

## Effect of Solvent on Photooxidation of Protoporphyrin–IX d.m.e. by Singlet Molecular Oxygen

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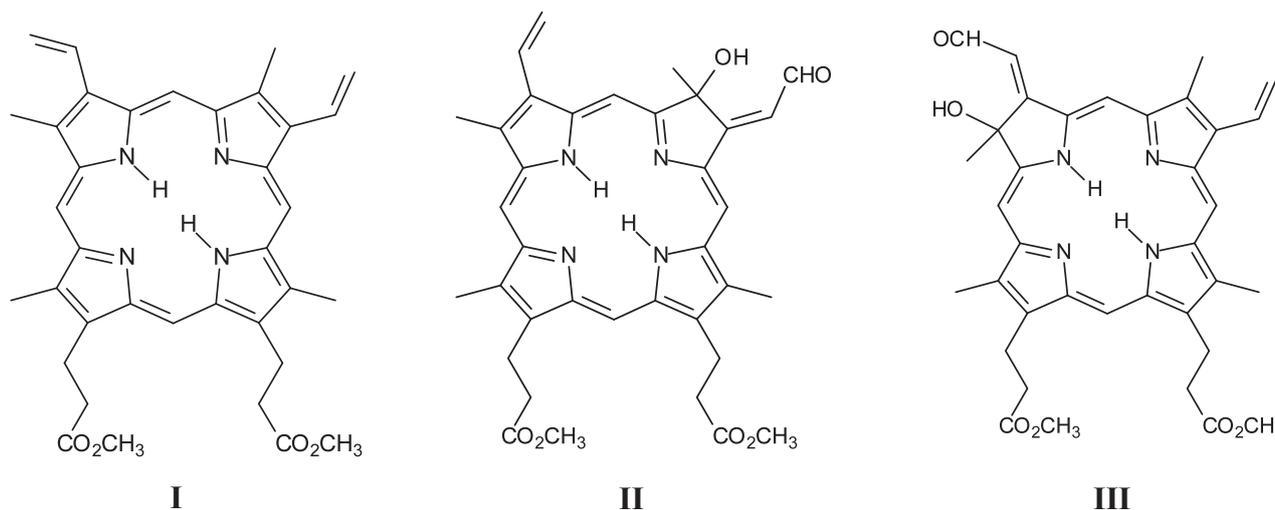
*The photooxidation of protoporphyrin - IX dimethyl ester by singlet molecular oxygen in various solvents was studied. It was shown that dielectric effect of a solvent is important in determining of the rate constant of this process.*

**Keywords:** Protoporphyrin - IX d.m.e., photooxidation, dielectric effect of a solvent.

### Introduction

Protoporphyrin - IX dimethyl ester (Figure 1, I) is one of the most important representatives of natural pigments,

the reactions of which with singlet oxygen ( $^1O_2$ ,  $^1\Delta_g$ ) continue to be interesting because of the wide use of I in biomedical photochemical technologies.<sup>[1-4]</sup> Therefore the photochemical stability is fundamental and important characteristic of I.<sup>[4]</sup>



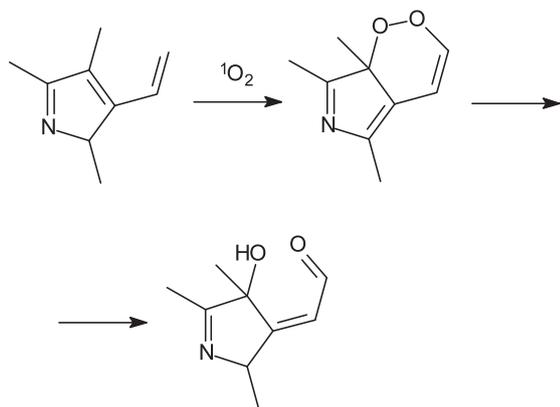
**Figure 1.** Structural formulae of protoporphyrin - IX dimethyl ester (I) and hydroxyaldehydes (II and III).

Dr. Evgeny Anatolievich Venediktov was born in 1951. After graduating from Ivanovo Institute of Chemical Technology he started to study porphyrin chemistry in the laboratory of Professor B. D. Berezin. He prepared his thesis "Influence of molecular structure on physico-chemical interaction of porphyrins and metal porphyrins with molecular oxygen" in the Institute of Biochemistry of USSR Academy of Sciences in Moscow with Prof. A.A. Krasnovskii Jr. and in 1980 received the Degree "Candidate of Chemical Sciences" (Ph.D.) in Physical chemistry from Ivanovo Institute of Chemistry and Technology. Since then he held positions at the Institute of Solution Chemistry of the Russian Academy of Sciences where he start to work in the laboratory headed by Prof. B.D. Berezin and currently is leading researcher. His research interests are connected with photochemistry of natural pigments and physical chemistry of singlet molecular oxygen.



Евгений Анатольевич Венедиктов родился в 1951 году. После окончания Ивановского химико-технологического института он начал заниматься химией порфиринов в лаборатории проф. Б.Д. Берёзина. Свою диссертацию "Влияние молекулярной структуры на физико-химическое взаимодействие порфиринов и металлопорфиринов с молекулярным кислородом" он подготовил в Институте биохимии АН СССР под руководством проф. А.А. Красновского мл. и в 1980 году получил степень кандидата химических наук по физической химии в Ивановском химико-технологическом институте. Он начал работать в в отделе, возглавляемом Б.Д.Берёзиным и в настоящее время он является ведущим научным сотрудником Института химии растворов Российской академии наук, где начал работать после защиты диссертации. Его научные интересы связаны с фотохимией природных пигментов и физической химией молекулярного кислорода.

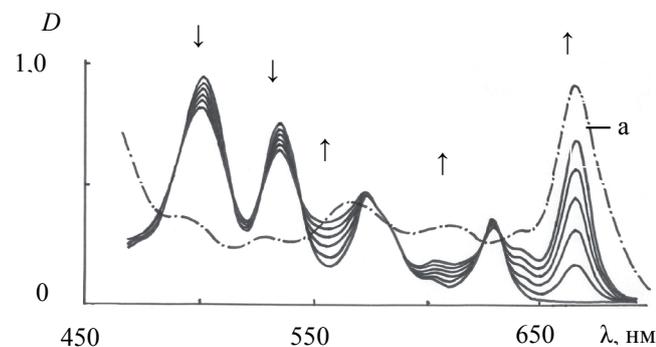
Earlier<sup>[3-10]</sup> it was demonstrated that **I** undergoes phototransformation in solution due to molecular oxygen. This reaction is highly specific. General oxidation products are hydroxyaldehydes **II** and **III** (Figure 1). The formation of these compounds formation involves the photochemical generation of  $^1\text{O}_2$  by energy transfer from the excited triplet molecules of **I** to the ground state of molecular oxygen and  $^1\text{O}_2$  transfer from photosensitizer to the ground state of **I**. Several reports<sup>[3,4,6,10]</sup> have postulated the concept of [4+2] cycloaddition of  $^1\text{O}_2$  to **I** which can be depicted as is shown below.



It was also shown<sup>[7,10]</sup> that the rate of **I** photooxidation by oxygen depends on solvent nature. Up to now, the discussion of this effect was limited to qualitative comparison. In this paper we demonstrate that in solution dielectric effect has a significant influence on the kinetics of **I** photooxidation by  $^1\text{O}_2$ .

## Experimental

**I** was obtained using the method outlined by Grinstein.<sup>[11]</sup> All solvents used in kinetic experiments were prepared as recommended in work.<sup>[12]</sup> Photolyses were conducted with a 70W halogen lamp equipped with SZS-21 glass filter ( $320 < \lambda_{\text{exc}} < 650$  nm). Spectra were obtained on SPh Model 18 spectrophotometer with glass cells of 1.0 cm path length. The  $^1\text{O}_2$  lifetimes were measured with LIF Model 200 fluorimeter.<sup>[13]</sup> The initial optical density of **I** solutions was about 1 at the band maximum of 502-506 nm depending on the solvent. The initial concentration of **I** was  $\sim 7 \cdot 10^{-5}$  M.



**Figure 2.** Examples of absorption spectra of protoporphyrin - IX in acetone measured after 0, 15, 30, 45, 60 и 75 min of exposition to light (a – absorption spectrum of hydroxyaldehydes).

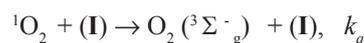
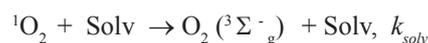
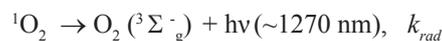
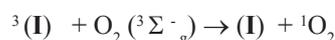
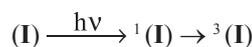
## Results and Discussion

The irradiation of **I** in air-saturated solutions results in rapid spectral changes (Figure 2) which are identical with that observed previously.<sup>[3,5-7]</sup> The key features are the decline of absorption attributed to **I** loss and the growth of the band at  $\sim 670$  nm associated with **II** and **III** formation. As it can be seen from Figure 3 these changes depend on solvent.

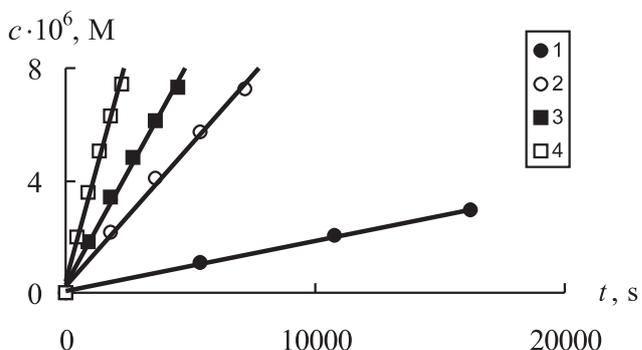
The observed rate constants ( $k = k_r[{}^1\text{O}_2]$ ) for **II** and **III** formation were calculated from evaluation of the initial increment  $d[\mathbf{II}, \mathbf{III}]/dt$  in Equation 1:

$$w = d[\mathbf{II}, \mathbf{III}]/dt = k_r[{}^1\text{O}_2][\mathbf{I}], \quad (1)$$

where  $[\mathbf{I}]$  is the initial concentration of **I**. The kinetics of **I** photooxidation by molecular oxygen can be depicted by the simplified process shown below<sup>[8-10]</sup>



where  $k_{\text{rad}}$ ,  $k_{\text{solv}}$ ,  $k_q$  and  $k_r$  are the rate constants of elementary processes.



**Figure 3.** Examples of increase of **II** and **III** concentration under protoporphyrin - IX photooxidation by  $^1\text{O}_2$  measured at 670 nm in diethyl ether (1), benzene (2), acetone (3) and dimethylformamide (4).

According to this kinetic scheme the rate of **II** and **III** formation can be expressed in a generalized form as

$$w = d[\mathbf{II}, \mathbf{III}]/dt = \frac{k_r \gamma I \tau [\mathbf{I}]}{1 + k_Q [\mathbf{I}] \tau} \quad (2)$$

Here  $k_r$  is the rate constant of **I** oxidation;  $\gamma$  is the  $^1\text{O}_2$  quantum yield;  $I$  is the light absorption intensity;  $\tau = 1/(k_{\text{rad}} + k_{\text{solv}}[\text{Solv}])$  is the  $^1\text{O}_2$  lifetime in pure solvent;  $k_Q$  is the rate constant of  $^1\text{O}_2$  deactivation by **I**. Assuming that  $k_Q$  is less than  $2 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$ <sup>[9,10,14]</sup> Equation 2 can be simplified as follows

**Table.** Kinetic parameter of protoporphyrin - IX photooxidation by  $^1\text{O}_2$ , lifetime of  $^1\text{O}_2$  in various solvents and their characteristics.

Solvent	$\tau^a$ , $\mu\text{s}$	$k_r/k_{r,bz}^a$	$\epsilon^{[12]}$	$n^{[12]}$	$\pi^{*[18]}$
Diethyl ether	30	0.15	4.23	1.3526	0.27
Toluene	29.5	0.73	2.38	1.4961	0.54
Benzene	31	1.00	2.27	1.5011	0.59
Acetone	50	1.03	20.56	1.3588	0.71
Pyridine	17	3.8	12.4	1.5095	0.87
Dimethylformamide	18	6.42	36.7	1.4303	0.88

<sup>a</sup>Errors of  $\tau$  and  $k_r/k_{r,bz}$  values are about 5 and 15 %, respectively.

$$w = k_r \gamma I \tau \quad [I] \quad (3)$$

Connection between  $k$  and  $k_r$  is derived from Equations 1 and 3

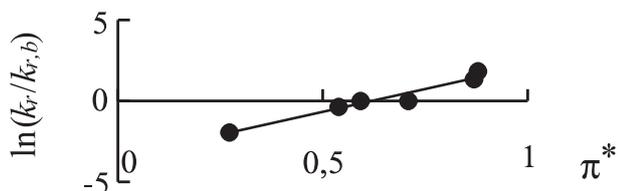
$$k = k_r \gamma I \tau \quad (4)$$

Thus  $k$  is dependent on  $\gamma$ ,  $I$  and  $\tau$  terms. As shown in works,<sup>[15-17]</sup> the quantum yield of  $^1\text{O}_2$  photogeneration by **I** is relatively constant in different solvents and has the value from 0.56 to 0.77. Therefore the relative change of  $k_r$  can be approximated by Equation 5

$$k_r/k_{r,bz} = k/k_{r,bz} \cdot \tau_{bz}/\tau, \quad (5)$$

where  $k_{bz}$ ,  $k_{r,bz}$  and  $\tau_{bz}$  are the kinetic parameters of reaction and the  $^1\text{O}_2$  lifetime in benzene as standard solvent. Using experimental data of  $k$  and  $\tau$  computed from the decay of  $^1\text{O}_2$  luminescence,<sup>[13]</sup> the relative rate constant may be calculated. The  $k_r/k_{r,bz}$  values of this reaction in various solvents are summarized in Table.

As it can be seen from the Table, reaction rate constant is sensitive to solvent. Thus, in diethyl ether the  $k_r/k_{r,bz}$  value is approximately 43 times smaller than in dimethylformamide. These data demonstrate the important role of solvent in **I** photooxidation. What is the origin of the solvent effect in this reaction? Early studies<sup>[9,14]</sup> indicated that an exciplex intermediate formation is a fundamental process of  $^1\text{O}_2$  interaction with porphyrins. In this system exciplex can occur through partial charge transfer from porphyrin to  $^1\text{O}_2$  and therefore it can possess polar character. From here we can assume that solvent kinetic effect reflects electrostatic interactions. However, the  $k_r/k_{r,bz}$  parameter does not exhibit dependence on solvent refractive index,  $n$ , and (or) solvent



**Figure 4.** Dependence of the logarithm of relative rate constant of protoporphyrin - IX photooxidation by  $^1\text{O}_2$  on the solvent dipolarity/polarizability parameter.

permeability,  $\epsilon$ . At the same time it was observed the increasing of  $k_r/k_{r,bz}$  with the growth of empirical parameter of solvent dipolarity/polarizability,  $\pi^{*}$ ,<sup>[18]</sup> characterizing the ability of solvent to stabilize a charge by dielectric effect, and this correlation is linear (Figure 4).

So it can be concluded that solvent dielectric effect is important in determining of the rate constant of this process.

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