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Application of Flash Photolysis in the Study of the Triplet State of Organic Substances

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Flash photolysis is a relaxation method for the investigation of the mechanism of rapid photochemical reactions. The fundamental design and constructional features of spectroscopic apparatus for flash photolysis have been examined. Considerable attention has been devoted to the description of the sources for flash photolysis. The application of flash photolysis in the study of triplet states of organic substances in solutions is considered. The results obtained for the quantum yields and the triplet-triplet absorption spectra of aromatic hydrocarbons, carbonyl compounds, dyes, and pigments have been presented. The mechanisms and the kinetics of the deactivation of triplet states, the quenching mechanisms, and the role of the triplet state in photochemical reactions have been discussed.
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1. INTRODUCTION

The study of excited electron states in chemical and biological processes constitutes an extremely urgent task. Primary photochemical reactions are known to take place with participation of both excited singlet and triplet states. Terenin[1] and Lewis and coworkers[2-4] put forward and justified experimentally the hypothesis that the transition from the excited singlet to the triplet state is due to the inversion of the spin of the optically excited electron. The longer lifetimes of triplet molecules (10^{-3}–10^{-4} s) compared with those in the excited singlet state (10^{-8}–10^{-9} s) in solutions are responsible for the dominant role of triplet states in the majority of photochemical reactions.

Until comparatively recently the sole source of direct information about triplet states of polyatomic molecules were data on the spectra and decay of phosphorescence[5]. Since most substances are not phosphorescent in liquid solutions, i.e. under conditions where diffusion processes take place, there was no information about triplet states of substances in solution. With the appearance of pulse excitation methods and in particular the method of flash photolysis† it became possible to follow directly processes involving the population and deactivation of the triplet states of substances in condensed and gaseous phases.

Recently many papers have been published on the triplet states of organic substances in solutions investigated under conditions of intense flash photolysis. Therefore it has become necessary to give a systematic account of the information and the properties of triplet states and their role in primary photochemical processes. The available reviews[6-8] by no means fully reflect the data on the physicochemical properties of the triplet states of organic substances. The present review deals exclusively with the results obtained in the study of the triplet states of organic substances by the method of flash photolysis. The aim of the review was also to illustrate the scope of the method of flash photolysis in the investigation of intermediate short-lived products of rapid reactions.

† In the Russian literature this method is also referred to as pulse photolysis, pulse photoexcitation, and pulse spectroscopy.

2. METHOD OF FLASH PHOTOLYSIS

Flash photolysis is one of the relaxation methods employing powerful brief light pulses which act on the given substance to give rise to a considerable non-equilibrium concentration of metastable states. The relaxation of the system to the initial or a new equilibrium state is "followed" from the absorption spectrum or some other characteristic recorded over a period of time after the pulse initiation.

Pulse illumination is achieved as a result of a pulse discharge, preferably in an inert gas (xenon, argon, and krypton)[9]. The source of the electrical energy of the flash ($E = CU^2/2$) is a battery of high-voltage condensers of capacity C (μF) charged to a potential U (kV). One or several gas-discharge flash tubes connected in series or in parallel serve as a source of the flash. The flash source connected by heavy leads to the battery of condensers constitutes the electrical circuit.

In the design of apparatus for flash photolysis much attention has been devoted to the electrical circuit and particularly to the flash source. The requirements which must be met by the source reduce to minimum duration and selectivity of the emission and also to maximum light yield. The electrical discharge in the circuit is oscillatory or shows simple decay depending on the relation between the resistance R, the inductance L, and the capacitance C of the circuit elements. When the relation $R = 2\sqrt{L/C}$ holds, the critical damping conditions are achieved, the duration of the emission τ is then a minimum which is most suitable for photoexcitation. A decrease of τ is obtained by lowering L and C ($\tau \propto \sqrt{LC}$). However, one must bear in mind that the compensation of the electrical energy of the flash on lowering C by increasing U is restricted by the load factor

($F \propto CU^4$), which determines the duration of the serviceability of the flash tubes. For electrical circuits with a low value of C (several microfarads), the duration of τ is determined largely by the self-inductances of the flash tubes. The inductance L of a circuit consisting of two series-connected elongated flash tubes (interelectrode distance 20 cm; 250 nH) connected to a condenser (5 μF; 6 nH) by a low-inductance circuit of the "sandwich" type (length 100 cm; 8 nH) is 264 nH.[10] The duration of the flash in this version $\tau = 2\pi\sqrt{LC}$ (according to the current) is 7.2 μs at $E = 1000$ J. The reduction of τ to 1.8 μs is achieved using a coaxial design for the flash tubes with $L = 6$ nH.[11]

Ultrashort (10^{-7}–10^{-12} s) light pulses are obtained by employing a self-contracting (the Z-pinch effect) pulse discharge ($\tau = 2 \times 10^{-7}$ s, $E = 4850$ J)[12] or lasers operating under giant pulse conditions[13–15].

In order to determine the time resolution of the spectrophotometric apparatus with flash photolysis, it is necessary to consider the flash duration τ_{light} in contrast to $\tau_{current}$. Due to the afterglow recombination process $\tau_{light} \geqslant \tau_{current}$. For $\tau_{current} = 5$ μs, the duration of the recombination afterglow τ_{light} may reach 150 μs (for 0.1 of the peak light amplitude) depending on the type of gas employed, the pressure, and the wavelength of the emission. The duration of afterglow can be reduced by increasing the internal surface area of the flash tube[16], by decreasing the length of the mean free path of the excited molecules[17], and by introducing quenching gases (N_2 and O_2).[18,19]

In the practical application of flash photolysis, flash lamps filled with both inert and molecular gases (O_2, N_2, and H_2) and their mixtures have found the greatest use[18–20]. Depending on the type of gas and its pressure (5 mm–10 atm‡), the spectral distribution of the pulse emission changes appreciably[21–23]. The emission maximum shifts towards the ultraviolet part of the spectrum when the energy of the flash increases as a result of the increase in U.[24] The application of flash lamps filled with various gases in combination with narrow-band light filters interposed between the source of radiation and the test object ensures the selectivity of excitation.

The number of quanta n emitted by the flash lamp during the flash depends on E, the type of gas, and the wavelength of the emission. According to actinometric measurements, $n = 1 \times 10^{20}$ quanta per flash in the range 220–440 nm at $E = 3000$ J ($\tau_{0.1} = 9.5$ μs; tube filled with O_2 at 20 mmHg).[19] With such high light intensity, the molecules of the light-absorbing substance (10^{-5}–10^{-6} mole litre^{-1}) undergo repeated (10^2–10^3) excitation during a single light pulse. A high concentration of intermediate, for example triplet, photoexcitation products is thereby achieved. Thus 100% population of the phosphorescent triplet level (5×10^{-7} mole litre^{-1}) is attained when an aqueous solution (0.01 N NaOH) of the dye is irradiated by a flash with $E = 6000$ J[25] (the probability of the transition to the triplet state is about 0.05)[26]. The high concentration of the intermediates generated by the photon excitation permits the use of spectroscopic methods for their recording and identification.

For semiquantitative measurements of the intermediate products of a reaction initiated by a light pulse, a spectrographic method of recording, described in the first version of the flash photolysis apparatus[27], is employed. Fig. 1 shows schematically the positions of the principal constructional elements of the flash photolysis apparatus with spectrographic recording[10]. The flash initiating the photochemical reaction is produced by the discharge of a high-voltage condenser (*1*) via two cylindrical flash lamps connected in series (*4*). The lamps are connected to the condenser via low-inductance leads (*2*) of the "sandwich" type. The flash is initiated by an electric pulse applied to the trigger (*3*) (a thyratron, ignitron, etc.). The test object is put in a cuvette (*5*) and is initially excited by light from photolysis flash lamps (*4*). The absorption spectrum of the intermediate product is "instantaneously" (about 10^{-6} s) recorded with the aid of a low-power monitoring flash lamp (*6*) and a spectrograph (*7*). The absorption spectrum of the intermediates is photographed an arbitrarily fixed delay time $\Delta\tau$ after the initiation of the excitation.

A series of absorption spectra of the intermediates are obtained in repeated measurements with variable delay times $\Delta\tau$. The change in the blackening of the photographic plate, which serves as a receiver of the radiation of the monitoring source, is proportional to the change in the optical density of the solution of the test substance, provided that the degree of blackening and the exposure are linearly related. The use of the spectrographic method for the recording of intermediates is valid for substances whose absorption spectra show fine (for example vibrational–rotational) structure. In this case the application of photoelectric recording requires many repetitions of the irradiation of the substance by light pulses, which frequently leads to its decomposition. In this respect the spectrographic method of recording is convenient for the study of the mechanism of irreversible photochemical processes.

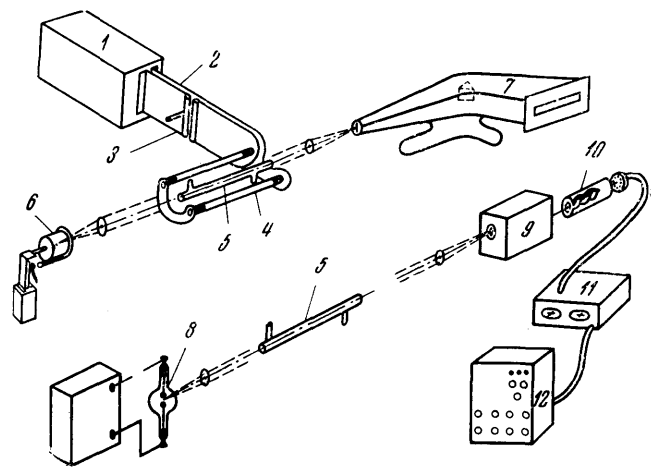


Figure 1. Diagram of flash photolysis apparatus[10] (for explanation, see text).

For accurate measurements of concentrations, the extinction coefficients of intermediates, and the kinetics of their reactions, the more sensitive photoelectric method of recording is employed. Photoelectric detectors cover a much wider range of wavelengths compared with the photographic plate, which in turn yields more information about short-lived products of photochemical reactions. Fig. 1 also shows schematically the positions of the principal elements of a flash photolysis apparatus with photoelectric

‡ For spherical flash lamps.

recording. In this version the monitoring flash lamp (6) is replaced by a source of continuous radiation (8)—an incandescent lamp or an ultrahigh pressure arc lamp filled with xenon or mercury. The spectrograph (7) is replaced by a monochromator (9) with a photomultiplier cell (10), a power source (11), and an oscilloscope (12). The spectral changes under the influence of the flashes from the photolysis lamp are recorded "point by point", the monochromator being set before each flash to a fixed wavelength in the relevant wavelength range.

The differential resolving power (on the basis of the change in the optical density ΔD) of the flash photolysis apparatus with photoelectric recording is determined by the level of fluctuation interference (noise) of the recording system. An increase of the signal-to-noise ratio is achieved by employing the maximum possible illumination of the photocathode of the photomultiplier by the continuous monitoring source, by using a low supply voltage for the photomultiplier, and with the aid of electric filters (RC) which limit the high frequency components of the transmitted signal[28-30]. CAT's combined with a source of pulse photoexcitation and operating under stroboscopic conditions have been employed recently to increase the signal-to-noise ratio[29,31]. When the illumination of the reaction system is repeated many times, the signal-to-noise ratio increases by a factor of $\sqrt{n}$, where n is the number of exciting light pulses.

As well as the above two methods for the recording of the absorption spectra of intermediates, fast scanning spectroscopy is employed[32-35]. In this method the absorption spectrum of the intermediates is scanned at a high speed with simultaneous oscilloscopic recording of the spectrum. In the single-beam high-speed spectrometer with a rotating system of three mirrors (optical accelerator) the range 400–1100 nm is scanned over a period of 4×10^{-5} s.[34]

The majority of the measurements of the absorption spectra of the intermediates have been made with flash energies in the range 100–1000 J. Approximate calculations show that an energy of 1000 J is sufficient for most photochemical studies[36]. As already mentioned, the time resolution of the flash photolysis apparatus is determined by the duration of emission from the photochemical flash source. The limiting rate constants for rapid reactions may be estimated from the resolution time of the apparatus and its sensitivity. For a first-order reaction, the maximum rate constant k_1 is estimated as $k_1 \simeq 10^5$ s^{-1} when the duration of the flash $\tau_{0.5}$ is several microseconds. For a second-order reaction, for example a reaction between radicals, $k_2 = \epsilon l \tau_{0.5}^{-1} \Delta D^{-1}$ is found from the relations $k_2 = \tau_{0.5}^{-1} C^{-1}$ and $\Delta D = \epsilon C l$, where ϵ is the extinction coefficient of the intermediate product (radical), C its concentration, and l the thickness of the absorbing layer (in the direction of the probing beam). For $l = 10$ cm, $\Delta D = 0.1$, and $\tau_{0.5} = 10^{-5}$ s, we have $k_2 = 10^7 \epsilon$. Consequently the maximum value is $k_2 = 10^{11}$ litre mole^{-1} s^{-1} when $\epsilon = 10^4$ litre mole^{-1} cm^{-1}.[36]

The reaction intermediates may be recorded in ways other than from absorption spectra. The charged species (ions) generated by the light pulse can be recorded from the change in electrical conductivity[37]; free radicals can be recorded using ESR spectra[38].

However, in the practical application of flash photolysis, the spectroscopic method for recording intermediate products, and in particular triplet states, has found the greatest use. In principle, this method can be used to solve two problems: the elucidation of the structure of intermediates from their absorption spectra, and of the mechanism and kinetics of the transformation of intermediates in rapid reactions.

3. QUANTUM YIELD OF THE TRIPLET STATE

Many molecules of aromatic hydrocarbons, carbonyl compounds, dyes, and pigments are effectively converted into the triplet state in liquid and solid solutions under the action of flash photolysis. The possibility of directly observing the population and deactivation processes of triplet states is determined, on the one hand, by the relatively long lifetime of triplet molecules and, on the other hand, especially by the capacity of triplet molecules to absorb from the triplet level (the triplet–triplet absorption spectrum). The last factor is a consequence of the transitions between states of the same multiplicity being allowed and constitutes the foundation of the spectroscopic recording of triplet molecules using pulse illumination.

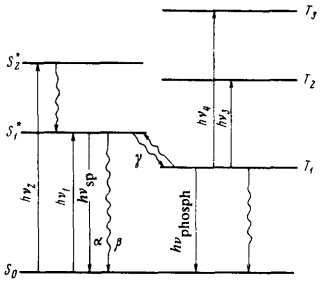


Figure 2. Schematic representation of the energy levels of the molecule: S_1^* and S_2^*—excited singlet levels; T_1, T_2, and T_3—excited triplet levels; for other explanations, see text.

The energy of the lowest excited singlet state is known to be degraded by several processes including fluorescence, non-radiative degradation, and transition to the triplet state[39-42]. Fig. 2 shows schematically the positions of the energy levels of the molecules, where α, β, and γ denote the probabilities of transitions giving rise to fluorescence (α), non-radiative degradation (internal conversion) (β), and transition to the triplet state (γ). There are simple relations between the probability of the γ transition, the quantum yield Φ_T in the formation of the triplet state, and the lifetime τ of the molecules in the S_1^* state: $\Phi_T = \gamma/(\alpha + \beta + \gamma)$ and $\Phi_T = \gamma\tau$. Using flash photolysis, it is possible to find Φ_T by the following two procedures. The first, the direct determination of $\Phi_T = C_\gamma/C_a = \Delta D/(\epsilon_T - \epsilon_S)\theta C_0 l$, is based on the direct determination of the concentrations of the triplet molecules C_γ and the molecules C_a excited by the light pulse[26,43-45]. ΔD is the change in optical density on formation of the triplet state, $\epsilon_T - \epsilon_S$ the difference between the extinction coefficients of the molecules in the triplet and singlet stage respectively, θ the fraction of light quanta absorbed by the molecules of the substance at an initial concentration C_0, and l the thickness of the absorbing layer. The expression for θ is $\theta = \int I_f(\nu)R(\nu)[1 - I_M(\nu)]d\nu / \int I_f(\nu)R(\nu)d\nu$, where I_f and I_M are the fractions of the light pulse transmitted by the light filter and the substance respectively and R is the relative

light yield of the flash excitation source[26]. The accuracy of such determinations of Φ_T could be within 20–30%. [46]

The second method for the determination of Φ_T [47,48] is based on the perturbation by heavy atoms of the spin–orbital coupling in the molecule[49]. The effect of heavy or paramagnetic atoms in one molecule leads to an increase of the probability of the transition to the triplet state of another[50] and the quenching of the fluorescence[51]. Thus in the presence of heavy atoms the relative yield F/F^0 of fluorescence falls with a parallel increase of the yield D_T/D_T^0 of the triplet molecules of the substance. The quantitative relation between the two processes is expressed by $F^0/F = (D_T F^0/D_T^0 F - 1)(1 + k_1/k_2)\Phi_T + 1$, where k_1 and k_2 are the rate constants for the quenching process:

$$S_1^* + Q \rightarrow S_0 + Q \quad , \qquad (1)$$

$$S_1^* + Q \rightarrow T_1 + Q \quad . \qquad (2)$$

Bromobenzene[47], potassium and sodium iodide and bromide, *p*-iodophenol, bromocyclohexane, *p*-dibromobenzene[52], and also gaseous xenon[48], etc. are used as heavy-atom quenching agents Q. Table 1 presents a number of values of Φ_T determined by one of the two methods. It shows that the values of Φ_T for xanthene dyes (fluorescein, eosin, and erythrosine) increase sharply on introduction of a heavy atom (bromine and iodine) into the fluorescein molecule. This is due to the effect of the heavy atom bound chemically to the molecular skeleton on the probability of transition to the triplet state[55].

Table 1. The quantum yields Φ_T of the transition to the triplet state determined by the method of flash photolysis.

Object	Solvent (20°C)	Φ_T	Refs.
Anthracene	liquid paraffin	0.58 ± 0.10	26
		0.75	47
9-Methylanthracene	liquid paraffin	0.44	47
9-Phenylanthracene	ethanol	0.51 ± 0.02	52
1,2,5,6-Dibenzanthracene	3-methylpentane	1.03 ± 0.16	26
Pyrene	ethanol (95%)	0.38 ± 0.02	48
Phenanthrene	3-methylpentane	0.70 ± 0.12	26
Fluorescein	water, pH 9	0.05 ± 0.02	26
	water, pH 12	0.08	53
6-Hydroxy-9-phenylfluorescein	water, pH 12	0.02	53
Dibromofluorescein	water, pH 9	0.49 ± 0.07	26
Eosin	water, pH 9	0.71 ± 0.10	26
Erythrosin	water, pH 9	1.07 ± 0.13	26
Chlorophyll a	ether	0.64	44
Chlorophyll b	ether	0.88	44
Phaeophytin a	–	0.3 ± 0.1	45
Mesoporphyrin	–	0.3 ± 0.1	45
Zn-mesoporphyrin	–	0.28 ± 0.1	45
Al-etioporphyrin	ethyl iodide (77°K)	0.8	54

A knowledge of Φ_T and the fluorescence quantum yield Φ_{fl} permits the determination of $\Phi_{n.d}$ for non-radiative degradation of many of the compounds listed in Table 1. Thus for pyrene[48] and also anthracene and its derivatives[47,52], $\Phi_T + \Phi_{fl} = 1$, which indicates the absence of a non-radiative degradation process. A value of $\Phi_{n.d}$ close to zero was also observed for xanthene dyes[44], chlorophylls[44,45], and etioporphyrins[57]. An appreciable contribution (≥ 50%) of non-radiative degradation to the deactivation of the excited singlet state was observed for mesoporphyrins[45] and 6-hydroxy-9-phenylfluorescein[3]. In the latter case $\Phi_{n.d} = 0.8$, while for fluorescein $\Phi_{n.d} \simeq 0.1$.[53] The difference between the values of $\Phi_{n.d}$ for the two compounds indicated above, which differ by the charge of the carboxy-group (in an alkaline solution), is due to the structure-forming effect of water molecules (solvent), which lowers the probability of the deformation of the molecular skeleton and hence of non-radiative degradation[41,53].

The values of Φ_T listed in Table 1 and determined indirectly, for example from the sensitisation of the *cis–trans* isomerism[56], are in good agreement with one another.

4. TRIPLET–TRIPLET ABSORPTION

In 1953 Porter and Windsor[58] observed the appearance in the spectrum of anthracene in hexane of a short-lived triplet absorption at 398 and 420 nm under the influence of pulse illumination. Subsequently the same workers[59] recorded the absorption spectra of the triplet molecules of 32 substances including aromatic hydrocarbons, ketones, and other compounds. The triplet–triplet absorption spectrum arises as a result of the absorption of light quanta by triplet molecules ($T_1 \xrightarrow{h\nu_3} T_2$; $T_1 \xrightarrow{h\nu_4} T_3$; etc., Fig.2). Fig. 3 shows the absorption spectra of the triplet states of condensed aromatic hydrocarbons ranging from benzene to pentacene. The triplet–triplet absorption of benzene was observed only in a solid matrix at 77°K[60], while the spectra of the triplet absorption of naphthalene, anthracene, naphthacene, and pentacene were measured at room temperature in liquid solution[59]. The wavelengths of the triplet absorption maxima of certain aromatic hydrocarbons (anthracene and its derivatives, naphthalene and its derivatives, naphthacene, pentacene, phenanthrene, chrysene, pyrene, rubrene, and others) have been given in a number of papers[59,61–65].

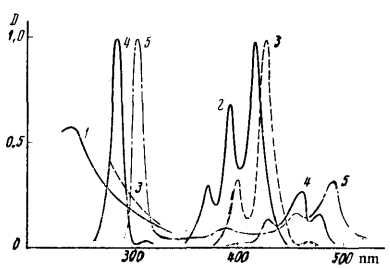


Figure 3. Triplet–triplet absorption spectra: *1*) benzene; *2*) naphthalene; *3*) anthracene; *4*) naphthacene; *5*) pentacene.

An important characteristic of absorption spectra is the oscillator strength f,[66] which is related to the experimental extinction coefficient ϵ: $f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu$. The ϵ_T for a triplet–triplet absorption is determined in several ways. One of them is based on the fact that the transition of a molecule to the triplet state is accompanied by the depletion of the singlet S_0 level. This method of determination of ϵ_T is convenient for those substances whose singlet–singlet and triplet–triplet absorption spectra do not overlap.

The degree of attenuation (decolorisation) of the singlet absorption band under the influence of pulse illumination is a measure of the concentration of triplet molecules. In this case $\epsilon_T^{\lambda_2} = \epsilon_S^{\lambda_1}(\Delta D^{\lambda_2}/\Delta D^{\lambda_1})$, where λ_1 and λ_2 correspond to the maxima in the singlet and triplet absorption. In the case of overlapping singlet–singlet and triplet–triplet absorption spectra, ϵ_T is found from the variation of ΔD with flash energy E. The limiting value ΔD^0, which is independent of E, corresponds to 100% conversion into the triplet state[25,67]. ϵ_T can also be estimated from the kinetic data for the deactivation of the triplet molecule. In this case one finds experimentally the relative rate constant for triplet–triplet annihilation: $\varphi = k/\epsilon_T$.[34] The rate constant k is usually close to the diffusion constant $k_D = 8RT/3000\eta$, where η is the viscosity of the medium[68].

Table 2. Extinction coefficients ϵ_T for triplet–triplet absorption and their oscillator strengths f for aromatic hydrocarbons.

Object	Solvent 20°C)	ϵ_T, litre mole^{-1} cm^{-1}	f	λ, nm	Refs.
Benzene	65% isopentane + 35% 3-methylpentane*	⩾1600	—	≃240	0
Naphthalene	liquid paraffin	10 000	0.06	415	59
	cyclohexane	22 600	—	412	9
	3:1 ethanol – methanol**	45 000	—	413	70
Anthracene	liquid paraffin	71 500	0.4	424	59
	hexane	46 000	—	420	63
	cyclohexane	57 200	—	420	9
	3:1 ethanol – methanol**	90 000	—	425	70
Naphthacene	liquid paraffin	52 600	0.4	460	59
	liquid paraffin	8000	0.05	312	59
	liquid paraffin	195 000	0.9	285.5	59
Pentacene	hexane	205 000	2.4	490	59
	hexane	630 000	2.0	305	59

* Measurements at 77°K.
** Measurements at 113°K.

Consequently $\epsilon_T = 8RT/3000\eta\varphi$. The values of ϵ_T for certain aromatic hydrocarbons found by one of the above methods and also the values of the calculated oscillator strength f are listed in Table 2. The high extinction coefficient ϵ_T for the triplet–triplet absorption of aromatic hydrocarbons is evidence of a high probability of the transitions $T_1 \rightarrow T_2$, $T_1 \rightarrow T_3$, etc. According to the literature[59,71], T_1, T_2, T_3, T_4, and T_5 are identified with the states $^3B^+_{2u}$, $^3A^-_{1g}$ (lower), $^3B^-_{1g}$ (lower), $^3B^-_{1g}$ (upper), and $^3A^-_{1g}$ (upper) respectively.[5] The positions of the excited triplet levels T_2, T_3, etc. are found from the positions of the lower triplet levels T_1 for polyacenes[2,50,72] and triplet–triplet absorption data[59]. The experimental values of T_2, T_3, T_4, and T_5 proved to be in good agreement with calculation[71].

The measurement of the triplet–triplet absorption spectra of aromatic compounds containing heteratoms, for example ketones, and also dyes and pigments, is in many cases more difficult than the measurement of the triplet spectra of aromatic hydrocarbons. In contrast to aromatic hydrocarbons, the flash photolysis of many heterocompounds yields both triplet and intermediate products (radicals, ions, isomers, etc.) as a result of the photoexcitation of the molecules. In many cases the absorption spectra of the intermediates are very similar to the triplet absorption spectra; moreover, radicals may be formed as a result of the reaction of triplet molecules with those of the medium, which leads to a considerable shortening of the lifetimes of the triplet states. Therefore, in order to identify the triplet absorption spectra, certain auxiliary procedures (triplet–triplet transfer, the method of matrix isolation, phosphorescence, etc.) are employed.

The absorption spectrum of the intermediate in the flash photolysis of benzophenone in liquid paraffin, identified as of the triplet type, was first reported by Porter and Windsor[59]. However, subsequently on the basis of data for the triplet–triplet energy transfer in the system benzophenone–naphthalene, it was shown[73] that the spectrum of the intermediate product of benzophenone is due to a ketyl radical and not to the triplet state. Probably the most reliable observations of the triplet state of benzophenone are reported by Bell and Linschitz[74] and by Melhuish[75]. Using a flash source with a duration of several microseconds, they observed the appearance of a short-lived (10^{-5} s) absorption in the photoexcitation of benzophenone in benzene[74]. Comparative data for the spectra of the triplet state of benzophenone and its ketyl radical were obtained using a poly(methyl methacrylate) matrix[75]. The difficulty of recording the spectrum of the triplet absorption of benzophenone is caused, on the one hand, by the short lifetime of the triplet in solution (10^{-5}–10^{-7} s[76–79]) and, on the other hand, by the similarity of the spectra of the triplet state of benzophenone and the ketyl radical. The short lifetime of the triplet state of benzophenone is due to its high reactivity for abstraction of hydrogen atoms from the molecules of the medium[74], and also to the quenching of the benzophenone triplet state by the photochemical reduction products[80]. Qualitatively analogous results were obtained from benzaldehyde and acetophenone[81]. The triplet states of carbonyl derivatives of naphthalene (naphthaldehyde, acetonaphthone, and naphthyl phenyl ketone) are less reactive in solutions in respect of photochemical reduction. This is indicated indirectly by the low quantum yield of the conversion into pinacols observed on irradiation in isopropyl alcohol[82]. For example, 2-acetonaphthone is not photochemically reduced in secondary alcohols[83]. This made it possible to record the triplet absorption spectrum of 2-acetonaphthone in benzene with a maximum at 430 nm[84]. Measurements have also been made of the triplet absorption spectra of certain aromatic alcohols. The maximum in the triplet absorption of 1-naphthol in benzene was observed at 390 nm[84] and that of 2-naphthol in water at 432 nm[85] and in a gelatine film at 443 nm[86].

The lower triplet level of aromatic hetero-compounds may be n,π^*, or π,π^*, or CTS (the charge-transfer state) depending on the nature of the substituents in the aromatic ring (amino-, hydroxy-, methoxy-groups, etc.) and the medium (hydrocarbons or solvents tending to form hydrogen bonds). For p-aminobenzophenone, the lower triplet level in isopropyl alcohol is CTS (T_1) and in cyclohexane n,π^*[87] (see Section 7 of this review).

The triplet absorption spectra of dyes have been investigated in less detail compared with aromatic hydrocarbons and oxygen-containing compounds. As in the case of aromatic ketones, the triplet molecules of dyes are capable of reversible electron-transfer reactions in the absence of external electron donors or acceptors[25]. In many cases this leads to the masking of the triplet absorption spectra of dyes by those of radicals. Moreover, in view of the tendency of dye molecules towards the formation of dimers and more complicated association complexes, triplet absorption measurements must be made in dilute dye solutions (10^{-6}–10^{-7} M). In order to detect triplet molecules

at a low concentration, highly sensitive flash photolysis apparatus is necessary.

The study of the triplet states of dyes using their absorption spectra is important in elucidating the mechanism of the sensitising action of dyes. Measurements have been made of the triplet absorption spectra of individual examples of xanthene[25,88-91], acridine[92], phenazine[93,94], thiazine[95-99], and polymethine[100] classes§. Fig. 4 presents the triplet absorption spectra of phenosafranine in aqueous solution at different pH; Table 3 lists the wavelengths λ_{max} of the maximum triplet–triplet absorption and the extinction coefficient ϵ_T for certain dyes. The dyes listed in Table 3 are characterised by an intense $S_0 \rightarrow S_1^*$ absorption band in the visible part of the spectrum. The transition to the triplet state is accompanied by a weakening of the $S_0 \rightarrow S_1^*$ band. Acridine Orange in triethylamine solution is an exception[92]. In the triplet state there are a number of transitions, $T_1 \rightarrow T_2$, $T_1 \rightarrow T_3$, etc., which appear experimentally as several triplet absorption bands usually located at the short-wavelength and long wavelength limits of the singlet absorption. A change in the pH of the medium leads to a displacement of the triplet absorption bands as a result of the shift of the acid–base equilibrium of the triplet molecule.

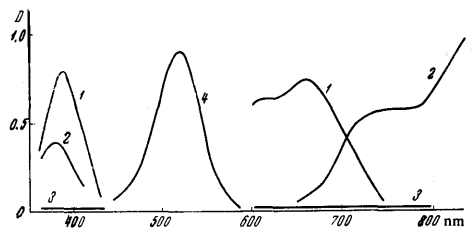


Figure 4. Triplet–triplet absorption spectra of phenosafranine in aqueous solution; *1*) pH 3–5; *2*) pH 5–7; *3*) pH 12; *4*) singlet–singlet absorption spectrum of phenosafranine at pH 7.[94]

The triplet absorption spectra of pigments of the type of chlorophyll and also porphyrins and phthalocyanines have been investigated in greater detail than those of dyes. This is due to the important role of chlorophyll as a sensitiser in the primary photosynthetic process. The triplet absorption spectra of chlorophylls a and b have been measured in a number of studies[67,101-110] on solutions of the pigment in various solvents (benzene, toluene, pyridine, ether, and others) with different flash energies (ranging from hundreds to several thousand joules) and in different excitation wavelengths ranges (blue and red). The principal findings in these investigations are that the triplet absorption spectrum of the pigments is independent of the exciting wavelength (blue or red), that the extinction coefficient is high ($\epsilon_T \simeq 10^4$ litre mole^{-1} cm^{-1}; π,π^* triplet absorption), and the triplet level of chlorophyll is readily populated (a high quantum yield Φ_T). The triplet absorption spectrum of chlorophyll is presented in Fig. 5; this shows that the most intense triplet absorption band of chlorophyll is located in the blue-green region; then in the region of the first transition $S_0 \rightarrow S_1^*$ (645 nm) the extinction coefficient $\epsilon_T^{645} \ll \epsilon_S^{645}$. This latter finding may be used to determine the "yield of triplet molecules per flash" and to find the values of ϵ_T. A triplet absorption with a maximum in the blue-green part of the spectrum is characteristic also of metal-free analogues of chlorophylls—phaeophytins a and b[67,102,104,108-110], chlorophyllin a[111], methyl chlorophyllide a[112], phaephorbide a + b[112], bacteriochlorophyll[107], and also certain porphyrins[102,104,107,113,114], and magnesium-phthalocyanine[104,113,115,116].

Table 3. The values of λ_{max} and ϵ_T for the triplet–triplet absorption of dyes.

Dye	Medium	λ_{max}, nm	ϵ_T, litre mole^{-1} cm^{-1}	Refs.
Fluorescein	H_2O, pH 12	520; >950	$8\cdot10^3$ (520 nm)	25
	H_2SO_4, 0.1 M	470	$9\cdot10^3$ (470 nm)	88
	H_2SO_4 .9 M	650	$7\cdot10^3$ (650 nm)	88
Eosin	H_2O, pH 7.2	410	—	91
	H_2O, pH 5.4	459; 540	$4.4\cdot10^4$ (459) nm	89
Erythrosine	H_2O, pH 9	—	$(2.6\pm0.7)10^4$ (526 nm)	26
Acridine Orange				
	acetic acid	≃650	—	92
Safranine T	H_2O, pH 9	380; 750; >850	—	93
	H_2O, pH 5	390; 650; 720	—	93
Thionine	H_2O, pH 8	690; 760	$9\cdot10^3$ (760 nm)	96
	H_2O, pH 1	375; 655	$1.5\cdot10^4$ (655 nm)	96
Methylene Blue	H_2O, pH 7	420; 780; 800; 870	—	97
	H_2SO_4, 0.1 *N*	280; 375	—	97
Methylene Green	H_2O, pH 9	410; 760; 790 >840	$1.5\cdot10^4$ (840 nm)	99
Novomethylene Blue	H_2O, pH 9	420; 780; >840	$4\cdot10^3$ (840 nm)	100

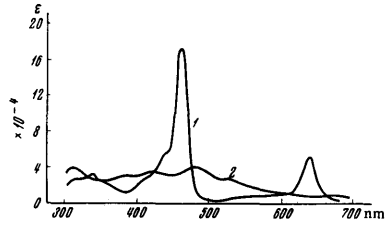


Figure 5. Triplet–triplet (curve *2*) and singlet–singlet (curve *1*) absorption spectra of chlorophyll b in benzene[106].

Study of the triplet–triplet absorption spectra of tetrapyrrole pigments made it possible to determine the effect of the structure of the molecule on triplet–triplet transitions. Even very considerable changes in the structure of pigments[46] have little effect on the nature of the triplet spectrum. The triplet absorption spectra of pigments are diffuse, differing significantly from the characteristic singlet–singlet absorption spectra. Moreover the triplet absorption spectra of chlorophylls are very similar to those of short-lived radicals—intermediate products of the photochemical oxidation-reduction reactions of chlorophylls[108,117] which makes it difficult to interpret the experimental results unambiguously using only spectroscopic data. In the latter case data for the kinetics of the deactivation of triplet states are valuable.

In many studies[108,118] the effect of "impurity" amounts of water on the spectroscopic properties of the triplet

§ Phthalocyanine dyes will be examined below together with pigments.

state of chlorophyll was investigated, and it was shown that the introduction of traces of moisture to a carefully dried solution of chlorophyll in toluene leads to an increase of the "yield of triplets per flash". The results did not confirm the hypothesis [119] that polar compounds affect the relative probabilities of fluorescence and the transition of chlorophyll to the triplet state. The familiar effect of the "activation" of the fluorescence of carefully dried solutions of chlorophyll in hydrocarbons (for example 3-methylpentane) in the presence of polar compounds [120,121] could not be explained by a decrease of the quantum yield Φ_T. The "activation" of the fluorescence of chlorophyll has been explained by the inversion of the positions of the n,π^* and π,π^* excited singlet levels [122,123]. To account for the results quoted by the present author [108] and Livingston [118], one must suppose firstly that the non-radiative degradation of energy in the n,π^* state is several times faster than the transition to the triplet state and secondly that the lifetime of the molecules in the π,π^* triplet state is much longer than in the n,π^* state. The latter assumption is probably unsound [40]. A more soundly based explanation of the observed effect has been put forward by Evstigneev et al. [124] and by Amster and Porter [125], who state that the absence of the fluorescence of chlorophyll in dried solutions is caused by the dimerisation of the pigment molecules. The introduction of moisture into the chlorophyll solution leads to the formation of monosolvates of the pigment as a result of the deaggregating effect of the water molecules and hence an increased concentration of "normal" (fluorescent) chlorophyll molecules.

In a number of studies measurements have been made of the triplet absorption spectra of retinene (the *trans*-form), which is one of the components of the visual pigments. A triplet–triplet absorption of retinene has been recorded in methanol [126,127], methylcyclohexane [128], toluene [129], and hexane [129] with a maximum at 440–450 nm. A triplet absorption was not observed for a solution of retinene in water containing 1% of digitonin or in 1 : 1 methanol–water mixtures. The quantum yield of the transition of retinene to the triplet state in methylcyclohexane decreased on addition of methanol to the solution, which is due to the formation of a complex between triplet retinene and methanol [128]. The triplet state of retinene is populated as a result of a transition from the n,π^* excited singlet level. The presence of water in the retinene solution leads to a change in the relative positions of the n,π^* and π,π^* excited singlet levels, accompanied by a decrease of the probability of the transition to the triplet state.

In connection with the postulated importance of the triplet state of chlorophyll in primary photosynthetic processes [130–132], repeated attempts have been made to detect the triplet–triplet absorption of chlorophyll *in vivo* [133,134]. Flash photolysis of photosynthetically active chloroplasts leads to eight types of spectral changes caused by electron and ion migration [135]. However, the triplet–triplet absorption spectrum of chlorophyll in photosynthesising organisms has not so far been observed. The likely explanation may be an effective transfer of energy from excited chlorophyll molecules to photochemically active centres [136]. The short-lived (about 10^{-5} s) absorption at 520 nm, observed on flash illumination of the cells of the alga *Chlorella*, was interpreted as due to the triplet state of carotenoids [137,138] as a result of energy transfer through triplet states with participation of chlorophyll. The triplet absorption spectrum of chlorophyll was observed only for chloroplasts [134] disrupted by surface-active substances (digitonin) and also for artificially isolated chlorophyll–protein complexes [139] and monomolecular layers of chlorophyll deposited on a glass support in the presence of aliphatic acid salts [140].

5. KINETICS OF THE DEACTIVATION OF TRIPLET STATES

The study of the mechanism and kinetics of the deactivation of triplet states is based on the direct measurement of the rate of decay of the triplet–triplet absorption bands. Numerous kinetic measurements of the decrease of the intensity of the triplet absorption of aromatic hydrocarbons, dyes, and pigments in a liquid solution have shown that the rate of deactivation of triplet molecules obeys the general equation

$$-\frac{dT}{dt} = k_1 T + k_2 T^2 + k_3 TS \ , \qquad [1]$$

where

$$k_1 = k_0 + \sum_i k_{Q_i} Q_i \qquad [2]$$

in accordance with the following deactivation processes:

$$T \rightarrow S \ , \qquad (0) \quad (k_0)$$
$$T + T \rightarrow S^* + S \ , \qquad (2) \quad (k_2)$$
$$T + S \rightarrow S + S \ , \qquad (3) \quad (k_3)$$
$$T + Q_i \rightarrow S + Q_i \ , \qquad (i) \quad (k_{Q_i})$$

where k_0 is the rate constant for the unimolecular deactivation, k_2 the rate constant for triplet–triplet annihilation, k_3 the rate constant for the self-quenching process, and k_{Q_i} the rate constant for the quenching of the triplet state by extraneous (impurity) molecular quenching agents Q_i.

The unimolecular reaction [reaction (0)] includes the following deactivation processes: phosphorescence (k_{phosph}), non-radiative degradation ($k_{n.r}$), and delayed fluorescence ($k_{r.fl}$)¶. The first two processes are shown schematically in Fig. 2 by straight and wavy arrows between T_1 and S_0 and the third is represented by a wavy arrow directed from T_1 to S_1^* and is due to the thermal excitation of the triplet molecule with its transition to the S_1^* level. Thus the expression for k_0 is written in the form $k_0 = k_{phosph} + k_{n.r} + k_{r.fl}$. In liquid solutions at room temperature the majority of complex molecules do not phosphoresce. The effect of heavy atoms on the spin–orbit coupling has been used [62] to elucidate the relation between the radiative and non-radiative degradation of the energy of the triplet state. On the basis of the dependence of k_0 and k_{phosph} on the nature of the heavy atom in the anthracene and its derivatives (anthracene, 9,10-dichloroanthracene, and 9,10-dibromoanthracene), it was concluded that the non-radiative degradation process makes a considerable contribution to the kinetics of the unimolecular deactivation of the triplet state.

The quenching of the triplet state by impurity molecules competes with unimolecular non-radiative degradation (according to Eqn. [2]) and is responsible for the discrepancies in the experimental values of k_1 (see Table 4). The minimum value of k_1 listed in Table 4 is closest to k_0. The constant k_0 may be determined in several ways. One of these is based on the Arrhenius relation between k_1 and temperature:

$$k_1 + k_0 + A \exp(-\Delta E/RT)[Q].$$

¶ This type of fluorescence is also called delayed fluorescence of the first kind [41].

As the temperature or the viscosity of the medium changes, k_1 is altered due to the largely variable contribution by kQ_i. The rate of deactivation of the triplet state is measured at different temperatures [145,146,149-151] and k_0 is found from the temperature variation of k_1. [150] Another procedure is based on measurements in a solid matrix where there are virtually no diffusion-dependent quenching processes. Thus the values of k_0 for anthracene in a polystyrene film [86] and in a poly(methylmethacrylate) matrix [152] are respectively 38 s^{-1} and 54 s^{-1}.

Table 4. The rate constants k_1 for the deactivation of the triplet state of anthracene.

Solvent	k_1, s^{-1}	Refs.	Solvent	k_1, s^{-1}	Refs.
Acetone	14 000±3000	59	Hexane	350	63
Hexane	13 000	142	Glycerol	180±20	59
Hexane	11 900±1500	141	Hexane	160	146
Cyclohexane	8000	62	Hexane	130	145
Bromobenzene	1600	143	Tetrahydrofuran	110	146
Ethylene glycol	1300±200	59	Isopentane	69	147
Cyclohexane	500	144	Glycerol	58	61
Cyclohexane	440	62	Hexane	56±76	148

Since oxygen is an extremely effective quenching agent for triplet states, the rate constants for the deactivation process must be measured in a carefully degassed solution. It has been shown [148] that k_1 for anthracene in tetrahydrofuran can be reduced to 40 s^{-1} on eliminating the oxygen remaining after degassing by allowing it to react with NaK. Small (trace) amounts of vacuum grease, which inevitably contaminate the solution during the degassing process, can also behave as quenching impurities. It has been shown [153] that the use of a vacuum grease at $p \geq 10^{-10}$ mmHg leads to the contamination of the solvent during degassing even under conditions excluding direct contact between the grease and the solvent. Traces of oxygen can be effectively removed from aqueous solution by "washing" the latter with an inert gas (argon) [25]. However, this method is ineffective for organic solvents [106].

In a number of studies [62,74,86] it has been shown that k_1 decreases with the number of flashes (from 8000 s^{-1} for anthracene in cyclohexane after the first flash to 440 s^{-1} after the fiftieth flash [62]) owing to irreversible reactions of the triplet molecules with the residual O_2. The procedure involving repeated preliminary flash illumination of the substance ("flash purification" [74]) can also be recommended for the determination of k_0 (provided that the substance is stable under repeated flash photolysis).

The constant k_0 is almost independent of the viscosity of the medium and temperature. Thus for anthracene the k_0 measured in hexane ($\eta = 0.320$ cP) and glycerol ($\eta =$ 1499 cP at 20°C) are 45 ± 25 s^{-1} and 30 ± 3 s^{-1} respectively [145]. A decrease of temperature leads to a slight decrease of k_0. The activation energy for the non-radiative degradation of triplet anthracene in a poly(methyl methacrylate) matrix is 60 cal $mole^{-1}$. [152] The constant k_0 depends significantly on molecular structure. For example, the experimental constants $k_0 + \sum_i k_{Q_i} Q_i$ for fluorescein are 220 s^{-1} (cation, 9 M H_2SO_4), 600 s^{-1} (neutral molecule, 0.1 N H_2SO_4), 600 s^{-1} (univalent anion, pH 5.5), and 50 s^{-1} (divalent anion, 0.01 M NaOH) [25,154]. The significant differences between the rate constants obtained for the neutral molecule and the divalent anion of fluorescein are not a result of the quenching effects of impurities [154].

The quenching of the triplet states by microimpurities and also triplet–triplet annihilation and self-quenching are bimolecular deactivation processes of triplet states. Triplet–triplet annihilation is due to the interaction of two triplet molecules with transition of one of them to an excited singlet state with subsequent fluorescence†. The value of k_2 is close to the diffusion constant and amounts to 10^9–10^{10} litre $mole^{-1}$ s^{-1} for non-viscous media. The activation energy for triplet–triplet annihilation, determined from the temperature variation of the rate of deactivation of the triplet state, agrees with ΔE_η. [149,150] The rate-limiting stage of the triplet–triplet annihilation is the diffusion of triplet molecules in the medium, and therefore the lifetime of triplet molecules in the gas phase is lower than in solution (when there is no quenching by impurities) [155]. For the triplet state of anthracene in the gas phase at 140°C, $k_2 = (1.4 \pm 0.4) \times 10^{11}$ litre $mole^{-1}$ s^{-1}. The constant k_2 is close to 3.8×10^{11} litre $mole^{-1}$ s^{-1} calculated on the basis of collision theory, whence it follows that triplet–triplet annihilation is extremely effective and occurs at every collision between triplet molecules [155]. The experimental observation of delayed fluorescence as a result of triplet–triplet annihilation has been reported by Parker [156] and Kikuchi et al., [157] who employed flash photolysis.

The self-quenching process, i.e. the deactivation of triplet molecules as a result of their interaction with non-excited molecules of the same substance, has been observed only for dyes [25,158] and pigments of the type of chlorophyll [105,109]. For triplet molecules of aromatic hydrocarbons, we have $k_3 \ll k_1 + k_2 T$, and for dyes and pigments, $k_3 \simeq 10^7$–10^8 litre $mole^{-1}$ s^{-1}. It follows from Eqn. [1] that the dominant processes in the kinetics of the deactivation of triplet states immediately after the flash are non-radiative degradation and triplet–triplet annihilation (under the conditions of 100% excitation to the triplet state). The self-quenching process is observed from the instant of the regeneration of non-excited molecules and makes an appreciable contribution to the deactivation kinetics only at high initial concentrations (10^{-4} M) of the substance.

6. MECHANISMS OF THE QUENCHING OF TRIPLET STATES

Depending on the form of the decay of the concentration of triplet molecules of a given substance, static and dynamic quenching of triplet states can be distinguished. Another classification is into "physical" and "chemical" quenching of triplet states depending on the products and on the nature of the quencher. In the static quenching of triplet states a decrease of the concentration of triplet molecules ("yield per flash") is not accompanied by a change in their lifetime. Static quenching is characterised by an equilibrium between molecules unperturbed by the quenching agent and those altered under its influence (a complex with a quenching agent in the ground or excited state, aggregate, etc.) and associated with a lower quantum yield for populating the triplet state. Thus when water is added to an alcoholic solution of chlorophyll, the observed fall of the yield of the triplet molecules of the pigment is caused by a decrease in the concentration of chlorophyll monosolvates as a result of the shift of the monomer–dimer equilibrium towards dimers.

† This type of delayed fluorescence is also called fluorescence of the second kind [41].

Dynamic quenching of the triplet state occurs in the collisions between triplet molecules and those of the quenching agent and is accompanied by a decrease of the lifetime of the triplets. Such quenching can yield the original molecules in the ground or excited state (physical quenching) or intermediate products, for example free radicals, ions, etc. (chemical quenching). Physical quenching processes include triplet–triplet and triplet–singlet energy transfer, paramagnetic quenching, quenching by heavy atoms, etc; among chemical quenching processes, one may include quenching by oxygen‡, by electron donors and acceptors, by transition metal ions, etc.

Table 5. Variation of the rate constants $k_{D,A}$ for the triplet–triplet energy transfer over a distance ΔE between a donor and an acceptor[162].

Donor	Acceptor	Solvent	$k_{D,A}$, litre mole^{-1} s^{-1}	ΔE, cm^{-1}
Diacetyl	1,2-benzanthracene	benzene	$3.0\cdot10^9$	3200
Benzophenone	naphthalene	benzene	$2\cdot10^9$	3100
Triphenylene	naphthalene	hexane	$1.3\cdot10^9$	2200
Phenanthrene	1-iodonaphthalene	hexane	$7.0\cdot10^9$	1100
Phenanthrene	1-bromonaphthalene	hexane	$1.5\cdot10^8$	900
Phenanthrene	naphthalene	hexane	$2.9\cdot10^6$	300
Naphthalene	phenanthrene	hexane	$2\cdot10^4$	−300

Triplet–triplet transfer was first observed in sensitised phosphorescence at low temperatures[159,160]. In liquid solutions the quenching of the phosphorescence by energy transfer was observed for diacetyl[161]. Triplet–triplet transfer between an energy donor (D) and acceptor (A) (which do not phosphoresce in liquid solutions) is accompanied by the quenching of the triplet state of D and the appearance of the triplet absorption spectrum of A. Measurements with different triplet energy donors and acceptors, including aromatic hydrocarbons[162–165], carbonyl compounds[73,84,166], and pigments[167–170] established in the first place that the effectiveness of the energy transfer (the rate constant $k_{D,A}$ for the quenching of the triplet donor) depends on the distance ΔT between the triplet levels of the energy donor and acceptor and in the second place that a diffusion mechanism obtains in the triplet–triplet transfer in liquid solutions. Table 5 lists the values of ΔT and $k_{D,A}$ for various triplet energy donor–acceptor pairs. It follows from the data in Table 5 that the rate constant for the transfer is close to the diffusion constant (10^9–10^{10} litre mole^{-1} s^{-1}) when $\Delta T \geqslant 1000$ cm^{-1}. The decrease of $k_{D,A}$ for smaller ΔT is probably due to the reverse energy transfer (from the acceptor triplet to the donor triplet)[171,172]. Using triplet–triplet transfer, the positions of the triplet levels in a number of non-phosphorescing compounds have been determined by flash photolysis. The positions of the triplet levels of *trans*-stilbene (17 500 cm^{-1}), *cis*-stilbene (20 200 cm^{-1})[164], phaeophytin a ($>$ 11 300 cm^{-1})[169], thionine (13 640 cm^{-1})[173], and others have been estimated on the basis of the correlation between $k_{D,A}$ and ΔT for various acceptor (the position of the triplet level unknown)–donor (the position of the triplet level known) pairs. Triplet energy transfer combined with flash photolysis is used also to elucidate the role of excited singlet and triplet states in photochemical reactions. By comparing the yields of products of a reaction initiated in one case by direct and in another by sensitised (transfer via triplet states) excitation, the important role of the triplet state of anthracene in the reaction with carbon tetrachloride in bromobenzene was demonstrated[163]. Using triplet–triplet transfer, evidence was obtained proving the participation of triplet and ground singlet tetramethylbenzoquinone molecules in the formation of semiquinone radicals in alcohol[174,175]. The participation of the triplet states was also demonstrated in the photochemical reduction of 2-acetophenone by tributyltin[84], the photochemical reduction of benzophenone by isopropyl alcohol[73,166], the photochemical oxidation of chlorophyll a by *p*-benzoquinone[169,170], etc.

The heavy atom effect (the "external" and "internal" effects of the heavy atom) on spin–orbital coupling in molecules increases the probability of forbidden intercombination transitions and consequently leads to a shortening of the lifetime of triplet molecules. The internal effect of the heavy atom has been demonstrated[62] in the kinetics of the deactivation of the triplet states of anthracene and its dichloro- and dibromo-derivatives. On passing from anthracene to 9,10-dichloroanthracene and 9,10-dibromoanthracene, the deactivation rate constant k_0 increases from 110 s^{-1} to 23 000 s^{-1}. The external effect of the heavy atom is shown in the quenching of the triplet state of safranine T by potassium iodide (quenching constant 1.0×10^8 litre mole^{-1} s^{-1})[93] and also of the triplet state of anthracene and its phenyl and methyl derivatives by bromobenzene[47]. The inhibiting effect of potassium iodide in the photochemical reduction of riboflavine has also been explained by the quenching of the triplet state of riboflavine by potassium iodide[176].

In a number of studies[105,142,177] it was observed that transition metal ions with paramagnetic properties are capable of quenching triplet states§. However, since Porter and Wright[142] did not find a correlation between the quenching rate constant and the magnetic susceptibility of transition metal ions, the shortening of the lifetime of triplet molecules in the presence of ions cannot be accounted for solely by "paramagnetic" quenching. On the basis of the effect of water on the rate constant for the quenching of the triplet states of anthracene and porphyrins (tetraphenylporphin and its zinc derivative) by Ni^{2+}, Co^{2+}, and Cu^{2+} ions[177] and also the effect of the ligand in the Ni^{2+}, Co^{2+}, and Cu^{2+} complexes of ethylenediamine, ethylenediaminetetra-acetate, pyridine, *o*-phenanthroline, and others[182,183], it was suggested that the quenching is due to the formation of a charge-transfer complex (CTC) between the excited molecule and the quenching agent. The excited complex $(S.MX_n)^*$ may be deactivated via the following pathway:

$$T + MX_n \rightarrow (S\cdot MX_n)^* \rightarrow S + MX_n^*, \qquad (4)(k_4)$$
$$\downarrow$$
$$(S\cdot MX_n) \rightarrow S + MX_n.$$

Measurements of the rate of quenching of the triplet state by oxygen showed that the quenching rate constant is close to the diffusion constant. Probably diffusion is the rate-limiting step for the quenching of the triplet states by oxygen only in moderately viscous media. In very viscous media, for example solid matrices at 77°K, the presence of O_2 at a concentration of 10^{-4} M does not affect the rate

‡ Quenching by oxygen can also be classified as physical quenching owing to the paramagnetic properties of O_2.

§ Quenching by oxygen which is paramagnetic, has been demonstrated for aromic hydrocarbons[59,63,142,143], dyes[25,89,96,178–180], and pigments[181].

of deactivation of triplet states[152]. The current view on the mechanism of the deactivating effect of oxygen involves paramagnetic quenching[142] and energy transfer from the triplet molecule to O_2 [1] and also the formation of a moloxide—the labile product of the addition of O_2 to the excited molecule[41]. At the same time it has been shown[25,178] that the quenching of the triplet state of fluorescein by oxygen leads to one-electron oxidation of the dye:

$$T + O_2 \rightarrow \dot{R}^+ + O_2^{\dot{-}}, \qquad (5)(k_5)$$

which takes place simultaneously with physical quenching:

$$T + O_2 \rightarrow S + O_2 . \qquad (6)(k_6)$$

The rate constants k_5 and k_6 are respectively[25,178] $k_5 = 1 \times 10^7$ litre mole^{-1} s^{-1} (pH 2.0), $k_5 = 1.4 \times 10^8$ litre mole^{-1} s^{-1} (pH 12.0), $k_6 = 1.2 \times 10^9$ litre mole^{-1} s^{-1} (pH 2.0), and $k_6 = 1.7 \times 10^9$ litre mole^{-1} s^{-1} (pH 12.0). Physical quenching is independent of the acidity of the medium, while chemical quenching is negligible in an acid medium (triplet cation of fluorescein) and increases with the pH (neutral triplet molecules and triplet anions).

As shown above in the discussion of the kinetics of the deactivation of triplet states, the rate of depletion of the triplet level depends on the rate of bimolecular triplet–triplet annihilation and self-quenching processes. Formally, these processes can also be regarded as quenching of the triplet state as a result of the collision of the triplet molecule with another such molecule or a ground state molecule (k_2 or k_3). In many cases the quenching of a triplet molecule by another triplet molecule or a ground state molecule leads to the formation of radicals produced by electron transfer and therefore quenching may be classified as being of the chemical type:

$$T + T \rightarrow R^{\dot{-}} + \dot{R}^+, \qquad (7)(k_7)$$

$$T + S \rightarrow R^{\dot{-}} + \dot{R}^+. \qquad (8)(k_8)$$

Table 6. The rate constants for the quenching of the triplet state by electron donors and acceptors.

Object	Medium	Quenching agent.	$k_9 + k_{11}$, litre mole^{-1} s^{-1}	k_9, litre mole^{-1} s^{-1}	$k_{10} + k_{12}$, litre mole^{-1} s^{-1}	k_{10}, litre mole^{-1} s^{-1}
Fluorescein	H_2O[185]	ethylenediamine tetra-acetate	$1.5 \cdot 10^5$	—	—	—
Fluorescein	H_2O[185]	Fe^{III} ethylenediamine tetra-acetate	—	—	$8 \cdot 10^8$	$1 \cdot 10^8$
Fluorescein	H_2O[25]	*p*-phenylenediamine	—	$5 \cdot 10^9$	—	—
Eosin	H_2O[158]	$K_3Fe(CN)_6$	—	—	$2.5 \cdot 10^8$	$1.5 \cdot 10^8$
Eosin	H_2O[89]	phenol	$1.5 \cdot 10^5$	—	—	—
Chlorophyll a	pyridine[187]	ascorbic acid	$\geq 10^4$	—	—	—
Chlorophyll a	ethanol[188]	methylviologen	—	—	$2.0 \cdot 10^9$	—
Phaeophytin a	ethanol[189]	phenylhydrazine	$3.0 \cdot 10^7$	—	—	—
Phaeophytin a	ethanol[189]	Methyl Red	—	—	$1.7 \cdot 10^8$	—

Reactions (7) and (8) were observed in aqueous solutions of xanthene[25,88,158,185], thiazine[91,98,186], and phenazine[93] dyes. The constants k_7 and k_8 were determined from the rate of accumulation of the radicals R$^\cdot$ and R$^+$. For fluorescein (pH 12), in particular, $k_7 = 6 \times 10^8$ litre mole^{-1} s^{-1} and $k_8 = 5 \times 10^7$ litre mole^{-1} s^{-1}.[25] The results show that electron transfer is most probable between two triplet molecules.

The quenching of triplet state by electron donors or acceptors is a consequence of a photochemical oxidation–reduction reaction with participation of triplet molecules. However, the quenching of the triplet state of the reducing agent (DH_2) or the oxidising agent (A) does not always lead to the formation of radical-ions:

$$T + DH_2 \rightarrow R^{\dot{-}} + \dot{D}H_2^+, \qquad (9)(k_9)$$

$$T + A \rightarrow \dot{R}^+ + A^{\dot{-}}. \qquad (10)(k_{10})$$

Chemical quenching of triplet molecules [reactions (9) and (10)] is accompanied by physical quenching, revealed experimentally by an inconsistency between the rate of quenching of the triplet state and the rate of accumulation of R$^\cdot$ and R$^+$:

$$T + DH_2 \rightarrow S + DH_2, \qquad (11)(k_{11})$$

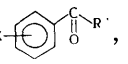
$$T + A \rightarrow S + A . \qquad (12)(k_{12})$$

Table 6 lists the rate constants for the quenching of the triplet molecules of dyes and pigments by various electron donors and acceptors. The mechanism of the quenching of triplet states by donors and acceptors is likely to include the formation of charge-transfer complexes as an intermediate stage in electron transfer. For instance, the probability of the conversion of charge-transfer complexes into radical-ions in the quenching of the triplet state of eosin by potassium hexacyanoferrate(III) is 0.6.[158]

7. PROPERTIES OF TRIPLET STATES AND THEIR ROLE IN PHOTOCHEMICAL REACTIONS

In contrast to the excited singlet state, a molecule in the triplet state is paramagnetic, which suggests that the triplet and phosphorescent states are identical[3,4]; this is supported by data on the kinetics of phosphorescence and photomagnetism[190]. Together with the optical properties of triplet molecules, the paramagnetic properties of triplet states are responsible for the ability of triplet molecules to absorb microwave radiation (ESR spectrum)[191].

Apart from the spectroscopic and kinetic properties and the characteristics of triplet states discussed above, triplet molecules exhibit a definite affinity for protons (the acid–base properties of triplets). The proton affinity of a molecule in an excited state may differ significantly from the affinity in the ground state. In a number of studies[192,193] this effect was investigated for aromatic acids and bases in terms of the changes in the absorption and fluorescence spectra with the acidity of the solvent. It was shown that aromatic acids dissociate in the excited singlet state over a period less than 10^{-9} s. The change in pK is then about 6. The measurements designed to determine pK_T for molecules in the triplet state by flash photolysis reveal a significant difference between pK_S (for the excited singlet state) and pK_T[85,194] together with a similarity between pK_g (for the ground singlet state) and pK_T. Similar values of pK_g and pK_T were obtained for a number of alcohols, acids, and amines[85,194]. However, for dyes of the thiazine (Methylene Blue, Methylene Green, Novomethylene Blue, Azur) and azine (safranine and phenosafranine) classes, pK_g differs from pK_T by more than 6 units[93,94,98,100,186]. Consequently the proton affinity of thiazine and azine dyes in the triplet state differs significantly from the affinity in the ground and excited singlet states.

The properties and reactivity of molecules in the triplet state depend in many respects on the distribution of electron density on excitation. For aromatic carbonyl compounds of the type , the lower excited triplet state (T_1) may be n,π^*, or π,π^*, or the charge-transfer state (CTS)[87]. A characteristic feature of the n,π^* triplet state of carbonyl compounds is a high quantum yield γ of the reaction involving the abstraction of a hydrogen atom from alcohols, hydrocarbons, and related compounds ($\gamma = 1$), which ultimately yields pinacols and also the occurrence of addition to the double bond of olefins and other unsaturated compounds[195]. Moreover, the n,π^* triplet level is characterised by a short-lived phosphorescence in the solid matrix at 77°K (10^{-3} s)[196], a small singlet–triplet splitting (< 3000 cm^{-1}), and a deficiency in electron density at the oxygen atom of the carbonyl group ($>C=\overset{+\delta}{O}$)[87]. The appreciably lower reactivity of the π,π^* triplet state is shown by a low quantum yield of the pinacol formation reaction ($\gamma = 0.1$). The π,π^* triplet level is then characterised by a greater singlet–triplet splitting (10 000 cm^{-1}) and also by the absence of an electron deficiency at the carbonyl group (>C=O)[87]. Thus the reactivity of molecules in the triplet state, and in particular of carbonyl compounds, depends on the distribution of electron density in the lower triplet state.

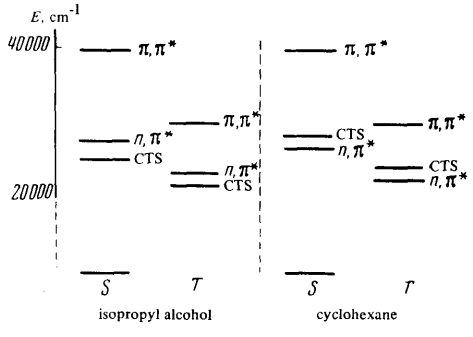
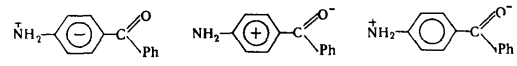


Figure 6. Schematic energy level diagram for *p*-aminobenzophenone in isopropyl alcohol and in cyclohexane[195].

The electron density distribution depends in turn on the nature of the substituents (X, R) and the effect of the solvent. For substituted benzophenones (R = C_6H_5 and X = a halogeno-, phenyl-, amino-, hydroxy-, and methoxy-groups in the *meta*- and *para*-positions), the quantum yield γ depends on the nature and positions of the X substituents and also on the polarity of the solvent. For benzophenone and also its *para*-substituted halogen derivatives, $\gamma \simeq 1$ (isopropyl alcohol, cyclohexane), which shows that the T_1 state is of the n,π^* type. *m*- and *p*-phenylbenzophenones have a low quantum yield of the pinacol-formation reaction ($\gamma = 0.1$) owing to the inversion of the positions of n,π^* and π,π^* triplet levels, the lower triplet level being π,π^*. The introduction of electron-donating (amino- and hydroxy-groups) substituents in the *para*-position of benzophenone leads to a variation of γ with the solvent. For amino- and hydroxy-derivatives of benzophenone, a long-wavelength absorption due to a charge-transfer state together with $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions was observed[195]. For *p*-aminobenzophenone, with the CTS configuration,



$\gamma = 0.00$ in isopropyl alcohol but in a non-polar solvent (cyclohexane) $\gamma = 0.02$. Similarly, for *p*-hydroxybenzophenone an increase of γ from 0.02 (isopropyl alcohol) to 0.9 (cyclohexane) was observed. The increase in γ on passing from a polar to a non-polar solvent is due to the reversal of the CTS and n,π^* triplet levels (Fig. 6).

Using direct or sensitised (triplet–triplet energy transfer) flash photolysis, the involvement of triplet molecules of organic and biologically important substances in many photochemical reactions has been demonstrated experimentally. Much information on the chemistry of triplet states has also been obtained by non-pulse excitation methods[197]. There is no doubt that the triplet state participates in various photochemical reactions but one must bear in mind that the real pathway of a photochemical reaction is not determined solely by the reactivity of the excited state. A significant factor which determines the primary photochemical step is the excitation conditions (pulse or stationary conditions and the density and duration of emission), the effect of the environment [the presence of extraneous molecules (additives) and the nature of the solvent], etc. In a consideration of the real pathway of a photochemical reaction involving excited singlet or triplet molecules, one must bear in mind the probability of transition to the triplet state, the lifetime in the triplet level, and also the concentration of the reacting (excited) molecules.

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The method of flash photolysis is undoubtedly one of the powerful modern procedures for the investigation of rapid reactions initiated by light. The applications of this method in the study of triplet states discussed above illustrate one of the possibilities of flash photolysis in the study of photochemical and photobiological processes. The present state of the experimental technique permits a considerable extension of the scope of the method in the investigation of the properties of the primary products formed under the action of radiation on matter (pulse radiolysis, lasers). This constitutes a stimulus for intensive research in the chemistry of excited states, short-lived products, and rapid processes.

REFERENCES

1. A. N. Terenin, Zhur. Fiz. Khim., 18, 1 (1944).
2. G. Lewis and M. Kasha, J. Amer. Chem. Soc., 66, 2100 (1944).
3. G. Lewis and M. Calvin, J. Amer. Chem. Soc., 67, 1232 (1945).
4. G. Lewis, M. Calvin, and M. Kasha, J. Phys. Chem., 17, 804 (1949).
5. P. Pringsheim, "Fluorescence and Phosphorescence", Interscience, New York, 1949.
6. A. V. Karyakin and V. I. Duzhenkov, Uspekhi Khim., 31, 1511 (1962) [Russ. Chem. Rev., No. 12 (1962)].

7. L. I. Grossweiner, Adv. Rad. Biol., 2, 83 (1966).
8. S. K. Lower and M. A. El-Sayed, Chem. Rev., 66, 199 (1966).
9. I. N. Marshak, "Impul'snye Istochniki Sveta" (Pulse Light Sources), Gosenergoizdat, Moscow, 1963.
10. J. W. Boag, Photochem. Photobiol., 8, 565 (1968).
11. S. Claesson and L. Lindquist, Arkiv Kemi, 12, 1 (1958).
12. E. Niemann and M. Klenert, Appl. Optics, 7, 295 (1968).
13. L. Lindquist, Compt. rend., C263, 852 (1966).
14. J. A. Giordmaine, P. M. Rentzepis, S. L. Shapiro, and K. W. Wecht, Appl. Phys. Letters, 11, 216 (1967).
15. P. M. Rentzepis and M. A. Duguay, Appl. Phys. Letters, 9, 219 (1967).
16. C. J. Hochanadel, J. A. Ghormley, J. W. Boyle, and J. R. Riley, Rev. Sci. Instr., 39, 1144 (1968).
17. G. Porter and E. R. Wooding, "International Congress of High Speed Photography, Cologne, 1958".
18. T. A. Gover and G. Porter, Proc. Roy. Soc., A262, 476 (1961).
19. L. Lindquist, Rev. phys. appl., 3, 15 (1968).
20. S. S. Brody, Rev. Sci. Instr., 28, 1021 (1957).
21. S. I. Andreev, M. P. Vanyukov, and E. E. Gavrilov, Zhur. Prikl. Spektrosk., 6, 27 (1967).
22. S. Claesson and G. Wettermark, Arkiv Kemi., 11, 561 (1957).
23. S. A. Charnaya, Svetotekhika, No. 6, 22 (1964).
24. V. M. Podgaetskii and A. N. Chernets, Optika i Spektrosk., 14, 424 (1963).
25. L. Lindquist, Arkiv Kemi., 16, 79 (1960).
26. P. G. Bowers and G. Porter, Proc. Roy. Soc., A, 299, 348 (1967).
27. G. Porter, Proc. Roy. Soc., A, 200, 284 (1950).
28. H. T. Witt, R. Moraw, and A. Müller, Z. phys. Chem. (Frankfurt), 20, 193 (1959).
29. B. Ke, R. W. Treharne, and C. McKibben, Rev. Sci. Instr., 35, 296 (1964).
30. N. O. Chechik, S. N. Fainshtein, and T. M. Lifshitts, "Elektronnye Umnozhiteli" (Electronic Multipliers), Tekhniko-Teor. Lit., Moscow, 1957.
31. G. Döring, H. H. Stiehl, and H. T. Witt, Z. Naturforsch., 22b, 639 (1967).
32. J. Koczewski and Z. R. Grabowski, Bull. Acad. polon. Sci. Ser. Sci., chim., geol., geog., 10, 165 (1963).
33. K. C. Herr and G. C. Pimentel, Appl. Optics, 4, 25 (1965).
34. O. D. Dmitrievskii, Symposium, "Elementarnye Fotoprotsessy v Molekulakh" (Elementary Photoprocesses in Molecules), Izd. Nauka, Moscow–Leningrad, 1966, p. 176.
35. O. D. Dmitrievskii, Optiko-Mekh. Prom., No. 4, 17 (1967).
36. G. Porter, Z. Elektrochem., 64, 59 (1960).
37. H. Rüppel and H. T. Witt, Z. phys. Chem. (Frankfurt), 15, 321 (1958).
38. T. H. Wilmshurst, T. J. Bennett, and R. C. Smith, Proc. Roy. Soc., A, 302, 305 (1968).
39. C. Reid, "Excited States in Chemistry and Biology" (Translated into Russian), Inostr. Lit., Moscow, 1960.
40. N. J. Turro, "Molecular Photochemistry" (Translated into Russian), Izd. Mir., Moscow, 1967.
41. A. N. Terenin, "Fotonika Molekul Krasitelei" (Photonics of Dye Molecules), Izd. Nauka, Leningrad, 1967.
42. J. G. Calvert and J. N. Pitts, "Photochemistry" (Translated into Russian), Izd. Mir, Moscow, 1968.
43. H. Labhart, "Abstracts of Papers. VIIIth European Congress on Molecular Spectroscopy, Denmark, 1965".
44. P. G. Bowers and G. Porter, Proc. Roy. Soc., A, 296, 435 (1967).
45. G. P. Gurinovich, A. I. Patsko, and A. N. Sevchenko, Dokl. Akad. Nauk SSSR, 174, 873 (1967).
46. G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev, "Spektroskopiya Khlorofilla i Rodstvennykh Soedinenii" (Spectroscopy of Chlorophyll and Related Compounds), Izd. Nauka i Tekhnika, Minsk. 1968.
47. T. Medinger and F. Wilkinson, Trans. Faraday Soc., 61, 620 (1965).
48. A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, Trans. Faraday Soc., 62, 3398 (1966).
49. M. Kasha and S. P. Mcglynn, Ann. Rev. Phys. Chem., 7, 403 (1956).
50. D. S. McClure, J. Chem. Phys., 17, 905 (1949).
51. M. Kasha, J. Chem. Phys., 20, 71 (1952).
52. A. R. Horrocks, T. Medinger, and F. Wilkinson, Photochem. Photobiol., 6, 21 (1967).
53. L. Lindquist and G. W. Lundeen, J. Chem. Phys., 44, 1711 (1966).
54. A. G. Gradyushko, V. A. Mashenkov, A. N. Sevchenko, K. N. Solov'ev, and M. P. Tsvirko, Dokl. Akad. Nauk SSSR, 182, 64 (1968).
55. S. P. McGlynn, T. Azumi, and M. Kasha, J. Chem. Phys., 40, 507 (1964).
56. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 44, 1711 (1966).
57. A. T. Gradyushko, V. A. Mashenkov, K. N. Solov'ev, and M. P. Tsvirko, Zhur. Prikl. Spektrosk., 9, 514 (1968).
58. G. Porter and M. W. Windsor, J. Chem. Phys., 21, 2058 (1953).
59. G. Porter and M. W. Windsor, Proc. Roy. Soc., A, 245, 238 (1958).
60. T. S. Godfrey and G. Porter, Trans. Faraday Soc., 62, 7 (1966).
61. U. Wild and H. H. Günthard, Helv. Chim. Acta, 48, 1843 (1965).
62. M. Z. Hoffman and G. Porter, Proc. Roy. Soc., A, 268, 46 (1962).
63. G. Jackson, R. Livingston, and A. C. Pugh, Trans. Faraday Soc., 56, 1635 (1960).
64. R. Livingston and D. W. Tanner, Trans. Faraday Soc., 54, 765 (1958).
65. D. S. McClure and P. S. Hanst, J. Chem. Phys., 23, 1772 (1955).
66. R. S. Mulliken and C. A. Riecke, Reports Progr. Phys., 8, 231 (1941).
67. A. K. Chibisov and A. V. Karyakin, Optika i Spektrosk., 15, 636 (1963).
68. A. M. North, Quart. Rev., 20, 421 (1966).
69. E. J. Land, Proc. Roy. Soc., A, 305, 457 (1968).
70. R. Astier and Y. H. Meyer, "The Triplet State", Cambridge, 1967, p. 447.
71. R. Pariser, J. Chem. Phys., 24, 250 (1956).
72. G. G. Hall, Proc. Roy. Soc., A, 213, 113 (1952).
73. G. Porter and F. Wilkinson, Trans. Faraday Soc., 57, 1686 (1961).
74. J. Bell and H. Linschitz, J. Amer. Chem. Soc., 85, 528 (1963).
75. W. A. Melhuish, Trans. Faraday Soc., 62, 3384 (1966).
76. F. S. Dainton, T. J. Kemp, G. A. Salmon, and J. P. Keene, Nature, 203, 1050 (1964).
77. H. L. J. Bäkström and K. Sandros, Acta Chem. Scand., 14, 48 (1960).

78. T. S. Godfrey, J. W. Hilpern, and G. Porter, Chem. Phys. Letters, **1**, 490 (1967).
79. H. Tsubomura, N. Yamamoto, and S. Tanaka, Chem. Phys. Letters, **1**, 309 (1967).
80. P. J. Wagner, Molec. Photochem., **1**, 71 (1969).
81. G. Porter and P. Suppan, Trans. Faraday Soc., **62**, 3375 (1966).
82. N. C. Yang, Pure Appl. Chem., **9**, 591 (1964).
83. F. Bergmann and Y. Hirschberg, J. Amer. Chem. Soc., 65, 1429 (1943).
84. W. A. Bryce and C. H. J. Wells, Canad. J. Chem., **41**, 2722 (1963).
85. G. Jackson and G. Porter, Proc. Roy. Soc., **A, 260**, 13 (1961).
86. A. V. Buettner, J. Phys. Chem., **68**, 3253 (1964).
87. G. Porter and P. Suppan, Pure Appl. Chem., **9**, 499 (1964).
88. L. Lindquist, J. Phys. Chem., **67**, 1701 (1963).
89. E. F. Zwicker and L. I. Grosweiner, J. Phys. Chem., 67, 549 (1963).
90. L. I. Grosweiner and E. F. Zwicker, J. Chem. Phys., **34**, 1411 (1961).
91. T. Ohno, S. Kato, and M. Koizumi, Bull. Chem. Soc. Japan, **39**, 232 (1966).
92. G. Blauer and H. Linschitz, J. Phys. Chem., **66**, 453 (1962).
93. A. K. Chibisov, B. V. Skvortsov, A. G. Karyakin, and N. N. Shvindt, Khim. Vys. Energii, **1**, 529 (1967).
94. A. K. Chibisov, B. V. Skvortsov, A. V. Karyakin, and L. N. Rygalov, Khim. Vys. Energii, **3**, 210 (1969).
95. C. G. Hatchard and C. A. Parker, Trans. Faraday Soc., **57**, 1093 (1961).
96. H. Fischer, Z. phys. Chem. (Frankfurt), **43**, 177 (1964).
97. S. Matsumoto, Bull. Chem. Soc. Japan, **37**, 491 (1964).
98. S. Kato, M. Morita, and M. Koizumi, Bull. Chem. Soc. Japan, **37**, 117 (1964).
99. A. K. Chibisov, G. P. Roitman, and A. V. Karyakin, Khim. Vys. Energii, **4**, 273 (1970).
100. A. K. Chibisov, V. A. Kuz'min, G. P. Roitman, I. I. Levkoev, and A. V. Karyakin, "XVIII Vsesoyuznoe Soveshchanie po Lyuminestsentsii Kiev, 1969, Tezisy" (XVIIIth All-Union Conference on Luminescence, Kiev, 1969, Abstracts), p. 95.
101. R. Livingston, G. Porter, and M. Windsor, Nature, **173**, 485 (1954).
102. R. Livingston, J. Amer. Chem. Soc., **77**, 2179 (1955).
103. S. Claesson and L. Lindquist, Arkiv Kemi, **11**, 535 (1957).
104. R. Livingston and E. Fujimori, J. Amer. Chem. Soc., 80, 5610 (1958).
105. H. Linschitz and K. Sarkanen, J. Amer. Chem. Soc., 80, 4826 (1958).
106. S. Claesson, L. Lindquist, and B. Holmstrom, Nature, **183**, 661 (1959).
107. L. Pekkarinen and H. Linschitz, J. Amer. Chem. Soc., 82, 2407 (1960).
108. A. K. Chibisov, "Issledovanie Fotoreaktsii Pigmentov Metodom Impul'snogo Fotoliza i Kineticheskoi Spektroskopii" (Investigations of the Photoreactions of Pigments by Flash Photolysis and Kinetic Spectroscopy), Candidate's Thesis, GEOKhI, Moscow, 1965.
109. A. V. Karyakin and A. K. Chibisov, Symposium, "Elementarnye Fotoprotsessy v Molekulakh" (Elementary Photoprocesses in Molecules), Izd. Nauka, Moscow–Leningrad, 1966, p. 296.
110. G. Zieger and H. T. Witt, Z. phys. Chem. (Frankfurt), **28**, 273 (1961).
111. V. A. Shakhverdov, Optika i Spektrosk., **10**, 933 (1965).
112. V. A. Shakhverdov, Symposium, "Elementarnye Fotoprotsessy v Molekulakh" (Elementary Photoprocesses in Molecules), Izd. Nauka, Moscow–Leningrad, 1966, p. 283.
113. A. Terenin, E. G. Lyubomudrov, and A. V. Shablya, Izv. Akad. Nauk SSSR, Ser. Khim., 1206 (1961).
114. G. P. Gurinovich and A. P. Patsko, Izv. Akad. Nauk SSSR, Ser. Fiz., **27**, 772 (1963).
115. J.-G. Villar and L. Lindquist, Compt. rend., **B264**, 1807 (1967).
116. G. A. Shakhverdov and A. N. Terenin, Dokl. Akad. Nauk SSSR, **150**, 1311 (1963); **160**, 1141 (1965).
117. A. K. Chibisov, Photochem. Photobiol., **10**, 331 (1969).
118. R. Livingston, Quart. Rev., **14**, 174 (1960).
119. J. Frank, Proc. Nat. Acad. Sci. USA, **44**, 941 (1958).
120. R. Livingston, W. F. Watson, and J. McArdle, J. Amer. Chem. Soc., **71**, 1542 (1949).
121. J. Fernandez and R. S. Becker, J. Chem. Phys., **31**, 467 (1959).
122. M. Kasha, Discuss. Faraday Soc., No. 9, 14 (1950).
123. R. Platt, Radiation Biology, **3**, 94 (1956).
124. V. B. Evstigneev, V. A. Gavrilova, and A. A. Krasnovskii, Dokl. Akad. Nauk SSSR, **70**, 261 (1950).
125. R. L. Amster and G. Porter, Proc. Roy. Soc., **A, 296**, 38 (1966).
126. E. W. Abrahamson, R. G. Adams, and V. J. Wulff, J. Phys. Chem., **63**, 441 (1959).
127. E. W. Abrahamson, J. Marquisee, P. Gavuzzi, and J. Roubie, Z. Elektrochem., **64**, 177 (1960).
128. W. Dawson and E. W. Abrahamson, J. Phys. Chem., 66, 2542 (1962).
129. K.-H. Grellmann, R. Memming, and R. Livingston, J. Amer. Chem. Soc., 84, 546 (1962).
130. E. I. Rabinowitch, "Photosynthesis" (Translated into Russian), Inostr. Lit., Moscow, 1959, Vol. 3.
131. A. N. Terenin, "Fotokhimiya Khlorofilla i Fotosintez" (The Photochemistry of Chlorophyll and Photosynthesis), Izd. Akad. Nauk SSSR, Moscow, 1951.
132. "Energy Conversion by the Photosynthetic Apparatus", Brookhaven Symposia in Biology, No. 19, New York, 1967.
133. J. L. Rosenberg, S. Takashima, and R. Lumry, "Research in Photosynthesis", New York, 1957, p. 85.
134. R. Moraw and H. T. Witt, Z. phys. Chem. (Frankfurt), 29, 25 (1961).
135. H. T. Witt, "Nobel Symposium 5", Interscience, New York, 1967, p. 261.
136. G. W. Robinson, "Energy Conversion by the Photosynthetic Apparatus", Brookhaven Symposia in Biology, No. 19, New York, 1967, p. 16.
137. H. T. Witt and R. Moraw, Z. phys. Chem. (Frankfurt), 20, 253 (1959).
138. P. Mathis, "International Congress of Photosynthesis Research, 1968, Abstracts", p. 91.
139. G. Zieger and H. T. Witt, Z. phys. Chem. (Frankfurt), 28, 273 (1961).
140. R. Reich, G. Döring, and H. T. Witt, Z. phys. Chem. (Frankfurt), **53**, 1 (1967).
141. G. Porter and M. W. Windsor, Discuss. Faraday Soc., No. 17, 178 (1954).
142. G. Porter and M. R. Wright, Discuss. Faraday Soc., No. 27, 18 (1959).

143. R. Livingston and D. W. Tanner, Trans. Faraday Soc., 54, 765 (1958).
144. G. E. Heppell, Photochem. Photobiol., 4, 7 (1965).
145. R. Livingston and W. R. Ware, J. Chem. Phys., 39, 2593 (1963).
146. G. Jackson and R. Livingston, J. Chem. Phys., 35, 2182 (1961).
147. J. W. Hilpern, G. Porter, and L. J. Stief, Proc. Roy. Soc., A, 277, 437 (1964).
148. H. Linschitz, C. Steel, and J. Bell, J. Phys. Chem., 66, 2574 (1962).
149. R. Livingston and P. J. McCartin, J. Phys. Chem., 67, 2511 (1963).
150. A. K. Chibisov and A. V. Karyakin, Dokl. Akad. Nauk SSSR, 153, 1132 (1963).
151. P. J. McCartin, Trans. Faraday Soc., 60, 1 (1964).
152. W. H. Melhuish and R. Hardwick, Trans. Faraday Soc., 58, 1908 (1962).
153. J. T. Dubois and F. Wilkinson, Appl. Spectroscopy, 18, 27 (1964).
154. L. Lindquist, J. Phys. Chem., 67, 1701 (1963).
155. G. Porter and P. West, Proc. Roy. Soc., A, 279, 302 (1964).
156. C. A. Parker, Adv. Photochem., 2, 305 (1964).
157. K. Kikuchi, H. Kokubun, and M. Koizumi, Z. phys. Chem. (Frankfurt), 62, 75, 79 (1968).
158. V. Kasche and L. Lindquist, Photochem. Photobiol., 4, 923 (1965).
159. V. L. Ermolaev and A. N. Terenin, Symposium, "Pamyati Sergeya Ivanovicha Vavilova" (In Memory of Sergei Ivanovich Vavilov), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 137.
160. A. N. Terenin and V. L. Ermolaev, Dokl. Akad. Nauk SSSR, 85, 547 (1952).
161. H. L. Bäckström and K. Sandros, Acta Chem. Scand., 12, 823 (1958).
162. G. Porter and F. Wilkinson, Proc. Roy. Soc., A, 264, 1 (1961).
163. S. Kusuhara and R. Hardwick, J. Chem. Phys., 41, 3943 (1964).
164. G. Herkstroeter and G. S. Hammond, J. Amer. Chem. Soc., 88, 4769 (1966).
165. A. Kellmann and L. Lindquist, "The Triplet State", Cambridge, 1967, p. 439.
166. A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).
167. M. Chessin, R. Livingston, and T. G. Truscott, Trans. Faraday Soc., 62, 1519 (1966).
168. A. K. Chibisov, A. V. Karyakin, and M. V. Zubrilina, Dokl. Akad. Nauk SSSR, 177, 226 (1967).
169. A. K. Chibisov, A. V. Karyakin, and M. V. Zubrilina, Biofizika, 14, 739 (1969).
170. A. K. Chibisov and A. V. Karyakin, "Progress in Photosynthesis Research", 2, 575 (1969).
171. K. Sandros and H. L. J. Bäckström, Acta Chem. Scand., 16, 958 (1962).
172. B. Stevens and M. P. Walker, Proc. Chem. Soc., 26, 109 (1964).
173. H. E. A. Kramer and M. Hainer, Z. Naturforsch., 24b, 452 (1969).
174. F. Wilkinson, G. M. Seddon, and K. Tickle, Ber. Bunsenges. Phys. Chem., 72, 315 (1968).
175. N. K. Bridge and G. Porter, Proc. Roy. Soc., A, 244, 259, 276 (1958).
176. B. Holmström, Bull. Soc. chim. belges, 71, 869 (1962).
177. H. Linschitz and L. Pekkarinen, J. Amer. Chem. Soc., 82, 2411 (1960).
178. V. Kasche and L. Lindquist, J. Phys. Chem., 68, 817 (1964).
179. A. Kira, S. Kato, and M. Koizumi, Bull. Chem. Soc. Japan, 39, 122 (1966).
180. V. Kasche, Photochem. Photobiol., 6, 643 (1967).
181. E. Fujimori and R. Livingston, Nature, 180, 1036 (1957).
182. C. Steel and H. Linschitz, J. Phys. Chem., 66, 2577 (1962).
183. V. A. Dagaev, "Kataliz Bezyzluchatel'nykh Perekhodov v Antratsene Nekotorymi Kompleksnymi Soedineniyami Kobal'ta(II), Nikelya(II), i Medi(II)" [Catalysis of Non-radiative Transitions in Anthracene by Certain Cobalt(II), Nickel(II), and Copper(II) Complexes], Candidate's Thesis, Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR, Kiev, 1968.
184. A. J. Fry, R. S. H. Liu, and G. S. Hammond, J. Amer. Chem. Soc., 88, 4781 (1966).
185. L. Lindquist, Acta Chem. Scand., 20, 2067 (1966).
186. A. K. Chibisov, B. I. Barashkov, G. P. Roitman, and A. V. Karyakin, "Soveshchanie po Fotokhimii Rastvorov, Tezisy" (Conference on the Photochemistry of Solutions. Abstracts), Izd. Naukova Dumka, Kiev, 1969, p. 4.
187. R. Livingston and P. J. McCartin, J. Amer. Chem. Soc., 85, 1571 (1963).
188. A. K. Chibisov, A. V. Karyakin, and B. B. Evstigneev, Biofizika, 11, 983 (1966).
189. A. K. Chibisov, A. V. Karyakin, B. B. Evstigneev, and I. P. Nazarova, Biofizika, 10, 1098 (1965).
190. D. F. Evans, Nature, 176, 777 (1955).
191. C. A. Hutchison and B. W. Mangum, J. Chem. Phys., 29, 952 (1958).
192. T. Förster, Z. Elektrochem., 54, 42, 531 (1950).
193. A. Weller, Z. phys. Chem. (Frankfurt), 3, 238 (1955).
194. G. Porter, Science, 160, 1299 (1968).
195. G. Porter and P. Suppan, Trans. Faraday Soc., 61, 1664 (1965).
196. G. Porter and P. Suppan, Trans. Faraday Soc., 62, 3375 (1966).
197. P. J. Wagner and G. S. Hammond, Adv. Photochem., 5, 21 (1968).

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