**THE PHOTODEGRADATION REACTION OF SOME
PORPHYRINS**

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ABSTRACT

One of the most important, but undesirable properties of the porphyrins is their oxidative photodegradation which can occur in non-polar solvents, under irradiation and in the presence of molecular oxygen. The mechanism of this oxidative photodegradation implies singlet oxygen and different radical species.

This paper is concerned with the mechanism of the photodegradation of some meso-tetra(4-X-phenyl)porphyrins(TXPP) and meso-tetra(4-X-1-naphthyl)porphyrins(TXNP), where X could have different organic structures (-NH₂, -NO₂, -SO₃H, -OH, -OCH₃, -CH₃).

Based on different spectral methods (UV-Vis and IR absorption spectroscopy, emission spectroscopy, X-ray diffraction, electronic microscopy and mass spectrometry, we propose a photodegradation mechanism and we evaluated the effect of some scavengers (2,6-di-tert-butyl-phenol (DTBF) for radical species, 1,3-diphenylisobenzofuran (DPBF) for singlet oxygen and nitro-blue tetrazolium (NBT) for superoxide anion) during the porphyrin photodegradation.

KEYWORDS porphyrins, photodegradation, spectral analysis, meso-substitution.

RESUMO

Este trabalho trata do mecanismo da fotodegradação de algumas meso-tetra(4-X-fenil)porfirinas (TXPP) e meso-tetra(4-X-1-naftil)porfirinas (TXNP), onde X corresponde a vários substituintes ($-NH_2$, $-NO_2$, $-SO_3H$, $-OH$, $-OCH_3$, $-CH_3$).

Usando métodos de espectroscopia UV-vível, infravermelho, espectroscopia de emissão, difração de raios-X, microscopia eletrônica e espectrometria de massa foi proposto um mecanismo de fotodegradação. O efeito de alguns compostos como 2,6-di-tert-butilfenol (DTBF) sobre radicais como as espécies do 1,3-difenilisobenzofurano (DPBF), oxigênio singlete e do nitro-azul tetrazólio (NBT) sobre ânion superóxido foi também estudado durante a fotodegradação das porfirinas.

1. INTRODUCTION

Porphyrins, both as free base and metallocomplexes, play an important role in many energy transfer processes from chemistry and biology ¹.

Porphyrins can be oxidized chemically, electrochemically or photochemically generating porphyrin-ring centered oxidized products, ²⁻⁷.

Competition between singlet oxygen (type II) and electron transfer (type I) photosensitization mechanisms has been observed in homogeneous and heterogeneous model systems, ⁸⁻¹⁰.

A possible photodegradation mechanism for different meso-tetra(4-X-phenyl)porphyrins (TXPP) and meso-tetra(4-X-naphthyl)porphyrins (TXNP), where X could have different organic structures ($-NH_2$, $-NO_2$, $-SO_3H$, $-OH$, $-OCH_3$, $-CH_3$) is discussed in this paper.

We could demonstrate this photodegradation mechanism by means of different spectral techniques: UV-Vis and IR absorption spectroscopy, emission spectroscopy, X-ray diffraction, electronic microscopy and mass spectrometry.

The effects of some traps for reactive species of oxygen (1,3-diphenylisobenzofuran (DPBF) for singlet oxygen, 2,6-di-tert-butylphenol (DTBF) for radical species and nitro-blue tetrazolium chloride (NBT) for the superoxide anion) on the photodegradation reaction of meso-substituted porphyrins, were analysed in this paper.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Methods

The structure of the meso-tetra(4-X-phenyl)porphyrins(TXPP), of the meso-tetra(4-X-naphtyl) porphyrins (TXNP), and the name of these porphyrins are shown in Tables 1, 2 and Figure 1.

All the porphyrins have been prepared and purified in the laboratory according to the literature data ¹¹⁻²⁰, or means of our own methods,².

The singlet oxygen trap, DPBF, obtained from Fluka (Purum grade) was used as received. Also, the superoxide anion trap (NBT) and the radical inhibitor (DTBF) were Fluka products and were used without further purification.

Potassium ferrioxalate, used as a chemical actinometer with a quantum yield of 1.11 at $\lambda = 420$ nm, was prepared by Parker's method ²¹.

Fig.1. The structure of meso-substituted porphyrins;

Table 1. The structure of meso-substituents and the name of meso-(tetra- X-phenyl)porphyrins

Meso-substituent (R)	Name of porphyrins	Abbreviation
1.	meso-tetra (4-phenyl) porphine	(TPP)
2.	meso-tetra (4-amino-phenyl) porphine	(TAPP)
3.	meso-tetra (4-nitro-phenyl) porphine	(TNPP)
4.	meso-tetra (4-sulphonato-phenyl) porphine	(TSPP)
5.	meso-tetra(4-hydroxy-phenyl) porphine	(THPP)
6.	meso-tetra(4-methyl-phenyl) porphine	(TMPP)
7.	meso-tetra(4-methoxy-phenyl) porphine	(TMOPP)

Table 2. The structure of meso-substituents and the name of meso-(tetra- X-phenyl)porphyrins

Meso-substituent (R)	Name of porphyrins	Abbreviation
8.	meso-tetra (4-naphthyl) porphine	(TNP)
9.	meso-tetra (4-sulphonato-naphthyl) porphine	(TSNP)
10.	meso-tetra (4-hydroxy-naphthyl) porphine	(THNP)

2.2. Irradiation Conditions and Measurements

The porphyrin (10^{-4}M) was added to a Pyrex flask containing 100 ml of benzene, with magnetic stirring and irradiated through the bottom optimal pyrex windows (transmitting wavelengths greater than 300 nm). The photoreactor was thermostated at 18°C by a water jacket. Oxygen was bubbled from a bottle at a rate of 3 l/h through a glass frit located inside the reactor. The light was focused by a parabolic reflector on a 420 nm filter (IAUC) which was placed in front of a quartz window.

After photobleaching, the medium was extracted (three times) with chloroform. The chloroform extracts were dried on sodium sulphate, filtered and concentrated before gas chromatography / mass spectrometry analyses.

Mass spectra were obtained with an Hewlett-Packard-5985 spectrometer. The following mass spectrometric operating conditions were employed: electron impact ionization - electron energy: 70 eV; source temperature: 200°C ; positive chemical ionization - electron energy: 150 eV; source temperature: 150°C ; methane pressure: 1 torr.

The final product of photodegradation reaction of the porphyrins was identified with an IR Specord M 80 - Carl Zeiss Jena type spectro photometer, from CCl_4 solution.

All the spectral changes of the porphyrins were analysed by means of the UV-Vis absorption spectra, recorded with a Specord M 400 spectrophotometer (Carl Zeiss Jena).

The chemiluminescence of some intermediate species resulted from the photodegradation reaction were analysed with a proper installation,^{22,23}. The device for measuring the chemiluminescence consisted of a cuvette placed in a light-tight compartment situated in front of a sensitive photomultiplier. The photocurrent from the photomultiplier was measured directly by a storage oscilloscope. Since the photodegradation of the porphyrin was very rapid, the photocurrent was integrated by charging a 1- μF condenser coupled between the input of the oscilloscope and ground. To increase the signal to noise ratio, the photons were collected by a six-branched fiber optics instead of an ellipsoidal light reflector and led to the photomultiplier cathode via a synchronising chopper, lens-assembly and filter cutoff-filters. The apparatus was suitable for recording both total light intensity and

spectra. The minimal light intensity with a signal ratio of 1 is 10^{-16} M, approximately 250 photons/s. The photocathode of the multiplier has been cooled to -20°C and the temperature of the reaction mixture (5 ml) could be regulated within $\pm 0.1^{\circ}\text{C}$. Addition of the sample can be carried out via syringe.

The singlet lifetime (radiative lifetime) of the porphyrins were calculated with an integration method, ruled on a ATARI computer.

The formula used was that given by Bowen and Wokes,³²

$$1/\tau_r = 2900 n^2 \tilde{\nu}_0^2 \int \epsilon d\tilde{\nu} \quad (\tau_r \text{ in seconds}) \quad (1)$$

where $\int \epsilon d\tilde{\nu}$ is the area under the curve of molar absorption coefficient plotted against wavenumber ;
 $\tilde{\nu}_0$ is the wavenumber of the maximum of the absorption band;
 n is the refractive index of the solvent.

The electronic micrograms were achieved with an apparatus Leitz REM -1600 T, (England). For each measurement, the samples were covered with a one Ag conducting silver film and with a fine Pt layer, by evaporation under high vacuum (10^{-6} torr)²³.

The X-ray diffraction measurements were achieved with an apparatus HZG-3 Freiberg PM, the X-ray being Cu-K α .

Twinned crystals of porphyrins in the form of purple needles were prepared by allowing methanol to diffuse into a saturated of the compound in toluene, to form hexagonal prisms. Some of these crystals could be cleaved into two nontwinned crystal fragments. A suitable nontwinned crystal fragment with approximate dimensions $0.05 \times 0.075 \times 0.5$ mm was used for the X-ray studies.

2.3. Quantum Yield Measurement

Quantum yield of photochemical degradation of the porphyrins upon excitation of the Soret band (420 nm), was determined using ferrioxalate actinometer²¹.

The photodegradation rate of the porphyrins (designated P), was evaluated by optical measurements using $\epsilon_{420 \text{ nm}}$ (molar absorption coefficient) ($\text{M}^{-1} \cdot \text{cm}^{-1}$), this value being determined independently,²³.

$$R = \Delta[P] / \Delta t \quad (2)$$

Quantum yield was calculated from the following equation :

$$\Phi = R / I_a \quad (3)$$

Based on Lambert-Beer law, the intensity of absorbed light, I_a [$\text{einstein} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$] may be expressed as:

$$I_a = I_0 - I = I_0 - I_0 \exp(-\epsilon l [P]) \quad (4)$$

where ϵ is the molar absorption coefficient of the photochemically active component of the porphyrin solution at the wavelength of initiating radiation and l is the effective length of the photoinitiating beam.

3.RESULTS AND DISCUSSION

Table 3 shows the main parameters for the photodegradation reaction of the porphyrins (the reaction rate at $t=0$ (V_R^0 ($\text{M} \cdot \text{s}^{-1}$)), the quantum yield (Φ) and the lifetime for the first excited singlet state ($\tau(s)$).

It can be seen that the TXNP derivatives have a photodegradation rate more higher than those from TXPP derivative. The former have a singlet lifetime for the first excited state much smaller than the latter.

Using X-ray diffraction we determined the spatial dimensions of the porphyrin crystals, by means of the interplanar distances ($\text{\AA}$) and the relative intensity of the diffraction maximum (I/I_0 in %),²³.

In the case of TXPP derivatives the most intensive diffraction maximum (I/I_0 in %), corresponds to an interplanar distance of $4.688 \text{ \AA}$, much less than for TXNP derivatives, where this parameter has two values: 5.56 and $4.448 \text{ \AA}$. From the two values of this parameter we could estimate the distorted spatial orientation of the naphthyl meso-substituents,²³.

Table 3. The correlation between the Hammett constants and the photochemical parameters of the photodegradation reaction for the meso-substituted porphyrins (solvent dodecanol) *

Porphyrin	$\Sigma\sigma_x$	$\tau(s)$	$V_R^0 (M.s^{-1})$	$\Phi \times 10^2$
TAPP	-2.52	3.15	0.7	1.07
THPP	-1.52	2.6	1.3	2.0
TMOPP	-1.3	0.71	2.01	3.09
TMPP	-1.5	0.38	2.4	3.19
TPP	0	0.33	2.5	3.3
TSPP	1.92	0.22	2.9	3.92
TNPP	3.08	0.16	3.2	4.38
THNP	-1.52	2.1	2.89	4.32
TNP	0	2.0	3.4	5.23
TSNP	1.92	1.422	4.76	7.44

*

$\Sigma\sigma_x$ =the Hammett constants;

$\tau(s)$ =lifetime for the first excited state;

$V_R^0 (M.s^{-1})$ = reaction rate;

$\Phi \times 10^2$ = quantum yield.

The electronic microscopy data show that the crystal dimensions for TXNP derivatives (50-60 μm) are much less than for TXPP derivatives (200 μm). From all these results we concluded that TXNP derivatives have a more distorted structure than TXPP, in good agreement with our previously published results,²³.

For both series of porphyrins, the compounds with the Hammett constant smaller than zero, show a less photodegradation because in such cases we have:

- a less intensive hyperconjugation macrocycle-meso-carbons,²⁹;
- a smaller inductive effect (from the meso-substituent to the porphyrinic macrocycle) and

-a greater conjugation between the macrocycle and the meso-substituent.

Under these conditions, the photodegradation mechanism for meso-porphyrins (designated P) could be:

To prove the existence of the species that appear in this mechanism we used different spectral methods:

A. From UV-Vis spectra, we could observe the photodegradation of the porphyrin system; some of the initial absorption bands disappeared and new absorption maxima were formed (for example, at TNP, Figure 2). This fact could be an evidence for the photodegradation reaction of these porphyrins which yield to some tetrapyrrolic rings chain (Eq. (12) and Eq. (14)),²³

Fig.2. The visible spectra of TNP (—) and its photodegradation product(-----);

Fig.3. The IR spectra of TNP(1) and its photodegradation product (2);

B. With IR spectroscopy we could observe the ketone products that resulted from the photodegradation reaction (Figure 3). For example, the spectrum for TNP shows the frequency from 1700 cm^{-1} , attributed to ketone group identified in the photodegradation product. This could be a evidence for Eq.(15);

C. The lability of the meso-substituent is different for different kind of porphyrins: the bond between the meso-substituent and the macrocycle could be break more rapidly for the porphyrins with Hammett positive constant,²⁸ The mass-fragment for meso-tetra (1-naphtyl)porphyrin is presented in Figure 4, and this could be a evidence for Eq.(15);

D. Wasser and Fuhrhop,^{22,23} proposed two ways of the photooxidative destruction of the porphyrins macrocycle; one of these implies a dioxetane state which was detected by chemiluminescence signal in agree with the literature data, Scheme 1.

Table 4. The correlation between the Hammett constants, the reaction rate and the ketone and peroxide concentration generated during the photodegradation reaction of the meso-substituted porphyrins*

Porphyrin	$\Sigma\sigma_x$	V_{R^0} ($M.s^{-1}$)	Ketone (mg/ml)	Peroxide (mg/ml)
TAPP	-2.52	0.7	5.12	3.13
THPP	-1.52	1.3	7.16	8.90
TMOPP	-1.3	2.01	23.46	17.45
TMPP	-1.5	2.4	34.15	12.15
TPP	0	2.5	43.12	34.00
TSPP	1.92	2.9	44.39	39.05
TNPP	3.08	3.2	50.80	69.07
THNP	-1.52	2.89	23.46	17.45
TNP	0	3.4	23.45	19.78
TSNP	1.92	4.76	46.21	68.00

*

$\Sigma\sigma_x$ = the Hammett constants;

V_{R^0} ($M.s^{-1}$) = reaction rate;

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Scheme 1. The photodegradation products of the porphyrins.

All these species were quantitative detected by spectrophotometric methods,³³(Table 4). From this table we can observe that the ketone and peroxides concentrations increase in the same way with the Hammett constants and the photodegradation rates for each class of meso-substituted porphyrins (TXPP and TXNP).

Table 5. Quantum yields of $^1\text{O}_2$ formation, standardized by taking Φ_Δ for all studied porphyrins (TPP or TNP as references).

Porphyrin	Φ_Δ
TPP(ref)	0.89
TAPP	0.69
THPP	0.70
TMOPP	0.77
TMPP	0.85
TSPP	0.85
TNPP	0.89
TNP(ref)	0.90
THNP	0.78
TSNP	0.80

Fig.4. The mass spectrum of the photodegradation product of TNP;

As we know, the porphyrins having no central metal atom had no chemiluminescence activity.³⁰ But, the photodegradation reaction of these compounds generates dioxetanes as chemiluminescent species. The decomposition of the dioxetane must produce one of the carbonyl products in an excited state. The wavelength maximum of the chemiluminescence is at 430-440 nm, this showing that the decomposition of the dioxetane is a concerted electrocyclic reaction which forms a carbonyl compound in the excited singlet state, and confirms the suggestion that the chemiluminescence is due to the decomposition of 1,2 dioxetanes, Scheme 1.

E. We tried to demonstrate the mechanism of the photodegradation reaction of the porphyrins. As we know, the photodegradation reaction of the porphyrins is preponderantly radical. We have studied the reaction between a meso-tetra(p-X-phenyl)porphyrin and a radical trap, DTBF. The photodegradation rate of TNP, measured at $t=0$, is very small than in the absence, Figure 5. This plot is specific for a radicalic reaction (with a proper induction period) and we could observe that the induction period for this plot is bigger than in its absence and than in the presence of only singlet oxygen trap. This fact could be an experimental evidence for the presence of radical states in this reaction. These radical states could come from the porphyrin or from the oxygen during the photodegradation, Eqs. (13), (11), (10), (8), (12);

F. Also, as we know the photodegradation reaction of the porphyrins is a concerted mechanism of singlet oxygen and radical species,³¹ The presence of singlet oxygen was demonstrated by means of the reaction between the porphyrin and a singlet oxygen trap, DPBF, Figure 5. The optimum concentration of the scavenger for this photodegradation reaction was 10^{-5} M, as we already published.³¹ In the presence of this scavenger, the photodegradation rate of the porphyrin is smaller than in its absence, this conclusion being a proof for the Eq. (7).

The explanations for this observation are:

- the porphyrins have a very strong absorption at 410 nm (and a very big molar absorption coefficient ($100,000-400,000 \text{ M}^{-1}.\text{cm}^{-1}$) by comparison with the scavenger at the same wavelength ($25,000 \text{ M}^{-1}.\text{cm}^{-1}$);
- in such conditions the porphyrin will generate less excited states and less singlet oxygen than the scavenger;
- the scavenger will be firstly destroyed, and the porphyrin will be degraded more slower in the presence of the scavenger. From Fig. 5, we can observe that the induction period of the plot $c_{\text{porphyrin}} \times 10^{-5} \text{ (M)}$ vs.

Fig.5. The variation of the porphyrin concentration during its photodegradation reaction in different conditions:

1. TNP 10^{-5} M in benzene;
2. TNP 10^{-5} M in benzene and in the presence of NBT 10^{-3} M;
3. TNP 10^{-5} M in benzene and in the presence of DPBF 10^{-5} M;
4. TNP 10^{-5} M in benzene and in the presence of DTBF 10^{-4} M.

t (min) ,in the presence of the scavenger is two times and half bigger than in its absence. The scavenger will firstly absorb the incident photons and the singlet oxygen generated will attack the porphyrin. This is the well known filter effect of the scavenger,³¹.

In the presence of DPBF, the singlet oxygen is desactivated as follows:

During a continuous irradiation process, the singlet oxygen has been observed from the absorption spectra of DPBF with the formula,²⁴⁻²⁷.

$$-1/\Delta A = 1/\epsilon \cdot l [\text{DPBF}] + (\beta/[\text{DPBF}]) \cdot (1/A) \quad (18)$$

where ΔA is the absorption changes of DPBF during the irradiation process measured at 410 nm ($\epsilon = 25000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ being the molar absorption coefficient and $l = 1 \text{ cm}$;

$[\text{DPBF}]$ is the mole number of DPBF oxidated in an unit of volume, where $A \longrightarrow \infty$, $\beta = k_d/k_r$ (k_d being the constant for the physical quenching of singlet oxygen, and k_r being constant for the chemical quenching of singlet oxygen).

The plot of $1/\Delta A = f(1/A)$ gives us β and $[\text{DPBF}]$; β values are in agreement with the literature data,²⁶.

The quantum yield for singlet oxygen generation has been determined by comparison with this value for TPP and TNP, Table 5.

$$\Phi_{\Delta} = \Phi_{\Delta \text{ref}} [\text{DPBF}] / [\text{DPBF}]_{\text{ref}} \quad (19)$$

Where $[\text{DPBF}]_{\text{ref}}$ and $\Phi_{\Delta \text{ref}}$ correspond to the unsubstituted meso-porphyrin. Under our conditions, the singlet oxygen is generated by an intermolecular process of energy transfer.

From this table, we can observe that for all porphyrins studied the photodegradation rate changes in the same way as Φ_{Δ} .

The presence of the radical species was evaluated by means of a specific scavenger, 2,6-di-*tert*-butyl-phenol (DTBF).

In the presence of this scavenger, the porphyrin radicals, generated during of the photodegradation reaction (see the eqs. 10-14), are quickly trapped. As we can see from the Figure 5, the induction period for the reaction in the presence of this scavenger is four time bigger than in its absence.

G. The superoxide anion that appeared in Eq. 8 also participates in the photodegradation reaction. To demonstrate this fact, we demonstrated the reaction between the porphyrins and NBT, Figure 5. The conclusion was the same: in the presence of this scavenger the photodegradation rate is smaller than in its absence. So, under these conditions it was evident that the superoxide anion participate in this reaction.

Doing this reaction in the presence of all three scavengers, we have observed that the photodegradation rate is twenty time smaller than in their absence (Figure 5).

Even qualitatively, all these experimental proofs are very useful for the application fields where the porphyrin solutions needs to be very photostable.

H. The eqs. (5) and (6) were considered from the literature data,³⁴.

4. CONCLUSIONS

In this paper we tried to elucidate a few of the complex aspects of the photodegradation reaction of the meso-substituted porphyrins.

As we saw, this reaction is a concerted process, the main active species of oxygen being singlet oxygen, superoxide anion, and different excited and radical states derived from the porphyrins and also from oxygen.

An important conclusion is that: when the Hammett constant for the meso-substituent has a positive value, the porphyrin undergoes a faster photodegradation reaction.

In this paper we have summed the results from different spectral technics, the cuantic and experimental photochemical methods to proof the intermediate states which concure to this reaction.

In this paper we have combined the experimental results from different spectroscopic techniques, photochemical methods, and quantum yields to prove the presence of intermediate states that participate in this reaction.

5. REFERENCES

1. P. Hambright, *Coord. Chem. Rev.*, 6, 247-258(1971);
2. R.M. Ion and L. Teodorescu, *Rev. Chim.*, 41,4,312-315 (1990).
3. R.M. Ion, L. Teodorescu, C. Mandravel, E. Volanschi and M. Hillebrand, *Rev. Chim.*, 2,129-133(1990).
4. R.M. Ion, L. Ceafalau, F. Moise and A. Iosif, *Anal. Univ. Buc.*, 1,51-58(1992).
5. R.M. Ion, *Rev. Chim.*, 44,11,957-960(1993);
6. R.M. Ion, S. Coca and D. Mardare, *Progr. Catal.*, 1,54-61(1993).
7. R.M. Ion, *Rev. Chim.*, 44,5,431-434(1993);
8. G.S. Cox, D.G. Whitten and G. Gianotti, *Chem. Phys. Lett.*, 67,511-512(1979);
9. M. Shopova, G. Braschiev and T. Ivanov, *Lasers Med. Sci.*, 2,91-96 (1987);
10. R.M. Ion, F. Moise, V. Gazdaru, C. Bercu and V. Badescu, *Progr. Catal.*, 1-2,9-14(1994);
11. R.G. Little, J.A. Anton, P.A. Loach and J.A. Ibers, *J. Heterocycl. Chem.*, 12,343-349(1975);
12. A.M.D'A. Rocha Gonsalves and M.M. Pereira, *J. Heterocycl. Chem.*, 22,931-933(1985);
13. C.M. Badger, R.A. James and R.L. Laslett, *Austr. J. Chem.*, 19,1928-1935 (1964);
14. K. Rousseau and D. Dolphin, *Tetr. Lett.*, 48,4251-4254(1974);
15. J.R. Miller and G.D. Dorough, *J. Amer. Chem. Soc.*, 74,20,3977-3981 (1952).
16. G.D. Dorough and F.M. Huennekens, *J. Amer. Chem. Soc.*, 74,20,3974-3976(1952);
17. R.H. Ball, G.D. Dorough and M. Calvin, *J. Amer. Chem. Soc.*, 68,2278-2281(1946);
18. P. Rothmund and A.R. Menotti, *J. Amer. Chem. Soc.*, 70,1808-1812(1948);
19. G.D. Dorough, J.R. Miller and F.M. Huennekens, *J. Amer. Chem. Soc.*, 73, 4315-4320(1951);
20. A.D. Adler, F. Longo, J.D. Finarelli, J. Golmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 32,476(1976).
21. C.A. Parker, "Luminescence of Solutions", Acad. Press, New York(1968), pp.208-214;
22. R.M. Ion and A. Ureche-Fotea, *Rev. Chim.*, 47,11,1064-1072(1996).
23. R.M. Ion, "Ph.D Thesis", (Bucharest University)1994, pp.38-44.

24. P.B. Merkel and D.R. Kearns, *J. Amer. Chem. Soc.*, **97**, 462-463 (1975).
25. C. Tanelian, L. Golder, C. Wolff, *J. Photochem.*, **25**, 117-125 (1984).
26. J.B. Verlhac, A. Gaudemer and J. Kraljic, *Nouv. J. Chim.*, **8**, 6, 401-406 (1984).
27. G. Roissbroich, N.A. Garcia and S.E. Braslavski, *J. Photochem.*, **31**, 37-47 (1985).
28. R.M. Ion and C. Mandravel, *Anal. Univ. Buc.*, **5**, 51-53 (1996).
29. J.A. Shelnutt and V. Ortiz, *J. Phys. Chem.*, **89**, 4733-4739 (1985).
30. M. Motsenbocker, Y. Ichimori and K. Kondo, *Anal. Chem.*, **65**, 397-402 (1993).
31. R.M. Ion, *Roum. J. Biophys.*, **6**, 3-4, 207-214 (1996).
32. E.J. Bowen and F. Wokes, *Fluorescence of solutions*, Longmans Green Co., London, 1953.
33. R.D. Arasasingham and T.C. Bruice, *Inorg. Chem.*, **29**, 1422-1427 (1990).
34. W. Busch, *Ph. D. Thesis*, Stuttgart, 1992.