LASER FLASH-PHOTOLYSIS OF METHYLENE BLUE SOLUTIONS

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Besides population and relaxation of T_1 state of methylene blue in methanolic solution it has been possible to observe increase and decomposition of a transient with longer lifetime which is probably a triplet excimer of the dyestuff. Kinetic measurements have enabled to determine the lifetime of the T_1 excimer, rate constants of energy-transfer to oxygen and electron-transfer from pyrrolidine to T_1 of the dyestuff.

Methylene blue is often used as a triplet sensitizer of photo-oxygenation reactions[1,2], decomposition of diazonium compounds[3], and in studies of photodynamic inactivation of biological objects[4,5]. In all these cases primary and decisive role is played by the lowest triplet excited state of the dyestuff from which energy is transferred to oxygen molecules in the system[2,6,7], or an electron-transfer takes place from a donor (substrate) to the excited dyestuff with formation of semiquinone radical[3,8-10].

Studies of these systems by flash-photolytic methods were concentrated on formation and reactivity of semiquinone radicals and the leuco-dyestuff[11,12]. Laser flash-photolytic measurements were directed, first of all, to study of the processes connected with electron-transfer from alkyl- and arylamines[8] and iron(II) ions[13]. Laser flash-photolysis of aqueous solutions of methylene blue[14] (time resolution 500 ns) showed the existence of three transients which were described by the authors as triplet excited states of the dyestuff dimer and monomer and charge-transfer state of the dimer.

This communication presents results of laser flash-photolytic measurements (time resolution better than 20 ns) of methanolic solutions of methylene blue of various concentrations with the presence and absence of oxygen and pyrrolidine.

EXPERIMENTAL

Methylene blue (Lachema, Brno) was recrystallized three times from 0·1M hydrochloric acid. The crystals were washed with pure ethanol and dried in vacuum dessiccator. Purity of the dyestuff was checked by chromatography on silica gel thin layer. Pyrrolidine (Merck-Schuchardt) was dried with sodium and distilled twice on a short column. The fraction boiling within 87 to 88°C was used. Methanol (Lachema, Brno) was rectified on a column and the fraction boiling within 63—65°C was used. The electronic absorption spectra were measured with a double-beam recording spectrophotometer Specord UV VIS (Zeiss, Jena). The laser flash-photolytic experiments were carried out in an apparatus constructed in our laboratory[15]. As a source of the excitation radiation we used a Q.switched ruby laser generating pulses of 20 ns half-width and energy 0·8 J (Tesla VÚVET). As a source of the analytical radiation we used a pulse xenon discharge lamp. The measurements were carried out in longitudinal arrangement with optical cells of 10 and 20 mm path length. Energy of the excitation pulses was reduced by aqueous solution of copper(II) sulphate. The spectral changes were detected with a photomultiplier RCA 1P28 in the range 405 to 590 nm. The vacuum deareated samples were prepared by the method cooling-heating-cooling (3 times) and sealed under vacuum.

RESULTS AND DISCUSSION

Fig. 1 represents electronic absorption spectrum of methylene blue in methanol at ambient temperature. The dyestuff absorbs both in UV and in the whole visible part of spectrum. The lowest absorption with molar absorption coefficient from 257 to 2408$\text{M}^{-1}\ \text{cm}^{-1}$ is in the region 19000 to 29000 cm^{-1}. An intensive absorption band with the maximum at 15200 cm^{-1} ($\varepsilon = 92330\text{M}^{-1}\ \text{cm}^{-1}$) belongs to transition to the lowest $\pi\pi^*$ singlet excited state of the molecule. In this state the contribution of highest weight is due to the monoexcited configuration described by transition of an electron from MO 9 to MO 10 (see ref.[16,17]). So far literature lacks detailed quantum-chemical calculations aimed at interpretation of higher-energy electronic transitions. Thus we cannot interpret satisfactorily the absorption bands in the region above 20000 cm^{-1}.

After excitation of the non-deareated methanolic solution of methylene blue (10^{-4}M) a steep absorption increase can be observed in the region 400 to 500 nm followed by a slower decrease of 10^2 ns order of magnitude (Fig. 2). This absorption is assigned to $T_1 \rightarrow T_n$ transitions, where the lifetime of the T_1 state is strongly reduced in the presence of oxygen[18]. At the wavelength 550 nm there occurs a change in the sense of the observed impulse. It is due to depopulation of the ground state of the dyestuff. The $T_1 \rightarrow T_n$ absorption is lower than the absorption of the ground

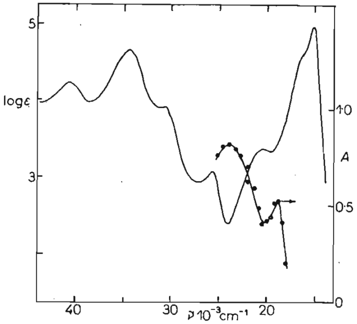

FIG. 1

Electronic Absorption Spectrum $S_0 \rightarrow S_n$ and $T_1 \rightarrow T_n$ (at the bottom) of Methylene Blue in Methanol state. In all the cases the absorption returns to the original value before excitation. Thus in the presence of oxygen no intermediate with a longer lifetime is produced which would absorb in the mentioned part of spectrum.

Kinetic courses after excitation of the deareated samples are given in Figs 2 and 3. After an abrupt absorption increase (similar to that in the non-deareated samples) there occurs a 100 × slower relaxation to the roughly original level of transparence. For the wavelengths 405 to 440 nm the kinetic course corresponds to the first-order reaction with respect to concentration of the molecule in the T_1 state. At higher wavelengths the kinetic course is more complex, and it seems to be a superposition of three subsequent processes (Fig. 3). In the scale of 500 ns/d there again occurs a steep absorption increase, the expected decrease does not practically take place, and a slower absorption increase can be observed reaching the maximum in the interval 4 μs. Then, within 50 μs the absorption decreases to the level of 33%.

Spectral course of the $T_1 \rightarrow T_n$ absorption is given in Fig. 1. Presuming negligible absorption of the T_1 state in the region 560 to 570 nm we calculated the concentration population of the T_1 state from the absorption decrease in the ground state. For excitation with one pulse this concentration is in average $0{\cdot}2 \,.\, 10^{-4}$M. The molar

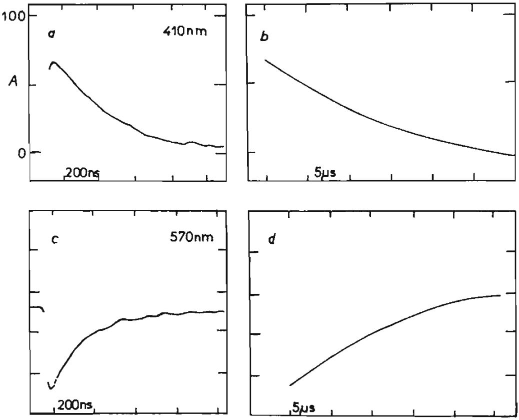

FIG. 2

Typical Oscillograms of Decrease of $T_1 \rightarrow T_n$ Absorption (*a*, *b*) and Repopulation of the Ground State (*c*, *d*) in Non-Deareated (*a*, *c*) and Deareated (*b*, *d*) Methanolic Solutions (10^{-4}M) absorption coefficient for the wavelength 410 nm (the maximum of the $T_1 \rightarrow T_n$ absorption) is then $2{\cdot}2 \,.\, 10^4 \text{M}^{-1}\, \text{cm}^{-1}$. The calculated value is approximative, it is loaded with considerable error especially in the wavelength region in which the superposition of the kinetic processes take place. The lifetime 11·0 ± 2 μs of the T_1 state calculated from the kinetic courses for concentration 10^{-4}M in the region 405 to 440 nm agrees well with the value found by Kearns[18] (7 μs).

As the triplet state of the dyestuff is efficiently quenched by molecular oxygen in solvent, the rate constant of energy transfer in the sense of Eq. (*A*) can easily be calculated[19–21].

$$^3\text{M} + {}^3\text{O}_2({}^3\Sigma_g^-) \rightleftharpoons [{}^3\text{M}\ldots{}^3\text{O}_2] \rightarrow {}^1\text{M}_0 + {}^1\text{O}_2({}^1\Delta_g, {}^1\Sigma_g^+) \qquad (A)$$

From our measurements (Fig. 2) the rate of decrease of ^{3}M can be expressed as

$$-\mathrm{d}[{}^3\text{M}]/\mathrm{d}t = (1/\tau + k_p[{}^3\text{O}_2])\,[{}^3\text{M}]\,, \qquad (1)$$

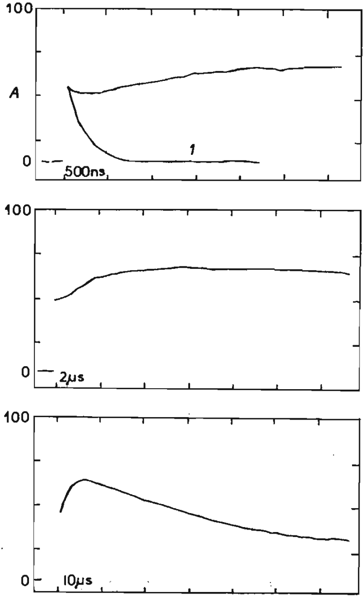

FIG. 3

The Complex Kinetic Course after Excitation of 10^{-4}M Deareated Methanolic Solution of Methylene Blue Observed at the Wavelength 525 nm (*1* in the presence of oxygen) where τ is the lifetime of ^{3}M, and k_p is rate constant of the energy transfer. Under normal conditions the oxygen concentration in methanol is $2{\cdot}12 . 10^{-3}$M (ref.[22]), hence, the energy transfer is pseudomonomolecular in nature. From slope of the straight line log (E_0/E) *vs* time it is possible to calculate k_p (see the Scheme below). The found value agrees very well with literature[18] ($2{\cdot}2 . 10^9\text{M}^{-1}\,\text{s}^{-1}$).

According to the reaction (*A*) two singlet excited states of oxygen can be populated viz $^1\Delta_g$ (92 kJ/mol) and $^1\sum_g^+$ (159 kJ/mol). As the T_1 state of methylene blue has lower energy than 142 kJ/mol, the energy transfer can populate the $^1\Delta_g$ state of oxygen only. The experiments carried out by Kearns and coworkers[2,23] confirm fully this fact. The state $^1\Delta_g$ of molecular oxygen thus must be considered in overall mechanism of sensitized decomposition of diazonium salts[3,24]. Molecules in this excited state are highly reactive in the sense of oxygenation reactions, and their lifetime 7 ± 1 μs (refs[18,25]) is long enough for interaction with the substrate even at long distance. The quantum yield of formation of singlet oxygen is 0·52 (see refs[26,27]), if the quantum yield of intersystem crossing for methylene blue is 0·52 (ref.[28]). With respect to the fact that increase in the observed signals is almost identical with the entering edge of the excitation pulse, it can be presumed that the rate of the intersystem crossing will be of nanosecond order of magnitude, and the rate constant will be of the order $10^{12}\,\text{s}^{-1}$, practically the same being true for $S_1 \rightarrow S_0$ nonradiative relaxation, because the quantum yield of the fluorescence $S_1 \rightarrow S_0$ is below 0·1 (ref.[29]).

The complex kinetic course at the wavelengths 480 to 550 nm (Fig. 3) could be interpreted as superposition of processes representing the relaxation of the T_1 state

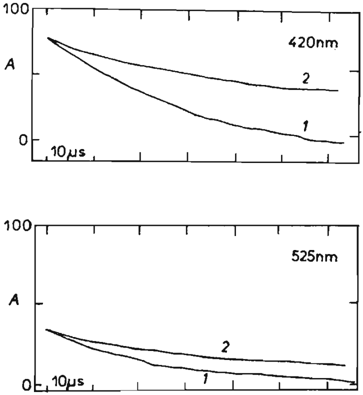

FIG. 4

Oscillograms of Decrease of $T_1 \rightarrow T_n$ Absorption in Glycerol Solutions

1 Non-deareated, *2* deareated.

of the dyestuff monomer and dimer[14], increase and decomposition of the triplet excimer, and formation of the semiquinone radical probably by decomposition of the excimer or by interaction of ^3M with the dyestuff in its electronic ground state[14] (residual absorption).

Our experimental results rather support the formation of the triplet excimer: *a*) Slow absorption increase after excitation (Fig. 3) is strongly affected by the presence of oxygen. In non-deareated solution under usual experimental conditions of excitation there is only simple kinetic process of the 1. order observable corresponding to the processes at shorter wavelenghts. *b*) Formation of the dyestuff dimer in the ground electronic state is strongly suppressed in alcohols within the concentrations $2 . 10^{-5}$ to 10^{-4}M (refs[30,31]). *c*) Formation of the triplet excimer must depend on diffusion and, hence, viscosity of the medium and on concentration of the interacting components. After excitation of the deareated solutions with $2 . 10^{-5}$M concentration the complex kinetic course was not observed (480–550 nm). The relaxation processes after excitation of glycerol solutions within the concentrations $2 . 10^{-5}$ to 10^{-4}M bear the marks of the first order kinetics and are little influenced by the presence of oxygen (Fig. 4) in the whole wavelength range measured. Table I gives kinetic constants for the wavelengths 450 and 525 nm. The lifetime of T_1 in deareated methanolic solution ($2 . 10^{-5}$) agrees very well with the data for the glycerol solutions. *d*) The complex kinetic course can also be observed in non-deareated solutions, if intensity of the excitation pulse is increased three times as compared with normal. This course is then observed also in the range of shorter wavelengths, its intensity being, however, four times smaller than the peak value of the $T_1 \rightarrow T_n$ absorption (Fig. 5).

Within the studied spectral range no rapid relaxation process corresponding to $S_1 \rightarrow S_n$ absorption and its relaxation was ever observed. These processes will be probably very fast, and population of the S_1 state will be small due to very fas

TABLE I

Lifetime of the T_1 State of Methylene Blue (μs, read for the wavelength 420 and 525[a] nm)

Solvent	Concentration, M	
	$2 . 10^{-5}$	10^{-4}
Methanol	27	11
Glycerol	30	29
	32[a]	27[a]

nonradiative processes to the T_1 and S_0 states. These views agree with the fact that so far inversed population in the S_1 state was not achieved, and stimulated emission of the dyestuff was not observed. The only successful experiments were those in sulphuric acid[32,33], where the protonated form has a quite different course of relaxation processes. For the mentioned reasons it is little likely that the non-linear optical phenomena (saturation, population of higher singlets) would have substantial influence on intersystem relaxation processes leading to higher population of the T_1 state. The T_n states can only be populated by the $T_1 \rightarrow T_n$ absorption. Their lifetime can be presumed to be of 10^{-12} s order of magnitude. On basis of general view it can be stated that the only significantly populated excited state of methylene blue able of primary photochemical reactions is the T_1 state.

The electron transfer producing semiquinone radical from a donor of the type of aromatic and aliphatic amines[8] is considered to be the primary step in sensitization of decomposition of diazonium salts[3,24]. We used 10^{-2}M pyrrolidine as the electron donor. After excitation with laser the usual absorption increase can be observed followed by abrupt decrease within 1 μs, whereafter there takes place a process slower than the relaxation of T_1 state in the absence of pyrrolidine (Fig. 6). This slower process can be assigned to formation of the semiquinone radical which absorbs relatively strongly in the mentioned spectral range[8,34]. The rate constant of the electron transfer for the pseudo-first order reaction was calculated from the beginning

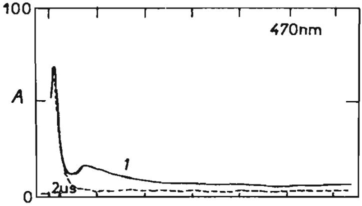

FIG. 5

Transition Absorptions in Non-Deareated Methanolic Solution (1 intensity of the excitation pulse increased about three times)

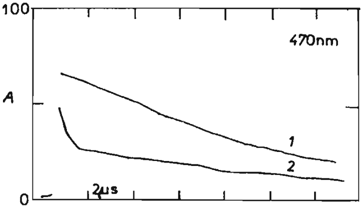

FIG. 6

Transition Absorption in Deareated Methanolic Solutions in the Absence (1) and in the Presence (2) of Pyrrolidine of the fast decrease of signal (Fig. 6) when the linear time dependence of log (E_0/E) is still obeyed. The calculated value $9{\cdot}05 \,.\, 10^7 \text{M}^{-1}\,\text{s}^{-1}$ is roughly ten times greater than that given by Joung and coworkers[8]. Our value was determined directly, the solution being carefully deareated, whereas Young and coworkers determined the rate constant indirectly and in non-deareated solution.

From the experimental results the folloving reaction scheme and rate constants can be suggested:

$$^3\text{M} \rightsquigarrow {}^1\text{M}_0 \qquad k_t = 3{\cdot}7 \,.\, 10^4\,\text{s}^{-1} \tag{B}$$

$$^3\text{M} + {}^3\text{O}_2(^3\Sigma_g^-) \rightarrow {}^1\text{M}_0 + {}^1\text{O}_2(^1\Delta_g) \qquad k_p = 1{\cdot}9 \,.\, 10^9\text{M}^{-1}\,\text{s}^{-1} \tag{C}$$

$$^3\text{M} + {}^1\text{M}_0 \rightarrow {}^3\text{MM} \qquad k_e \sim 10^9\text{M}^{-1}\,\text{s}^{-1} \tag{D}$$

$$^3\text{M} + :\text{P} \rightarrow \text{M}\cdot + \cdot\text{P} \qquad k = 9{\cdot}05 \,.\, 10^7\text{M}^{-1}\,\text{s}^{-1} \tag{E}$$

$$^3\text{M} + {}^3\text{M} \rightarrow {}^1\text{M}_1 + {}^1\text{M}_0 \qquad k_a \sim 10^9\text{M}^{-1}\,\text{s}^{-1} \tag{F}$$

$$^3\text{MM} \rightarrow 2\,{}^1\text{M}_0 \qquad k_{te} = 2{\cdot}4 \,.\, 10^4\,\text{s}^{-1} \tag{G}$$

$$^3\text{MM} + {}^3\text{O}_2(^3\Sigma_g^-) \rightarrow 2\,{}^1\text{M}_0 + {}^1\text{O}_2(^1\Delta_g) \qquad k'_p \sim 10^9\text{M}^{-1}\,\text{s}^{-1} \tag{H}$$

$$^3\text{MM} + :\text{P} \rightarrow {}^1\text{M}_0 + \text{M}\cdot + \cdot\text{P} \qquad k' \sim 10^7\text{M}^{-1}\,\text{s}^{-1} \tag{I}$$

In the overall reaction sequence anihilation of the triplets (F) is considered which can play an important role at high levels of excitation. The annihilation is limited usually by diffusion, therefore the estimate of its rate constant is of the same order of magnitude as that of (D) and (H). Also we consider the energy transfer from the triplet excimer (^{3}MM) to oxygen, and electron transfer from pyrrolidine (P) to the excimer.

The lifetime of T_1 measured in methanolic solution ($2 \,.\, 10^{-5}\text{M}$) is practically identical with those in glycerol (Table I), where there is, in addition, agreement in the measured concentration range. This fact is probably due to the nonradiative relaxation process of T_1 having predominant intramolecular character. It means that the proper dissipation system of the molecular vibronic states (a great molecule) forms an efficient pseudocontinuum for degradation of energy to the ground vibronic states. The lower lifetime of T_1 in 10^{-4}M methanolic solutions is probably due to the competitive process of formation of the excimer (D).

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