LIGHT ABSORPTION AND PHOTOCHEMISTRY
(including photo-polymerisation and the effects of light on dyes)

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To advance the subject of light absorption by molecules, chemists need (A) a pictorial standpoint to understand the phenomena qualitatively, and (B) means of calculating from simple principles the wave-lengths of absorption bands, the band intensities, their polarisations, whether a band corresponds to photodissociation or to a vibrationally stable excited state, the coupling of nuclear vibrations to the excitation and the contour of the band, the relations between absorption and fluorescence or phosphorescence, and the effect of solvent medium on absorption. A number of reviews have dealt with some of these matters.[1-8]

Progress towards solutions of these problems has consisted, first, in a clear understanding of the application of wave-mechanical principles to the spectra of the hydrogen atom and the molecule H_2, and secondly, in attempts to relate more complicated molecular examples to hydrogen by successive approximations from simplified initial assumptions. Round the nucleus of a hydrogen atom a series of wave-patterns or orbitals are theoretically assumed whose amplitude squares give the charge distribution of an electron " occupying " the orbital. The magnetic properties of the electron require each orbital to have two forms of opposite magnetic direction or " spin ", and no more than one electron can occupy any one magnetic form of any one orbital (Pauli principle). The different energy levels of the atom are represented by the electron occupying different orbitals. The orbitals resemble the three-dimensional wave-patterns of vibrations in a medium about a point in space; the fundamental, $1s$, of lowest energy being a spherical-shaped wave with maximum amplitude at the centre. First harmonics have a nodal surface, spherical for $2s$ and planar for $2p$. Second harmonics have two nodes; besides the $3s$ and $3p$ types there are $3d$ with two nodal planes. The process of light absorption is conceived as in Fig. 1. The energy of the light here causes a $1s$ orbital to change to a $2p$ orbital, and the hour-glass shape of the latter, with its separation of negative charge into two halves, may be visualised as due to the directional action of the electric vector of the light. The intensity of the transition is measured by the square of the " dipole moment of transition ", which may here be pictured as measured by the separation distance d of the " centres of gravity "

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[1] W. C. Price, *Ann. Reports*, 1939, **36**, 47.
[2] G. N. Lewis and M. Calvin, *Chem. Reviews*, 1939, **25**, 273.
[3] R. A. Morton, *Ann. Reports*, 1941, **38**, 7.
[4] E. J. Bowen, *ibid.*, 1943, **40**, 12.
[5] E. A. Braude, *ibid.*, 1945, **42**, 105.
[6] C. A. Coulson, *Quart. Reviews*, 1947, **1**, 144.
[7] A. Maccoll, *ibid.*, p. 16.
[8] L. N. Ferguson, *Chem. Reviews*, 1948, **43**, 385.

of the two halves of the p orbital. $1s \longrightarrow 2s$ transitions are " forbidden " because no " transition moment " is involved, and $1s \longrightarrow 3d$ because two new nodes would have to be simultaneously developed, which would need " quadrupole " radiation. The energy levels of the H atom are accurately calculable from the Schrödinger equation.

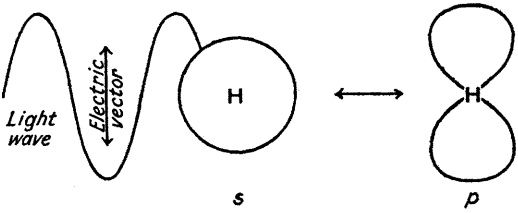


FIG. 1
Light absorption by a hydrogen atom.

The hydrogen molecule is then treated as a two-centre atom ; spherical s orbitals become elongated σ orbitals rotationally symmetrical about the molecular axis.[6] Two electrons in a σ_g orbital form the ground state. There are two first harmonics with one nodal plane corresponding to atomic p orbitals, σ_u with the plane crossing the axis and π_u containing the axis,

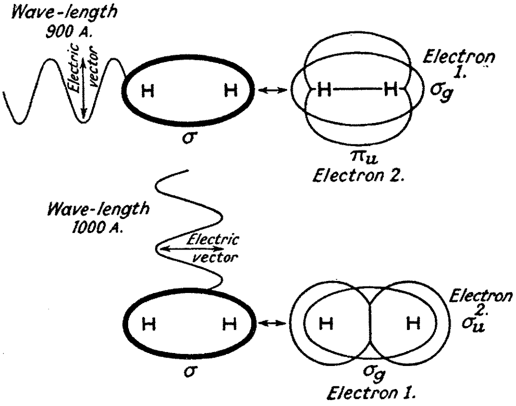


FIG. 2
Absorption by a hydrogen molecule.

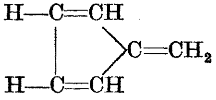
(Note : σ orbitals are rotationally symmetrical about the molecular axis ; π orbitals have a nodal plane through the atomic nuclei. The suffixes g and u mean that if a straight line is drawn in any direction through the centre of the molecule the wave-function has the same or the opposite sign respectively as the centre is passed. On light absorption one electron passes to an orbital having an extra node, *i.e.*, surface at which the wave-function changes sign, which is at right-angles to the electric vector direction of the incoming plane-polarised light.)

the latter not being rotationally symmetrical. The absorption bands of hydrogen at 1000 and 900 A. arise from " permitted " transitions of one electron to these orbitals, and are highly directional since the new node is developed at right-angles to the electric vector (see Fig. 2) (*i.e.*, transitions are polarised along and across the molecular axis respectively). No change of spin normally occurs on light absorption by undisturbed atoms. Triplet levels of H_2 reached by transitions similar to the above with change of spin of the electron occur at lower energies than the singlet levels, and theoretically might be observed as excessively weak absorption bands at longer wave-lengths in hydrogen molecules whose symmetry is distorted by collisions, etc. The principles on which to find answers for many of the queries above are therefore all illustrated by the molecule H_2. Other queries depend on the shapes of the potential-energy curves of the molecule. Electronic excitation does not immediately alter inter-atomic distances (Franck–Condon principle). The excited molecule is thus usually formed in a compressed condition and begins to vibrate. Vibrations may also be coupled with electronic excitation because of symmetry requirements.

In organic chemistry the first molecule of interest from the point of view of light absorption is ethylene, $H_2C{=}CH_2$. The double bond may be regarded as composed of two electrons in an essentially σ_g-shaped orbital (Fig. 2) and two in one resembling the π_u of H_2. The longest wave-band at 1750 A. is treated as the transition of one electron from the π_u to an " antibonding " π_g orbital, having an additional nodal plane crossing the molecular axis. For light absorption to occur most efficiently, therefore, the electric vector must lie along the C—C link. This has been experimentally verified for C=C- and N=N-containing molecules oriented in crystals.

To obtain quantitative predictions about absorption bands the direct route would be to treat the molecule as a two- or more centred system of positive nuclei surrounded by electrons whose orbital energies are to be calculated. This being impossibly difficult, the problem is broken down by attempting to approximate to the molecular orbitals by combining atomic orbitals, which themselves are approximations for atoms other than hydrogen. Two ways of combining atomic orbitals have been developed by different schools, the valence bond (V.B.) and the linear combination (L.C.A.O.) methods. The details of these methods, both involving great mathematical complexity, have been given elsewhere.[6, 7] Judged by their quantitative capabilities there is little to choose between them. The present purpose of the Reviewer is to compare them from the " pictorial " point of view. In ethylenic and azo-type molecules the L.C.A.O. method proceeds as outlined above, representing light absorption as a $\pi_u \rightarrow \pi_g$ transition. The V.B. method regards ethylene as a " resonance hybrid " of valency forms $CH_2{=}CH_2$ and $\overset{+}{C}H_2{-}\overset{-}{C}H_2$. The energy levels of the molecule are derived by mathematical treatment, giving a series of " combinations " of the above structures in varying proportions. Depending on the proportions, each level is " stabilised " or lowered in energy by what is called " resonance energy ". To a first approximation, however, the ground level is mostly $CH_2{=}CH_2$ and the excited level $\overset{+}{C}H_2{-}\overset{-}{C}H_2$. The fact that azo-compounds absorb at longer wave-lengths than ethylenic is attributed to a relatively smaller resonance energy of the former in the ground state and a larger in the excited state, diminishing the energy difference of the levels.[2] A similar explanation can be given to the fact that compounds of type =C—C=

absorb at longer wave-lengths than those of type =N—N=. Here the excited states are mostly composed of the resonance forms —C=C— and —N=N—, and the relatively greater resonance energy of the former brings its energy level down towards the ground state. Similarly, the longer-wave absorption of fulvene (I) compared with that of benzene may be attributed to an unusually large lowering of the energy of the ground level of the latter because of resonance between Kekulé and Dewar structures of nearly equal energy. Further comparisons have been made of absorption band positions between compounds whose "resonance", either in the ground or in the excited state, is increased or diminished by strain, steric effects, etc.[8]



(I.)

Although this use of the V.B. standpoint, applied in a non-quantitative way to explain trends in light absorption, is simple and successful up to a point, it does not seem to lend itself to wide development. It is therefore important to see how far interpretations based on the L.C.A.O. method can be employed ; for although this method takes one away from the "valency" picture it more closely follows the fundamental concepts of wave-mechanics in treating electrons as wave-patterns. On the molecular-orbital picture every electron is in principle distributed over the molecule as a whole ; some may be treated as almost entirely localised as lone pairs on atoms or in particular bonds ; others, as the π electrons of conjugated systems, as largely delocalised. The differences in the absorption band positions of the carbon and nitrogen compounds discussed above is then referred to differences of extents of "localisation" of electrons involved in the transitions, "delocalisation" being analogous to "resonance" and lowering energy levels. For pictorial use, the molecular orbital standpoint seems to have special advantages in affording clearer insight into the light absorption of highly conjugated molecules, into the directional properties of electronic transitions, into triplet levels, and into transitions involving non-bonding electrons. The following discussion is intended to bring out these points. The V.B. method relies for its appeal to chemists (as distinct from its use by mathematicians) on its representation of molecules by valency structures. The precision of this attempt, however, fades as the molecule becomes more conjugated. Naphthacene, for example, has 5 Kekulé structures, 110 Dewar-like structures, and 649 doubly excited structures. Its ground state must be conceived as a resonance hybrid of 40% of the Dewar forms, 60% of the doubly excited forms, with a negligible contribution from the Kekulé forms.[9] The molecular orbital concept applied to benzene treats the atomic skeleton as a multi-nuclear atom, and assigns the six "aromatic" electrons in pairs to wave-patterns with one node, two nodes, etc.[10] These patterns are shown in Fig. 3 on the top line, all (being π-type electrons) having a nodal plane coincident with the plane of the ring and 1 having no additional node, 2 and 3 having a node crossing the ring (electron waves of opposite phase on the two halves), 4 and 5 with two nodes. A sixth, not shown,

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[9] A. and B. Pullman, *La Revue Scientifique*, 1946, 145.

[10] K. F. Herzfeld, *Chem. Reviews*, 1947, **41**, 233.

would have three crossing nodes and therefore opposite wave phases on consecutive carbon atoms. The ground level has orbitals 1, 2, and 3 filled, as shown by the dots (black and white circles indicating opposite spins). Observed absorption bands correspond to the electron transitions given in the figure. The orbital energies increase from 1 to 5 and the levels increase in energies downwards. The strongest band, at 1800 A., arises from a permitted transition resembling a $1s \longrightarrow 2p$ atomic transition. The 2600 A. band, the " benzene band " usually observed in ultra-violet spectrographs, is weak since it is " allowed " only when the molecular symmetry is distorted by a particular type of nuclear vibration. At 3400 A. is an extremely weak band which has been recognised only from phosphorescence effects, the excitation being normally " forbidden " because of change of spin of the electron. Since ordinary instruments permit measurements on the 2600 A. band and on part of a band at 2000 A. only, comparisons of absorption-band

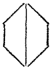
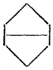
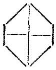
	1	2	3	4	5	
Symmetry symbol of level.						Absorption band, A.
$^1A_{1g}$	● ○	● ○	● ○			(Ground level)
$^3B_{1u}$	● ○	●	● ○	●		(Unobserved triplet level)
^3E_u	● ○	●	● ○		●	(Unobserved triplet level)
$^3B_{2u}$	● ○	● ○	●	●		3400 Very weak triplet level
$^1B_{2u}$	● ○	● ○	●	○		2600
$^1B_{1u}$	● ○	●	● ○	○		2000
^1E_u	● ○	●	● ○		○	1800 Very strong

Fig. 3

Orbitals of benzene.

data on benzene and its derivatives have been confined to these wavelengths. Recent work has shown a much greater regularity of the effects of substituents on the 2000 A. band than on that at 2600 A.[11] This clearly points the way to an extension of the work to the 1800 A. band where the complications due to the largely " forbidden " nature of the others, particularly in respect of band intensity, may be minimised.

Anthracene has absorption bands in the near ultra-violet at 3700 A. and at 2500 A. The former has a vibrational structure, the latter not. The fluorescence excited in either band corresponds with the transition from the 3700 A. level to the ground state. The molecule excited at 2500 A. must therefore revert in a time short compared with a vibration period to the 3700 A. level, and radiate from thence. This is remarkable in view of recent work on the directional nature of these transitions.[12] Molecular orbitals of anthracene are shown in Fig. 4. The 14 " aromatic " electrons in the ground level are disposed in the 7 lower wave-patterns, while above are shown (dotted) the unfilled orbitals to which electrons pass on excitation. The transitions are such that the electric vector of the light must lie along the short axis of the molecule for the 3700 A. band and along the long axis for the 2500 A. band. Anthracene crystals thus possess strong dichroism in the ultra-violet. This treatment of the problem is attractive because of its relations to molecular symmetry. Just as the V.B. method, however, becomes blurred for highly conjugated molecules, so the molecular-orbital method encounters similar difficulties when developed mathematically. The original L.C.A.O. method of constructing molecular orbitals has to be refined by allowance for electron interaction which results from simple superposition of electron orbitals and further by the possibilities of interactions of configurations of electrons of the same symmetry.[13] This is

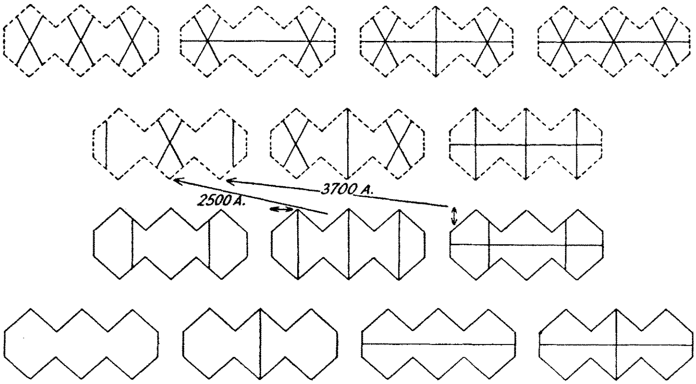


FIG. 4
Molecular orbitals of anthracene.

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[11] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.
[12] C. A. Coulson, *Proc. Physical Soc.*, 1948, **60**, 257.
[13] J. Jacobs, *ibid.*, 1949, **62**, 710; D. P. Craig, *Proc. Roy. Soc.*, 1950, **200**, 474.

virtually equivalent to a concept of " resonance " of electrons between orbitals in the representation of a molecular energy level.

In spite of this complication, the molecular-orbital picture is useful for visualising triplet levels of conjugated molecules (see Fig. 3) which are now recognised as responsible for phosphorescence bands and for some weak absorption bands.[14] Considerations of band strength are now as important as those of band wave-length. The latter gives the energy of the orbital transition, and the former, defined by the band area $\int \varepsilon . d\omega$, where ε = molar extinction coefficient of a dilute solution and ω = wave-number of centre of band, gives the mean life τ of the excited level ; all the excited molecules being assumed to revert by radiation to the ground level, we have (approximately) : [15]

$$1/\tau = 2{\cdot}88 \times 10^{-9}\omega^2 \int \varepsilon . d\omega$$

Weak bands therefore correspond to large τ values, *i.e.*, to transitions forbidden in either direction. (Actual mean lives of excited levels may be shorter because of internal or collisional energy degradation.) It is not easy, however, to decide whether a weak band arises from a singlet–singlet transition forbidden by symmetry principles or from a singlet–triplet transition. The weak band at 3000 A. shown by aldehydes and ketones is attributed to the former ; [16] the red bands of nitroso-compounds to the latter.[15] Magnetic measurements can be used to decide in favourable cases,[17] but more useful may be a study of the effect of substituents in changing the band wave-length and intensity, together with theoretical expectations, mostly as yet undeveloped. A complication in these matters is the effect of one absorption band on another. Weak bands may " borrow " intensity from neighbouring strong bands, and may also " borrow " polarisation directions as well, destroying the sharpness of some of the above considerations.[18]

For an electronic transition where every molecule absorbs light when its " target area " is struck, the maximum possible extinction coefficient can be calculated from geometrical principles alone.[19] These give $\varepsilon_{\max} = 0{\cdot}87 \times 10^{20}a$, where a = " chromophore area ", which can be approximated to from bond dimensions. It is interesting to compare this with the approximate expression $\varepsilon_{\max} = 1{\cdot}24 \times 10^{20}d^2$, which may be derived from the theory given above for an absorption band at 4000 A. with a " half-width " of 5000 cm.$^{-1}$, where d = distance electronic charge is transferred during the absorption (cf. Fig. 1 and discussion). For an elongated conjugated molecule a is a product of a large length and a small width, while d appears as a square. Unfortunately detailed comparisons of the significance of these quantities and their extended quantitative application are limited by " intensity borrowing " between absorption

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[14] M. Kasha, *Chem. Reviews*, 1947, **41**, 401.

[15] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.

[16] H. L. McMurry, *J. Chem. Physics*, 1941, **9**, 231, 241.

[17] G. N. Lewis and M. Calvin, *J. Amer. Chem. Soc.*, 1945, **67**, 1232.

[18] R. S. Mulliken and C. A. Ricke, *Rep. Prog. Physics*, 1941, **8**, 231.

[19] E. A. Braude, *J.*, 1950, 379.

bands and non-fulfilment of the condition of fully allowed transitions in most examples.

A simplified method of calculating both the wave-lengths and the intensities as well as determining the orbital symmetries for aromatic hydrocarbons and dyes has recently been developed.[20] The π electrons of the conjugated system are treated mathematically as a problem of " electrons in a box " [21] which has been successfully used in the theory of metals. Such calculations avoid the use of individual atomic orbitals in constructing the molecular ones and are relatively easy to understand and work with.

Electron Transfer Spectra.—The brown solutions of iodine in aromatic hydrocarbons, alcohol, etc., show an intense ultra-violet absorption band closely resembling that of the ion I_3^-.[22] The effect is favoured by substitution of methyl groups in the ring, which tend to increase the π-electron donating power. The interaction of the molecules must be by polarised complex formation held together by van der Waals forces, and the strong band intensity indicates that light absorption causes a considerable shift of electron density distribution within the complex. Whether the iodine molecule is oriented parallel or perpendicular to the hydrocarbon ring, and the direction of the charge displacement on light absorption is not yet known.

The intense absorption bands of ferric ion complexes have been interpreted as electron-transfer spectra.[23] The ferric ion has five *d* electrons, which occupy three of the 3*d* orbitals in complexes, the remaining two 3*d*, one 4*s*, and three 4*p* orbitals being filled by electrons supplied by the co-ordinating groups. Very weak bands at 5500 A. and 7000 A. are ascribed to forbidden $d \longrightarrow d$ transitions among the five atomic *d* electrons. Intense bands whose wave-lengths depend on the electron-donating powers of the co-ordinate groups are found for complexes in the ultra-violet or visible region, *e.g.*, at 5000 A. for ferric thiocyanate. Excitation has been attributed to the passage of an electron from one of the co-ordinate links to an atomic *d* orbital, giving a ferrous ion and a radical, *e.g.*, SCN with thiocyanate. The further reactions of such radicals account for the light-sensitiveness of ferric complexes, particularly in presence of reducing or oxidising agents. The photochemical decompositions of ferric, cobaltic, and manganic oxalates, tartrates, etc., may be imagined to be of this nature:

$$Co^{3+}(C_2O_4{}^{2-})_3 + h\nu \longrightarrow Co^{2+}(C_2O_4{}^{2-})_2 + C_2O_4{}^-$$

$$2C_2O_4{}^- \longrightarrow C_2O_4{}^{2-} + 2CO_2$$

Proof of the reality of such electron transfers has been found from the effects of the radicals in initiating polymerisation.[47] What may be queried, however, is the special use of the term " electron-transfer spectra " for certain absorption bands. The bands may be compared with those of the molecule HI

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[20] H. Kuhn, *J. Chem. Physics*, 1949, **17**, 1198 ; J. R. Platt and H. B. Klevens, *ibid.*, pp. 470, 481, 484.

[21] See ref. 24, p. 61.

[22] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[23] E. Rabinowitch and W. H. Stockmayer, *ibid.*, 1942, **64**, 335 ; *Rev. Mod. Physics*, 1942, **14**, 112.

or the other hydrogen halides. Here the excited state is anti-bonding and photo-dissociates into atoms.[24] The ground state is only partly ionic, however, and to attribute the absorption band to an electron-transfer mechanism would be an exaggeration, particularly for hydrogen iodide. The linkages in the complexes must also be partly covalent and partly ionic. Secondly, there is the important question whether the long-wave limit of the so-called electron-transfer band provides a value for the energy of the electron transference. We have to distinguish between bands of this kind, characterised by high extinction coefficients because of the large " dipole moment of transition ", and bands due to atomic $d \rightarrow d$ transitions of the metallic ion, which, being " forbidden ", must be weak. In ferric complexes the distinction is experimentally very clear. Other evidence is available for chromic complexes. Chromium is the only transitional element whose spark spectrum has been analysed to give the ground level of the ion (Cr^{3+}) in the gaseous state. Its two lowest $d \rightarrow d$ forbidden transitions are ${}^4F \rightarrow {}^2G$ at about 6700 A. and ${}^4F \rightarrow {}^2H$ at about 4900 A. Practically all chromic complexes in solution have absorption bands near these positions, *e.g.*, chrome alum, 6400—5300 and 4700—3700 A., and chromitartrates, maxima at 6100 and 3750 A. It is reasonable to conclude that these rather weak bands in solution correspond to the atomic $d \rightarrow d$ transitions, and this accords with the low light sensitivity of chromic complexes. Cobalt salts, however, show features which complicate the simple picture. Solutions of cobaltioxalate have two fairly weak bands at 6050 and 4260 A., and a strong one at 2500 A. The last would be identified as the electron-transfer band, and the first two as $d \rightarrow d$ transitions. Although the solutions are stable under 6050-A. illumination, however, they decompose with a quantum efficiency of about unity at 4260 A.[25] Here the reduction of the cobaltic ion to cobaltous by electron transfer appears to be a secondary change following an initial *d–d* orbital shift, the transfer occurring at a much lower energy than the concept of the 2500 A. band as the " electron transfer band " would indicate. The time seems ripe now for a systematic exploration of inorganic complex-ion spectra, and a clearer insight into the problem awaits new measurements.

Photochemistry in Relation to Textiles

The photochemical behaviour of dyes on fabrics has been discussed at a recent symposium.[26] The observed effects may be regarded from two aspects, that of the practical dyer and that of the physical chemist. The subject also divides itself into two parts, the fading or changes of colour of dyes on long illumination, and the " tendering " of fabrics, particularly cotton, found when certain dyeings are exposed to light. The practical man requires data corresponding closely to the behaviour of dyes under conditions of use, evaluated by practical judgments. He is interested not so much in the extent of photochemical action as in what the changes in

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[24] E. J. Bowen, " Chemical Aspects of Light ", Clarendon Press, 1946, p. 94.

[25] J. Vranek, *Z. Eleckrochem.*, 1917, **23**, 336.

[26] *J. Soc. Dyers Col.*, 1949, **65**, 585—788.

appearance or strength are. Considerable fading of some shades is less objectionable than a little fading in others. In attempting to define resistance to the effect of light the difficulty is met that in some cases the observed change is slow in the early stages and accelerates later, while in others a small initial rapid change quickly slows down with time.[27] Changes of humidity,[28] temperature, accessibility of dye to air, presence of other dyes, traces of impurities such as copper or iron, differences in spectral distribution between testing lamp and sunlight,[29] and other factors all contribute to make the practical assessment of the effect of light on dyes a very complex matter.[30]

The physical chemistry of the photoreactions of dyes is now in process of taking shape as a coherent picture. It was first shown for basic fluorescent dyes,[31, 32] and later for azo [33, 34] and vat dyes,[35] that excitation of the dye molecule by light may lead to the formation of a reduced dye radical and oxidation of some substance present. This process competes with loss of excitation energy by fluorescence, internal degradation, or collisional degradation. Fluorescent dyes, by reason of their relatively long life in the excited state, have a greater opportunity of reaction, unless very long-life triplet levels of the dye are formed.[36] The possible part played by triplet levels arising from partial degradation of the excitation energy is still obscure. If D represents a dye molecule, we have :

$$\mathrm{D} + h\nu \longrightarrow \mathrm{D}^* \quad \text{(singlet excited level)} \quad . \quad . \quad . \quad (1)$$

$$\mathrm{D}^* \longrightarrow \mathrm{D} + h\nu' \quad \text{(fluorescence)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{D}^* \longrightarrow \mathrm{D} \quad \text{(degradation of energy to heat)} \quad . \quad (3)$$

and possibly the change of D* into a triplet excited level (not distinguished below from D*).

If a substance AH capable of being oxidised is present in the system, the following reaction may occur, giving a pair of reactive radicals :

$$\mathrm{D}^* + \mathrm{AH} \longrightarrow \mathrm{DH} + \mathrm{A} \quad \text{or} \quad \mathrm{D}^- + \mathrm{AH}^+ \quad . \quad . \quad (4)$$

Factors influencing the efficiency of this reaction will be the redox potentials of D* and AH, the rate of encounter of D* and AH, and the extent of reverse change after dissipation of the excitation energy. The rate of encounter will depend on whether D* and AH are linked as a complex or have to diffuse together ; if the latter, rates of diffusion and the mean life

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[27] T. H. Morton, *J. Soc. Dyers Col.*, 1949, **65**, 597 ; T. Vickerstaff and D. Tough, *ibid.*, p. 606.

[28] W. L. Lead, *ibid.*, p. 723.

[29] B. S. Cooper and F. S. Hawkins, *ibid.*, p. 586.

[30] S. Burgess, *ibid.*, p. 732 ; G. Nordhammar and N. Gralen, *ibid.*, p. 741.

[31] J. Franck and F. Haber, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1931, **13**, 250 ; F. Haber and J. Weiss, *Proc. Roy. Soc.*, 1934, *A*, **142**, 332.

[32] J. Weiss, *Trans. Faraday Soc.*, 1939, **35**, 48 ; 1946, **42**, 133.

[33] B. E. Blaisdell, *J. Soc. Dyers Col.*, 1949, **65**, 618.

[34] E. Atherton and I. Seltzer, *ibid.*, p. 629 ; N. F. Desai and C. H. Giles, *ibid.*, p. 639.

[35] C. H. Bamford and M. J. S. Dewar, *ibid.*, p. 674.

[36] M. Kasha, *Chem. Reviews*, 1947, **41**, 401 ; E. J. Bowen, *J. Soc. Dyers Col.*, 1949, **65**, 613.

of D* are important. Hemming in of the reactants by solvent molecules, so that they cannot drift apart before they react again in the reverse direction (having lost the original excitation energy) (Franck–Rabinowitch " cage " effect), usually makes the measurable efficiency of reaction (4) very small.

A decision between the possibilities of DH + A or $D^- + AH^+$ in reaction (4) is not easy to make ; each has been championed by different investigators.[32, 37] It is probably true to say that experimental observations favour the first possibility of a hydrogen-atom transfer where the reactants collide bimolecularly, and favour the electron-transfer mechanism where the reactants are initially bound in a complex (cf. cobaltioxalates). If A is a ferric or similar ion the electron transfer would seem more probable.

The production of radicals by reaction (4) leads to complicated secondary changes which are gradually becoming unravelled.[38] Many of these complexities are due to the effects of molecular oxygen. Dyes are relatively stable to light and oxygen in non-oxidisable solvents such as water ; in presence of organic compounds a number of types of effect may be observed, some of which are illustrated below.

Azo-dyes in organic solutions free from oxygen are reduced by light to the hydrazine derivatives, and later to substituted anilines.[33] Here AH in reaction (4) is the solvent, which is dehydrogenated in reactions (4) and (5) :

$$DH + AH \longrightarrow DH_2 \text{ (hydrazine)} + A \quad . \quad . \quad . \quad (5)$$

The solvent radicals mutually interact :

$$A + A \longrightarrow \text{non-reactive products} \quad . \quad . \quad . \quad (6)$$

In presence of oxygen the dye remains undecomposed and the solvent is photo-oxidised. It is probable that the DH radicals react thus :

$$DH + O_2 \longrightarrow D + HO_2 \quad . \quad . \quad . \quad . \quad (7)$$

The solvent is then oxidised by a complex radical reaction involving the attack of HO_2 on AH and of O_2 on the radicals A. A very complete study of the photosensitised oxidation of tetralin by certain vat dyes indicates a similar mechanism.[37] Here it has been possible to interpret the chain process of oxidation as :

$$A + O_2 \longrightarrow AO_2 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$AO_2 + AH \longrightarrow AO{\cdot}OH + A \quad . \quad . \quad . \quad (9)$$

with chain-ending reactions :

$$\left.\begin{array}{r} A + A \longrightarrow \\ A + AO_2 \longrightarrow \\ AO_2 + AO_2 \longrightarrow \end{array}\right\} \text{non-reactive products} \quad . \quad . \quad . \quad (10)$$

In addition it was found that molecular oxygen deactivated the excited dye molecule :

$$D^* + O_2 \longrightarrow D + O_2 \quad . \quad . \quad . \quad . \quad (11)$$

Reaction (11) may possibly involve the production of less reactive triplet levels of D and O_2.

Some dyes of a reactive nature are photo-bleached irreversibly by oxygen.

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[37] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1949, *A*, **198**, 252.

[38] R. Livingston, *J. Soc. Dyers Col.*, 1949, **65**, 781.

The effect of traces of reducing agents in accelerating the reaction is significant.[39] This indicates that reactions (7) and (8) provide intermediate peroxide radicals which in some circumstances can oxidise and destroy the original dye.

Examples are known of reversible photo-reductions of dye molecules by other molecules, *e.g.*, the effect of phenylhydrazine sulphate on illuminated methylene-blue : [40]

$$D^* + Ph{\cdot}NH{\cdot}NH_3^+ \longrightarrow DH_2 + Ph{\cdot}N{:}NH_2^+ \qquad . \quad . \ (12)$$

Reaction (12) reverses itself in the dark. It must take place as a two-stage reduction beginning with reaction (4), both stages being reversible when the excitation energy is dissipated.

The same general scheme of reactions is capable of explaining in outline the photosensitised change of one dye in presence of another.[41] The interaction of radicals with ions of variable valency affords a qualitative reason for the effect of inorganic impurities on the stability of dyed materials to light.

An important type of photo-reaction of dyes on fabric, especially cotton, is " tendering ".[42, 43] Certain vat dyes, particularly yellow ones, behave in this way. After exposure to light the cotton is depolymerised and oxidised, so that it falls to pieces, while the dye remains essentially unchanged. The effect is not explicable by reaction (4), where AH is cellulose, but has been shown to result from the intermediate formation of hydrogen peroxide.[42] The effect requires oxygen and is enhanced by moisture and by alkalinity. It has therefore been suggested that the first reaction after excitation of the dye by light is : [35]

$$D^* + OH^- \longrightarrow D^- + OH \quad \text{or} \quad DH + O^- \qquad . \quad . \ (13)$$

followed by reaction (7), giving HO_2 radicals. The OH radicals then oxidise the cellulose giving some carbon dioxide in the neighbourhood of the dye, while the HO_2 radicals dismute to give hydrogen peroxide which diffuses into the fabric and oxidises it to give oxycellulose. Under dry conditions reaction (4) may play a part, followed by (8) and (11), the slowness of the reaction being ascribed to the reversibility of (4).

It is an observed fact that yellow vat dyes are usually much more active photo-tenderers than blue ones. A probable reason is that reaction (13) is bound to be largely reversed by the Franck–Rabinowitch effect. Yellow dyes absorb short-wave visible quanta of greater energy than those absorbed by blue dyes, and this may supply the local thermal energy required for some of the resultants of (13) to break loose from their molecular " cage ".

These effects of dyes in " tendering " cotton are quite distinct from the direct action of ultra-violet light on cellulose.[44] Under 2537-A. illumination

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[39] K. Weber, *Ber.*, 1936, **69**, 1026.

[40] G. Holst, *Z. physikal. Chem.*, 1937, *A*, **179**, 172 ; **180**, 161 ; 1938, **182**, 321.

[41] F. Scholefield and C. Patel, *J. Soc. Dyers Col.*, 1928, **44**, 268 ; F. Scholefield and H. Turner, *J. Textile Inst.*, 1933, **24**, 130 ; J. Böhi, *Helv. Chim. Acta*, 1929, **12**, 121.

[42] G. S. Egerton, *J. Soc. Dyers Col.*, 1949, **65**, 764.

[43] D. Ashton, D. Clibbens, and M. E. Probert, *ibid.*, p. 650 ; A. Landolt, *ibid.*, p. 659.

[44] H. F. Launer and W. K. Wilson, *J. Amer. Chem. Soc.*, 1949, **71**, 958.

cellulose is degraded by C–C and C–O bond splitting, moisture but not oxygen being necessary. At longer wave-lengths some photo-oxidation occurs, but the rates are low because of the small light absorption.

Reversible colour changes in dyed materials exposed to intense illumination are sometimes observed.[45] This phenomenon, called phototropism, is probably due to *cis–trans*-changes in the molecular structures of the dye molecules.

Photosensitised Polymerisations

Vinyl-type polymerisations are chain reactions initiated by free radicals. A convenient way of introducing radicals into the system is by their photochemical production *in situ*, either by opening an ethylene bond to give a diradical, or by the photo-dissociation of benzoyl peroxide, benzoin, diacetyl, and similar organic molecules which give mono-radicals.[46] Ferric complexes in aqueous solution, such as $\mathrm{Fe^{3+}F^-}$, $\mathrm{Fe^{3+}Cl^-}$, and $\mathrm{Fe^{3+}OH^-}$, which yield on illumination ferrous ions and a free radical, are also effective.[47] The rates of photochemically initiated polymerisations are usually proportional to the square root of the intensity of the light, owing to the chain-termination mechanism of bimolecular radical combination. It is now recognised that chain-transfer processes occur during polymerisation ; so that four velocity constants at least are necessary to interpret the rate, those of initiation, propagation, transfer, and termination. For styrene and methyl methacrylate polymerisations the steps may be represented as : [48]

$$\begin{array}{rcll}
2\mathrm{M} & \longrightarrow & 2\mathrm{X} \text{ or } \mathrm{D}_2 & k_1 \quad \text{(Initiation)} \\
\mathrm{X}+\mathrm{M} & \longrightarrow & \mathrm{X} & k_2 \quad \text{(Propagation)}
\end{array}$$

$$\left.\begin{array}{rcll}
\mathrm{D}_2+\mathrm{M} & \longrightarrow & \mathrm{D}_1+\mathrm{R} & 2k_3 \\
\mathrm{D}_1+\mathrm{M} & \longrightarrow & \mathrm{P}_2+\mathrm{R} & k_3 \\
\mathrm{R}+\mathrm{M} & \longrightarrow & \mathrm{P}_1+\mathrm{R} & k_3
\end{array}\right\}\text{(Chain transfer)}$$

$$\left.\begin{array}{rcll}
\mathrm{D}_2+\mathrm{X} & \longrightarrow & \mathrm{D}_1+\mathrm{Q} & 2k_4 \\
\mathrm{D}_1+\mathrm{X} & \longrightarrow & \mathrm{P}_2+\mathrm{Q} & k_4 \\
\mathrm{R}+\mathrm{X} & \longrightarrow & \mathrm{P}_1+\mathrm{Q} & k_4 \\
2\mathrm{X} & \longrightarrow & 2\mathrm{Q} & k_4
\end{array}\right\}\text{(Chain termination)}$$

where D_2 = initial polymer growing at both ends,
D_1 = ,, ,, ,, ,, one end,
R = growing transfer polymer,
P_2 = " dead " initial polymer,
P_1 = " dead " transfer polymer,
X = any active centre,
Q = any " dead " centre.

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[45] E. Stearns, *J. Opt. Soc. Amer.*, 1942, **32,** 282.

[46] H. W. Melville, *Proc. Roy. Soc.*, 1937, *A*, **163,** 511 ; T. T. Jones and H. W. Melville, *ibid.*, 1940, *A*, **175,** 392 ; G. M. Burnett and H. W. Melville, *ibid.*, 1947, *A*, **189,** 456 ; *idem, Nature*, 1945, **156,** 661 ; P. D. Bartlett and C. G. Swain, *J. Amer. Chem. Soc.*, 1945, **67,** 2273 ; 1946, **68,** 2377, 2381 ; R. B. Whyte and H. W. Melville, *J. Soc. Dyers Col.*, 1949, **65,** 703.

[47] M. G. Evans and N. Uri, *ibid.*, p. 709 ; *Nature*, 1949, **164,** 404.

[48] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192,** 309, 329 ; 1949, *A*, **197,** 356.

These four constants can be evaluated by measuring the rate of polymerisation with different initial rates of initiation (light intensity), by the use of a rotating sector or a shutter to " chop " the light beam, and by following the " after-effect " or continuation of the reaction after the illumination is cut off. The photochemical after-effect in vinyl polymerisations is very much longer than those of atom reactions such as the hydrogen and bromine combination.[49]

Miscellaneous Photo-reactions

The quantum efficiency of oxidation of rubber solutions by oxygen in ultra-violet light has been shown to be initially unity.[50] This indicates the formation of a hydroperoxide by direct addition. Only when the concentration of this substance rises high enough for it to absorb light and be itself photochemically decomposed to radicals does an oxidation chain reaction of high photo-sensitivity set in.

Zinc tetraphenylchlorin has been shown to react in light with *o*-quinones, losing two atoms of hydrogen to the latter to give zinc tetraphenylporphin.[51] The rate of reaction is independent of the quinone concentration to such high dilutions that clear evidence is provided to show that a long-life triplet level of the zinc compound is involved. This can be associated with its phosphorescence of mean life 8×10^{-3} sec.

The photolysis of gaseous hydrogen peroxide at 2537 A. proceeds by the mechanism :

$$\begin{aligned} H_2O_2 + h\nu &\rightarrow 2OH \\ OH + H_2O_2 &\rightarrow H_2O + HO_2 \\ 2HO_2 &\rightarrow H_2O_2 + O_2 \end{aligned}$$

with an experimental quantum efficiency of 1·7 (theoretical maximum 2),[52] indicating very little back reaction. The photolysis of persulphate solutions is more complicated.[53] No OH radicals seem to play a part, but other intermediates must be present in the decomposition to sulphate because of the observed effects on the rate of H_3O^+, SO_4^{2-}, OH^-, and Cl^-. In spite of careful and accurate work the mechanism is still obscure.

Nitrobenzene vapour in the short-wave ultra-violet decomposes to give nitrosobenzene and *p*-nitrophenol : [54]

$$\begin{aligned} C_6H_5\cdot NO_2 + h\nu &\rightarrow C_6H_5\cdot NO + O \\ C_6H_5\cdot NO_2 + O &\rightarrow HO\cdot C_6H_4\cdot NO_2 \end{aligned}$$

tert.-Butyl nitrite vapour exposed to ultra-violet light gives acetone and the hitherto unprepared nitrosomethane : [55]

$$(CH_3)_3C{-}O{-}N{=}O + h\nu \rightarrow (CH_3)_2CO + CH_3\cdot NO$$

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[49] F. Briers, D. L. Chapman, and E. Walters, *J.*, 1926, 562.

[50] E. J. Hart and M. S. Matheson, *J. Amer. Chem. Soc.*, 1948, **70**, 784.

[51] M. Calvin and G. D. Dorough, *ibid.*, p. 699.

[52] D. H. Volman, *J. Chem. Physics*, 1949, **17**, 947.

[53] L. J. Heidt, J. B. Mann, and H. R. Schneider, *J. Amer. Chem. Soc.*, 1948, **70**, 3011.

[54] S. H. Hastings and F. A. Matsen, *ibid.*, p. 3514.

[55] C. S. Coe and T. F. Doumani, *ibid.*, p. 1516.

The latter substance, often invoked to explain the chain-stopping power of nitric oxide in hydrocarbon reactions, readily dimerises, and gives formaldoxime on heating.

A fundamental difficulty in interpreting experimental results of photodissociations involving radicals in gaseous systems is caused by the diffusion of radicals to the vessel walls. This has been the subject of theoretical treatment and applied to ketone decompositions.[56]

When exposed to ordinary intense light sources, reversibly photodissociating gases such as nitrogen dioxide or chlorine give small stationary atom or radical concentrations only, because of the high rates of recombination. A new arrangement has been described whereby up to 10,000 Joules of electrical energy, stored in condensers, can be discharged in a few thousandths of a second through a column of rare gas, giving intensities of light 10^4 times greater than steady sources.[57] Very high photo-stationary radical concentrations can thus be obtained, and under these conditions new final products may be formed by inter-radical reactions.

Much work at present is concentrated on photo-changes induced by high-velocity particles or very short waves. This has been recently summarised.[58] The importance of one short-wave photo-reaction seems to have escaped general notice. Geologists have for some time maintained that the free oxygen of the air was wholly derived from photosynthesis by plants. It now appears that the major source was the photo-reaction of water vapour in very short ultra-violet light.[59] Water vapour and carbon dioxide react photochemically in short-wave light to give oxygen and formaldehyde, and this reaction is suggestive as a possible source of living matter on the earth. Recent developments in the production of lithium fluoride plates make work in the region 1800—900 A. more practicable, and doubtless new papers will soon appear on this little explored field.

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[56] T. L. Hill, *J. Chem. Physics*, 1949, **17**, 1125.

[57] R. G. W. Norrish and G. Porter, *Nature*, 1949, **164**, 658 ; *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.

[58] F. S. Dainton, *Ann. Reports*, 1948, **45**, 5.

[59] W. Groth, *Z. Elektrochem.*, 1939, **45**, 262.