Photosolvation Reactions and Their Quantum Yields of Hexacyanocobaltate(III) in Non-aqueous Solvents

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The photoreactions of hexacyanocobaltate(III) in non-aqueous solvents (methanol, ethanol, acetonitrile, DMF, pyridine) caused by irradiation at 365 nm or 313 nm are found to be the photosolvation

$$[Co(CN)_6]^{3-} + \text{Solv.} \xrightarrow{h\nu} [Co(CN)_5(\text{Solv.})]^{2-} + CN^-$$

In pyridine, in addition to the photosolvation product, a fluorescent substance which is perhaps an aromatic compound is also formed by the irradiation at 365 nm. The quantum yields are almost the same as that in aqueous solution. In ethanol, the quantum yields irradiated at both 313 nm and 365 nm are the same, indicating that the quantum yield is independent of the exciting wavelength. The sensitized photosolvation using several donors failed to occur because of the solubility limitation. Interesting spectral results are also reported.

A large number of investigations have been performed on the photochemical[1,2] and photophysical[2,3] behaviors of transition metal complexes in the last decade. Most of these studies, however, have been done in aqueous solutions, except for the carbonyl complexes, and this seems to be due to the fact that most transition metal complexes have very low solubilities in non-aqueous organic solvents. It is mainly in aqueous solutions that many investigators have studied the photochemistry of transition metal complexes with great interest.

Recently several papers on the photochemistry and photophysics of transition metal complexes in non-aqueous solvents were reported. The photosolvation of tetrabutylammonium hexacyanochromate(III) in *N*,*N*-dimethylformamide (DMF) was studied and some evidence against the doublet hypothesis for the photoreactive state of the Cr(III) complex was obtained.[4] The same system was investigated from the standpoint of the sensitized photoaquation and photosolvation reaction and the photoreactive state was also identified as the lowest quartet excited state.[5] On the other hand, the intersystem crossing efficiency of hexacyanochromate(III) was reported from the results of the direct and $[Ru(bipy)_3]^{2+}$-sensitized phosphorescence intensities in DMF solutions.[6] Other papers dealt with the phosphorescence quenching of $[Ru(bipy)_3]^{2+}$ in ethanol–benzene,[7] and in DMF or methylformamide.[8] As for Co(III) complexes, however, neither photochemical nor photophysical studies have been made in non-aqueous solvents.

In the field of the photochemistry of transition metal complexes in aqueous solutions, it is well known that the Co(III) complexes show the photoredox reaction and/or the photoaquation and that the photoredox reaction is more likely to occur when irradiated at the shorter charge transfer band than at the longer ligand field band and that the phosphorescence cannot be seen except in a few cases even with the crystal at low temperature.[1] It is particular in the Co(III) complexes, however, that hexacyanocobaltate(III) shows only the photoaquation and does not exhibit any photoredox reaction even when the complex is irradiated at the charge transfer absorption band, 254 nm,[9] and that, moreover, it shows the phosphorescence with the crystal at low temperature (4.2 K or 77 K).[10] The reason for this unusual behavior of hexacyanocobaltate(III) has not been clarified yet. Therefore, taking account of the fact that the phosphorescence of hexacyanochromate(III) is observed in DMF but not in water,[4] photochemical and photophysical studies seem to be necessary for Co(III) complexes in non-aqueous solvents. First of all, hexacyanocobaltate(III), which shows the unusual behavior mentioned above, attracted our attention and we report in this paper the preliminary results obtained from the photochemical experiments of tetrabutylammonium hexacyanocobaltate(III) ($[Bu_4N]_3[Co(CN)_6]$) in several organic solvents.

Experimental

Materials. Tetrabutylammonium hexacyanocobaltate(III)($[Bu_4N]_3[Co(CN)_6]$) was prepared from $K_3[Co(CN)_6]$ and tetrabutylammonium bromide.[11] The spectrum of $[Bu_4N]_3[Co(CN)_6]$ in water agreed with that of $K_3[Co(CN)_6]$.[9] Potassium pentacyanopyridinecobaltate(III)($K_2[Co(CN)_5py]$) was prepared according to the literature.[12] Fluoranthene was purified by passing it through a column of silica gel. Michler's ketone was recrystallized twice from ethanol. Triacetylacetonatorhodium(III) ($Rh(acac)_3$) was recrystallized from chloroform. Reagent grade pyrazine and triphenylamine were used without further purification. Reagent grade methanol and ethanol were dried by the literature method.[13] Acetone, acetonitrile, and DMF were dried by the method reported.[14] Reagent grade pyridine was purified by distillation. Chloroform was of spectrograde and used without further purification. All these solvents were stocked in a desiccator in the dark.

Apparatus. The irradiation equipment was used in the usual way. The excitation wavelength 313 nm was isolated from a Toshiba SHL-100UV-2 mercury lamp by means of a combination of the chemical filter described by Murov[15] and the Toshiba UV-D25 glass filter. Light of 365 nm was isolated by using a Toshiba UV-D1C glass filter and a glass plate. Light of 436 nm was isolated by the method described.[16] The light intensity was measured by a ferrioxalate actinometer.[17] The absorption spectrum was measured with a Hitachi 124 double beam spectrophotometer and the emission spectrum was measured with a Aminco-Bowman spectrophotofluorometer.

Procedures. Although $[Co(CN)_6]^{3-}$ in organic solvents did not cause any thermal reactions, the sample solutions used for the irradiation were always prepared just before the measurements. When the organic sensitizers were added to the solution of $[Co(CN)_6]^{3-}$, no change of the absorption of the complex was observed. The sensitization experiments were carried out under the condition that the donors absorbed most of the incident light. Degassed solutions were obtained by successive freeze-pump-thaw cycles. The quantum yields were determined spectrophotometrically using the molar extinction coefficients(ε) of the photoproducts, which were obtained by the complete photolysis of $[Co(CN)_6]^{3-}$. In the case of $[Co(CN)_5py]^{2-}$, the ε of the synthesized sample was used because the isosbestic points in the photolysis of $[Co(CN)_6]^{3-}$ in pyridine were not seen at later stages. In benzonitrile, the quantum yield could not be obtained because the reaction did not proceed with clean isosbestic points.

Results and Discussion

Absorption Spectra. $[Co(CN)_6]^{3-}$ shows three characteristic bands in the ultraviolet region which are assigned as follows, in the order of decreasing wavelength: ${}^1A_{1g}\rightarrow{}^1T_{1g}$ (the first absorption band), ${}^1A_{1g}\rightarrow{}^1T_{2g}$ (the second absorption band), and metal to ligand charge transfer(MLCT) band, respectively.[1,18,19] The first two bands are spin-allowed ligand field transitions and have rather low molar extinction coefficients (ε). The last one is an allowed $t_{2g}\rightarrow\pi^*$ transition and hence is a very intense band. The spin-forbidden, lowest energy ligand field transition, ${}^1A_{1g}\rightarrow{}^3T_{1g}$, is observed in the crystalline spectrum, but not in solution.[10]

The absorption data obtained in several organic solvents are summarized in Table 1, together with the values of the dielectric constants in the second column. At first sight, there seems to be no regularity in the position of the absorption maximum of $[Co(CN)_6]^{3-}$ in these solvents, but it may be seen that there are two groups of solvents: (a) one is water, methanol, ethanol, ethylenediamine, and chloroform; (b) the other is acetonitrile, benzonitrile, pyridine, and DMF. In the former group, as the values of dielectric constants decrease, the absorption maximum shifts to longer wavelengths (red shift). On the other hand, the behavior of the latter group is unusual: despite the values of the dielectric constants, they all show greater red shifts than the (a) group. For example, acetonitrile, which is next to water in the order of the dielectric constants of the solvents used, shows a longer maximum wavelength, 320 nm, than does chloroform, 318 nm, which has the smallest dielectric constant. The second absorption bands show a similar tendency to the first absorption bands. This phenomena cannot be explained only from the difference in the polarity of solvents. When we note that all the solvents in the (b) group have double or triple bonds, it can be said that the π-electrons of the solvents in the (b) group are responsible for the greater red shift in the spectra of $[Co(CN)_6]^{3-}$ in these solvents. It is known that the spectrochemical series should reflect the π-bonding properties of the various ligands and, in fact, strong π-acceptor ligands such as CN^- and NO_2^- cause larger Δ(the energy separation of the t_{2g} and e_g metal d orbitals in an octahedral complex) values. Hence, the π-electron interactions between the ligand CN^- of $[Co(CN)_6]^{3-}$ and the organic solvents in the (b) group may play an important role.

The various maximum wavelengths of the photoproducts can be reasonably explained from the standpoint of spectrochemical series. It may be noted that acetonitrile cannot coordinate at a position other than an N atom and that $[Co(CN)_5(CH_3CN)]^{2-}$ shows a peak at longer wavelengths than that of $[Co(CN)_6]^{3-}$. Thus a CN^- which coordinates at a C atom is at a higher position than CH_3CN in the spectrochemical series.

Photosolvation Reactions. The solutions of $[Co(CN)_6]^{3-}$ in ethanol, methanol, acetonitrile, DMF, pyridine, benzonitrile, acetone, chloroform, and ethylenediamine were irradiated at 365 nm (in ethanol, also at 313 nm) and the spectral changes are shown in Fig. 1 to Fig. 5.

In ethanol, upon irradiation at 365 nm, $[Co(CN)_6]^{3-}$

TABLE 1. SPECTRAL DATA AND PHOTOSOLVATION QUANTUM YIELDS OF $[Co(CN)_6]^{3-}$ IN WATER AND VARIOUS NON-AQUEOUS SOLVENTS

Solvent	Dielectric constant[a]	$\lambda^1_{max}(\varepsilon)$[d]	$\lambda^2_{max}(\varepsilon)$[d]	$\lambda^p_{max}(\varepsilon)$[d]	Φ_{313}[e]	Φ_{365}[e]
H_2O[f]	78.3[b]	311 (199)	258 (136)	382 (294)	0.31	0.32
CH_3CN	38.0[c]	320 (186)	264 (137)	353 (190)		0.28
DMF	36.1[c]	322 (188)	265 (135)	399 (276)		0.28
CH_3OH	32.6[b]	313 (191)	259 (136)	391 (283)		0.32
C_6H_5CN	25.2[b]	320 (190)				[j]
C_2H_5OH	24.3[b]	314 (190)	261 (136)	392 (184)	0.28	0.28
en[g]	14.2[b]	317				[k]
py[h]	12.3[b]	321 (198)		361 (271[i])		0.31
$CHCl_3$	4.81[b]	318 (200)	261			[k]

a) Values at 25 °C except en ($CHCl_3$ at 20 °C). b) Data from J. A. Dean (editor), "Lange's Handbook of Chemistry," McGraw-Hill, New York, (1973). c) Data from Ref. 14. d) λ^1_{max}, λ^2_{max}, and λ^p_{max} are the maximum wavelengths of the first and second absorption bands and that of the photoproduct, at room temperature, respectively. e) Φ_{313} and Φ_{365} are the photosolvation quantum yields irradiated at 313 nm and 365 nm, at 25 °C, respectively. f) Photoaquation quantum yield irradiated at 436 nm is 0.31 in aqueous solution. g) Ethylenediamine. h) Pyridine. i) Value of $K_2[Co(CN)_5py]$ in aqueous solution. j) Φ cannot be obtained. See Experimental Section. k) No reaction occurred.

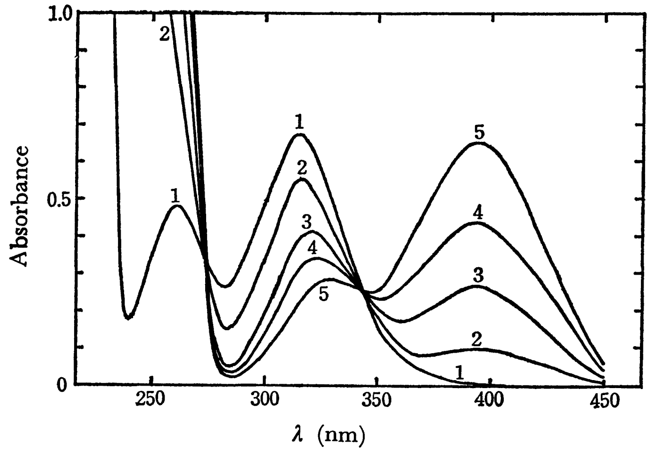

Fig. 1. Spectral change of $[Co(CN)_6]^{3-}$ in the aerated ethanol solution upon irradiation at 365 nm ([complex] 3.532×10^{-3} M, 25 °C). Time of irradiation, 1) 0, 2) 18 min, 3) 55 min, 4) 1 hr and 50 min, 5) 5 hr and 5 min.

undergoes a reaction and shows the spectral changes in Fig. 1, which are different from that in aqueous solution.[9] The peak at 314 nm decreases gradually and instead the peak at 392 nm increases. After sufficient irradiation time, this peak does not show any substantial increase. Two isosbestic points are seen at 280 nm and 342 nm, indicating that the primary photoproduct is photochemically stable. When the irradiated solution is left alone in the dark, the peak at 392 nm decreases and the peak at 314 nm recovers, but this back reaction is very slow and the recovery is not complete. Thus this thermal reaction is negligible during the irradiation. As for the photoproduct, it may be considered that ethanol has the ability to coordinate with the excited state transition metal complexes and, in fact, in the ethanol solution of $W(CO)_6$ which is studied in many coordinative organic solvents,[1] it is known that a solvent ethanol coordinates as a ligand by the irradiation.[20] Besides, we examined the effect of the addition of water to the ethanol solution. In this mixed solvent, $[Co(CN)_6]^{3-}$ undergoes a reaction also, but the isosbestic points cannot be seen cleanly. Moreover, the features of the spectral change upon irradiation become the same as that in aqueous solution[9] as the content of water increases, on the one hand, and it becomes the same as that in ethanol solution when the content of ethanol increases, on the other hand. Thus, we may consider from this preliminary result that in the dried ethanol solution, the following photosolvation reaction occurs:

$$[Co(CN)_6]^{3-} + EtOH \xrightarrow{h\nu} [Co(CN)_5(EtOH)]^{2-} + CN^- \qquad (1)$$

The quantum yield of reaction (1) is 0.28 and almost the same as that in aqueous solution, 0.32 in our experimental conditions. When light of 313 nm is used for the excitation wavelength, the same reactions as described above occur and the quantum yield is also 0.28. Although, because of the solubility limitation, the photosolvation reaction irradiated at 436 nm could not be studied in ethanol as well as in other solvents, it seems that the same results obtained by the irradiation at both 313 nm and 365 nm show that the quantum yields are independent of the wavelengths and this agrees with the results in aqueous solution (we found that the quantum yield at the excitation wavelength of 436 nm was also 0.31 in aqueous solution). O_2 had no effect on the photosolvation quantum yield.

In methanol, as shown in Fig. 2, the reaction which occurs upon the irradiation at 365 nm can be regarded as a photosolvation similar to Eq. (1), for we found that when the photoproduct in methanol was redissolved in water, its spectrum had a peak at 388 nm which did not coincide with that of $[Co(CN)_5H_2O]^{2-}$ in aqueous solution, 382 nm. The quantum yield 0.32 is the same in aqueous and in ethanol solution. The back reaction is also slow and the degree of recovery is smaller than that in ethanol.

In acetonitrile and DMF, as shown in Fig. 3 and Fig. 4, respectively, the change of the spectra caused

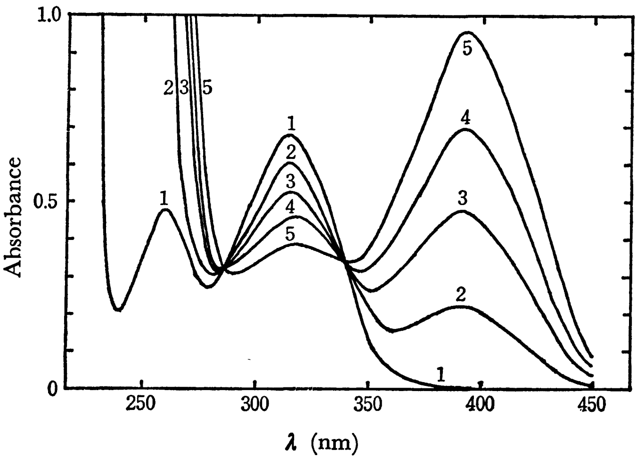

Fig. 2. Spectral change of $[Co(CN)_6]^{3-}$ in the aerated methanol solution upon irradiation at 365 nm ([complex] 3.524×10^{-3} M, 25 °C). Time of irradiation, 1) 0, 2) 35 min, 3) 1 hr and 35 min, 4) 3 hr, 5) 8 hr.

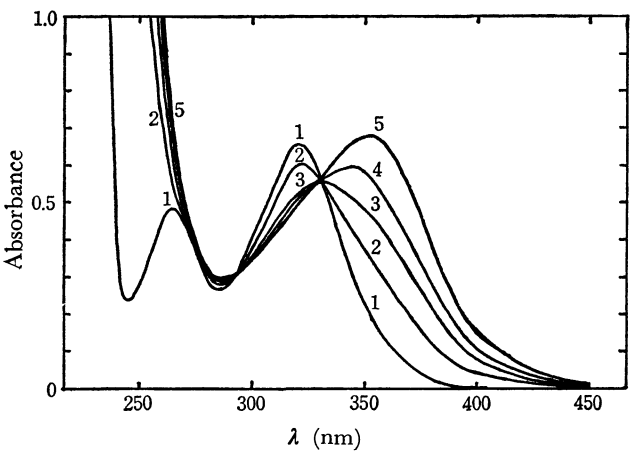

Fig. 3. Spectral change of $[Co(CN)_6]^{3-}$ in the aerated acetonitrile solution upon irradiation at 365 nm ([complex] 3.538×10^{-3} M, 25 °C). Time of irradiation, 1) 0, 2) 40 min, 3) 1 hr and 40 min, 4) 3 hr and 30 min, 5) 14 hr.

by the irradiation at 365 nm is also explained by the photosolvation

$$[Co(CN)_6]^{3-} + CH_3CN \text{ (or DMF)}$$
$$\xrightarrow{h\nu} [Co(CN)_5(CH_3CN)(\text{or DMF})]^{2-} + CN^- \qquad (2)$$

The quantum yield of the reaction in both solvents is 0.28. In DMF, O_2 had no effect on the quantum yield.

In pyridine solution (Fig. 5), the situation is greatly different from that in the above solvents; a fluorescent compound is formed by the irradiation at 365 nm. At the beginning, the fluorescence cannot be seen, but after about 30 minutes from the beginning of irradiation, the blue fluorescence becomes visible and the intensity increases with time. After about two hours, the intensity reaches a maximum. From this stage, however, the isosbestic points gradually disappear. The fluorescence and its excitation spectrum are given in Fig. 6. The absorption spectrum of the photoproduct shows a peak at 352 nm when measured in aqueous solution. Since $K_2[Co(CN)_5py]$ which is prepared has an absorption maximum at 352 nm in water and exhibits no fluorescence at room temperature, and since the excitation spectrum of the fluorescent solution does not coincide with the absorption spectrum of $[Co(CN)_5py]^{2-}$, we can consider that the fluorescent product is not $[Co(CN)_5py]^{2-}$ but perhaps some organic compound. Therefore the total reaction is written as

$$[Co(CN)_6]^{3-} + py$$
$$\xrightarrow{h\nu} [Co(CN)_5py]^{2-} + \text{fluorescent compound} \qquad (3)$$

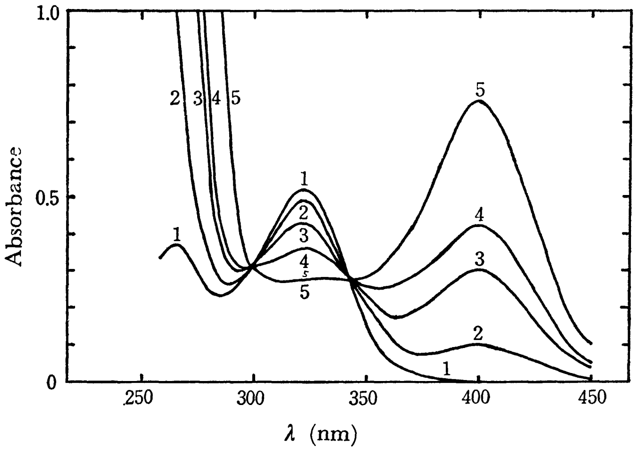

Fig. 4. Spectral change of $[Co(CN)_6]^{3-}$ in the aerated DMF solution upon irradiation at 365 nm ([complex] 2.746×10^{-3} M, 25 °C). Time of irradiation, 1) 0, 2) 10 min, 3) 40 min, 4) 1 hr, 5) 6 hr and 20 min.

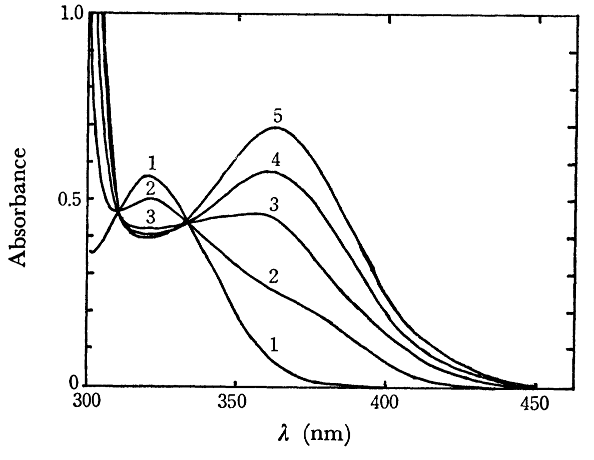

Fig. 5. Spectral change of $[Co(CN)_6]^{3-}$ in the aerated pyridine solution upon irradiation at 365 nm [(complex] 2.828×10^{-3} M, 25 °C). Time of irradiation, 1) 0, 2) 30 min, 3) 1 hr and 30 min, 4) 3 hr, 5) 6 hr.

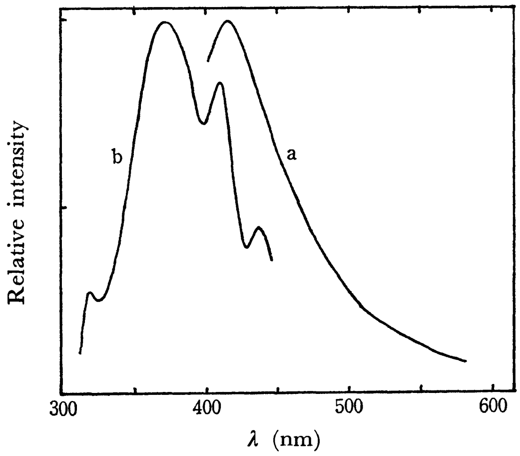

Fig. 6. Emission and excitation spectrum of the photoproduct of $[Co(CN)_6]^{3-}$ in the aerated pyridine solution produced by the irradiation at 365 nm for 6 hr at 25 °C.

a) emission spectrum, b) excitation spectrum measured at room temperature, respectively.

The deaerated solution causes the same reaction also and there is no difference in the quantum yield. Interestingly, the preliminary experiments show that the benzonitrile solution of $[Co(CN)_6]^{3-}$ gives rise to the fluorescent compound also (in this case the isosbestic points cannot be seen from the initial stage), whereas the acetonitrile solution does not give any product other than $[Co(CN)_5(CH_3CN)]^{2-}$. It is therefore reasonable to consider that the aromatic ligand is required in order to form the fluorescent compound. A reaction analogous to Eq. (3) is found in the case of $[Cr(CN)_6]^{3-}$ in the aerated pyridine.[21] These types of reaction involving the formation of the fluorescent compound have not been known till now and though at this stage we have not been able to determine the structure of the fluorescent compound, we will report all the features of this interesting reaction in the near future.

The quantum yields obtained in several organic solvents are also summarized in Table 1. It can be seen from this Table that the quantum yields are almost the same in our experimental conditions except those in chloroform and ethylenediamine where no reaction occurred. Thus, in these coordinative solvents, the rate-determining step may be regarded as the elimination process of CN^-.

Sensitization Experiments. The donors used are pyrazine, $Rh(acac)_3$, triphenylamine, Michler's ketone, and fluoranthene, and the concentration of $[Co(CN)_6]^{3-}$ varies from 1×10^{-3} M to 1×10^{-2} M. Higher concentrations than this cannot be obtained because of the solubility limitation. It is found that in both the cases of using as donors the first three sensitizers irradiated at 313 nm and the latter two sensitizers irradiated at 365 nm, no sensitized photosolvation reactions in ethanol occur.

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21) In the deaerated pyridine solution of $[Cr(CN)_6]^{3-}$, the irradiation at 365 nm causes predominantly the photosolvation. A little formation of the fluorescent compound can be seen also. It is clear that O_2 plays an important role in this system.