The Lightfastness or the Non-Photochemistry of Dyes**

Horst E. A. Kramer*

Dedicated to Professor Josef Goubeau on the occasion of his 85th birthday

The following classification of dyes, UV stabilizers, sensitizers, and optical brighteners is proposed in the light of the Jablonski diagram. The fastest deactivation process should be: (a) internal conversion (k_{IC}) for dyes on textile fibres and UV stabilizers acting as absorbers, (b) fluorescence emission (k_F) for optical brighteners and laser dyes, and (c) intersystem crossing process (k_{ISC}) for sensitizers. – The photochemistry of dyes is discussed according to Koizumi's classification of D-R, D-D, and D-O processes (D = dye, R = reducing agent, O = oxygen). The «reacticity» of the excited singlet and triplet state is defined with respect to the D-R process. While the reactivity of the excited singlet is higher than that of the triplet state (energetic aspect), the triplet state is favoured by its longer lifetime (kinetic aspect). Contributions to the internal conversion were determined separately for some aminoanthraquinone dyes and the following order has been found: inter*molecular hydrogen bonds (from the solvent methanol to the amino and to the carbonyl groups of the dye) > introduction of a methyl group on the amino moiety >* intra*molecular hydrogen bond.*

1. Introduction

By absorbing light of appropriate frequency a molecule is transferred from its electronic ground state ($^1S_0$) to its first excited ($^1S_1$) or even higher excited singlet states (^1S_n), whereby higher vibrational levels may be reached (cf. Fig. 1). In the condensed phase the molecule undergoes a fast radiationless deactivation within $\approx 10^{-13}$ s to the vibrational ground state of the first excited singlet state ($^1S_1$). There exist at least three deactivation pathways, namely internal conversion (k_{IC}) – a radiationless process to the ground state ($^1S_0$) –, fluorescence emission (k_F) into the ground state, and finally an intersystem crossing process (k_{ISC}) to the triplet term system.

The intersystem crossing process is forbidden by first approximation since one electron spin has to be reversed. The singlet state can be characterized by the fact that both the excited and the remaining electron have antiparallel spins whereas both electrons have parallel spins in the triplet state. Although spin reversal is forbidden by first approximation, spin orbit coupling in large molecules may accelerate the forbidden intersystem crossing process to such an extent that the triplet state is populated. Once the molecule is in the triplet state (T_1) transitions within the triplet term system ($T_1 \rightarrow T_n$) occur with normal intensity since they are spin-allowed transitions; they can be observed with flash spectroscopy. The transitions from the triplet (T_1) to the ground state ($^1S_0$) are again forbidden by first approximation. Therefore, both the radiationless deactivation process ($k_{L'}$) and the emission process (k_P) (phosphorescence) are slow. Compared to the fluorescence, the phosphorescence is shifted to longer wavelengths by the amount of the so-called singlet-triplet splitting energy. These slow deactivation processes ($k_{L'}$, k_P) impart a long lifetime to the triplet state which varies in a wide range from 10^{-6} to 1 s depending on the chemical nature of the compound and on the surrounding conditions (low temperature, absence of oxygen). The lifetime of the excited singlet state, however, is much shorter on the order of 10^{-8}–10^{-9} s.

Now the question arises: which of the excited states, singlet or triplet, the photochemical reactions start from? At first glance we may be tempted to give preference to the excited singlet state since it has the higher energy and therefore the higher reactivity. However, a more detailed analysis reveals that this is not the crucial point.

Let us consider a bimolecular photochemical reaction: the reagent has to diffuse to the excited molecule during its lifetime and to undergo the photochemical reaction. If the molecule were already deactivated when the reagent approaches, no photochemical reaction would occur. Here, the triplet state is favoured due to its longer lifetime and thus is the origin of many photochemical reactions. On the other hand the excited state can be forced to react if the concentration of the reagent will be so high that the above mentioned kinetic conditions (diffusion and reaction during the short lifetime of the excited singlet state) are fulfilled. Such a reaction can be detected by the quenching of the fluorescence of the excited state.

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Analogous considerations are applicable to unimolecular photochemical reactions such as, for example, bond scission, rotation about bonds, isomerization, etc. Generally, the reactivity of the excited singlet state will be higher than that of the triplet state, however, the time available for the reaction is shorter for the excited singlet than for the triplet state.

2. Classification using the Jablonski Diagram

In the light of the Jablonski diagram (Fig. 1) a classification scheme can be envisaged, not only of the dyes, but for all substances which are important due to their interaction with light.

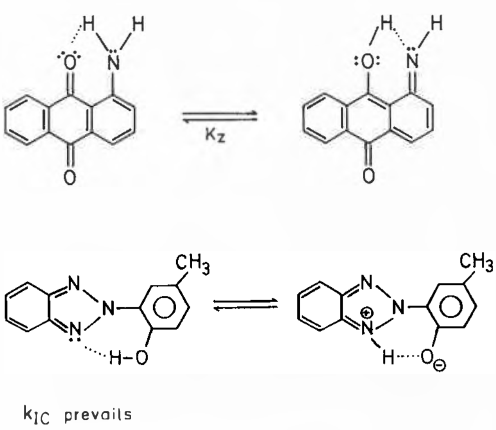
The classification could be done according to which of the three processes: internal conversion, fluorescence, and intersystem crossing is the fastest for the molecule under consideration.

2.1. Internal Conversion

This should be the fastest process in dyes on textile fibres. In Scheme 1 1-aminoanthraquinone is depicted with its *intra*molecular hydrogen bond. The intramolecular hydrogen bond provides fast radiationless deactivation by means of a rapid internal conversion process. The same principle holds for compounds like 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Scheme 1), representative of UV stabilizers acting as UV absorbers which have been studied very thoroughly by *Heller*[1] and *Blattmann*[2,3].

Due to their strong UV absorption these substances prohibit the polymer with which they are admixed from absorbing light and undergoing a photodegradation reaction (inner filter effect); the excited UV stabilizer molecule itself, however, should be rapidly deactivated without radiation. In this case the *intra*molecular hydrogen bond plays the decisive role[4-11]. It obviously mediates the strong coupling which is necessary to convert the electronic excitation energy into vibrational energy, probably of the out-of-plane bending vibration of the OH group[7] (concept of the promoting and accepting modes). In this context it is important to recognize that, according to *Förster*[12], the acidity or basicity is changed in the excited state. Consequently a proton of the NH_2 or OH group (in the excited state more acid) is transferred to the corresponding partners (CO group or aza nitrogen atom which are more basic in the excited state, Scheme 1).

Scheme 1

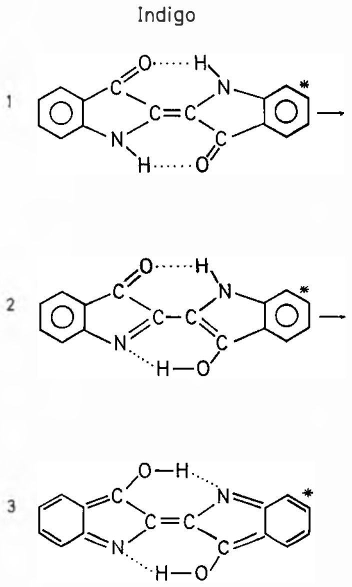


The same principle is also realized in the indigo molecule where the internal conversion is so fast that the fluorescence emission process cannot compete effectively (Scheme 2)[13,14,103].

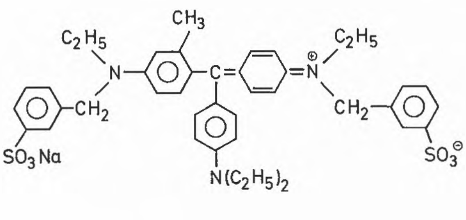
In the triphenylmethane dyes a different type of vibration, namely the rotation-vibration of the whole phenyl group, is supposed to be the origin of the fast internal conversion of these dyes. *Förster* and *Hoffmann*[15] found that the fluorescence yield of crystal violet increases strongly with increasing viscosity (for example in glycerol or at low temperatures) where the rotation-vibration of the phenyl groups is hindered and therefore the corresponding deactivation mechanism is ineffective[13,104]. In fluid media with low viscosity, however, the fluorescence yield of the dye is small. In Scheme 3 the formula of a somewhat more complicated triphenylmethane dye is shown which acts as No. 1 of the (German) blue standard scale of lightfastness.

In this context the well known fact should be mentioned[8] that fluorescent dyes often have low lightfastness. Strong fluorescence demonstrates the absence of fast processes competing effectively with emission and consequently the molecule remains in the excited state longer and the probability increases that it will undergo a photochemical degradation reaction.

Scheme 2



Scheme 3



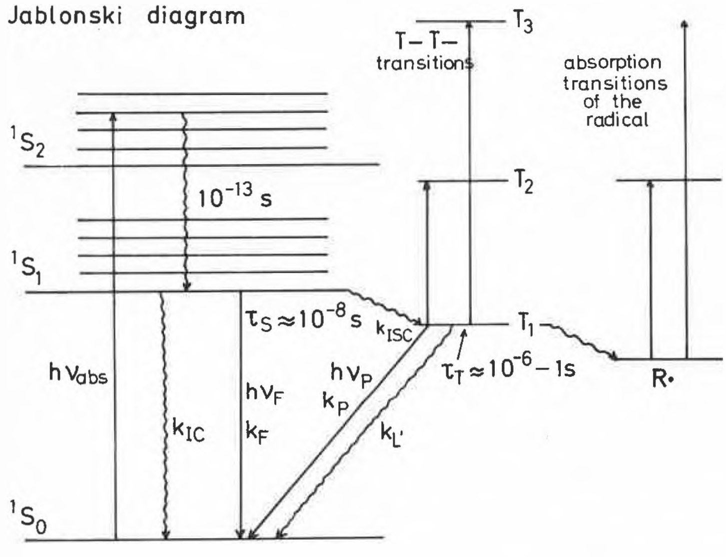


Fig. 1. Jablonski diagram, see text.

A vibration also brings about the fast deactivation of azo dyes[16] which is the origin of their high lightfastness. According to the investigations auf *Rau* et al.[17-19,96] one has to differentiate whether the ($n\pi^*$) or the ($\pi\pi^*$) state is of lowest energy. If the ($n\pi^*$) state is lowest practically no fluorescence is observed. The lifetime of the excited state is < 25 ps as shown by *Struve*[20], in which case the dye is very stable against light. The very detailed studies of *Rau* and *Lüddecke*[19] showed that in the azobenzenophanes no twisting around the N=N bond (rotation mechanism) takes place, rather only an *inversion* within the molecular plane occurs. Thereby one C-N-N angle is varied thus performing a *trans-cis* isomerization. In the qualitative potential energy diagram of Fig. 2 (in analogy to *Rau* [19,96]), the $^1(n\pi^*)$ state exhibits an energy minimum at an angle of inversion at about 135° whereas the ground state shows a maximum at that angle. This means that the energy gap between ground and excited state becomes smaller and therefore the rate of the radiationless process increases.

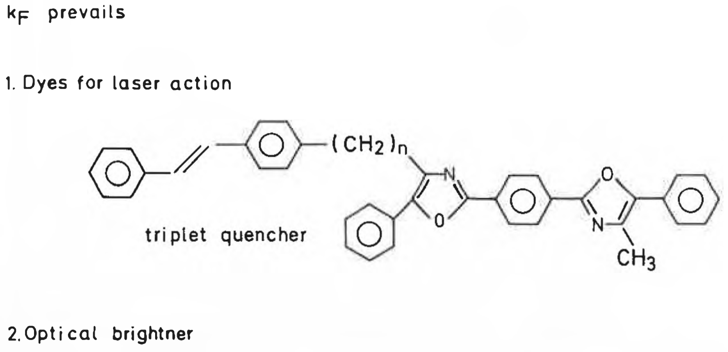
On the other hand, if the $^1(\pi\pi^*)$ state is lowest the *trans-cis* isomerization proceeds by twisting (rotation analogous to that in stilbene)[19]. The lifetime of the excited state is longer and possibly even fluorescence arises.

For *N*-alkyl substituted aminoazobenzenes and some diaminoazobenzenes *Bisle* et al.[97] detected a weak $n \leftarrow \pi^*$ fluorescence which they discussed in terms of (n,π^*)-$(\pi\pi^*)$-coupling. In addition to fluorescence, triplet-triplet absorption spectra of azo dyes were observed[98].

2.2. *Fluorescence*

Fluorescence emission should be the predominating process for signal dyes, laser dyes, and for a completely different class of substances, namely optical brighteners. Optical brighteners absorb in the UV region while their fluorescence occurs in the visible region due to their Stokes shift. The laser dyes should have fluorescence quantum yields near 1 (Scheme 4). It is unfavourable when the long-lived triplet state is populated because it may be the origin of degradation processes and thus of inadequate long-time stability of the laser dye. Furthermore, the population of the triplet state also diminishes the laser output. Both disadvantages can be overcome by a so-called triplet quencher (the stilbene moiety in Scheme 4) which quenches the triplet state of the laser dye to its ground state by a triplet-triplet energy transfer process. The quenching efficiency is highest if the quencher molecule is fixed directly to the laser dye according to *Lüttke* et al.[21,22].

Scheme 4



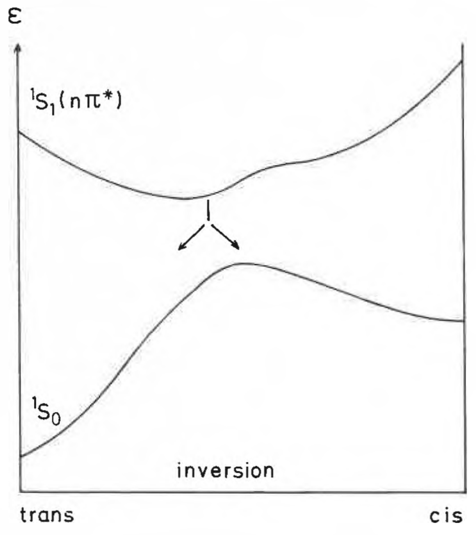


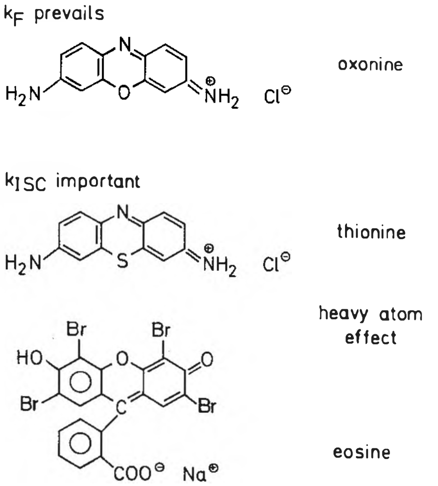
Fig. 2. Potential energy surface diagram in analogy to Rau [96] *for cis/trans isomerization of azo compounds by inversion within the plane; the lowest singlet state has* $n\pi^*$ *character.*

2.3. *Intersystem-Crossing*

For the oxonine molecule (Scheme 5) fluorescence emission is still the predominating process and the triplet state is not populated. The triplet yield of the thionine molecule, however, where oxygen is replaced by sulfur, amounts to 0.55[37]. The origin of the acceleration of the intersystem crossing process is due to the spin-orbit coupling which is proportional to the fourth power of the effective nuclear charge number ($\sim Z^4_{\rm eff}$, so-called heavy atom effect) and in this respect sulfur obviously has to be considered here as a heavy atom. In the eosine molecule four bromine atoms provide a high triplet yield. For the selenine molecule, where the sulfur atom of thionine is replaced by selenium, the rate of the intersystem crossing process (and possibly the triplet yield too) is expected to increase (however, this is not fulfilled for selenine with respect to the triplet yield[24]). The first experiments gave puzzling results. The dye triplet state is converted by a reducing agent (allylthiourea (ATU), high concentration) into the semiquinone radical. When changing from selenine to thionine, the amount of the semiquinone formed decreased although we had expected just the opposite. A more detailed study revealed the following. Not only the triplet formation process ($k_{\rm ISC}$, Fig. 1) becomes more allowed and is accelerated therefore but also the rates of the deactivation processes from the triplet state to the ground state ($k_{\rm P}$, $k_{\rm L'}$, Fig. 1) increase – or in other words the lifetime of the triplet state is shortened (for example, acid triplet form of thionine $^3TH_2^{2\oplus}$:$\tau_0' = 17.5$ μs; acid triplet form of selenine $^3SelH_2^{2\oplus}$: $\tau_0' = 0.39$ μs[23,24]). Consequently even at high ATU concentration the dye triplet state has no longer the opportunity to be converted completely into the semiquinone since it is deactivated mainly by unimolecular reaction into the ground state, i.e. the yield of the semiquinone decreases when going from thionine to selenine.

This result opens a new aspect: Until now we assumed the triplet formation to be unfavourable with respect to the long-time stability of the dye and it to be avoided in the best possible way since the triplet state can undergo degradation reactions due to its long lifetime. On the other hand, if we accelerate the intersystem crossing rate very strongly the triplet state is formed *rapidly* and possibly with *high yield* and then it is also deactivated *rapidly* into the ground state, i.e. the triplet state could possibly become a *short-lived intermediate* consequently, which due to its short lifetime probably no longer has the opportunity to undergo degradation reactions.

Scheme 5



Preliminary studies of the aminoanthraquinones give some hints. When bromine atoms are introduced the triplet yield $\eta_{\rm ISC}$ (Table 1) increases. However, we

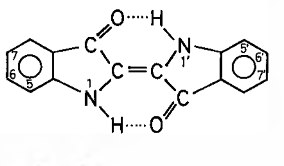
Table 1. Triplet yields $\eta_{\rm ISC}$ of aminoanthraquinones in toluene[25], 25 °C.

	$\eta_{\rm ISC}$
1-aminoanthraquinone	0.02
1-amino-2,4-dibromoanthraquinone	0.5
2-aminoanthraquinone	0.4
2-amino-1,3-dibromoanthraquinone	0.5
1,5-diaminoantraquinone	0.6
1,5-diamino-2,4,6,8-tetrabromoanthraquinone	0.75

have not yet observed a pronounced decrease of the long-time stability of these dyes[25].

Within the series of indigo, 6,6'-dibromoindigo (purple), 5,5',7,7'-tetrabromoindigo (Cibalblau C.I.73065), and 5,5',7,7',8,8'-hexabromoindigo (Anthrasol 06 B (Hoechst)) the lightfastness increases with the number of the bromine atoms. It is worth noting that the last mentioned dye represents number 7 within the (German) blue standard scale of lightfastness, i.e. it has a very high lightfastness. Further studies could reveal whether or not the above mentioned mechanism is the origin of the high lightfastness (Scheme 6). In this context one should also keep in mind that changes in lightfastness can only be related with variations of the chemical structure of the dyes if the physical state of the dyes is equal (see Section 4). For Anthrasol 06 B aggregation may also contribute to its high lightfastness.

Scheme 6



purple ≙ 6,6'-dibromindigo
5,5',7,7'-tetrabromindigo (Cibalblau)
5,5',7,7',8,8'-hexabrom indigo
(Anthrasol 06B(Hoechst))

The intersystem crossing process should be the predominating process within photosensitizer molecules. The synthesis of ascaridole according to *Schenck*[26] is mentioned as an example (Scheme 7). According to the Kautsky mechanism[27], the triplet state of the dye (sensitizer) reacts with molecular oxygen in its triplet ground state ($^3\Sigma_g^-$). Both molecules are converted into singlet states, namely the sensitizer to its ground state and the O_2 molecule into its $^1\Delta_g$ state. The overall reaction is spin-allowed and therefore proceeds very fast. The transition $^3\Sigma_g^- \leftarrow {}^1\Delta_g$ is doubly forbidden (spin- *and* symmetry-forbidden) and that gives a long lifetime to the O_2 molecule in its $^1\Delta_g$ state (where it may be considered an electrophile). The long lifetime enables $O_2(^1\Delta_g)$ to diffuse to its reaction partner (the dienophile α-pinene in the above mentioned example) and to undergo the reaction.

This singlet oxygen mechanism (or Type II mechanism of photooxygenation, for the notation see *Schenck*[28]) plays an important role for the *photodynamic effect*[29–31]. A second contribution to the photodynamic effect is made by the Type I mechanism of photooxygenation whereby radicals are formed in the same way as in the D-R mechanism (cf. section 3.2). The photodynamic effect means the damage of living cells and tissue containing dye molecules by light in the presence of oxygen whereby malignant tumors may arise under certain conditions[31]. On the other hand malignant tumors containing the dye hematoporphyrin are damaged by light more rapidly than normal tissue. According to *Dougherty* et al.[101], *von Tappeiner* and *Jesionek*[102] reported the earliest attempt to use the photodynamic effect for treatment of human tumors. However, it is only very recently that this phototherapeutic effect has started to be developed more thoroughly[32]. Walls of cells are damaged among other things by the photodynamic effect and besides that singlet oxygen can react with several amino acids (histidine, tryptophan, methionine) in enzymes[33] and inactivate them[34].

The *photogalvanic effect* was discovered by *Rabinowitch*[35] in 1940 when he irradiated a dye solution containing a reducing agent. Whereas no reaction occurred in the ground state, the triplet state of the dye molecule is indirectly reached upon irradiation and can now be reduced due to the (measurable) change of the electrochemical potential of the system dye/reduced forms of the dye upon irradiation. The energy of the light is converted into chemical energy of the radicals produced. The radicals, however, will recombine rapidly unless measures can be taken to hinder them. This behavior clearly describes the problem of solar energy conversion with these dyes[36].

3. The photochemistry of dyes in fluid solution

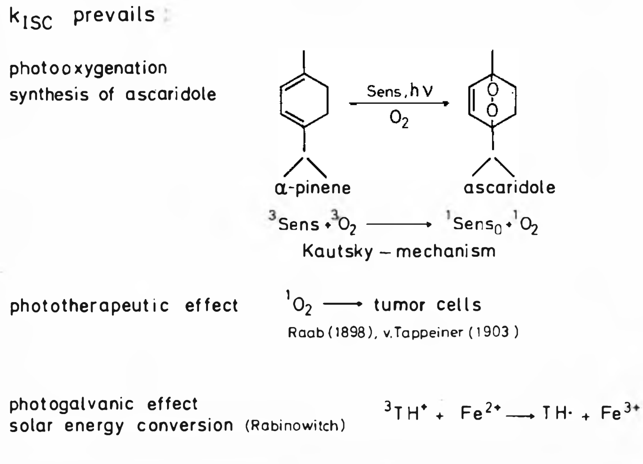
3.1 Survey

After this survey of substances which are important because of their interaction with light, we turn to the photochemistry of dyes in fluid solution and use the classification of *Koizumi* (Scheme 8). For review articles see *Koizumi* et al.[37,38], *Chibisov* et al.[39,40], *Meier*[31,63], and *Traber* et al.[55]. D-R, D-D, and D-O processes are distinguished where D, R, and O represent the dye, reducing agent, and oxygen, respectively.

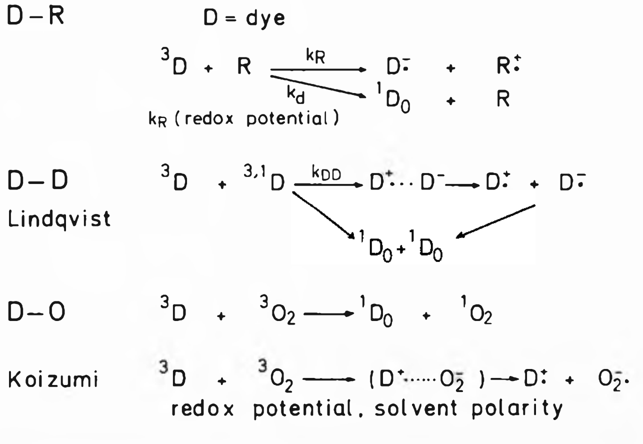
In the *D-R process* one redox equivalent is transferred whereby radicals are formed. In competition with this process the bimolecular deactivation of the triplet state of the dye molecule into its ground state takes place, possibly via an intermediate which is common to both processes (k_R and k_d)[41,42]. The redox process depends on the redox potentials of the molecules involved (see section 3.2).

The *D-D process* was discovered by *Lindqvist*[43]. Here a dye molecule in its triplet state reacts with a second dye molecule which may be either in its singlet ground state or in its triplet state (*at high light intensities*, for example using flash photolysis, the reaction of two molecules in their triplet state is favoured). In competition with the deactivation process to the ground state an electron transfer process takes place thus producing a half-oxidized ($D^{\oplus\odot}$) and a half-reduced ($D^{\ominus\odot}$) dye radical. If both radicals diffuse apart two half-reduced dye radicals undergo a dismutation reaction to form the dye (D) and the leuco dye (DH_2) while the half-oxidized

Scheme 7



Scheme 8



dye radical is degraded irreversibly by a reaction with the solvent or it recombines with a half-reduced dye radical. If the dye radicals cannot escape (agglomeration of the dyes on the fibre[44]) they can recombine and two dye molecules in the ground state are regenerated. This chemical deactivation of the dye molecules in their triplet state opens an additional pathway to the ground state thus shortening the triplet lifetime. The probability, therefore, decreases for degradation reactions which improves the long-time stability (lightfastness) of the dye.

The *D-O process* means the reaction with oxygen. The formation of singlet oxygen has already been described (see section 2.3). In competition with this process an electron transfer can occur – if the redox potential of the dye triplet state is favourable – whereby a half-oxidized dye radical $D^{\oplus\odot}$ and $O_2^{\ominus\odot}$ are produced[45]. High polarity of the solvent supports this process which may be one of the origins of the oxidative degradation of the dye.

The photooxygenation of allylthiourea (ATU) sensitized by thionine can be switched from a Type I mechanism (high ATU concentration; primary reaction: redox process between thionine triplet and ATU with subsequent formation of the corresponding *radicals*) to a Type II mechanism (low ATU concentration; primary reaction between thionine triplet and oxygen with subsequent formation of *singlet oxygen*)[46–48].

3.2 *Redox process (D-R)*

Rehm and *Weller*[49,50] investigated the quenching of the fluorescence of excited molecules $^1D^*$ by reducing agents R. In Fig. 3 the logarithm of the rate constant of this quenching reaction is plotted versus the oxidation potential of the reducing agents R. With strong reducing agents R (low values of the oxidation potential E^{ox}) the reaction proceeds diffusion-controlled (horizontal part of the curve). However, using weak reducing agents R (high values of the oxidation potential E^{ox}) the rate constant of the electron transfer reaction decreases and a linear relationship between $\log k_q$ and E^{ox} or ΔG_{ET} (change of the free reaction enthalpy of the electron transfer process), respectively, is found (linear free energy relationship[49]). The position of this straight line within the diagram gives some information about the reactivity of the excited state of the molecule to be quenched: If for example the straight line were shifted to lower values of the potential E^{ox}, this would mean that the excited state of the molecule D reacts only with very strong reducing agents R, with weak reducing agents, however, it does not, or in other words: The excited state of the molecule D has a lower reactivity than that given by the former straight line and vice versa (Fig. 3).

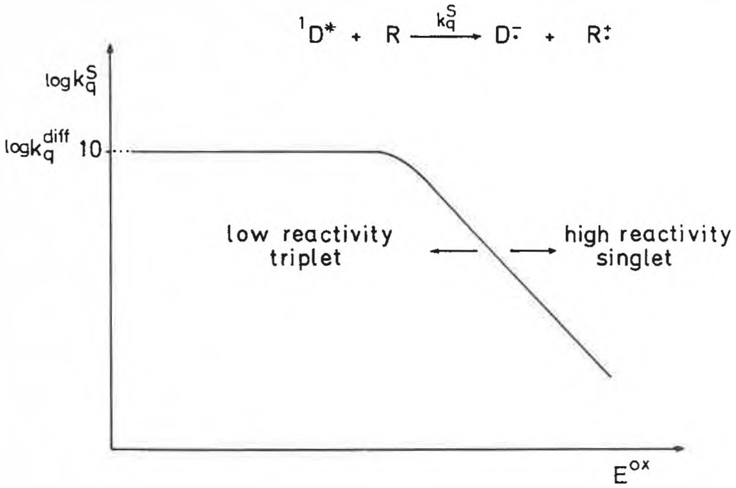


Fig. 3. Schematic Rehm-Weller diagram for the quenching of an excited electron acceptor (dye D) by various reducing agents R with oxidation potential E^{ox}. Ordinate: logarithm of the quenching rate constants ($\log k_q$); abscissa: oxidation potential E^{ox} of the various reducing agents R.*

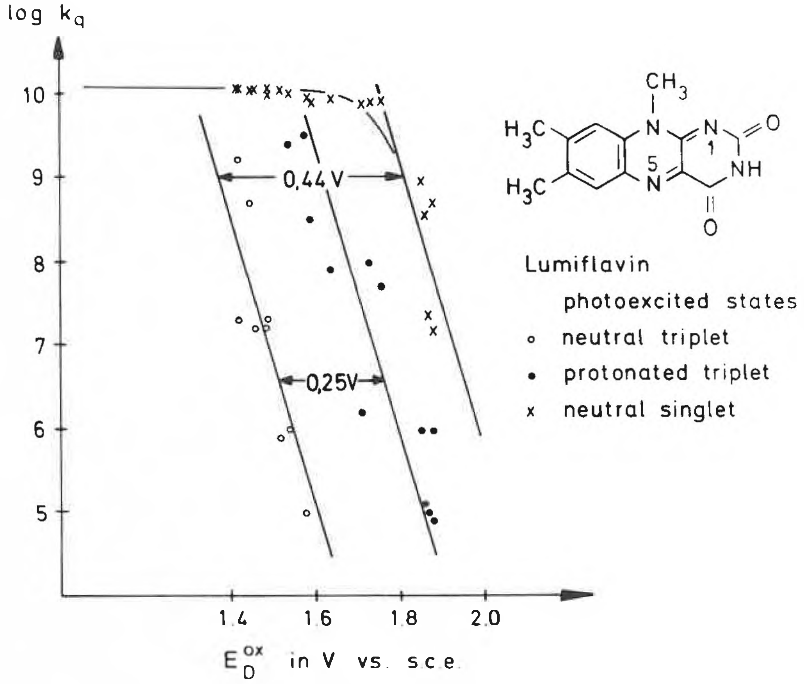


Fig. 4. The dependence of rate constants of flavin photoexcited state quenching on the oxidation potential of the reducing agents in methanolic solution[53].

For some dyes[51–58] (thionine[51], acridine orange[52,54], methylene blue[56], lumiflavin[53,55]) separated straight lines of the excited singlet and triplet state have been found[53,54], the reactivity of the singlet state being always higher than that of the triplet state. The horizontal distance of the straight lines of the singlet and triplet state of the dye, that means the reactivity difference between singlet and triplet state, corresponds approximately to the amount of the singlet-triplet splitting energy of the dye. Closer examination reveals the distance between the singlet and the triplet straight line to be even higher, or in other words, the reactivity of the triplet state is even lower than properly expected from the singlet-triplet splitting energy (for an explanation see[54,55]).

For lumiflavin[53,55] (Fig. 4) the protonated triplet form ($^3F1H^{\oplus}$) should exhibit a higher reactivity with respect to the electron transfer process than the neutral triplet form ($^3F1$). This difference of the reactivity should correspond to the difference of the redox potentials of the different protolytic triplet forms. Using a Michaelis cycle the difference of the redox potentials can be calculated from the difference of the pK values of triplet (pK_T) and semiquinone (pK_S) which were determined by flash photolysis[51,53],

$$E^{red}(F1H^{\odot}/^3F1H^{\oplus}) - E^{red}(F1^{\ominus\odot}/^3Fl) = 2.303\,\frac{RT}{F}\,(pK_S - pK_T) \qquad (1)$$

where F is the Faraday constant. According to the right hand side of equation (1) the difference of the redox potentials is predicted to be 220 mV using the pK values while a value of 250 mV is found from the horizontal displacement of the straight lines in Fig. 4[53] which agrees well with the above mentioned result.

Summing up we may say the «reactivity of the excited state of a molecule» with respect to a redox process can be defined in a quantitative manner by the position of its straight line in a Rehm-Weller diagram.

From Fig. 5 the following expression is derived for the change of the free reaction enthalpy of the electron transfer process ΔG_{ET}: The ionization energy (proportional to the oxidation potential $E^{ox}(R/R^{\oplus\odot})$) of the reducing agent R has *to be supplied* by the system whereas on the other hand the electron affinity (proportional to the reduction potential $E^{red}(D^{\ominus\odot}/D)$ of the dye (electron acceptor)) *is gained*. If the dye is excited (D*), its electron affinity increases by the amount of the electronic excitation energy ΔE_{exc}, equations (2) and (3).

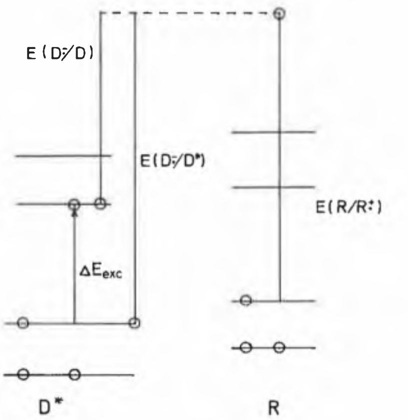


Fig. 5. Change of the free reaction enthalpy ΔG_{ET} of the electron transfer process from a reducing agent R to an excited acceptor dye D: $D^* + R \rightarrow D^{\ominus\odot} + R^{\oplus\odot}$; $E^{ox}(R/R^{\oplus\odot})$: oxidation potential of the reducing agent R, $E^{red}(D^{\ominus\odot}/D)$: reduction potential of the dye D in its electronic ground state, ΔE_{exc}: electronic excitation energy of the dye D, $E^{red}(D^{\ominus\odot}/D^*)$: reduction potential of the excited dye D*.*

$$\Delta G_{ET} = F \cdot E^{ox}(R/R^{\oplus\odot}) - F \cdot E^{red}(D^{\ominus\odot}/D) - \Delta E_{exc} + \frac{e_0^2}{4\pi\, \varepsilon_0\, \varepsilon\, a} \tag{2}$$

$$F \cdot E^{red}(D^{\ominus\odot}/D^*) = F \cdot E^{red}(D^{\ominus\odot}/D) + \Delta E_{exc} \tag{3}$$

The last member of equation (2) represents a Coulomb term if the radicals $R^{\oplus\odot}$ and $D^{\ominus\odot}$ are charged (e_0 = elementary electronic charge, ε_0 = permittivity of the vacuum, ε = permittivity of the solvent, a = distance of the radicals).

The electronic excitation supports not only reduction processes but also oxidation processes of the excited dye molecule D*. The ionization energy to remove the excited electron is smaller by the amount of the electronic excitation energy. Generally speaking: Both oxidation and reduction processes proceed easier in an excited molecule as compared to a molecule in its ground state. Which of these processes really does occur, depends on the *reaction partner available during the lifetime of the excited molecule D**.

With these remarks we will leave the photochemistry of dyes *in fluid solutions* and turn to dyes *on fibres*.

4. Dye/Fibre

Some review articles pertinent to this subject should be quoted[16, 59–63]. According to *Giles* and *Strevens*[64] the following factors are important with respect to the lightfastness of the dye on fibres:

- the photochemistry of the dye (as discussed in section 3);
- the fading reaction of the dye, which is oxidative on non-protein fibres whereas on protein fibres it is reductive[65];
- the degree of association of the dye[66];
- the diffusion of oxygen (and possibly water) to the dye within the fibre[67];
- the influence of the surrounding atmosphere (temperature, humidity, oxygen content, content of sulfur dioxide, nitrogen oxide);
- the polarity of the fibre.

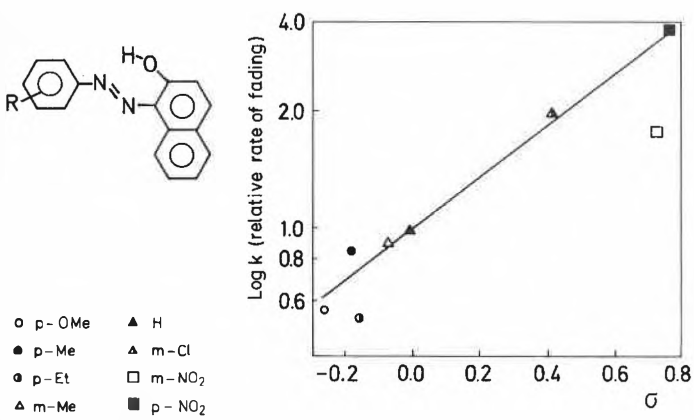


Fig. 6. Relation between relative rates of fading in logarithmic scale and Hammett's constants for phenylazo-β-naphthol dyes on polypropylene (exposure to long-wavelength ultraviolet radiation in nitrogen atmospheres)[70].

Aggregation of the dye: As was pointed out by *Giles* et al.[66] only dye molecules placed just on the surface of the aggregated particle can undergo a reaction with oxygen according to the D-O mechanism (Scheme 8) which was applied by *Egerton*[68, 69] to dyes on fibres. Dye molecules lying within the aggregated particle are protected until the outer layer is removed. On the whole the dye in the aggregated state is less likely to undergo a fading reaction (reaction rate $\sim 1/a^2$, where a is the radius of the particle) than the dye in monomolecular distribution (reaction rate independent of a)[66].

Generally speaking the physical state of the dye on fibres is very important with respect to its lightfastness. Using different dyes one may only expect to reveal the influence of the chemical structure of the dyes if all other parameters are held constant, that is, especially if the physical state of the dyes on fibres is equal.

The D-D process (Scheme 8) will improve the lightfastness if in the aggregated dye particle the half-oxidized and the half-reduced dye radical do not undergo any other reaction than to recombine and to regenerate thus the dye in its ground state[44]. This opens an additional deactivation pathway for the triplet state to the ground state. This shortening of the lifetime of the triplet state improves its lightfastness (see also section 3.1). On the other hand, according to *Bough* et al.[44] reactions between $D^{\ominus\odot}$ and O_2 and between $D^{\ominus\odot}$ and H_2O or $OH^{\ominus}$ respectively are conceivable.

Mallet and *Newbold*[70] studied the fading of the azo dyes given in Fig. 6 on polypropylene in nitrogen atmosphere in dependence of the substituent R. If the fading rate (in a logarithmic scale) is plotted versus Hammett constants σ a straight line of positive slope is found, that means, it is a reductive fading process. If oxygen is added again a straight line of positive slope is found, but a second line of negative slope may be traced using the points of *m*- and *p*-methyl- and *p*-methoxy-phenylazo-*β*-naphthol, and the parent dye. This can be explained if some of the dye fades via an oxidative route, while the rest decomposes by a predominating reductive mechanism.

Generally speaking, one can draw the conclusion from these results that in an oxygen containing atmosphere an oxidative fading mechanism in addition to the reductive mechanism has to be taken into consideration.

From the above mentioned considerations the following points arise:

(i) For the excited dye molecule *both the oxidizing and the reducing capacities are increased by the electronic excitation energy* (energetic aspect), see section 3.2.

(ii) Which of these reactions, namely oxidation or reduction, really does occur, depends on the reaction partner which can *undergo the reaction with the excited state of the dye molecule during its lifetime* (kinetic aspect).

Both aspects have to be met to enable a photochemical reaction to occur. In this context the classical results of *Joussot-Dubien, Bonneau* et al.[71,72] concerning the protonation of triplet states of dyes should be mentioned: It is not sufficient to choose a pH value below the pK value of the triplet state (thermodynamic or energetic aspect, respectively) but also the *concentration of the buffer acid must be high enough* as to make sure that the protonation reaction can be accomplished during the short lifetime of the triplet state of the dye (kinetic aspect).

It is worth noting that in the excited states of the dye molecule not only the reactivity in one-electron transfer reactions but also the electrophilicity, that is the tendency to undergo nucleophilic addition reactions (two-electron transfer reactions), are higher than in the ground state; for flavins see[55,73].

Possible reaction partners of the excited dye molecule are *fibres* and *oxygen*. There is no doubt that the excited singlet state of the dye molecule has a higher reactivity than the triplet state but, on the other hand, the lifetime of the excited singlet state is shorter. From this, it follows that the *short-lived singlet state* can only react with a partner which does not have to move to the dye molecule: So to speak the partner must be already present such as, for example, the *fibre* since the dye is in close contact with it. A reaction between oxygen and the dye molecule in the excited singlet state is not very probable since oxygen cannot diffuse to it during the short lifetime. In agreement with this consideration the short-lived fluorescence of dyes is normally not quenched by oxygen of the atmosphere within experimental error (that is, the yield of a possible reaction between oxygen and the excited singlet state of the dye molecule must be smaller than the experimental error of these fluorescence measurements). The conditions for the *triplet state* of the dye molecule are different. Although its reactivity is lower than that of the singlet state, for kinetic reasons it can react as well with fibres as with oxygen. It now depends on the energetic aspect which reaction or reactions, respectively, occur.

4.1. Cellulose

It was reported[16,74,75] that, on cellulose, dyes (preferably azo, anthraquinone, and vat dyes) fade oxidatively in the presence of oxygen (also methylene blue[74]). At first glance this experimental result seems to be at variance with our statement according to which the excited dye molecule is more easily oxidized *and* reduced.

Reduction of the dye (for example of methylene blue[74]) by cellulose is observed in *oxygen-free* atmosphere where the corresponding reduced forms of the dye (e.g. Leuko Caledone Jade Green ($\lambda_{irr} = 253.7$ nm)[76]) are produced. In the presence of oxygen, however, reoxidation takes place[76] possibly already at the stage of the dye semiquinone (DH$^{\ominus}$), whereby the dye is regenerated again and again. Model systems were studied under continuous illumination (anthraquinone-2,6-bis(sodium sulfonate) in aqueous ethanol solutions[77]) and by flash photolysis (duroquinone in aqueous ethanol[78], 9,10-anthraquinone in ethanol and in hexane[94]). Therefore in the presence of oxygen this reduction pathway does *not* bring about any *permanent fading*. The oxidative process with oxygen[69], however, leads to *permanent fading* and only this is *measured* (Scheme 9). Further reactions of cellulose[61,64] (irradiation with light of short wavelength[79]) and the phototendering of fibres[61,62,80,81] can only be referred to.

4.2. Wool

According to *Giles* et al.[60,65,75] the process leading to permanent fading of dyes on wool (especially azo dyes are used) is reductive in nature. Since the reductive fading on methylethylcellulose increases upon addition of histidine, and to a smaller extent perhaps also of tryptophan, both amino acids are considered to be responsible for the *permanent reductive fading process* (obviously no regeneration of the dye with oxygen takes place). Now an explanation has to be found why the oxidative fading process on wool is of minor importance[82]. Two points have to be taken into consideration:

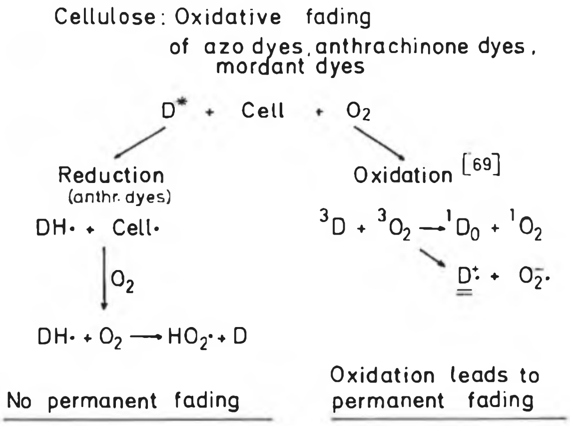
(a) Since the reductive process already leads to permanent fading, the relative contribution of an oxidative process to the total permanent fading on wool is smaller as compared to cellulose, where only the oxidative process effects a permanent fading.

(b) It has been demonstrated[33] that singlet oxygen reacts with histidine, tryptophan, and methionine (photodynamic effect, see section 2.3).

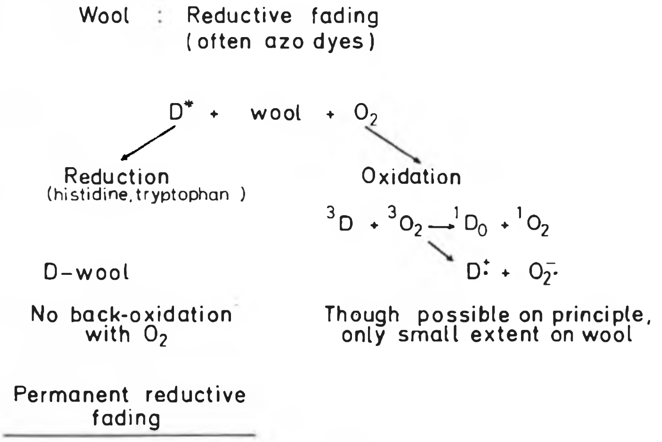
Griffiths[16] first recognized the applicability of these results and considerations (b) to wool. According to *Griffiths*, singlet oxygen is quenched by the above mentioned amino acids and therefore, it is only available to a small extent for an oxidative fading of the dye (Scheme 10).

These considerations could also make understood why a dye (such as indigo) which can be applied to both fibres has high lightfastness on one fibre and low lightfastness on the other[62]. If the dye considered fades oxidatively, it exhibits low

Scheme 9



Scheme 10



lightfastness on cellulose whereas it is stable on wool where the oxidative process is of minor importance. If the dye fades reductively just the opposite holds[60].

4.3. Influence of humidity

Humidity accelerates the fading process considerably on cellulose whereas it is not so important for wool[82]. Water causes the fibre to swell which facilitates oxygen transport to the excited dye molecules[82]. Therefore, oxidation is accelerated and fading is supported on cellulose where the oxidative fading process is the most important. However, the facilitation of oxygen transport is practically of no importance for the fading process on wool, here the oxidative fading plays only a minor role.

5. Catalytic Fading – Internal Conversion Processes for Aminoanthraquinones

Catalytic fading can be observed for example if blue or violet anthraquinonoid dyes are mixed together with a yellow azo dye and if only the blue dye is excited selectively using light of the corresponding wavelength: The yellow azo dye undergoes catalytic fading[16,83,84]. Energy transfer phenomena can be excluded for energetic reasons. The mechanism is depicted in Fig. 7. The triplet state of the anthraquinonoid dye is formed which produces singlet oxygen in the well known way, and finally singlet oxygen reacts with the azo dye[89] (catalytic fading of other systems, cf.[85–88]). On the other hand, *Griffiths* et al.[100] and *Gruen* et al.[99] report that some azo dyes (substituted arylazonaphthols[100], substituted *trans*-4-dialkylamino-4′-nitroazobenzenes[99]) produce singlet oxygen thus self-sensitizing their photooxidation[100].

The individual anthraquinonoid dyes exhibit different activities with respect to catalytic fading. The first group with high activity contains 1,5- and 1,8-diaminoanthraquinone which are distinguished by a high triplet quantum yield whereas 1,2- und 1,4-diaminoanthraquinone belong to the second group with low activity with respect to catalytic fading and which are characterized by only a small triplet quantum yield.

Using the experimental results of fluorescence quantum yield η_F, fluorescence lifetime τ_F, and triplet quantum yield η_{ISC} the rate constants of fluorescence emission k_F, internal conversion k_{IC}, and intersystem crossing k_{ISC} can be determined from equations (4)–(6)[90,91].

$$\eta_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}} \tag{4}$$

$$\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}} \tag{5}$$

$$\eta_{ISC} = \frac{k_{ISC}}{k_F + k_{IC} + k_{ISC}} \tag{6}$$

We studied 1-aminoanthraquinone, 2-aminoantraquinone, 1,4-diaminoanthraquinone, and 1,5-diaminoanthraquinone in toluene and methanol[90,91].

The highest fluorescence quantum yield ($\eta_F = 0.25$ in toluene) and the longest fluorescence lifetime ($\tau_F = 5 \cdot 10^{-9}$ s in toluene) are found for 2-aminoanthraquinone where no intramolecular hydrogen bond exists. All other dyes with *intra*molecular hydrogen bonds exhibit lower fluorescence quantum yields and fluorescence lifetimes. Fluorescence quantum yield and fluorescence lifetime decrease when going from toluene to methanol as solvent where *inter*molecular hydrogen bonds are formed in addition to the intramolecular ones.

1,5-Diaminoanthraquinone has a higher intersystem-crossing rate constant than 1,4-diaminoanthraquinone and this has to be considered the origin of the higher triplet yield of 1,5-diaminoanthraquinone.

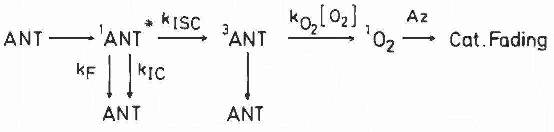


Fig. 7. Reaction scheme[83] *of catalytic fading for a mixture of blue or violet anthraquinonoid dyes (ANT) and yellow azo dyes (AZ) which fade catalytically*[89].

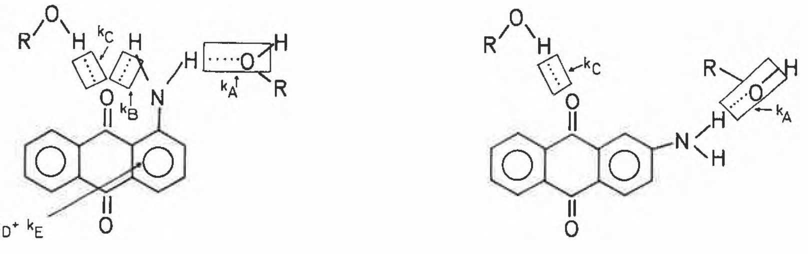


Fig. 8. Contributions to the internal conversion of aminoanthraquinones in the excited singlet state.

This result can be interpreted using the energy term scheme of singlet and triplet states (relative energetic position of singlet S_1 and triplet T_2[90,91]). The results of our kinetic investigations are in agreement with the stability of these dyes as studied by *Egerton* and *Roach*[92].

The following contributions to the internal conversion of the excited dye molecule have to be taken into consideration (Fig. 8):

(A) Intermolecular hydrogen bonding between the NH_2 group and solvent methanol;
(B) Intramolecular hydrogen bonding;
(C) Intermolecular hydrogen bonding of the CO group to methanol;
(D) Contribution from the skeleton of the molecule;
(E) Contribution of a methyl group introduced into the amino group.

Assuming that all these contributions are constant in the molecules studied, one succeeds in determining the individual contributions to k_{IC} for the above mentioned compounds (including the compound methylated at the amino group) in the solvents toluene (no intermolecular hydrogen bonding) and methanol. The following contributions to k_{IC} are found: Skeleton of the molecule, $k_D \approx 5 \cdot 10^7$ s^{-1}; intramolecular hydrogen bonding, $k_B \approx 3 \cdot 10^8$ s^{-1}; introduction of a CH_3 group into the amino group, $k_E \approx 1.6 \cdot 10^9$ s^{-1}; intermolecular hydrogen bonding, $k_A \approx 3.2 \cdot 10^9$ s^{-1}; intermolecular hydrogen bonding, $k_C \approx 3.3 \cdot 10^9$ s^{-1}.

For these aminoanthraquinones the intermolecular hydrogen bonding gives a higher contribution to the internal conversion than the intramolecular hydrogen bonding whereas the very opposite holds for 2-(2′-hydroxy-5′-methylphenyl)benzotriazole[5,6] (Scheme 1). According to *Kelemen*[93] the explanation of this different behaviour may be seen in the fact that the conditions for tautomerization (proton transfer) in the excited state are not as favourable for the aminoanthraquinones as for the hydroxyphenylbenzotriazoles (cf. also[95]).

Intermolecular hydrogen bonds can stabilize these aminoanthraquinonoid dyes if the activity of the donor in the hydrogen bond is restricted to the acceleration of the internal conversion (and e.g. does not transfer in addition an H-atom with low yield).

6. Conclusion

Besides the physical state of a dye on fibres above all rapid deactivation processes of the excited states of the dye are of decisive importance for its lightfastness. Radiationless deactivation to the ground state (internal conversion) is brougth about by internal rotation-vibration (triphenylmethane dyes) and inversion for azo dyes if the lowest excited singlet state has

$n\pi^*$ character. Intramolecular and intermolecular hydrogen bonds are very effective: In the UV stabilizers of the hydroxyphenylbenzotriazole class the intramolecular hydrogen bond makes the most important contribution to the internal conversion whereas for the aminoanthraquinonoid dyes the intermolecular hydrogen bonds are more effective than the intramolecular hydrogen bond. Moreover, the D-D processes may be considered as chemically induced deactivation which contribute to the well known fact that the aggregated dye is more stable than the dye in monomolecular distribution; however, the most important reason is that the dye molecules lying within the aggregated particle are not exposed to the reaction with oxygen.

The transition into the long-lived triplet state is considered to be unfavourable for the longtime stability of the dye since the long-lived triplet state can undergo degradation reactions. Using some preliminary results about the influence of bromine substitution the following question was discussed. If the intersystem crossing rate is accelerated very strongly the triplet state is formed rapidly and possibly with high yield. On the other hand, the triplet state is also rapidly deactivated into the ground state and thus the triplet state could possibly become a short-lived intermediate which due to its short lifetime probably no longer has a chance to undergo degradation reactions. High intersystem crossing rates can be achieved by the internal heavy atom effect (for example by introducing bromine atoms into the dye molecule).

The reactivity of the excited state (of a dye molecule) was defined considering the reduction process (D-R process) and using Rehm-Weller diagrams. The Rehm-Weller diagram is a linear free enthalpy relationship where a kinetic value, namely the rate constant of the redox process, is related to a thermodynamic value, the change of the reaction free enthalpy of the redox process. The higher reactivity of the acid triplet form of the dye as compared to the neutral triplet form for an electron accepting process corresponds to the difference of the redox potentials of both protolytic forms of the triplet state. Using a Michaelis cycle this difference of the redox potentials is available from the difference of the pK values of triplet and semiquinone of the dye; these pK values can be determined by flash photolysis. The reactivity difference between the more reactive singlet state and the less reactive triplet state corresponds approximately to the singlet-triplet splitting energy which amounts for dyes to only 29–37 kJ/mol (for aromatic hydrocarbons it is much higher). For this reason redox reactions of the excited singlet and of the triplet state of the same molecule can be easily followed on dyes.

For a photochemical reaction to occur both aspects (energetic and kinetic aspect) have to be fulfilled. Kinetic aspect means that the reaction can be accomplished only within the lifetime of the excited state under consideration. Whereas the excited singlet state has a higher reactivity, the triplet state is distinguished by its longer lifetime. Applying this to the system dye/fibre/O_2 the following conclusion can be drawn. Despite of its higher reactivity the excited singlet state cannot react with oxygen since the oxygen has to diffuse to the dye molecule during the short lifetime of its excited singlet state (kinetic aspect). The excited singlet state of the dye can only react with the fibre which it is in close contact with. On the other hand, from kinetic reasons, due to its longer lifetime the triplet state of the dye can react as well with oxygen as with fibres. It now depends on the energetic aspect which reaction or reactions of the triplet state occur.

For the excited dye molecule both the oxidizing and reducing capacities are increased by the electronic excitation energy (energetic aspect). Which of these reactions occurs depends on the reaction partner that can undergo the reaction with the excited state of the dye molecule during its lifetime.

At first glance the experimental results on cellulose and wool seem to be inconsistent with our conclusions. The excited dye (e.g. anthraquinonoid dyes) undergoes both reductive and oxidative processes on cellulose in presence of oxygen. However, the reductive process does not lead to permanent fading since the dye is reoxidized possibly already at the stage of the dye semiquinone by oxygen. Only the oxidative process brings about permanent fading and only this is finally measured. – The reductive process is the origin of the permanent fading on wool, whereas the oxidative process is of minor importance since singlet oxygen (which is responsible for this process) is quenched by histidine present in wool. – On this basis the different influence of humidity on the fading process can be interpreted. Water causes the fibre to swell which facilitates oxygen transport to the excited dye molecules. Therefore, oxidation is accelerated and fading is supported on cellulose where the oxidative fading process is the most important. However, the facilitation of oxygen transport is practically of no relevance to the fading on wool where the oxidative fading plays only a minor role.

A dye such as indigo which can be applied to both fibres exhibits low lightfastness on cellulose since it can be easily oxidized; on wool, however, the oxidative process is of minor importance and therefore the dye is stable. Just the opposite would hold if the dye faded reductively.

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