthracene which has absorbed radiation directly is 0·001% while the observed yield of dimer is approximately 1%. Anthracene has a correspondingly large quenching action on the phosphorescence of biacetyl in solution.

The large volume of careful work on hydrocarbons of the anthracene series has enabled many of the primary processes in Fig. 4 to be identified and their probabilities unambiguously computed. However, even in these apparently straightforward cases, the natures of the solvent and of the substituent in the anthracene nucleus, as well as the position of the substituent, may drastically alter the importance of any one process. For example, 9,10-diphenylanthracene has nearly a unit quantum yield of fluorescence between temperatures of −70° and +20° and in this case the quantum yield of photo-oxidation depends on the oxygen concentration and on the hydrocarbon concentration.[68] This suggests that the oxidation occurs directly by union of oxygen with the singlet state, or that oxygen-catalysed singlet–triplet conversion always results in photo-oxidation (cf. step 7 of Fig. 4). The high quantum yield of fluorescence in oxygen-free solutions and the absence of dimerisation suggest that the peripheral phenyl groups, which are constrained to be out of the plane of the anthracene nucleus, sterically prevent solvent interactions that would otherwise result in the internal conversion of the excitation energy into the ground state. This steric explanation is probably the more correct as the rate of the photo-oxidation is considreably enhanced in a heavy-atom solvent.

Chlorophyll.—Most of the concepts discussed above are applicable to the primary processes in the photochemistry of photosynthetic molecules. The absorption and emission spectra, and the photochemistry, of compounds such as chlorophyll have been studied *in vitro* (purified samples in solution) as well as *in vivo*. In the latter case interpretation is complicated by the uncertain state of aggregation of chlorophyll and by the intermolecular energy-transfer processes which are part of photosynthesis.

Chlorophyll *a* is discussed in detail here as a representative example of a molecule which is involved in the primary process of photosynthesis. The absorption spectrum, shown in Fig. 7, shows two main bands, one centred at 6700 Å, the "red" bands (^1Q), and the other at 4200 Å, the Soret band (^1B).[69] Although measurements *in vivo* are somewhat uncertain because of the presence of other pigments, the chlorophyll bands are not appreciably shifted.

Fluorescence is observed in the red region of the spectrum only, as shown in Fig. 7. The fluorescence spectrum and quantum yield are independent of the exciting wavelength from 4360 to 6980 Å.[70] The absolute

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[68] Livingston, *J. Chim. phys.*, 1958, **55**, 887.

[69] Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins," in "Radiation Biology", ed. by A. Hollaender, McGraw-Hill Book Co., Inc., New York, 1956, Vol. III, pp. 71—123.

[70] Forster and Livingston, *J. Chem. Phys.*, 1952, **20**, 1315.

quantum yield of fluorescence *in vitro* is 0·24, independent of solvent used, *e.g.*, methanol, ethyl ether, acetone, benzene, and cyclohexanol, except that for dry chlorophyll in a dry hydrocarbon solvent the yield is quite low. *In vivo* the fluorescence quantum yield is very low, 0·02. This point is discussed more fully in the following section on the photo-oxidation of solids. As with polyacene solutions, internal conversion of excited states above the lowest singlet state occurs very rapidly in chlorophyll solutions (and probably *in vivo* also), and hence it is unlikely that the higher excited singlet states can play any important role either in the photochemistry of these molecules or in photosynthesis itself.

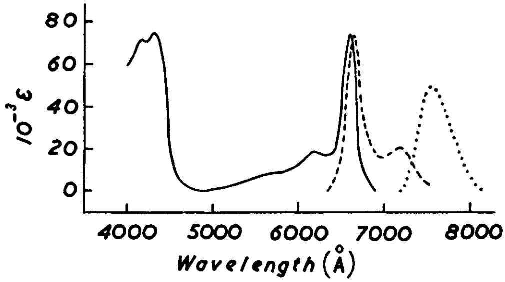

FIG. 7. *The absorption and emission spectra of chlorophyll* a.[73,77] ——— *Absorption spectrum in ether at room temperature,* - - - - - - - *fluorescence spectrum in ether at room temperature, ordinate in arbitrary units,* .... *phosphorescence spectrum in a rigid glass (dry hydrocarbon) at* −183°, *ordinate in arbitrary units.*

The fluorescence of chlorophyll is quenched in the presence of dissolved oxygen, but less than that of other porphyrins or polynuclear aromatic hydrocarbons.[71] The quenching by oxygen is apparently not related to photo-oxidation, since the yield of the latter process is very small[72] (*ca.* 5×10^{-4}).

Chlorophyll *a* also exhibits strong phosphorescence ($\tau_0 \approx 10^{-3}$ sec.), but only in solution in a dry hydrocarbon at low temperature (rigid glass).[73] Its spectrum is shown in Fig. 7. This emission is assigned to the transition from a $^3(n,\pi^*)$ state to the ground state. Phosphorescence had not previously been observed for chlorophyll *a*.[74] Fernandez and Becker[73] attribute the phosphorescence in dry media to a change in the nature of the lowest singlet state from $^1(\pi,\pi^*)$ in hydroxylic solvents to $^1(n,\pi^*)$ in dry solvents. In the former case, the radiative lifetime of the singlet state is short, and fluorescence is favoured; in the latter case, intersystem crossing to the triplet state is more important and hence phosphorescence is observed.

The presence of the triplet state has been demonstrated by flash-photolysis.[75] Solutions of chlorophyll show new absorption bands immediately

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[71] Livingston and Ke, *J. Amer. Chem. Soc.*, 1950, **72**, 909.
[72] Aronoff and Mackinney, *J. Amer. Chem. Soc.*, 1943, **65**, 957.
[73] Fernandez and Becker, *J. Chem. Phys.*, 1959, **31**, 467.
[74] Becker and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 3669.
[75] Livingston and Ryan, *J. Amer. Chem. Soc.*, 1953, **75**, 2176.

after flash-excitation. Since these bands disappear rapidly, they are considered to represent absorption by molecules of chlorophyll in the lowest triplet state, *i.e.*, triplet–triplet absorption. The decay characteristics of the triplet state show, not only first-order quenching (internal conversion), but also efficient quenching by unexcited chlorophyll molecules and by triplet molecules. Oxygen causes reversible and irreversible photobleaching of chlorophyll and a simultaneous disappearance of triplet molecules. An intermediate "moloxide" has been postulated as being formed from triplet molecules and molecular oxygen and able to dissociate (reversible bleaching or quenching) or be converted into a photo-oxide (irreversible bleaching). In any case, the quantum yield of the latter process is small.

In the process of photosynthesis (which is yet to be duplicated *in vitro*) the situation is more nearly analogous to that in the solid state than in solutions. The chloroplast consists of grana, in which the concentration of chlorophyll is high (of the order of 0·3M).[76] Hence the distance between the chlorophyll molecular centres in the grana is about 20 Å for completely random orientation or considerably less if the chlorophyll molecules are collected into aggregates or into monolayers. The small red shift in the absorption spectrum of chlorophyll in live cells is evidence against the existence of "crystalline" chlorophyll in the grana, but tends to support the concept of unimolecular layers.

Intermolecular energy-transfer must be a fundamental part of photosynthesis. Fluorescence of chlorophyll is excited *in vivo* by other pigments, *e.g.*, phycoerythrin and phycocyanin.[77] Exactly how the excitation energy of the chlorophyll molecules initiates reduction in photosynthesis is unknown. Rabinowitch[78] cites three possibilities: (i) migration of excitation energy from chlorophyll to the enzyme or photosynthetic unit in the grana, (ii) migration of photoproducts formed in the neighbourhood of excited chlorophyll molecules to the enzyme, and (iii) migration of the enzyme itself. The known energy transfer from accessory pigments such as carotenoids, phyobilins, and chlorophyll *b* to chlorophyll *a* supports mechanism (i). Even if further evidence for this is obtained, it will prove difficult to determine the extent of the other possible modes of transfer. The problem of energy transfer *in vivo* is treated further in the following section.

6. Photo-oxidation of solids

A considerable amount of work on this topic has been reported for quite complex systems. Most of it has an industrial bias in as much as the workers have been mainly interested in the effect of oxygen on commercial substrates (pigments, mordants, fibres, etc.) under the influence of light. In order to interpret these results in terms of primary process and mechanism, it is first necessary to study comparatively simple systems under very

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[76] Rabinowitch, "Photosynthesis," Interscience Publishers, London, 1956, Vol. II, Part 2, p. 1735.

[77] French and Young, *J. Gen. Physiol.*, 1952, **35**, 873.

[78] See ref. 76, p. 1298.

strict experimental conditions of purity and incident light. This discussion will be confined to molecular crystals.

The generality of photo-oxidation of crystalline materials has only recently become apparent through detailed studies of the photoconductivity and emission spectroscopy of molecular crystals. For example, an examination of the surface photoconductivity of anthracene single crystals has clearly indicated the formation of chemical adducts of surface molecules of anthracene and molecular oxygen.[79] Oxygen is unable to penetrate deeply into the crystal as bulk photoconductivity is not affected by the oxygen atmosphere of the crystal. It is not known whether the surface "oxide" is formed through the absorption of light initially by the crystal as a whole or by imperfect pseudocrystalline surface layers, so it is not possible to say much regarding the primary processes involved in this case. Other examples often arise in crystal spectroscopy. A recent study of the luminescence of toluene single crystals has indicated that previous assignments have probably been based on emission by oxidative impurities:[80] in this case, the impurity was benzaldehyde.

The packing in benzene, naphthalene, anthracene, and tetracene crystals is very close and it is unlikely that oxygen molecules would be able to penetrate the surface layers of the crystals. However, when substituted tetracene molecules are examined in the crystalline state, one can observe a bulk oxidation effect.[81] The product is the transannular peroxide produced also by photo-oxidation in solution.

It has been demonstrated that the rate of production of photo-oxide, which is identical with the rate of uptake of oxygen, is controlled by the rate of diffusion of oxygen through the surface layers of photo-oxide and not by the intensity or wavelength of the exciting light.[82] If this is a true surface effect, as is presumed to be the case, the primary process involves the transport of excitation energy to the surface layers of the crystal.

A consideration of the nature of the energy levels in crystals is necessary at this stage. According to the theory of Frenkel[83] and Davydov,[84] the energy levels in a molecular crystal bear a definite relation to these levels in the isolated molecule. During light absorption there appear in the crystal waves of excitation (a transfer of excitation from one molecule to another). The solution of the equation that defines the movement of the molecules in the excited states can be obtained for two limiting cases, corresponding to the appearance in the crystal of two types of excitation waves: (i) the excitation passes from one molecule to another so rapidly that the molecules cannot be displaced to new equilibrium positions; and (ii) the excitation passes from one molecule to another so slowly that the molecules

[79] Chynoweth, *J. Chem. Phys.*, 1954, **22**, 1029.
[80] Kanda and Sponer, *J. Chem. Phys.*, 1958, **28**, 798.
[81] Hochstrasser and Richie, *Trans. Faraday Soc.*, 1956, **52**, 1363.
[82] Hochstrasser, *Canad. J. Chem.*, 1959, **37**, 1123.
[83] Frenkel, *Phys. Z. Sowjet.*, 1936, **9**, 158.
[84] Davydov, *J. Exp. Theoret. Phys.* (*U.S.S.R.*), 1948, **18**, 210.

have time to take up new equilibrium positions. In the latter case there arises a local deformation which travels slowly throughout the crystal. Internal conversion of excitation energy, that is, the conversion of optical excitation energy into heat, manifests itself through case (ii). Transfer of excitation energy between the two types mentioned above is possible and the direction of transfer will depend on the relative frequencies of absorption leading to these modes of excitation. Possibly, in the crystal, intersystem crossing will manifest itself as localisation of excitation energy. The passage of triplet excitation throughout the crystal will be very slow and depend on the movement of crystal imperfections, as in case (ii). The Frenkel–Davydov theory predicts that in the crystal the states of the isolated molecule will be split into a broad band (the exciton band). The width of this band depends on the magnitude of the transition probability between the excited state and the ground state in the isolated molecule. Consequently the triplet levels will not be split into a band as the extinction coefficient for $T \leftarrow S$ absorption is virtually zero in the molecule. Thus intersystem crossing involves energy transfer from a non-localised state to a localised state (molecular level) which does not move with the exciton wave. Such considerations probably apply, not only to molecular crystals, but also to dimers and molecular aggregates. McRae and Kasha[85] have discussed these cases and have shown the manner in which one would expect the fluorescence and phosphorescence yields to behave in such systems. Although the general features of the Frenkel–Davydov theory have been confirmed by absorption and emission spectroscopy of molecular crystals, there has been very little work done on the photochemistry of such systems which might aid in the elucidation of the nature of the primary processes.

Measurements of the temperature-dependence of fluorescence in conjunction with quantum yields of photo-oxidation should be made to decide whether or not photo-oxidation and fluorescence are competitive processes.

There are three distinct types of luminescence observed from pure crystals. When reference is made to crystal luminescence, it is necessary to distinguish between these. The first is the short-lived fluorescence which has a spectral location and a lifetime similar to those of the isolated molecule, *i.e.*, singlet–singlet emission. The second is the long-lived phosphorescence which resembles the normal phosphorescence in its approximate spectral location. The third is a luminescence of longer lifetime than the fluorescence, the two appearing in the same spectral region. The nature and origin of the third type is not certain although it appears to be quite a general phenomenon.[86] Each of these emissions arises initially through the absorption of light into the singlet state of the crystal, and no significant direct excitation of a metastable state is involved.[87]

[85] McRae and Kasha, *J. Chem. Phys.*, 1958, **28**, 721.
[86] Blake and McClure, *J. Chem. Phys.*, 1958, **29**, 722.
[87] Belikova, *Opt. i Spekt.*, 1959, **6**, 117.

During the formation of a transannular peroxide, a drastic structural change must occur, as is illustrated in Fig. 8 for tetramethylrubrene. A large

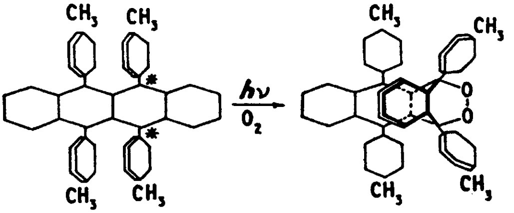

FIG. 8. *The photo-oxidation of tetramethylrubrene.*[82]

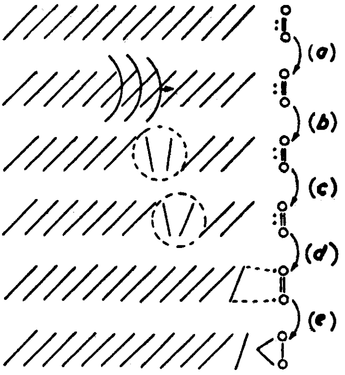

FIG. 9. *A model to represent the photo-oxidation which takes place on the surface of a molecular crystal.*

amount of lattice distortion is necessary to allow the hydrocarbon to twist about the 5,12-positions and this can be explained in terms of the scheme shown in Fig. 9. The lines represent a linear aggregate of molecules as, for example, along a particular crystal dimension. Step (*a*) is the initial light absorption which gives rise to the excitation of a non-localised crystal excited state. The arrowed arcs represent wave-fronts moving very rapidly through the crystal, or along the aggregate when no resultant configurational change occurs. Step (*b*) involves the trapping of a quantum of excitation energy which then moves along the aggregate very slowly and hence separates from the exciton wave. Steps (*c*) and (*d*) show the movement of the imperfection until the surface is finally reached; at (*e*) the reaction with oxygen physically adsorbed on the surface takes place. The variation of the slope of the dislocated molecule in this two-dimensional representation is intended to represent a damping of the localised excitation energy as the excess of energy is taken up in the lattice vibrations. There appear to be three factors which determine the extent of the oxidation, if any, of a molecular crystal: (i) the crystal must not have unit quantum yield of fluorescence, otherwise none of the electronic energy would become localised in this sense; (ii) the imperfections can move rapidly enough for the surface of the crystal to be reached before the electronic energy is transferred into the vibrations of the lattice and within the radiative lifetime of the triplet–singlet emission; and (iii), should conditions (i) and (ii) be favourable, the oxygen molecules can reach the hydrocarbon crystal surface, *i.e.*, permeate the oxide layer during the period that the surface molecules retain some electronic excitation energy. In the photo-oxidation of pure crystals of tetramethylrubrene, it was apparent that (iii) was the limiting factor. The measured quantum yield of oxidation in one system was 0·001, but this could be momentarily increased by at least one order of magnitude if the crystals, after preliminary oxidation, were allowed to stand in oxygen for a few hours and were then re-irradiated.[82]

Whether or not the model presented here approaches reality still remains to be seen. However, when dealing with molecular crystals it is important to realise the scope of the Frenkel–Davydov theory.

So far we have used the term exciton only in the sense described by the Frenkel–Davydov theory. Many workers use this term to describe a different type of excitation and, although the latter usage is normally confined to ionic crystals, the extension to molecular crystals is often obvious. The primary act after light absorption by a crystal is the production of mobile excitons, which, as before, are waves of excitation energy. These lose thermal energy to the lattice until they come to rest and the excited electrons revert to the ground state with accompanying phonon emission.* As an alternative the mobile excitons may, during their lifetime, interact with crystal imperfections where they are ultimately trapped. The resultant species, which is a trapped exciton, consists of an electron held by its mutual attraction for the trap and the hole. This trapped exciton will have a characteristic lifetime before it finally reverts to a localised exciton. The trapped excitons may also dissociate into an electron and a mobile hole, but to effect this dissociation some extra energy is required. The ionisation potential of an aromatic molecule is normally about 7·5 ev. The energy of the exciton cannot be greater than *ca.* 3 ev if near-ultraviolet light is employed. However, such extra energy could be obtained from high-energy trapping centres in the crystal.

Another possibility arises and this involves the "bimolecular" reaction between the trapped exciton and a mobile exciton. This interaction may result in chemical reaction as, for example, in the photolysis of azides.[88] In order that a reaction can occur at a surface according to this description, traps or imperfections must be present at the surface. The excitation energy

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*A *phonon* is a quantum of linear motion of crystal-lattice vibrational energy. In gases and liquids an excess of molecular vibrational-energy is rapidly removed by collisions, which lead to the transfer of this energy. In crystals the excited molecular vibrations are only acceptable to the crystal lattice as the much smaller quanta *phonons*. Thus internal conversions between excited states in crystals of the molecular type occur through phonon–exciton interactions in the lattice.

[88] Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **209**, 550.

is transported to these traps rapidly *via* mobile excitons, and the trapped exciton which results can react with adsorbed gas if this is available. The photochemical yield is then determined by the rate of union of the trapped exciton with oxygen in relation to the rates of the various processes which result in deactivation of the trapped exciton.

The extension of such ideas to explain transfer of excitation energy and electronic conduction in aggregates of more complex molecules, such as chlorophyll in lamellae, has been discussed by Kasha.[89] This author presents a simplified, though accurate, account of the exciton theory, with particular reference to the photosynthetic system. In an aggregate such as that of chlorophyll in the chloroplast, excitations to the exciton band will have an "allowedness" which depends on the relative orientation of the molecules in the lamellae. The molecular triplet level lies below the exciton band and the probability of populating this level depends on the relative rates of fluorescence and internal conversion compared with intersystem crossing from the *thermally equilibrated* crystal band to the triplet level. In some aggregates, the lowest component of the exciton band combines with the ground state with very low probability. Thus the band remains populated for a long time compared with the intersystem-crossing time. It is to be expected on this basis that the phosphorescence of the aggregate will be enhanced over that of the monomer and in turn the fluorescence is reduced. These considerations could account for the very low quantum yield of fluorescence for chlorophyll *in vivo.*

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[89] Kasha, *Rev. Mod. Phys.*, 1959, **31**, 162.