

## PHOTOLYSIS OF KRYPTOCYANINE IN SOLUTIONS

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The photolysis rate of methanolic kryptocyanine solutions depends on the excitation wave length and oxygen concentration. Only ultra violet radiation is photoactive, *i.e.* excitation to  $S_2$  and energetically higher states. Photooxidation of the dyestuff is the decisive process, although a slower process proceeds simultaneously (which is probably a photoreduction) and predominates in de-aerated solutions. The photooxidation processes are substantially slowed down by the presence of piperidine. A probable explanation of the photoreactivity of kryptocyanine after excitation into the  $S_2$  state is given.

Methanolic kryptocyanine solution is used as a passive Q-switch for modulation of resonator quality of the ruby laser enabling generation of giant nanosecond and picosecond pulses. A long-period use of this solution is complicated first of all by its relatively low light stability. This is especially disadvantageous, if stability of the output parameters of the laser are requested. The light stability of polymethine dyestuffs in a colloid film was studied by Lazarev for the first time<sup>1</sup>; he found that discolouring of the dyestuffs is affected in decisive way by the oxygen concentration resp. partial pressure in the reaction system. Later on more detailed studies were started concerning light stability of kryptocyanine and polymethine dyestuffs under the conditions of polychromatic excitation in the ultraviolet and visible regions<sup>2,3</sup>, in samples placed directly in the resonator of a ruby laser<sup>4,5</sup> and with monochromatic excitation by light from a pulse ruby laser<sup>3</sup>. Thermal stability of kryptocyanine solutions was not systematically studied up to now. Fragmentary information can be obtained from the paper by Miyazoe and Maeda<sup>6</sup> who dealt with the problems only marginally. In ethylene glycol<sup>6</sup> and glycerol<sup>7</sup> solutions the thermal stability is very low.

With respect to the fact that the previous papers were not focused on the quantitative specification of the factors affecting the light stability of kryptocyanine in solutions, we started a study of kinetics and quantum yields of the photolysis under the conditions of monochromatic excitation. The experiments were carried out in methanol and other solvents in deaerated and aerated solutions and with addition of piperidine.

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## EXPERIMENTAL

Kryptocyanine (Lachema, Brno) was recrystallized three times from methanol. Its purity was checked by thin-layer chromatography ( $Al_2O_3$  Reanal Brockman II neutral) with an acetone-methanol 9 : 1 mixture as eluent. Methanol *p.a.* (Lachema, Brno) was distilled through a rectification column, and the middle runnings boiling at 63–65°C were used. The other solvents used were distilled through rectification column, and the fractions corresponding to the published boiling point data were used. Purity of the solvents was checked by absorption spectra in the ultra violet region and by gas chromatography in some cases.

The electronic absorption spectra were measured at the room temperature with a two-beam recording spectrophotometer Specord UV-VIS (Zeiss, Jena), in the region 50000 to 13000  $cm^{-1}$ .

The spectral changes taking place in the photolyte after definite time intervals of irradiation were followed qualitatively with an apparatus constructed in our laboratory<sup>8</sup>. The photolysis kinetics were measured at the room temperature with an apparatus described in another report<sup>9</sup>. A sample with suitable concentration was irradiated by monochromatic radiation in a cylindrical cell having volume 10.8 ml and optical thickness 2 cm. Time changes of transparency were recorded by a recorder G1B1 (Zeiss, Jena). Simultaneously with the photolysis, another recorder G1B1 and calibrated photocell MQGS recorded the intensity of photolytic radiation (einstein  $\cdot min^{-1}$ ). The photolysis was applied to the samples from which oxygen was completely removed by vacuum deaeration (the sequence: freezing–evacuation–heating was repeated several times), or partially removed (by bubbling with argon), and to the samples saturated with pure oxygen and the samples prepared in contact with normal atmosphere (under the latter conditions the oxygen concentration was  $7 \cdot 10^{-3} M$ ). The samples were irradiated with the light of the wavelength 334, 365 and 690 nm separated from the total emission spectrum of the discharge tube HBO 500 by means of interference filters HgSIF (Zeiss, Jena).

Calculation of the quantum yields of the photolysis was related to the intensity of the excitation radiation absorbed only by kryptocyanine according to the relation derived by Becket and Porter<sup>10</sup>.

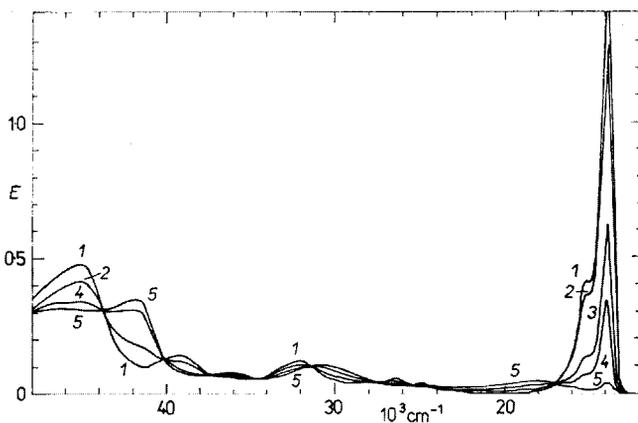


FIG. 1

Spectral Changes during Photolysis of  $10^{-5} M$  Non-Deaerated Methanolic Kryptocyanine by Light of Wavelength 334 nm

1 0, 2 10, 3 24, 4 31, 5 41 minutes of irradiation.

## RESULTS AND DISCUSSION

During photolysis the light of the wavelength 365 and 334 nm causes considerable spectral changes both in ultra violet and visible regions of the spectrum (Fig. 1 and 2). Especially the absorption decrease in the region of long-wavelength absorption band is marked, and here it is possible to obtain the most accurate quantitative data about the decrease of kryptocyanine in the photolyte. In the close neighbourhood of this band an absorption band with the maximum at  $17000\text{ cm}^{-1}$  is increasing (Fig. 2). In the ultra violet region there are no such drastic changes. In all the absorption maxima of kryptocyanine it is possible to observe an absorption decrease which is clearly seen in the region of the third and fifth maxima and an absorption increase in the regions about  $31000$  and  $41000\text{ cm}^{-1}$ . The second absorption band practically disappears.

The occurrence of eight isosbestic points indicates that most probably a photochemical reaction is taking place, the photoproducts being not subjected to any further photochemical changes. The same type of spectral changes is observed also in deaerated solutions or in those bubbled with dry argon free from oxygen.

*Kinetics and Quantum Yields of Photolysis*

Fig. 3 shows the time changes of the absorbance ( $\lambda\ 654\text{ nm}$ ) during irradiation of three samples (aerated, deaerated, and a sample which was bubbled with dry oxygen-free argon for three hours) of a  $10^{-5}\text{ M}$  kryptocyanine solution with light of the wavelength 334 nm. Saturation of the solution with pure oxygen accelerates the photolysis. Hence photooxydation with oxygen is the decisive process of photo-destruction of kryptocyanine in aerated solutions. Under such conditions the concentration of molecular oxygen in alcohols reaches the value up to  $7 \cdot 10^{-3}\text{ M}$  (ref.<sup>11,12</sup>).

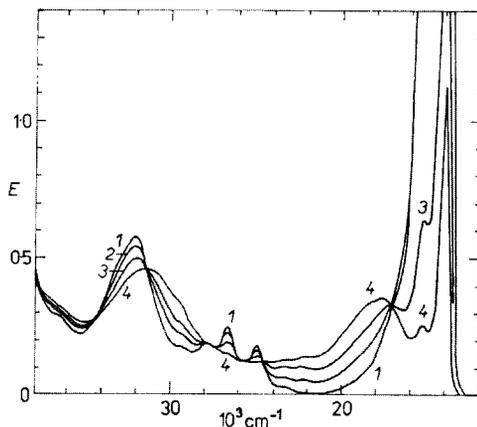


FIG. 2  
Spectral Changes during Photolysis of  $10^{-5}\text{ M}$   
Non-Deaerated Methanolic Kryptocyanine  
Solution by Light of Wavelength 365 nm  
1 0, 2 30, 3 60, 4 120 minutes of irradiation.

With respect to the fact that a slower photolysis of kryptocyanine proceeds even in deaerated solutions, *i.e.* in the absence of oxygen, a further photochemical reaction can be considered resulting in destruction of the molecule by a mechanism different from the photooxidative one. It is possible that the predominant reaction consists in photoreduction by alcohol which, under similar conditions, proceeds with many compounds and dyestuffs<sup>13,14</sup>.

On the basis of the present conception of elementary photophysical and photochemical processes proceeding in polyatomic molecules<sup>13,15,16</sup> the overall photolysis process of kryptocyanine can be divided into the following steps:

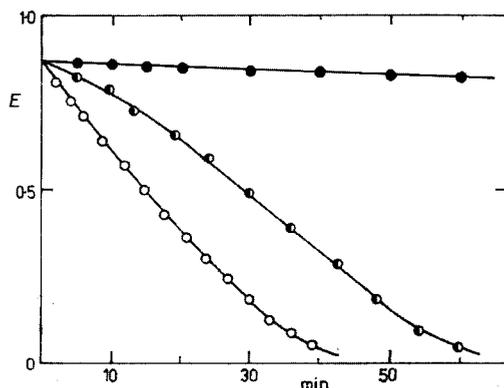
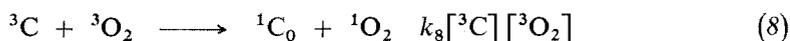
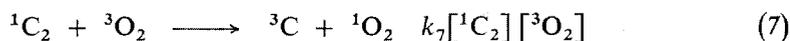
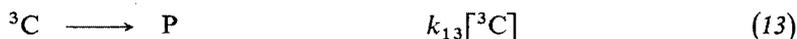


FIG. 3

Photolysis Kinetics of  $10^{-5} \text{ M}$  Methanolic Kryptocyanine Solution on Irradiation with Light of Wavelength 334 nm ( $I_0 = 13.8 \cdot 10^{-7} \text{ e. min}^{-1}$ )

○ Non-deaerated, ● bubbled with argon for 3 h, ● vacuum deaerated.



The scheme considers excitation into the second singlet of kryptocyanine, because first this excitation results in photolysis. Fluorescence from the second singlet (process (4)) was proved after two-photon excitation with pulse ruby laser<sup>7</sup> and by us, too<sup>17</sup>. In Eqs (9) to (11) we presume the formation of one oxidation product COX. We also presume that two singlet states of molecular oxygen  ${}^1\Sigma_g^+$  and  ${}^1\Delta_g$  which are formed to a certain extent during energy transfer<sup>18-20</sup> oxidize kryptocyanine to the same compound. Eqs (12) and (13) represent photoreduction processes. The last equation represents oxidation of another compound A present in the solution.

The given kinetic scheme makes it possible to express the rate of decrease of kryptocyanine, that of formation of  ${}^1\text{C}_2$  and of the singlet oxygen. With respect to the fact that many of the rate constants, especially those of the deactivation processes, are unknown values, it is useful to introduce the following simplification. We shall consider only a certain excited state of kryptocyanine  $\text{C}^+$  (triplet or singlet) which expresses, in common, the excited form of the molecule. The rate constants  $k_2$  and  $k_6$  will be summarized to give a common constant of deactivation  $k_d$ , and the processes (7), (8) connected with energy transfer will be characterized by a single rate constant  $k_p$  of energy transfer. The rate constants of photoreductions  $k_{12}$  and  $k_{13}$  will be unified under  $k_r$ .

The equilibrium concentrations  $[\text{C}^+]$  and  $[{}^1\text{O}_2]$  can be calculated as it follows:

$$[\text{C}^+] = I_a / ((k_p + k_9)[{}^3\text{O}_2] + k_d + k_r) = I_a / Z, \quad (15)$$

$$[{}^1\text{O}_2] = k_p I_a [{}^3\text{O}_2] / Z (k_{10}[{}^1\text{C}_0] + k_{14}[\text{A}]). \quad (16)$$

If the quantum yield of kryptocyanine photolysis is given by Eq. (17), and no oxygen neither the compound A are present in the system of photolysis (Eq. (18)), then it is possible to write Eq. (19), where  $q$  is given by Eq. (20), and  $q_0$  is the quantum yield of the photolysis in the absence of the compound A.

$$q_p = -I_a^{-1} d[{}^1\text{C}_0] / dt, \quad (17)$$

$$q = k_r / (k_r + k_d), \quad (18)$$

$$q_p = \varrho + (q_0 - \varrho) k_{10} [{}^1\text{C}_0] / (k_{10} [{}^1\text{C}_0] + k_{14} [\text{A}]), \quad (19)$$

$$\varrho = (q(k_9 [{}^3\text{O}_2] - k_d) + k_t) / (q(k_p + k_9) [{}^3\text{O}_2] + k_t). \quad (20)$$

Eq. (19) gives the dependence of  $q_p$  on the concentration of A for constant  ${}^1\text{C}_0$  concentration. If A concentration equals zero, then the curve expressing this dependence will cut the  $q_p$  axis at the point  $q_0$ . If  $k_{14}[\text{A}] \gg k_{10}[{}^1\text{C}_0]$ , then the curve will approach the value  $\varrho$  in the limit. Hence in the absence of oxygen it will approach the value  $q$ . Such conditions will exist then under which kryptocyanine will undergo only photoreduction.

In our case piperidine was used as the compound A, being a good acceptor of singlet oxygen; it also does not absorb in the spectral region of excitation, and on photooxidation it gives hydroxy and dihydroxy derivatives *i.e.* compounds structurally similar to alcohols<sup>21</sup>.

Table I gives the changes of the quantum yield related to oxygen and piperidine concentrations. The quantum yield of photolysis of aerated methanolic kryptocyanine solutions is roughly five times greater than that of the deaerated solutions or those ones containing piperidine in concentrations higher than  $2 \cdot 10^{-3}\text{M}$ . Fig. 4 represents the photolysis kinetic curves for various piperidine concentrations. Graphical dependence of the quantum yield  $q_p$  on piperidine concentration agrees qualitatively with the theoretically presumed dependence (Fig. 5). Also the value of the quantum yield for the piperidine concentrations higher than  $2 \cdot 10^{-3}\text{M}$  agrees well with that of photolysis of the deaerated solution.

It is possible to introduce  $\varrho = 0.043$  into Eq. (19) and calculate the ratio of the rate constants  $k_{14}/k_{10}$  for various piperidine concentrations (Table I). The average result

TABLE I  
Photolysis Quantum Yields of Methanolic Kryptocyanine Solutions under Various Conditions

$c_{\text{pip}} \cdot 10^4 \text{M}$	$c_{\text{O}_2} \cdot 10^3 \text{M}$	$I_0^{334} \cdot 10^7 \text{ e min}^{-1}$	$q_p$
0.0	0.0	14.4	0.0054
0.0	argon 3 h	15.5	0.012
0.0	7.0	40.0	0.023
5.0	7.0	40.0	0.015
7.0	7.0	14.5	0.012
9.0	7.0	15.5	0.009
20.0	7.0	15.5	0.0043
30.0	7.0	15.5	0.0041
50.0	7.0	15.5	0.0043

is  $k_{10} \approx 50k_{14}$ . With respect to that the photooxidation processes are limited by diffusion<sup>22</sup>, their rate constants are of the maximum order  $10^9 \text{ s}^{-1}\text{M}^{-1}$ , then it can be expected that  $k_{14}$  will be lower than the given limit.

Photolysis of the areated kryptocyanine solutions in various solvents (Table II, Fig. 6) indicate that the fastest decomposition takes place in chloroform and tetrahydrofuran, *i.e.* in the solvents where thermal stability is very low, too. In the course of the photolysis in chloroform a transient absorbance increase is observed followed

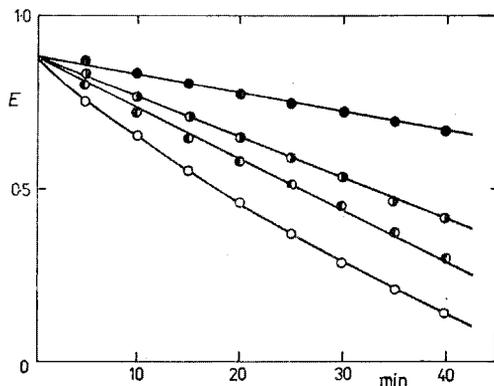


FIG. 4

Photolysis Kinetics of  $10^{-5}\text{M}$  Non-Deaerated Kryptocyanine Solution with Added Piperidine

○ 0.0; ● 5.0; ● 9.0; ● 20.0 ·  $10^{-4}\text{M}$ .

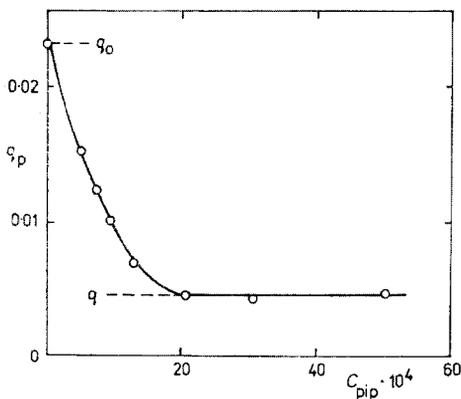


FIG. 5

Dependence of Photolysis Quantum Yield on Piperidine Concentration

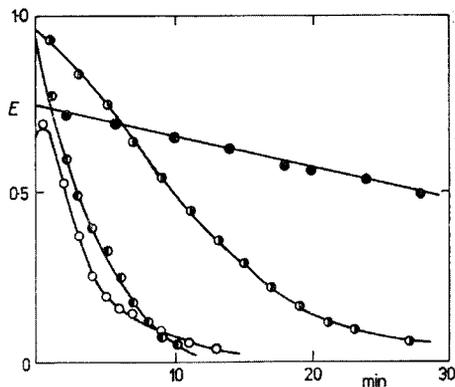


FIG. 6

Photolysis Kinetics of  $10^{-5}\text{M}$  Non-Deaerated Kryptocyanine Solutions in Chloroform ○, Acetone ●, Acetonitrile ●, and Pyridine ●

TABLE II  
 Photolysis Quantum Yields of Kryptocyanine in Various Solvents (Non-Deaerated Solutions)

Solvent <sup>a</sup>	$I_0^{334} \cdot 10^7 \text{ e min}^{-1}$	$q_p$
Pyridine	15.5	0.005
Acetone	14.7	0.1
Acetonitrile	15.0	0.037
Chloroform	17.0	0.1
Tetrahydrofurane	16.0	0.1

<sup>a</sup> Oxygen concentration of these solutions varies within the limits  $2-3 \cdot 10^{-3} \text{ M}$  at  $25^\circ \text{C}$  (ref. <sup>24</sup>).

by its steep decrease. A surprisingly high quantum yield of photolysis was obtained in acetone and acetonitrile. The pyridine solution are the most stable.

If we take into account the individual excited states of kryptocyanine molecule, we can give the following statements<sup>23</sup>. The  $S_1 \rightarrow S_0$  fluorescence lifetime is  $37 \cdot 10^{-12} \text{ s}$ , its quantum yield being  $q_f = 7 \cdot 10^{-3}$ . The quantum yield of the inter-system crossing  $S_1 \rightsquigarrow T_1$  is smaller than  $6.3 \cdot 10^{-4}$ . Thus it can be presumed that the radiationless relaxation  $S_1 \rightsquigarrow S_0$  is the fastest and, at the same time, the most efficient process of deactivation of the  $S_1$  state (the rate constant of the order  $10^{12} \text{ s}^{-1}$ ). Current excitation cannot give any measurable concentration of molecules in the  $T_1$  state<sup>23</sup>. Therefore, these facts explain satisfactorily why the excitation to the  $S_1$  state does not result in photodestruction of the dyestuff. Another situation can take place, if kryptocyanine is excited directly to the  $S_2$  state. The big energy difference between the  $S_1$  and  $S_2$  states (more than 1 eV) decreases the probability of radiationless relaxation to such an extent that it is possible to observe the fluorescence  $S_2 \rightarrow S_0$  even under normal excitation conditions<sup>17</sup>. It can be presumed that the lifetime of  $S_2$  is greater than that of  $S_1$  and, at the same time, that the inter-system crossing from  $S_2$  to the triplet states is more efficient than that from the  $S_1$  state. Under such conditions the energy transfer to oxygen and also the photooxidation processes are possible.

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