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Polymer photostabilisers. Photophysical properties and stabilising efficiency

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ABSTRACT. The photophysical characteristics and luminescence-spectroscopic properties of molecules with a high photostabilising efficiency are examined. It is shown theoretically that the short lifetime and (or) low population of the triplet state of the molecule are essential (but not sufficient) conditions for its use as a photostabiliser. Both these conditions or one of them are fulfilled when systems in which non-radiative conversion processes, initiated by adiabatic reversible photochemical processes or systems with heavy atoms, are used. Experimental data confirming these postulates are presented.

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I. Introduction

The problem of increasing the photostability of polymeric materials has not lost its interest over a long period of time despite the advances achieved both in the understanding of the scientific principles of the problem and in the practical application of the results.[1–4] The reason for this is the expansion of the range of polymeric materials and their applications together with increasing requirements for their photostability, including photostability under extreme conditions.

One of the most common and promising ways of solving the problem involves the use of special additives which are introduced into polymers and polymer compositions to increase their photostability. In terms of the mechanism of their protecting action, the additives can be divided (albeit not entirely unambiguously) into two types: compounds whose action has a chemical mechanism and systems whose stabilising effect is manifested already in the initial, physical stage of the polymer phototransformation process.

The role of compounds with a chemical stabilisation mechanism involves chemical reactions of their molecules with the products of the photolysis of polymers (usually radicals) and convert the latter into an inactive state, interrupting the chain of transformations. Such compounds can be used to protect not only against the action of light but also against other factors which induce the appearance of radical polymer degradation processes (oxidation, the action of heat, mechanical stress, ionising radiation, etc.). Compounds of this type include antioxidants and thermostabilisers.

Compounds with the physical photostabilisation mechanism prevent the occurrence of the primary stage of the photolysis of polymer or impurity molecules. These compounds are intrinsic photostabilisers and in employing this term below we shall have only them in mind.

The significant advances achieved during the last decades in the creation of antioxidants and associated to a large extent with the development and introduction of a new class of stabilisers — sterically hindered amines (SHA)[3,4]—have not reduced the interest in the study and practical employment of photostabilisers. This has arisen for a number of reasons.

Photostabilisers include compounds of different classes with a broad range of protecting properties and which absorb the energy of the light radiation in different spectral regions. In contrast to the sterically hindered amines, photostabilisers have more universal applications: they can be used both for carbochain and for different kinds of heterochain polymers which undergo a short chain of photochemical transformations — in filled, dyed, and incombustible polymers. Sterically hindered amines and other compounds with a chemical stabilisation mechanism have a limited period of activity, because they are consumed after a time. The mechanism of the action of photostabilisers in the absence of side processes does not involve their consumption and can ensure a long operating life of the polymer. Photostabilisers are able to manifest a synergistic effect in mixtures with stabilisers whose action has a chemical mechanism, which makes it possible to increase the lifetime of polymeric materials and to reduce the concentration of additives.

It is noteworthy that the requirements imposed on the molecular and electronic structures of effective photostabilisers are the same or are similar to the requirements which must be satisfied by intrinsically photostable polymers (see Section IV). The development of ideas about the mechanism of the action and causes of the high efficiency of photostabilisers has thus promoted the elucidation of ways of creating photostable polymer molecules. The study of the physical stages in the stabilisation process is important also for antioxidant molecules, because on formation of complexes with electronically excited molecules (for example, with the O_2 molecule[5,6]) many of them induce their quenching. All the foregoing discussion demonstrates the current interest of the study of the mechanism of the action of photostabilisers and of the principles of their selection.

Two physical processes underlie the action of photostabilisers: the process involving the absorption of light by the stabiliser which shields the polymer molecule against the action of incident photons and the transfer of energy from the electronically excited polymer molecules to the stabiliser molecules with their subsequent deactivation. Systems in which the former process occurs preferentially are called absorbers (UV absorbers), while systems of the latter type are called quenching agents. The determination of the leading mechanism of the stabilisation process is important for the selection of the stabiliser. UV absorber photostabilisers should evidently absorb the light which photolyses the polymer molecules. The essential condition for the effective action of quenching agent molecules is the overlap of the luminescence spectrum of the polymer and of the absorption spectrum of the stabiliser.[1,2,7–12]

However, by no means all molecules satisfying these requirements can be effective photostabilisers. Furthermore, these conditions can be satisfied also by molecules of photosensitisers of the decomposition of polymers. The molecule of the effective photostabiliser should possess also a definite set of photophysical properties. Theoretical analysis of this problem is the subject of the present review. Clearly, with this formulation of the problem one can elucidate only the necessary but not sufficient conditions for the application of a molecule as a stabiliser, because the latter conditions include also a large number of parameters (compatibility with the polymer, molecular mobility, etc.).[1,2]

II. Photophysical processes in polyatomic molecules

The transformations of electronically excited molecular systems can occur with emission of photons (radiative transitions) or via a non-radiative pathway. The non-radiative routes to the decomposition of electronic states include non-radiative conversion processes in which the electronic excitation energy is converted into the vibration energy of the system without chemical transformations of the latter, autoionisation processes, electronic energy transfer and migration processes. All the processes enumerated are in the nature of physical processes involving the transformation of the electronic excitation energy and are referred to as photophysical. Apart from the photophysical routes to the transformation of molecular systems, there is also a possibility of photochemical routes, which lead to the formation of new chemical products. Photochemical processes are non-radiative.

The subdivision of the non-radiative pathways in the transformation of the electronically excited molecules into photophysical and photochemical is not always possible. In particular, it fails in molecules of many effective photostabilisers. Nevertheless, such subdivision must be used as the initial step in these cases too.

Very many studies[13–15] have been made on the characteristic features of photophysical processes in photostable molecules and on the development of their theory. Here we shall discuss briefly only the results which will be useful in the subsequent exposition.

Electronically excited molecular states can be classified[16] in terms of their multiplicity and orbital nature. The majority of molecules have a singlet ground state (S_0). In aromatic and heteroaromatic molecules the lowest excited singlet state is the $S_{\pi\pi^*}$ or $S_{n\pi^*}$ state. Triplet (T) states can also be of the $\pi\pi^*$ or $n\pi^*$ type. The lowest excited state of the molecules is a T state. There is a possibility of five types of relative dispositions of the singlet and triplet $\pi\pi^*$ and $n\pi^*$ states.[15,17]

The characteristic value of the rate constant for the radiative decomposition of $S_{\pi\pi^*}$ states (k_r^S) is $\sim 10^8-10^9$ s^{-1}, while that for the decomposition of the $S_{n\pi^*}$ state is $\sim 10^5-10^6$ s^{-1}. Since the $T-S$ transitions are forbidden as regards multiplicity, the rate constants k_r^T for the radiative decomposition of the T state are much smaller. In molecules without heavy atoms, k_r^T is $10^{-1}-10^2$ s^{-1} for $T_{\pi\pi^*}$ states and 10^3-10^4 s^{-1} for $T_{n\pi^*}$ states. The introduction of heavy atoms into the molecule leads to a significant (by several orders of magnitude) diminution of the lifetime of the T states. The above features are determined by the characteristics of the spin–orbital interaction in the molecule.[15,18–22]

There are three types of non-radiative conversion processes: internal conversion processes, which take place between states with the same multiplicity ($S-S$ or $T-T$), singlet–triplet ($S-T$) conversion processes, and triplet–singlet ($T-S$) conversion processes. We shall examine the characteristic rate constants for these processes.

The rate constants for internal conversion (k_{ic}) processes between excited states are very large ($\gtrsim 10^{11}$ s^{-1}). As a result of this, polyatomic molecules are seen to emit a luminescence with a high yield only from the lowest excited state of the given multiplicity (Kasha's rule[23]). On the other hand, it has been established for a large number of molecules that internal conversion S_1-S_0 processes make a small contribution to the decomposition of the lowest excited state,[24] i.e. that the constant k_{ic} for the S_1-S_0 conversion process is smaller than the constant k_r^S for the radiative decomposition of the S_1 states and the rate constant for the $S-T$ conversion (k_{ST}).

Theoretical study showed[25] that the above features of the internal conversion process are a consequence of the marked dependence of k_{ic} on the transition energy E_{if}. The dependence of k_{ic} on E_{if} is described approximately by the exponential law $\exp(-\alpha E_{if})$ with the parameter $\alpha \simeq 4-5$ eV^{-1}. For low values of $E_{if} \lesssim 1$ eV, the constant k_{ic} is $\gtrsim 10^{11}$ s^{-1} and exceeds the values of k_r^S and k_{ST}. Such values of E_{if} are characteristic of transitions between electronically excited states. For $E_{if} \gtrsim 2.5$ eV, the constant k_{ic} becomes smaller than k_r^S and k_{ST}. For a large number of polyatomic molecules, the energy difference between the S_1 and S_0 states satisfies this requirement and the internal conversion process is therefore unimportant in the degradation of the S_1 state. If the energy of the lowest excited state lies in the range 1.5–2.5 eV, the quantity k_{ic} is comparable to k_r^S and k_{ST} and in such molecules the S_1-S_0 internal conversion process may make an appreciable contribution. Experimental data confirming the foregoing can be found in a number of publications.[14,15,25–27]

The rate constant for the $S-T$ conversion between states of different nature ($\pi\pi^*$ and $n\pi^*$) reaches $\sim 10^{10}-10^{11}$ s^{-1} and the $S-T$ conversion process suppresses the fluorescence process.[15,21,22] The constant k_{ST} for the conversion between states of the same orbital nature is significantly lower and amounts to 10^6-10^9 s^{-1}. The $S-T$ conversion and fluorescence processes can compete in this instance.

The five types of relative positions of states of different orbital nature and with different multiplicities, mentioned above, and the characteristic features of the spin–orbital interaction and $S-T$ conversion processes serve as the basis of the luminescence-spectroscopic systematic treatment of molecules.[15,17]

Numerous studies have been devoted to the characteristics of $T-S$ conversion processes.[28–32] Of the general results, we shall mention here the energy gap law, in conformity with which the constants k_{TS} and k_{ic} diminish approximately exponentially with increase in the energy of the T state; here too the quantity α

amounts to approximately $4-5$ eV^{-1}. For many molecules in solid solutions, the constant k_{TS} is comparable to the rate constant for the radiative decomposition of the corresponding triplet state. (In liquid solutions this is not the case because different bimolecular processes involving the quenching of T states assume a significant role and the lifetime of such states falls sharply[33]).

In concluding this Section, it is important for our purpose to emphasise that the non-radiative degradation of the electronic excitation energy in the majority of photostable molecules takes place with a significant population of the triplet states, whose lifetimes are relatively long.

III. Initiation of non-radiative conversion processes by adiabatic photochemical reactions

Photochemical reactions are known to be capable of occurring via non-adiabatic or adiabatic mechanisms. The non-adiabatic reactions are similar to non-radiative conversion processes and reduce to a non-adiabatic transition between electronic states, one of which (the final state) is the state of the reaction products (for example, a predissociative state). In this case, the duration of the transition between the states is appreciably smaller than the reciprocal of the transition rate constant (i.e. the transition expectation time). The evolution of the system is therefore described with the aid of the usual kinetic scheme consisting of a series of independent competing processes, each of which is characterised by the corresponding rate constant.

Adiabatic photochemical reactions proceed without change in the electronic state of the system. They are usually described by the equation for the motion of the system on one potential surface from the minimum (region) for the initial system to the minimum (region) for the reaction products. The duration of the transition is in this case comparable to the reciprocal of the photoreaction rate constant. When an adiabatic photochemical reaction takes place, the probabilities of all the photophysical processes begin to depend on the reaction coordinate (x) and the usual kinetic treatment of the evolution of the system becomes inapplicable†. The dependence of the rate constants for the conversion processes on x becomes particularly significant.

We shall consider the possible cases where this dependence can be manifested most strongly. To make the system concrete, we shall have in mind initially S_1-S_0 internal conversion processes.[34]

The possibility of the occurrence of a photochemical reaction in the S_1 state during a period shorter than $\sim 10^{-8}$ s implies that the potential surface for this state either has no maximum, separating the initial state from the state of the reaction products, or that the maximum is small. In contrast to the S_1 state, in the S_0 state, the system is stable and the $U_0(x)$ potential surface has a deep minimum for certain equilibrium values of x. This minimum is separated by a high ($\gtrsim 1$ eV) potential barrier from the state of the reaction products in the electronic ground state. The form of the potential curves is illustrated schematically in Fig. 1*a* (continuous curves).

It is possible to distinguish another type of potential surface (Fig. 1*b*). If the reaction is impossible in the S_0 state, then that surface corresponds to repulsion. The possibility of the occurrence of the reaction in the excited state implies that the function $U_1(x)$ has a minimum corresponding to the reaction product. Isomerisation reactions (especially *cis–trans* isomerisation reactions), reactions), proton or hydrogen atom transfer reactions, etc. belong to the first type, while reactions involving the formation of excimers (an excited complex of two identical molecules) or exciplexes (an excited complex of different molecules) belong to the second type.

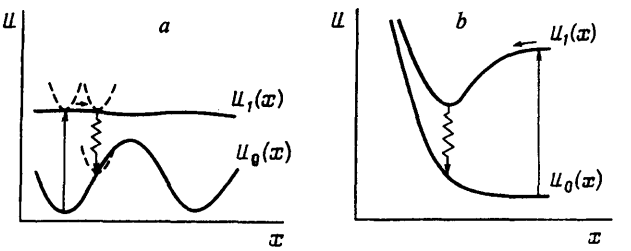


Figure 1. Schematic illustration of the potential surfaces for the isomerisation (*a*) and complex formation (*b*) reactions; the horizontal arrows indicate the movement of the system along the reaction coordinate.[34]

In the case of a condensed phase, subject to the condition that the vibrational relaxation rate constant exceeds the rate constants for all the remaining processes, the movement of the system along the reaction coordinate can be represented by a series of successive transitions through a series of quasi-equilibrium states. Their quasi-equilibrium is determined by the effect of the solvent on the molecular system—the finite orientational and translational relaxation time of the solvent (Fig. 1*a*, dashed curves). According to the theory of the condensed state put forward by Frenkel',[35] the lifetime of the system in each quasi-equilibrium state (the period between the jumps executed by solvent molecules from one state to another) exceeds $\sim 10^{-11}$ s and is much greater than the vibration period of the atoms in the system. The conversion process should therefore be regarded as one occurring between states of the system corresponding to the potential curves shown by dashed lines in Fig. 1*a*. This constitutes the difference between the mechanism of the conversion process occurring in the course of an adiabatic reaction and the mechanism of conversion in photostable systems, where the process takes place between two potential surfaces. The rate of the adiabatic photoreaction and its influence on photophysical processes and hence on the luminescence properties of the system depend on the characteristics of the medium (viscosity, intermolecular interaction, etc.).[36]

The significant decrease in the energy gap between the $U_0(x)$ and $U_1(x)$ potential curves leads to an increase in k_{ic}, which is greater the smaller the minimum difference $U_1(x)-U_0(x)$. Specific estimates can be made for certain reactions.

One of the widely occurring photoreactions with an adiabatic stage is the *cis–trans* isomerisation reaction, which can occur in the S_1 state of molecules having isolated or conjugated double bonds

† It is useful to note the analogy between this situation and the energy transfer process between diffusing molecules where the transfer rate constant depends on the distance between the moving molecules.

(stilbene and its derivatives, carbocyanine dyes, etc.).[36,37] In this case, the angle of rotation of the fragment about the double bond serves as the reaction coordinate. The activation energy $U°$ for this reaction in the S_0 state is 1–2 eV.[37] Neglecting the difference between the *cis*- and *trans*-isomers (1–3 kcal), the potential surface of the ground state can be described by the equation:

$$U_0(x) = \frac{U^0}{2}(1 - \cos 2x). \quad (1)$$

The $U_1(x)$ relation is known only for certain systems.[38] For our purposes, it is important to know only that the function $U_1(x)$ varies within narrow limits (~0.2 eV) and that the variation of the S_1-S_0 transition energy can be described satisfactorily by the expression:

$$E_{if} = E_{if}^0 - \frac{U^0}{2}(1 - \cos 2x), \quad (2)$$

where E_{if}^0 is the transition energy at $x = 0$. Using Eqn. (1) and (2) and the expressions for the rate constants k_{ic},[25] the $k_{ic}(x)$ relation has been calculated. The results are presented in Fig. 2. It follows from the data in this figure that k_{ic} increases with x to a greater extent the greater the parameter $U°$. The increase in k_{ic} becomes appreciable (by about two orders of magnitude) already in the initial stage of the reaction, where the angle of rotation of the fragment is ~45°. At $x = \pi/2$, k_{ic} reaches a maximum and diminishes on further increase in x.

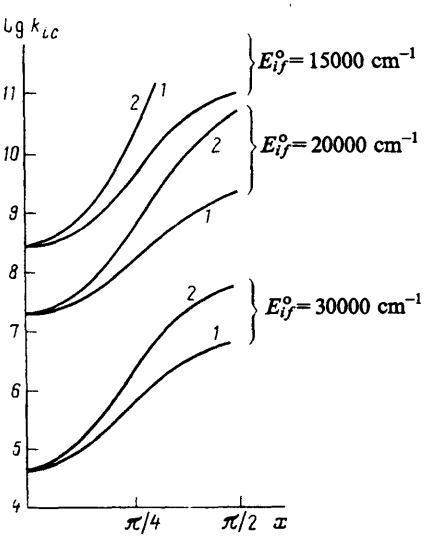


Figure 2. Dependence of k_{ic} on x for *cis–trans* isomerisation reactions with $U° = 8000$ cm^{-1} (curves *1*) and $U° = 12000$ cm^{-1} (curves *2*).[34]

If k_{ic} at $x = 0$ amounts to 10^6 s^{-1} ($E_{if}^0 \simeq 25000$ cm^{-1}), whereupon it is possible to neglect the contribution of the S_1-S_0 internal conversion process under conditions ruling out a photoreaction, then when a photoreaction occurs there is a possibility of the quenching of the fluorescence and the suppression of the $S-T$ conversion process. This effect is even more important for smaller values of E_{if}^0, whereupon the constant k_{ic} becomes $10^{10}-10^{11}$ s^{-1} during the photoreaction, which can lead to the suppression not only of the fluorescence and the $S-T$ conversion but also of the photoreaction itself. This conclusion has been confirmed experimentally[39,40] (see below).

As can be seen from Fig. 1*b*, in the case of complex formation reactions the maximum value of k_{ic} is attained at the minimum on the $U_1(x)$ curve. When excimers are formed, the decrease in the transition energy at this point reaches 5000–6000 cm^{-1}.[33] This change in the transition energy leads to a significant suppression of the fluorescence if E_{if}^0 for the isolated molecule does not exceed ~25000 cm^{-1}. It has been noted[34] that the mechanism of the initiation of the internal conversion process by the excimer formation reaction is the cause of the phenomenon of the concentration-induced quenching of the luminescence.

The initiation of the internal conversion process has been observed for proton transfer reactions.[40] For these reactions (as for any processes with a redistribution of the charge), processes involving the reorganisation (repolarisation) of the medium play a significant role. For such systems, we therefore find that, firstly, the influence of the polarity of the medium on the probability of the process is significant and, secondly, that there are difficulties in an unambiguous determination of the reaction coordinate. However, the general claim that the potential surfaces of the ground and excited states must approach one another for the initiation of the conversion process remains in force. This conclusion is consistent with experimental data, because the quenching of the S_1 states is most effective in systems where the proton acceptor is a weak base in the S_0 state, i.e. when the activation energy for the H^+ transfer process in this state is high.[40]

All that has been said above about the initiation of the internal conversion processes by adiabatic photoreactions refers directly also to the $S-T$ and $T-S$ conversion processes,[41,42] because the rate constants for the latter also increase with decrease in the energy gap. Furthermore, the change in the spin–orbital interaction (β_{s0}) as x varies is also significant for these processes. The increase in β_{s0} can be observed during reactions where fragments of the system are displaced from the plane[15] and on formation of complexes with a non-planar structure or complexes with molecules containing heavy atoms.[16] There is yet another cause of the initiation of the $S-T$ conversion process by a photoreaction: the change in the relative positions of the $\pi\pi^*$ and $n\pi^*$ states of different multiplicity during photoreactions.[41] Since the terms of the S and T states are usually of a similar form, the initiation of the $S-T$ conversion as a consequence of the change in the energy gap alone is relatively weak. In the case of the $T-S$ conversion, the occurrence of the latter is significantly reflected in the phosphorescence yield, because $k_r^T \simeq k_{TS}$ even in photostable systems.

The equation for the probability of finding the system at time t in the initial electronic state at the point x on the reaction coordinate is fairly simple and at the same time makes it possible to analyse the behaviour of the system. It assumes the form:[42,43]

$$\frac{\partial W_S}{\partial t} = D\frac{\partial^2 W_S}{\partial x^2} - v\frac{\partial W_S}{\partial x} - [k_r^S + k_{ic}(x)]\,W_S. \quad (3)$$

This follows from the more general Focker–Planck equation. Eqn. (3) has been formulated for the initiation of the S_1-S_0 internal conversion process. The parameter D characterises the diffusional movement of the system along the S_1 surface and v is the velocity of the system along the reaction coordinate under the influence of the force determined by the dependence of the S_1 term value on x, which

is assumed in this instance to be linear. It has been suggested that the rate constant for the radiative decomposition of the S_1 state is independent of x and $S-T$ conversion processes may be neglected. [For an unchanged value of k_{ST}, Eqn. (3) retains its form, but k_r^S should be understood as the sum of the rate constants for the radiative decomposition of the S_1 state and for decomposition as a consequence of the $S-T$ conversion.]

We shall consider certain special cases. Suppose that $D = 0$ and that the system is in the initial instant at the point $x = 0$ [$W_S(x, 0) = \delta(x)$] and begins to move in the positive direction of the x axis along the sloping term of the S_1 state. After the attainment of the point $x = L$, the photoreaction is assumed to be completed (at this point the potential energy increases sharply). The rate of movement of the system along the S_1 term is linked to the reaction time by the relation $\tau_R = Lv^{-1} = k_R^{-1}$. The population of the S_1 state

$$W_S(t) = \int_0^L W_S(x, t)\,dx \quad \text{at} \quad t \leqslant \tau_R ,$$

is given by the expression:

$$W_S(t) = \exp[-k_r^S t - v^{-1}k_{ic}(vt)],$$

where

$$k_{ic}(x) = \int_0^x k_{ic}(x')\,dx'.$$

The law governing the decomposition of the S_1 state is not exponential. For $t > \tau_R$, the system is in the S_1 state of the photoproduct and its further evolution is described by the usual law: $Q_R^S exp\text{-}\{[k_{ic}(L) + k_r^S]t\}$, where Q_R^S is the yield of the photoproduct in the S_1 state and $k_{ic}(L)$ is the constant for the internal conversion of this state. If during the movement along the S_1 term the energy diminishes by an amount ΔE, then the dependence of k_{ic} on x can be represented in the form $k_{ic}(x) = k_{ic}^\circ \exp(\alpha \Delta E x L^{-1})$, where k_{ic}° is the conversion constant in the initial system (for $x = 0$) and α is a coefficient in the exponential dependence of k_{ic} on the transition energy (see Section II).

The quantum yields of the fluorescence (Q_r), internal conversion (Q_{ic}), and the photoproduct (Q_R^S) are given by the expressions

$$Q_r = e^a b^b [\Gamma(-b, a) - \Gamma(-b, ae^A)],$$
$$Q_{ic} = e^a a^b [\Gamma(1-b, a) - \Gamma(1-b, ae^A)],$$
$$Q_R^S = 1 - Q_r - Q_{ic}, \qquad (4)$$

where $a = k_{ic}^\circ Z^{-1}$, $b = k_r^S Z^{-1}$, $Z = Ak_R$, $A = \alpha \Delta E$, and $\Gamma(x,y)$ is an incomplete gamma-function. The radiation and photoproduct conversion quantum yields are calculated from the usual expressions with $k_{ic} = k_{ic}^\circ \exp(\alpha \Delta E)$.

Fig. 3 presents the dependence of Q_r, Q_{ic}, and Q_R^S on the parameter A. Evidently in the range of values of A where $k_{ic}(x)$ exceeds k_r^S and k_R (for $A \geqslant 5$ or $\Delta E \gtrsim 1$ eV), the internal conversion suppresses not only the fluorescence process but also the very photoreaction which has accelerated the internal conversion.

Fig. 4 presents the dependence of Q_{ic} on D for the case where the energy of the S term is independent of x, $v = 0$, and the movement of the system along the term is diffusional in character. The initial condition has the same form as above, while $k_{ic}(x)$ is given by the expression $k_{ic}(x) = k_{ic}\exp(c \sin^2 x)$, which corresponds to Eqn. (1) for the energy of the S_0 term. The boundary condition $(\partial W_S/\partial x)_{x=\pm\pi/2} = 0$ models the situation where the photochemical reaction cannot be completed as a consquence of steric hindrance [the function $U_1(x)$ at these points becomes infinite]. The boundary condition $[W_S(x,t)]_{x=\pm\pi/2} = 0$ describes the situation where the system undergoes instantaneous photochemical decomposition after the attainment of the boundaries. (One can then introduce the reaction rate constant $k_R \simeq D$.[42]) The value of the parameter $c = \ln 10^3$ employed corresponds to the value of U° in Eqn. (2), which is ~ 1.5 eV. Evidently even when the reaction can occur under conditions such that it cannot reach completion, the internal conversion process is rapidly accelerated, which can lead to the suppression of both fluorescence and the photoreaction itself.

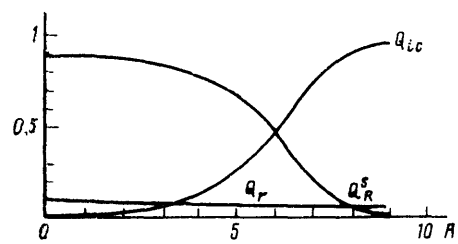


Figure 3. Dependence of Q_r, Q_{ic}, and Q_R^S on the parameter $A = \alpha \Delta E$; $k_r^S = 1$, $k_{ic}^\circ = 1$, $k_R = 10$.

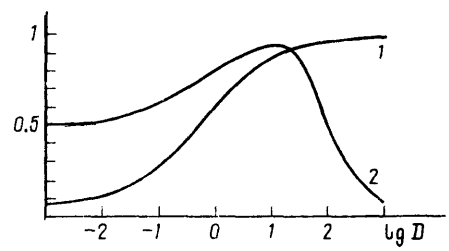


Figure 4. Dependence of Q_{ic} on D for a system with a *cis–trans* isomerisation reaction: *1*, boundary condition $(\partial W_S/\partial x)_{x=\pm\pi/2} = 0$, $k_r^S = 1$, $k_{ic}^\circ = 0.1$; *2*, boundary condition $[W_S(x,t)]_{x=\pm\pi/2} = 0$, $k_r^S = 1$, $k_{ic}^\circ = 1$.

Two main conclusions follow from the foregoing. (1) A significant initiation of the internal conversion process is observed when the minimum energy gap between the S_1 and S_0 terms does not exceed 2–2.5 eV. (2) Provided that $k_{ic}(x) \gg k_R$, $k_{ic}(x) \gg k_R^s$ for $0 < x < L$, and $k_r^S \simeq k_R$, when the first condition is fulfilled the internal conversion process leads not only to the quenching of the fluorescence but also to the suppression of the photoreaction. In the range of values $k_R \gg k_r^S$ and $k_{ic}(x) \ll k_R$, the evolution of the excited state is determined by the ratio of the quantities k_r^S and k_{ic} for the photoproduct. The latter conclusion holds also for other types of conversion.[42]

It was suggested above that the rate constant for the vibrational relaxation significantly exceeds the rate constants for other processes involved in the evolution of the system and that the movement of

the system along the reaction coordinate is limited by the relaxation of the solvent. In certain cases, this condition may break down. Thus, in the concluding stage of the reaction involving the formation of excimers or exciplexes, where there are no solvent molecules between the reacting molecules, the mutual approach of the reactants is not limited by the relaxation of the solvent. In this situation, there is a possibility of the formation of the reaction product in a highly excited vibrational state, as happens in the gas phase. A similar situation can occur also for other reactions.

This case has been analysed in detail.[44] It has been shown that the internal conversion process can compete with the vibrational relaxation process, provided that the terms of the ground and S_1 states intersect in the region of the energies of the vibrational states of the reaction product. The conversion process can occur with an appreciable probability even from states of the continuous spectrum of the collision complex, provided that the point of intersection of the surfaces is located in the classically accessible region or in its vicinity. For H atom and H^+ transfer reactions, the probability of the conversion process is high also in the sub-barrier region.

The position of the point of intersection of the terms for the excimer formation processes is determined by the oscillator strength f of the S_1-S_0 transition. It has been shown[44] that the quenching of the excimers from vibrationally excited states is possible if $f \gtrsim 0.5$, which is characteristic of many dye molecules which undergo concentration-induced quenching of their luminescence. For exciplexes with a significant charge transfer contribution, such a situation is more probable the higher the electron affinity of one of the reactants and the lower the ionisation potential of the other. The latter makes it possible to understand the characteristic features of the quenching of singlet oxygen by electron donors, in particular the observed increase in the quenching constant with decrease in the ionisation potential of the quenching agent.[5,6]

In concluding this Section, we may note that, in the case of systems with sensitised conversion processes, on the one hand, there is a significant decrease in the lifetime of the excited states and, on the other, the pathway leading to the degradation of the energy changes: as a consequence of the acceleration of the internal conversion process, the degradation of the excitation energy takes place without the triplet states being populated or with a significant decrease in their population.

IV. Photophysical properties of effective photostabilisers

Using the results described above, here we shall discuss the question which photophysical properties effective photostabilisers should possess in addition to the requirements specified in the Introduction.[1,2,7–12] It is not difficult to satisfy the requirements set out above using π-electron and especially aromatic (heteroaromatic) molecules. However, this is not sufficient.[45]

Indeed the photostabiliser molecule in an excited state can itself undergo irreversible phototransformations. It would appear that, in order to eliminate this undesirable effect, it should be sufficient to employ molecules exhibiting photostability in the lowest S and T states, which has been observed for a large number of π-electron molecules. However, it is important to take into account the following factor. The molecule in the lowest relatively long-lived T state can absorb a second light quantum and undergo a transition to highly excited T states.[46] In these states, all molecules without exception are reactive,[46,47] decomposing into fragments or ionising (auto-ionising). Although the probability of two-quantum $T-T$ excitation is low, the efficiency of the action of photostabilisers depends significantly on the contribution of these excitations, because one is dealing with the long term behaviour of this system.

The number of molecules excited to the highest triplet states increases with increase in the quantum yield of the lowest triplet states and their lifetime. An additional requirement which must be met by the properties of effective photostabilisers is therefore that the populations and lifetime of the lowest T states of the molecules should be as small as possible. We shall discuss different cases from this standpoint.

We shall consider initially molecules which are photostable in the lowest electronically excited state. In the absence of intermolecular $T-T$ energy transfer processes, the population of the lowest T state is determined by the relation between the constants for the radiative decomposition of the S_1 state and the value of k_{ST}, because in most cases S_1-S_0 conversion processes will not play a significant role. If the rate of the $S-T$ conversion process is determined by the transitions between the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ or between the $S_{n\pi^*}$ and $T_{\pi\pi^*}$ states (molecules belonging to luminescence spectroscopic types II–IV [15,17]) or if the molecule contains heavy atoms, then $k_{ST} \gg k_r^S$ [16] and the quantum yield of the T state is almost unity. For molecules belonging to luminescence spectroscopic types I and V, the $S-T$ conversion process takes place between states of the same orbital nature and $k_r^S \simeq k_{ST}$.[15] Only for isolated dye molecules and effective phosphors is the relation $k_r^S \gg k_{ST}$ observed. It arises from the characteristic features of the disposition of the excited $T_{\pi\pi^*}$ states relative to the $S_{\pi\pi^*}$ state and the spin–orbital interaction selection rules.[16,48] Such molecules have a high fluorescence quantum yield and their photostabilising efficiency is frequently also high, but they cannot always be used. On the other hand, for most photostable molecules the yield of the T states cannot be very low, especially since the latter can arise also via the $T-T$ energy transfer route.

The lifetime of the $T_{\pi\pi^*}$ states of molecules without heavy atoms in solid solutions (and not only at low temperatures)[49] is very long. Photostable molecules with the lowest $T_{\pi\pi^*}$ state are therefore not very effective photostabilisers and can in fact function as photosensitisers. The $T_{n\pi^*}$ states are short-lived and the $T-T$ absorption processes are relatively unlikely for such states.[46] However, the majority of molecules with the lowest $T_{n\pi^*}$ state are reactive. In particular, they participate in photodehydrogenation reactions.[36]

The lifetime of the $T_{\pi\pi^*}$ states may be sharply reduced (by 3–4 orders of magnitude) after the introduction of heavy atoms into the molecule. It changes in inverse proportion to the fourth power of the effective charge on the heavy atom. Many organometallic compounds are therefore good photostabilisers.[1,2] (Unfortunately, some of them behave as catalysts of oxidation reactions.[50])

As is already clear from the foregoing, there exists yet another possibility of reducing the lifetime of the T states with the simultaneous decrease in their population, which is associated with the initiation of S_1-S_0 and $T-S$ conversion processes by reversible adiabatic photoreactions.

We shall consider the behaviour of a system with potential surfaces ensuring the occurrence of a reversible photoreaction in S and T states (Fig. 5). Neglecting diffusion, the population of the S_1 state $W_S(x,t)$ is specified by an equation which is analogous to Eqn. (3) for $D = 0$:

$$\frac{\partial W_S}{\partial t} = -v\frac{\partial W_S}{\partial x} - [k_r^S + k_{ST} + k_{ic}(x)]\,W_S. \qquad (5)$$

We shall assume that the constants k_r^S and k_{ST} are independent of x, that $k_{ic}(x)$ increases exponentially with increase in x, and that the initial condition is $W_S(x,0) = \delta(x)$. Using the above results, one can write the following expression for the quantum yield of the T state:

$$Q_T = k_{ST} I_1 + Q_R^S k_{ST} [k_r^S + k_{ST} + k_{ic}(L)]^{-1}, \quad (6)$$

where Q_R^S is the quantum yield of the photoproduct in the S_1 state, amounting to $1-(k_r^S + k_{ST})I_1 - I_2$, I_1 and I_2 being defined by the same expressions as Q_r and Q_{ic} respectively in Eqn. (4). The quantity $b = (k_{ST} + k_r^S)Z^{-1}$ is overdetermined.

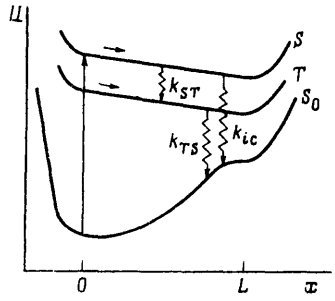


Figure 5. Schematic illustration of the terms for a molecular system with a reversible photochemical reaction; the horizontal arrows indicate the movement of the system along the reaction coordinate.[45]

Table 1. Dependence of the quantum yield of T states on the parameters $A = \alpha\Delta E$ and $k_R = v/L$ [$k_{ic}^\circ = 0.1$, $k_{ic}(x) = k_{ic}^\circ \exp(AxL^{-1})$, $k_{ST} = 0.5$, $k_r^S = 0.4$].

A	k_R					
	0	10^{-1}	1	10	10^2	10^3
4	0.5	0.435	0.269	0.107	0.08	0.077
6	0.5	0.424	0.220	0.049	0.016	0.012
8	0.5	0.412	0.188	0.037	0.006	0.002

Table 1 presents the quantum yields of the triplet state for different values of the parameters A and k_R. It is seen from these data that the yield of the T state diminishes sharply with increase in k_R and tends to the limiting value $k_{ST}[k_{ST} + k_r^S + k_{ic}(L)]^{-1}$ at $k_R \to \infty$, which is equal to the yield of the triplets in the photoproduct. The decrease in Q_T is more notable the higher the value of the parameter A, i.e. the greater the difference between the energies of the S_1-S_0 transition at the points $x = 0$ and $x = L$.

We shall now consider the influence of the initiation of $T-S$ conversion processes on the probability of secondary reactions. The population of the lowest T state is given by the equation:

$$\frac{\partial W_T}{\partial t} = -v\frac{\partial W_T}{\partial x} - [k_r^T + k + k_{TS}(x)]\, W_T, \quad (7)$$

where k is the rate of a secondary reaction [for example, the rate of $T-T$ absorption or transfer of energy to reactive molecules (in particular O_2)]. Subject to the initial condition $W_T(x,0) = \delta(x)$ and the exponential dependence of k_{TS} on x: $k_{TS} = K_{TS}^\circ \exp(AxL^{-1})$, and for $k \ll k_r^T + k_{TS}^\circ$, one can find the following expression for the relation for the yield of the secondary reactions to its yield corresponding to $A = 0$:

$$\overline{Q} = (k_r^T + k_{TS}^\circ) I_1 + \frac{k_r^T + k_{TS}^\circ}{k_r^T + k_{TS}^\circ e^A} Q_R^T . \quad (8)$$

The quantum yields of the photoproducts in the T state, Q_R^T and I_1, are calculated from formulae similar to those presented above. The dependence of $\overline{Q}$ on the rate of an adiabatic photoreaction is illustrated in Fig. 6. Evidently, for realistic values of the parameter $A = 4-8$ ($\Delta E = 1-2$ eV), we have $\overline{Q} < 10^{-1}$, provided that k_R exceeds the sum $k_r^T + k_{TS}^\circ$. A significant decrease in $\overline{Q}$ is observed even when Q_R^T is very low. $\overline{Q}$ diminishes to an even greater extent when account is taken of the effect of the occurrence of the S_1-S_0 internal conversion both as a result of the decrease in the yield of the T state and because the point from which the system begins to move along the T state surface may be one with a coordinate $x > 0$ where k_{TS} is greater than k_{TS}°. The initiation of S_1-S_0 conversion processes suppresses the unlikely but possible two-quantum reactions in S states.

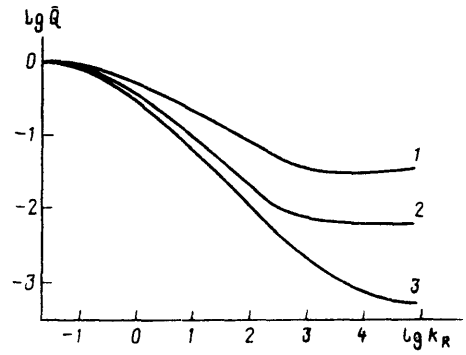


Figure 6. Dependence of $\overline{Q}$ on k_R for $k_r^T = k_{TS}^\circ = 1$: *1*, $A = 4$; *2*, $A = 6$; *3*, $A = 8$.[45]

Similar results have been obtained also for more complex models of potential surfaces, in particular for the *cis–trans* isomerisation reaction for which the maximum values of $k_{ic}(x)$ and $k_{TS}(x)$ correspond not to the reaction product but to an intermediate region and movement along the term of the excited state is diffusional.

Thus in the case of the most effective photostabilisers the population of the T states and (or) their lifetime should be the smallest possible. The fulfilment of one of the conditions specified may be sufficient. The compositions formulated supplement the generally known requirements[1,2] imposed on photostabilisers. When molecules with a fluorescence quantum yield equal or close to unity are used, the first condition holds, for molecules with heavy atoms the second condition holds, while both conditions can be fulfilled in the case of molecules for which the S_1-S_0 and $T-S_0$ conversion processes are initiated by reversible photochemical reactions. Clearly the most

characteristic feature of systems of the latter type is the absence of an appreciable luminescence yield.

We emphasise that the initiation of the conversion processes by an adiabatic photoreaction is important and not the actual occurrence of the photoreaction itself.

The occurrence in the molecular system of luminescence with a large Stokes shift, which may be a consequence (although not always; see, for example, Frank-Kamenetskii and Lukashin[51]) of an adiabatic photochemical reaction, is not a sufficient condition for using the system as an effective photostabiliser.

The above requirements and the ways in which they are met hold also for intrinsically photostable polymers, since the inclusion in the polymer chain of fragments with the photophysical properties listed above increases its photostability.

The experimental data for the photostabilising efficiency of molecular systems will be considered below on the basis of the ideas described above.

V. Principal structural types of photostabiliser molecules

The agreement between the ideas set out above and the available experimental data will be demonstrated in this Section in relation to the most typical examples of systems possessing photostabilising properties. The systematic treatment of these data is based on the photophysical characteristics of photostabiliser molecules and, in particular, on the type of adiabatic photoreaction accelerating the non-radiative conversion.

1. Systems with an intramolecular hydrogen bond (IAHB)

Until recently, photostabilisers of this type have found the greatest practical application in thermoplastic, thermoelastoplastic, and reactoplastic materials[52] and they are being manufactured on a large scale by a number of undertakings in the USSR and abroad.[53–55] It is of interest to trace the development in the course of time of ideas about the mechanism of the action of photostabilisers with an intramolecular hydrogen bond.

A high capacity to absorb UV light in the range 300–400 nm is characteristic of aromatic derivatives with an intramolecular hydrogen bond. In the first publications devoted to the study of such stabilisers (derivatives of benzophenone, benzotriazole, and salicylic acid), their stabilising effect was attributed[56] to their ability to absorb UV light (shielding effect). From the middle 1940's until the beginning of the 1960's, this was the only explanation of the photostabilising capacity of such substances. However, it had long been noted that the proposed mechanism is unable to account fully for the observed protecting effect. For example, a decrease in the molar extinction coefficient ε of phenyl salicylate derivatives leads to an increase in the photoprotecting effect.[57] It was also not understood why certain structurally similar substances with an intermolecular hydrogen bond and with a high extinction coefficient ε (for example, 2-hydroxyphenyl-1,2,4-triazole) do not exhibit a photostabilising effect.[58]

Later the view was expressed in a number of studies[59–62] that, together with the absorption of UV light, UV absorbers can quench excited polymer centres or impurities which are always present in real industrial polymers. The absorption of light in the range 280–400 nm in polymers such as polyolefins (PO), poly(vinyl chloride) (PVC), and polystyrene (PS) is associated with the presence in these substances of oxidation products, variable-valence metallic impurities (for example, catalyst residues), and polycyclic hydrocarbons adsorbed from the atmosphere.[63,64] Furthermore, in the presence of oxygen in polymers [polyethylene (PE), polypropylene (PP), etc.], complexes are formed whose absorption spectra have undergone a bathochromic shift compared with the spectrum of the [pure] polymer owing to the appearance of a charge-transfer band.[65–67] The oxygen molecule is an effective quenching agent for excited states[58] but it does not exhibit photostabilising effects in polymers. On the contrary, it accelerates the photodecomposition of many polymeric materials.[68]

In 1966–1968, Pivovarov and Lukovnikov and co-workers[7–10] and later George[69,70] published a series of studies which significantly altered the ideas about the mechanism of the action of UV absorbers with an intramolecular hydrogen bond. It was shown convincingly in relation to polypropylene that typical UV absorbers such as *p*-(*t*-butyl)phenyl salicylate, 2-(2-hydroxy-5-methylphenyl)benzotriazole, and 2-hydroxy-4-octyloxybenzophenone effectively quenched the luminescence of the polymer with energy transfer to the stabiliser. Depending on the polymer irradiation conditions, the cross-section of the specimens, the exposure time, and the type of stabiliser, the contributions of the shielding and quenching effects may vary and quenching can predominate.[8] Furthermore, after prolonged exposure of the polymer specimens, the quenching of the photochemical oxidation products (carbonyl groups) may become important.[70]

The rules specified above, according to which the stabiliser must absorb light energy to the maximum extent in the region where the polymer absorbs and in the region of its luminescence, were formulated in these studies.[9] In polymers which luminesce in their initial state (before irradiation), the greatest protecting efficiency may be achieved by using mixtures of stabilisers one of which ensures the protection of the polymer molecules and the other must deactivate the oxidative degradation products.[70,71] The validity of these conclusions was confirmed in subsequent investigations.[72–74]

Until recently there was no unanimous view in the literature concerning the role of the intramolecular hydrogen bond in the appearance of the photostabilising effect. The stabilising properties of UV absorbers have been attributed[75–77] to the presence in their structure of a quasi-aromatic ring with a strong hydrogen bond in the ground state of the molecule. However, the estimate of the efficiency of these compounds based on the strength of the intramolecular hydrogen bond[78,79] reflects only the shielding capacity of the stabiliser (the intensity of the absorption band in the range 310–370 nm increases with increase in the energy of the intramolecular hydrogen bond) and does not indicate the practical possibility of using the compound as a photostabiliser. On the other hand, if account is taken of the fact that the energy of the intramolecular hydrogen bond changes when the molecule passes to an excited state and the bond frequently breaks,[80] the possibility of correlation between the strength of the intramolecular hydrogen bond and the stabilising efficiency looks problematical.

It is essential to note yet another approach to the explanation of the mechanism of the deactivation of energy by UV absorbers with intramolecular hydrogen bonds. It has been suggested[81,82] that the most effective stabilisers should be aromatic compounds with an intramolecular hydrogen bond which fluoresce with an anomalously large Stokes shift (derivatives of 2-hydroxyphenylbenzotriazole and 2-hydroxyphenylbenzoxazole) but no experimental data confirming the high efficiency of these compounds are quoted. On the other hand, it is known from literature data[58] that 2-hydroxyphenylbenzoxazole is not efficient as a photostabiliser. Furthermore, in

highly dilute solutions in hydrocarbons, 2-hydroxy-derivatives of benzotriazole exhibit a weak fluorescence with a normal Stokes shift[83] and λ_{max} = 25 000 cm^{-1}, while the glow of this compound observed by Betin[82] is due to the crystalline phase (λ_{max} = 15 000 cm^{-1}). The glow of the crystalline phase at λ_{max} = 22 000 cm^{-1}, erroneously attributed to fluorescence with an anomalously large Stokes shift, has been observed[84] for 2-hydroxyphenylbenzoxazole whose crystals fluoresce with λ_{max} = 21 500 cm^{-1}.[85]

A significant step towards the understanding of the problem under discussion was made in a number of studies[83,86–89] carried out in 1979–1986 using luminescence-spectroscopic methods. The authors analysed the results of investigations of the photostabilising efficiencies of compounds with an intramolecular hydrogen bond on the basis of modern ideas concerning the nature of non-radiative conversion processes in polyatomic molecules, in particular, taking into account the effect of the initiation of these processes by adiabatic photoreactions.[89,90] *It was concluded that molecules with an intramolecular hydrogen bond, for which the lifetime and population of the triplet state are low, exhibit a high photostabilising efficiency as a consequence of the initiation of the S_1-S_0 and $T-S$ conversion processes by reversible intramolecular proton transfer reactions.* This effect leads to the suppression of secondary reactions of T states and ensures a high photostabilising efficiency of systems of this kind.

In conclusion of this Section, we may note that during the last ten years no information has appeared in the literature concerning new types of photostabilisers with an intramolecular hydrogen bond. Benzotriazole[91–96] and benzophenone[97–101] derivatives, modified by different substituents in order to diminish their migration from the polymer and to improve their toxicological properties, are still being patented and recommended for use. A fairly complete survey of the methods of synthesis and applications of different derivatives of 2-hydroxyphenylbenzotriazole has been published.[102]

2. Molecules in which there is a possibility of the *cis–trans* isomerisation reaction

The *cis–trans* isomerisation photoreaction is possible in molecules of azo-compounds, azomethines, stilbenes, chalcones, etc. The rotation of the molecular fragments in the electronically excited state is about the –N=N–, –N=C–, and –C=C– bonds. The reaction can take place both in the liquid phase and in solid polymer matrices.[103] Data on the mechanism of the *cis–trans* isomerisation reaction can be found in a number of communications.[104–107]

A characteristic feature of the majority of arylazo-compounds is the absence of luminescence in liquid and solid solutions and in polymer matrices (alkylamino- and dialkylamino-azobenzenes luminesce weakly in solid matrices at 77 K[108]). Very intense fluorescence has been observed only in *o*-hydroxyarylazo-compounds which tend to undergo the azo-hydrazone tautomerism. The fluorescence has been attributed to the hydrazo-form,[109] which is incapable of *cis–trans* isomerisation.

Among azo-compounds there are dyes of virtually every colour ranging from yellow to black. Depending on the nature of the substituent in the aromatic ring, the photostability and photochemical activity of azo-compounds can vary significantly—from the sensitisation of photochemical reactions to the pronounced photostabilisation effect. It has been observed experimentally that, as a rule, the fluorescent azo-dyes are sensitisers of the photodegradation of polymeric materials.[1] On the other hand, in the majority of photostable dyes, which are capable of increasing the photostability of the polymer (polyamide fabrics), there is no luminescence or it is observed to occur with a very low quantum yield.[110,111] The results of studies on the use of arylazo-compounds as photostabilisers of block-copolymers of isoprene with styrene (IST-30) have been published.[112–114] It has been shown that many azo-compounds, particularly those with amino- or hydroxy-groups in the *para*-position in the benzene ring, as well as nitro- or phenylazo-groups in the 4-position relative to the azo-group are more effective photostabilisers of polydienes than the photostabiliser Tinuvin P used in industry. On the other hand, compounds containing a hydroxy-group in the *ortho*-position relative to the azo-group are relatively ineffective as photostabilisers. The reason for the low efficiency of *ortho*-substituted derivatives and the high efficiency of the *para*-substituted derivatives is that in the series of derivatives of azo-benzene, *para*-derivatives do not luminesce as a consequence of the effective non-radiative deactivation initiated by the *cis–trans* isomerisation reaction, while *ortho*-hydroxy-derivatives do exhibit a luminescence with a high quantum yield[115] and therefore their excited states have a relatively long lifetime.

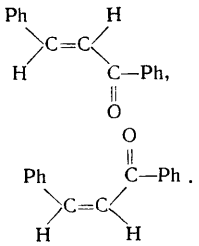
Although the wide-scale practical application of arylazo-compounds as photostabilisers of polymeric materials is limited because of their intrinsic colour (they are unsuitable for the manufacture of white or colourless articles from polymers), they have been recommended for use in polyolefins and in PVC,[116,117] in vulcanised butyl rubbers dyed to give light colour shades,[118] in linear polyesters,[119] and in styrene and rubber block-copolymers.[120] They exhibit a high stabilising effect in polyamides.[121]

Compounds with C=N bonds, namely benazine,[122] furfurylazine,[123] salicylazine,[124] and tetrazine,[125] have already been known for many years as photostabilisers of polymers of different types. There is a high probability of deactivation processes involving the non-rigid molecules of these compounds, which are capable of *cis–trans* isomerisation. Thus benazine (dibenzylideneazine) Ph–CH=N–N=CH–Ph does not luminesce either as a crystal or in solution (at room temperature and at 77 K).[85] Benzylideneaniline and many similar azomethines having different substituents in the benzene ring behave similarly. The effective non-radiative conversion in these systems is associated with the change in the steric structure in the excited state.[126,127] Molecules with a rigid structure, where the C=N group is incorporated in a ring (for example, phenylbenzimidazole) or having rings with intramolecular hydrogen bonds (salicylideneanilines, *o*-tosylaminobenzaldehydes), become luminescent.[128–130] In this case the *cis–trans* isomerisation reaction is impossible or is greatly hindered and the photostabilising properties of the molecules are impaired.

Diarylethylenes (stilbenes) are typical representatives of systems in which *cis–trans* isomerisation takes place. There exists an extensive literature on studies of the luminescence-spectroscopic properties of these compounds and of the isomerisation reaction mechanism.[85,131–138] As a rule, molecules in the *trans*-form fluoresce, while the *cis*-isomers hardly fluoresce. Apparently the difference in the behaviour of the *cis*- and *trans*-forms limits the applicability of stilbenes as stabilisers.

The molecules of indigoid and thioindigoid dyes having a central C=C bond also undergo *cis–trans* isomerisation. A high photostability and ability to increase the resistance to light-induced ageing of dyed materials are characteristic of these compounds.[139,140] It has been shown[141] that only the *trans*-isomers fluoresce, while the *cis*-isomers do not fluoresce and do not phosphoresce. The luminescence-spectroscopic properties of indigoid dyes have been surveyed.[115,142]

The *cis*—*trans* isomerisation reaction is characteristic also of α,β-unsaturated ketones with aromatic rings (chalcones). The isomerism of these compounds is determined by the relative positions of the substituents in relation to the C=C bond of the vinylene group:



These compounds do not luminesce, like other compounds with a non-rigid structure,[142] because the conversion processes occurring in them are accelerated by *cis*—*trans* isomerisation reactions. They have been recommended as effective photostabilisers.[143,144]

Thus many systems in which conversion processes are initiated by the *cis*—*trans* isomerisation reaction are effective photostabilisers.

3. Systems in which there is a possibility of the formation of excimers and exciplexes

As stated in Section IV, the non-radiative conversion processes can be accelerated on formation of excimers and exciplexes. Some data on the properties of these systems can be found in a number of communications.[31,145,146] Apart from intermolecular excimers and exciplexes, it has become usual to refer also to intramolecular ones. The formation of the latter is attributed to a rearrangement of the structure of the molecule in the excited state such that the different fragments undergo a significant change in their positions in space and the distance between them diminishes. Examples of the formation of intramolecular excimers have been published.[147–149]

Among systems used as photostabilisers in which there is a possibility of the formation of excimers (exciplexes), mention should be made of derivatives of acrylic acid,[150–152] benzylidenemalonates,[56] phenyl benzoates and carboxylic acid amides,[153] and aromatic derivatives of phosphoric acid.[154] The mechanism of the photoprotecting action of these compounds was not understood until attention was turned to the relation between the stabilising properties of molecules and the initiation of non-radiative conversion by reversible photoreactions.[45]

A detailed analysis of the mechanism of conversion for aromatic derivatives of phosphoric acid has been carried out[155] on the basis of quantum-chemical calculations by the CNDO/2 method.[156] Compounds having the structure Ph—X—PO(Y—Ph)—X—Ph, where X = Y = O, X = Y = NH, and X = O, Y = NH, were investigated. It was established that, in the equilibrium configuration of the excited S_1 state, these molecules have a sandwich structure with an almost parallel disposition of benzene rings, as in the excimers of benzene[157] and polystyrene.[158] This entails a decrease in the difference between the energies of the S_1 and S_0 states, the acceleration of the internal conversion process, and a decrease in the population of the T states. Furthermore, the non-planar structure of these systems and the presence of the central heavy P atoms ensure a high rate of T—S conversion processes. Accordingly, aromatic derivatives of phosphoric acid do not luminesce in solutions either at room temperature or at 77 K and exhibit very pronounced photostabilising properties.[154]

A similar conversion mechanism operates in other known photostabilisers which do not contain an intramolecular hydrogen bond in their structure (oxanilides, benzamides, benzoates, and acrylate esters). Their steric rearrangement in the excited state is sufficiently rapid (over a period $\lesssim 10^{-11}$ s[159]) to ensure conditions for the initiation of conversion processes.

The unusual behaviour of phenyl benzoates in polymers has for a long time attracted attention.[2] The stabilising capacity of these systems has been traditionally attributed to the Fries photorearrange-ment,[160] which results in the formation of 2-hydroxybenzophenones which protect the polymer as molecules with an intramolecular hydrogen bond. However, this explanation proved to be over-simplified because it has been shown[57] and then confirmed[161] that phenyl benzoates are themselves photostabilisers. An even more direct proof of this postulate was obtained in a study[162] where it was shown that chloro-substituted phenyl benzoates, in which the Fries rearrangement is impossible, exhibit a stronger photoprotecting effect than compounds in which such rearrangement is possible.[125] The mechanism of such conversion in phenyl benzoate has been examined in an investigation[163] where it was shown that the absence of luminescence and the high photostabilising efficiency of this compound are associated with the initiation of conversion processes as a consequence of a conformational rearrangement of the type involving the formation of an intramolecular excimer.

Aromatic derivatives of acrylic acid, investigated by luminescence spectroscopic methods,[164] also have a low luminescence yield as a consequence of sensitised conversion processes. Since in addition they do not undergo irreversible photoreactions,[165] their photostabilising efficiency is high.

Diaryloxamides,[166–171] having the general formula R^1—Ph—NH—CO—CO—NH—Ph—R^2 and exhibiting a high stabilising efficiency in polymer-containing coatings, varnishes, and polycarbonates, have similar properties. The conversion mechanism under discussion operates also in the recommended derivatives of benzoic and benzacrylic acids[170–174] and in benzoylmethane[175–177] (stabilisers of butadiene rubber and cosmetic preparations).

There are fairly numerous literature data on the quenching of the excited states of polymers by electron-donating complex-forming agents. Thus it is well known that the formation of complexes between amines and the carbonyl groups of polymeric molecules entails the initiation of conversion processes and the quenching of excited states in exciplexes.[145] Other compounds having a relatively low ionisation potential behave similarly.[145]

The question of the deactivation of singlet oxygen molecules occupies an important place in the problem of the photostabilisation of polymers. They arise as a result of energy transfer from different sensitiser molecules (aromatic hydrocarbons, dyes, pigments, carbonyl compounds)[1,2,104,178] and participate in reactions involving the formation of hydroperoxides, the oxidation of C=C bonds, addition to diene systems, etc.[179–182] Tertiary amines, substituted phenols, chelate complexes, and β-carotene are used to suppress polymer photochemical oxidation processes.[179–182] Singlet oxygen is then quenched in exciplexes and in the case of β-carotene this is accompanied also by the *cis*—*trans* isomerisation reaction.

Thus many systems in which there is a possibility of the formation of intermolecular or intramolecular exciplexes, which initiate conversion processes, exhibit effective photostabilising properties.

4. Compounds containing a metal atom

As mentioned in Section II, a molecular system with a heavy atom usually has a short lifetime of the T state and can therefore be an effective photostabiliser. An example of systems of this type is provided by organometallic compounds (for example, ferrocenes) and metal chelates.[1,2] These compounds can be both UV radiation absorbers and quenching agents for excited states of the polymer or impurity molecules. We shall consider this question briefly.

Apparently the first experimental indication of the possibility of energy transfer from the polymer to the molecules of phenylferrocene and *o*-hydroxybenzoylferrocene, used to photostabilise melamine-alkyd coatings, was obtained by Schmitt and Hirt.[184] Ferrocene derivatives also protect other polymers against the action of light.[1]

Chelate complexes of heavy metal ions (Ni, Cr, Eu, etc.) with thiobisphenols quench the triplet state of the carbonyl group[185] and other chromophores.[1] For this reason alone, they exhibit photostabilising properties. However, it is known that not all metal chelates are quenching agents for the excited states of carbonyl groups.[2] Thus nickel thiophenoxide does not quench the T states of ketones but nevertheless exhibits photostabilising properties, which have been attributed to the involvement of this chelate in processes leading to the quenching of singlet oxygen molecules.[186,187] In terms of the efficiency of the quenching of singlet oxygen, metal chelates can be arranged in the following sequence depending on the nature of the metal: $Mn^{2+} \simeq Cu^{2+} < Co^{2+} < Ni^{2+} \simeq Fe^{3+}$. As already mentioned above, singlet oxygen may be quenched by the formation of complexes. In the case of metal chelates, the spin–orbit interaction, which is determined by the charge on the metal nucleus, is important for this quenching mechanism. This problem has not yet been considered theoretically.

If the quenching of excited states in polymers is associated with energy transfer to the photostabiliser molecule, it is subject to the same rules as in other molecular systems:[14] energy transfer takes place only when the energy at the lowest excited state of the acceptor is lower than the energy of the donor; triplet–triplet transfer occurs via an exchange-resonance mechanism while singlet–singlet transfer involves an inductive-resonance mechanism; the efficiency of the transfer increases with increase in the overlap integral for the emission spectrum of the donor and the absorption spectrum of the acceptor. When the photophysical properties of the photostabilising molecule are known, this permits conclusions about the mechanism of its action and a description of the dependence of the transfer constants on the type of photostabiliser molecule and the type of polymer.[188,189]

It is essential to note that the photostabilising effect of metal chelates does not reduce to the physical mechanism of their action, because they function also as activators of the non-radical decomposition of hydroperoxides and their efficiency depends also on the type of ligand.[190–192] Detailed studies have been made on the mechanism of the action and efficiency of the complexes most widely used to stabilise polydienes.[193] Similar results were also obtained in another investigation.[194]

New metal chelate stabilisers for butadiene rubber, polystyrene, and polyolefins have been proposed in recent years.[195–198] As a rule, their action does not reduce to a single mechanism but involves shielding processes, the quenching of excited states, and chemical inhibition of photoreactions.

VI. Synergistic mixtures of photostabilisers

Under the real conditions of industrial processing and use of articles made of polymer materials, the polymer is acted upon by different ageing factors (heat, light, oxidants, mechanical stresses, etc.), and different ones can predominate. In order to impart to polymer articles an increased useful lifetime, in practice one usually employs not individual stabilisers but their mixtures, which frequently exhibit a synergistic effect. Such synergistic mixtures can comprise UV absorbers and quenching agents, antioxidants (including PZA) and UV absorbers, quenching agents, and antioxidants of various types, etc. Ternary mixtures of stabilisers are sometimes used.

Thus a mixture of the 2-hydroxy-4-octyloxybenzophenone photostabiliser and PZA (Tinuvin 770) in proportions of 9:1 imparts a significantly greater photostability to polypropylene than when each stabiliser is used separately.[199] It has been shown[200] that the employment of PZA in a mixture with physical mechanism stabilisers makes it possible to increase the photostability of polypropylene and high- and low-pressure polyethylenes by a factor of 6–8. It has been reported that sheeting for agricultural purposes with a useful lifetime of 3–4 years has been developed in Hungary using mixtures of this type. A synergistic effect has been observed[201,202] when a mixture of Tinuvin 770 with the Tsissorb [Cis-sorb?] 531 photostabiliser (2-hydroxybenzophenone) was used.

The causes of the synergism between PZA and photostabilisers have been investigated.[203–205] It was shown for the first time in these studies that the synergistic effect depends on the cross-section of the polymer article: a significant effect is observed in articles with a cross-section greater than 1 mm. A diffusion mechanism of the synergistic effect has been put forward to account for this finding. The diffusion of photostabiliser molecules to the PZA from the bulk of the polymer and from its surface ensures the protection of the surface layer undergoing further chemical oxidation (the "depot" effect).

Similar ideas have been put forward in another study,[206] where the photostabilisation of polypropylene, polystyrene, high pressure polyethylene, and ABC resins was investigated using synergistic mixtures of PZA and UV absorbers. According to these ideas, in the case of thin-profile articles the synergistic effect is either small or is altogether absent. Apparently this was observed in a study[207] where mixtures of Tinuvin 770 with the Tsissorb 531 photostabiliser, Tinuvin 327, and the UV-1084, Negopex B, and Irgastab 2002 nickel chelates failed to give a synergistic effect when films up to 200 μm thick were used.

Interesting results for the stabilisation of polyurethane systems have been obtained.[208] The authors investigated the protection of these systems against photooxidative ageing using PZA, photostabilisers, and phenolic antioxidants as well as their mixtures. It was established that in the case of polymers containing aromatic fragments the use of synergistic mixtures of these three types of stabilisers is the most effective.

The most complete survey and theoretical consideration of numerous experimental data on the synergism between various types of stabilisers and auxiliary substances were carried out by Ivanov and Shlyapintokh.[209] They considered the nature of the synergistic effect in the photostabilisation of polymers and they assumed that the effect is based on the following mechanisms: (1) diffusional transfer of the antioxidant to the photoreaction zone generated by the UV absorber; (2) protection of the photostabiliser by the antioxidant; (3) the action of the main stabiliser during use and of

the additional stabiliser during the processing of the polymer; (4) the increase in the efficiency of the UV absorber in the presence of an antioxidant as a consequence of the change in the mechanism of chain termination; (5) protection of the polymer by auxiliary additives during the activation of the main stabiliser in the initial stage of the ageing process; (6) the effect of one stabiliser as a radical acceptor and of another as a compound decomposing hydroperoxides; (7) quenching of the excited states of the antioxidant by the photostabiliser; (8) the use of special additives to improve the distribution of stabilisers in the polymer; (9) the formation of effective stabilisers on reaction of stabilising additives; (10) regeneration of the effective stabiliser. The authors estimated the maximum synergistic effects based on these mechanisms and the optimum component ratios. They analysed the probable changes in the effects as the thickness of the polymer specimens, the light intensity, and temperature were varied. Mechanisms 1–5 and 7–9 were studied experimentally.

Synergistic mixtures containing photostabilisers have been proposed recently for the stabilisation of polyethylene,[210,211] automobile enamels,[212] enamels for polyurethane coatings,[213] and other polymer systems.[214–218]

It is important to emphasise that all the photostabilisers used in synergistic mixtures are systems in which the T states are either not populated or have a short lifetime.

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Thus analysis of theoretical and experimental data makes it possible to formulate requirements, in addition to those already well known, which must be satisfied by the photophysical properties of molecular systems with a high photostabilising efficiency. The possibilities in the search for new types of photostabilisers have been by no means exhausted since only a small number of systems with a limited set of the simplest reversible adiabatic photoreactions, initiating non-radiative conversion processes, have been used hitherto. The ideas described determine to a large extent the pathways followed in such search.

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