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The effect of solvent on tetracene oxidation by singlet molecular oxygen ($^1\Delta g$): aspects of specific solvation

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Abstract—It is evident that the solvent effect on tetracene oxidation by singlet molecular oxygen is predominantly conditioned by a specific solvation of the reaction intermediate in aprotic media that is assumed to be a state with a stressed anionic center.

The involvement of oxygen in reactions proceeding in biological and chemical systems has generated considerable interest in the properties of singlet molecular oxygen ($^1O_2$).

The mechanism of $^1O_2$ addition to organic molecules has been a subject of both theoretical and experimental studies.[1–4] A significant problem concerns defining the structure of the intermediate implicated in this process.

Two previous works have related the independence of the [4+2]-cycloaddition of $^1O_2$ to 1,3-dienes from the solvent with the formation of a weak polar intermediate state[2,3] and consequently with a concerted reaction mechanism. On the other hand, intense susceptibility to solvents was observed during the oxidation of naphthalene derivatives.[4] The authors interpreted these results in the framework of an electrostatic mechanism for solvation of the intermediate which pointed to its polar nature and hence to the identification of an exciplex structure.

Here we report the application of the dependence of oxidation kinetics on solvent to investigate the structure of the intermediate involved in [4+2]-cycloaddition of $^1O_2$ to tetracene.

The rate constants of tetracene oxidation were obtained from photochemical measurements. Irradiation ($\lambda_{\text{ex.}}$ >520 nm) of a $\sim 6\times10^{-5}$ M tetracene solution in the presence of $\sim 3\times10^{-5}$ M Pd-mesoporphyrin-IX dimethyl ester as sensitizer resulted in rapid solution bleaching. The changes in absorption monitored by spectrophotometry fitted a pseudo-first-order kinetic law. The values of the observed rate constant, k_{obsd}, were determined from the kinetic measurements according to the equation:

$$-\mathrm{d}[T]/\mathrm{d}t = k_{\text{obsd}}[T] \qquad (1)$$

The oxidation is explained as proceeding via a $^1O_2$ reaction.[5] Thus, k_{obsd} is given by the following kinetic expression:[6]

$$k_{\text{obsd}} = k_r \gamma_\Delta I_o (1-10^{-A})\tau \qquad (2)$$

where k_r is the true rate constant; γ_Δ is the $^1O_2$ quantum yield; I_o is the light intensity; A is the optical density of the sensitizer solution in the excitation range; τ is the $^1O_2$ lifetime in solution, which takes into account the interaction of $^1O_2$ with solvent, substrate and sensitizer. At low concentration of reagents the τ values are equal to the lifetime of $^1O_2$ in pure solvent. In the revised expression (2) we also postulate γ_Δ value independence on the nature of the solvent. In order to estimate changes of the true rate constants, k_{obsd} values were normalized to that in benzene. Thus, the reactivity parameter $k_r/k_{r(\text{bz})}$ is calculated in the following way:

$$k_r/k_{r(\text{bz})} = k_{\text{obsd}}/k_{\text{obsd(bz)}} \times \tau_{(\text{bz})}/\tau \qquad (3)$$

where $k_{r(\text{bz})}$, $k_{\text{obsd(bz)}}$ and $\tau_{(\text{bz})}$ are the kinetic parameters of tetracene oxidation and $^1O_2$ deactivation in benzene.

The kinetic data obtained as a function of solvent properties are listed in Table 1. It is obvious that k_r increases on increasing the solvent acceptor ability. This fact reflects the specific character of the solvation of the reaction intermediate. Dependence of the natural loga-

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Keywords: tetracene; oxidation; singlet oxygen; specific solvation; intermediate.

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Table 1. Lifetime and quenching rate constants (k_q) of $^1O_2$ luminescence, solvent parameters, experimental and calculated kinetic data of tetracene oxidation

Solvent	τ^a (μs)	$k_q{}^a \times 10^{-7}$ (M^{-1} s^{-1})	$k_{obsd}/k_{obsd(bz)}$	$k_r/k_{r(bz)}$		AN^b	n^c	ε^d
				Exp.	Calcd from Eq. 5			
Diethyl ether	30		0.22	0.23	0.2252	3.9	1.3526	4.34
Benzene-h_6	31		1.00	1.00	0.9248	8.2	1.5011	2.28
Benzene-d_6	480	1,4						
1,4-Dioxane	28		1.02	1.13	1.1971	10.8	1.4224	2.21
Acetone-h_6	50		2.51	1.56	1.6487	12.5	1.3588	20.70
Acetone-d_6	352	2,3						
Pyridine	16		1.91	3.70	4.1891	14.2	1.5095	12.30
N,N-Dimethylformamide	18		3.20	5.51	4.7432	16.0	1.4303	36.70

[a] Measured by time-resolved luminescence spectroscopy;[7] errors of τ values and k_q are about 5 and 10%, respectively.

[b] Gutmann's parameter from Ref. 8.

[c] n values are quoted from Ref. 9.

[d] ε values are quoted from Ref. 9.

rithm of $k_r/k_{r(bz)}$ on the Gutmann's acceptor number, AN, is approximated by the linear equation:

$$\ln(k_r/k_{r(bz)}) = -(2.39\pm0.31)+(0.25\pm0.03)\times AN \qquad (4)$$

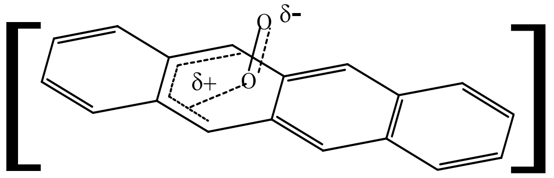
The correlation coefficient of this dependence is 0.978. It becomes 0.994 in the case of including the influence of refractivity n as $(n^2-1)/(n^2+2)$ into the approximation and it increases to 0.996 when also including the influence of dielectric permeance ε as $(\varepsilon-1)/(2\varepsilon+1)$ so generating the following equation:

$$\ln(k_r/k_{r(bz)}) = -(4.24\pm0.73)+(0.22\pm0.03)\times(AN)+(7.41\pm2.62)\times(n^2-1)/(n^2+2)+(0.85\pm0.92)\times(\varepsilon-1)/(2\varepsilon+1) \qquad (5)$$

The $k_r/k_{r(bz)}$ values calculated from Eq. (5) conform better to the experimental data (Table 1), but this fact is not so essential because the electrostatic mechanism of intermediate state solvation is not general.

From the research of tetracene oxidation by singlet molecular oxygen in aprotic solvents it follows that the specific solvation of a reaction intermediate has a predominant effect in this process. An increase of oxidation rate with the increase of Gutmann's acceptor number value enables us to predict that the reaction intermediate has a stressed anion center on the oxygen molecule and delocalized positive charge on the molecule of tetracene.

Solvent dependent kinetics of $^1O_2$ luminescence quenching, at least in benzene-d_6 and acetone-d_6, are similar to that of tetracene oxidation. This similarity suggests the presence of an excited complex (exciplex) with a high degree of charge transfer **1** as a key intermediate in the [4+2]-cycloaddition of $^1O_2$ to tetracene.



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