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COMPARATIVE STUDY OF THE SENSITIZED PHOTOOXIDATION OF N-METHYL PHENOTHIAZINE IN HOMOGENEOUS AND MICROHETEROGENEOUS MEDIA

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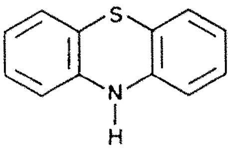
Abstract - Apparent rate constants and quantum yields have been determined for the rose bengal sensitized photooxidation of 10-methyl phenothiazine in methanol and in O/W and W/O microemulsions. A Stern-Volmer analysis of the luminescence of singlet oxygen in solutions of CD_3OD containing different concentrations of the phenothiazine derivative revealed a very efficient quenching of the triplet state of rose bengal by the substrate. No such energy transfer is found in micelles of sodium 12-(10'-phenothiazinyl)dodecyl-1-sulfonate which show an enhanced rate of photooxidation. Evaluation of rate constants and local concentrations leads to the conclusion that the rather low quantum yields of photooxidation of 10-methyl phenothiazine in the three media investigated is mainly due to the efficiently competing deactivation of the triplet state of the sensitizer by the substrate.

INTRODUCTION

Phenothiazine (1) derivatives have found many industrial applications as dyes[1], antioxidants and in pharmaceutical preparations. Substances of physiological activity are primarily employed for their neuroleptic properties[2], and chloropromazine (2) is one of the best known examples of phenothiazine derived tranquilizers[3]. However, drugs containing a phenothiazine moiety may provoke rather severe photosensitizing effects, e.g. allergic skin reactions[4] and occular opacity, resulting from light exposure during therapy.

Light and oxygen being likely to play an important role in the initiation of those side effects, photooxidation reactions of phenothiazine derivatives have been widely investigated. Within this large domain of interdisciplinary research, we have focussed our interest on model investigations on the sensitized photooxidation of 10-alkyl phenothiazines[5] in biomimetic microheterogeneous environments[6-9], more specifically, in micelles[10,11] and microemulsions[11,12]. These systems are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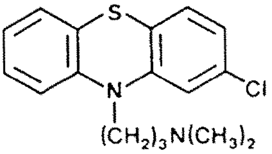
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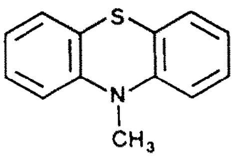
fluid, transparent, stable and macroscopically homogeneous and may be employed easily for photochemical and photophysical investigations[13]. At concentrations slightly above CMC, surface active molecules form roughly spherical aggregates (micelles) in water[10,11,14-16], the hydrocarbon chains forming a lipophilic core as their polar head groups are directed outwards interacting with the aqueous pseudo-phase. Microemulsions, as used in this work, can be considered as dispersions of microdroplets of a hydrocarbon in water (O/W), or of water in a hydrocarbon at low water content (W/O), stabilized by an interfacial film of surfactant and cosurfactant molecules[12,17-19]. In both, micellar media and microemulsions, the layer of surfactant molecules presents some similarities with biological membranes, and these systems are often used instead of the more complex biological materials[6-9].

In applying microheterogeneous systems to chemical and photochemical reactions, some quite interesting effects have been observed, including rate and yield enhancements, variations in regioselectivity and stereoselectivity, enhanced charge separation and magnetic effects[13,20-28]. Many of these observations can be interpreted by a high local substrate concentration, or, in general, by the preferential localization and/or accumulation of the substrate or intermediate at a given site within the structural organization of the environment. In preparative applications, microemulsions may show a net advantage with respect to micelles due to their greater capacity of solubilizing organic substrates.

As already shown earlier, the sensitized photooxidation of 10-methyl phenothiazine (MPT, **3**) yields specifically the corresponding sulfoxide **4**[5,29]. In this reaction, singlet oxygen, produced by a suitable sensitizer (reactions 1 to 3), reacts with ground state MPT. Starting from the mechanistic hypothesis of Foote and Peters[30,31] for the sensitized photooxidation of organic sulfides (reactions 4 and 5), a higher local concentration of sulfide R_2S would enhance the rate of dismutation of the intermediate peroxo compound R_2SOO (reaction 5).



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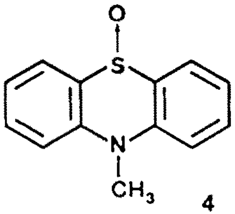

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$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens}^* \qquad (1)$$

$$^1\text{Sens}^* \xrightarrow{\text{ISC}} {}^3\text{Sens}^* \qquad (2)$$

$$^3\text{Sens}^* + {}^3O_2 \longrightarrow {}^1O_2 + \text{Sens} \qquad (3)$$

$$^1O_2 + R_2S \longrightarrow [R_2SOO] \qquad (4)$$

$$[R_2SOO] + R_2S \longrightarrow 2\ R_2SO \qquad (5)$$

High local concentrations of the substrate can be achieved in microheterogeneous systems, such as e.g. microemulsions. However, if such a rate enhancement should be verified experimentally, other effects due to the microheterogeneous environment have to be taken into account:

1) high local concentrations of the sensitizer and its aggregation may affect ist triplet quantum yield (Φ_{ISC})[5],

2) the efficiency of the singlet oxygen production ($\Phi(^1O_2)$) depends on this Φ_{ISC}, as well as on the concentration of oxygen assuming that this reaction is diffusion controlled,

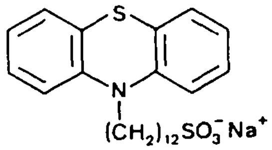
3) the rate of reaction 4 depends on the concentration of the substrate R_2S and on the lifetime of singlet oxygen, the latter depending primarily on the nature of the medium (reaction 6)[32,33] and, again, on the concentration of the substrate (provided the compound is a more or less efficient

physical quencher of singlet oxygen (reaction 7)).

We report in this publication the results of the sensitized photooxidation of the phenothiazine moiety (MPT, 3) in two types of microemulsions (O/W and W/O), as well as in methanol as a reference, and compare the results with the sensitized photooxidation of 12-(10'-phenothiazinyl)dodecyl-1-sulfonate (PTDS, 5), a functionalized surfactant molecule containing a phenothiazine as a reactive species at the end of the hydrocarbon chain[5,34].

$$ {}^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (6) $$

$$ {}^1O_2 + R_2S \xrightarrow{k_q} {}^3O_2 + R_2S \qquad (7) $$



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RESULTS

1. Apparent rate constants - We measured apparent rate constants of the rose bengal sensitized photooxidation of MPT (3) in methanol, in an O/W and in a W/O microemulsion, respectively. The two microemulsions chosen contain the same weight percent of surfactant (sodium dodedyl sulfate, SDS) and cosurfactant (1-butanol); we may, thus, consider the interfacial area as similar in both systems. Details of the composition of the two microemulsions are given in the experimental part and in figure 1[35].

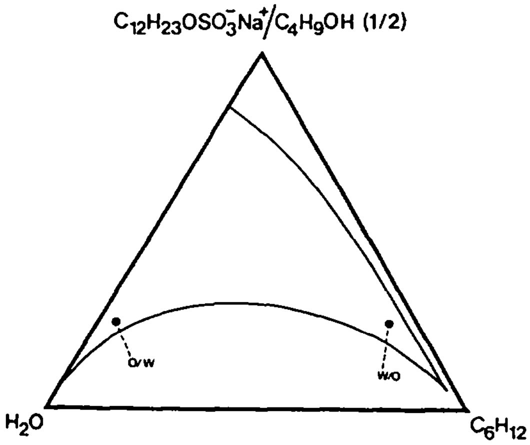

Figure 1 - Composition of the O/W and W/O microemulsions used as reaction media for the sensitized photooxidation of MPT (3). The pseudo-ternary phase diagram has been drawn in weight percent (Ref. 35).

Considering the short lifetime of singlet oxygen in alcoholic and aqueous solutions, the observation of a rather inefficient sensitized photooxidation requires the use of relatively high substrate concentrations. In all reported experiments, the initial concentration of MPT (3) has been 10^{-2} mole.l^{-1}. The concentration of rose bengal has been such as to assure total absorption of the incident light (5×10^{-5} mole.l^{-1})

In microemulsions, as well as in methanol, sulfoxide 4 is the only product formed during the sensitized photooxidation. Product formation has been followed spectrophotometrically and the sulfoxide concentrations have been calculated using the molar absorption coefficients (ε) determined in all three media in establishing the respective Lambert-Beer plots with the analytically pure compounds 3 and 4. Figure 2 shows the kinetics of the formation of 4 in function of the reaction medium under similar experimental conditions as far as electronic excitation is concerned.

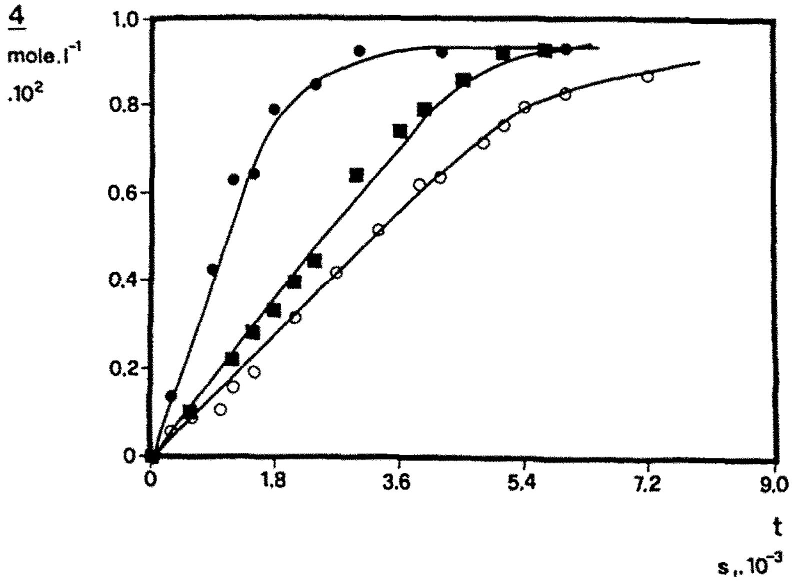

Figure 2 - Kinetics of product 4 formation upon sensitized photooxidation of 10-methyl phenothiazine (MPT, 3) in methanol (■), O/W microemulsion (●) and W/O microemulsion (○), $[MPT]_0 = 0.01$ mole/l

Although, the kinetics of product formation in methanol and in the O/W microemulsion seem to indicate a certain period of initiation, we may plot a straight line through the experimentally determined points which is within the respective limits of error up to 60% of conversion. From those lines, we calculated the apparent rate constants of the sensitized photooxidation of MPT (3) which are given in table 1.

Table 1 - Apparent rate constants and quantum yields of the sensitized photooxidation of 10-methyl phenothiazine (MPT, 3) in different media; sensitizer: rose bengal.

Medium	Sulfoxide formation k_{app} (mole.l^{-1}.s^{-1})	k_{app}^{rel}	Φ_{-O_2}
Methanol	2.0(±0.3) x 10^{-6}	1	3.0(±0.6) x 10^{-3}
O/W microemulsion	4.5(±0.5) x 10^{-6}	2.25	7.0(±1.5) x 10^{-3}
W/O microemulsion	1.5(±0.2) x 10^{-6}	0.75	2.2(±0.4) x 10^{-3}
PTDS (5)/water			1.1(±0.1) x 10^{-1}

The results show a rate enhancement of the sulfoxide 4 production in the O/W microemulsion compared to experiments in methanol. In the W/O microemulsion, the reaction is, however, slower than in the reference experiments. Effects of the organized media can be seen, the apparent rate constant in e.g. the O/W microemulsion being higher by a factor of 2.25 and 3 when compared to those in methanol and in the W/O microemulsion, respectively.

2. Quantum yields - Quantum yield determinations have been made by combined measurements of oxygen consumption in a closed system and actinometry, using a Clark oxygen electrode and an electronically integrating actinometer[36-38]. Oxygen measurements have been made during the first 10% of of oxygen consumption (diminuation of [3] < 2%), where the reaction follows strictly pseudo-zero order kinetics, and, hence, the decrease of oxygen concentration is linear in function of the time of irradiation.

As could be expected from the observed low chemical reactivity of the substrate (table 1), the corresponding quantum yields are rather small. But, owing to the very good stability of the oxygen electrode, measurements could be made for a sufficiently high concentration of MPT (3) in methanol and in the O/W microemulsion.

The quantum yield of oxygen consumption in the rose bengal sensitized photooxidation of MPT (3), Φ_{-O_2}, has been determined to be 3.0(±0.6) x 10^{-3} in methanol solution.

The determination of quantum yields by this method requires the knowledge of the initial oxygen concentration in the reaction medium[39]. Those concentrations are not known for the microemulsions used. However, the respective quantum yields can be evaluated from the relative rates of sulfoxide 4 production under the conditions of pseudo-zero order kinetics, knowing the quantum yield in methanol. The calculated quantum yields in the O/W and W/O microemulsions are then 7.0(± 1.5) x 10^{-3} and 2.2(±0.4) x 10^{-3}, respectively (table 1).

The initial oxygen concentration in the aerated O/W microemulsion can now be calculated using equation 8

$$\Delta n_{O_2} = \Phi_{-O_2} \cdot N_{abs} = \frac{\mathcal{N} \cdot (\Delta O_2\%) \cdot [O_2]_0 \cdot V}{100} \qquad (8)$$

where Δn_{O_2} : number of oxygen molecules consumed during the time of irradiation

N_{abs} : number of photons absorbed during the time of irradiation (measured with the integrating actinometer)

$\mathcal{N}$: 6.023 x 10^{23}

$\Delta O_2\%$: percent of the initial concentration of oxygen consumed during the time of irradiation (determined with the oxygen electrode)

$[O_2]_0$: initial concentration of oxygen in the sample (mole.l^{-1})

V : volume of the irradiated sample (l)

The resulting 5.7(± 1.2) x 10^{-4} mole.l^{-1} of oxygen in the O/W microemulsion respresent an increase of the oxygen concentration by a factor of about 2.3 when compared with the known initial concentration in air saturated aqueous solutions (2.5 x 10^{-4} mole.l^{-1}). The experimental result compares favourably with the concentration calculated from the volume fractions of water, cyclohexane and 1-butanol of the O/W microemulsions used and the respective oxygen concentrations under condition of air saturation[40] (6.9 x 10^{-4} mole.l^{-1}).

The rate of reaction in the W/O microemulsion being below the acceptable limit with respect to the stability of the oxygen electrode, the corresponding measurements have not been made.

DISCUSSION

The quantum yield of singlet oxygen production ($\Phi(1_{O_2})$) sensitized by rose bengal in methanolic solution has been determined by ways of quantitative chemical trapping using furane derivatives to be 0.76[41,42]. Quantitative chemical trapping under those conditions requires that the rate of the chemical reaction of the substrate with singlet oxygen (reaction 4) must be at least 100 times faster than the rates of physical deactivation of singlet oxygen by the solvent (reaction 6, k_6 = 10^5 s^{-1} in methanol[32]) and by the substrate (reaction 7). The very low quantum yield of the sensitized photooxidation of MPT (3) in methanol ($\Phi_{-O_2} = 3.0(\pm 0.6) \times 10^{-3}$) would imply that this substrate must be a very inefficient chemical acceptor of singlet oxygen. As postulated earlier[5], physical deactivation of singlet oxygen by MPT (reaction 7) might be relatively efficient due to charge transfer interactions. Consequently, the rate of the chemical reaction would be smaller than both rates of physical deactivation.

In addition, a Stern-Volmer experiment where the luminescence of singlet oxygen (1270 nm) has been measured in CD_3OD, using continuous excitation at 546 nm[43], for different concentrations of MPT (3) reveals that the substrate is not only deactivating singlet oxygen but the triplet state of the sensitizer as well (figure 3).

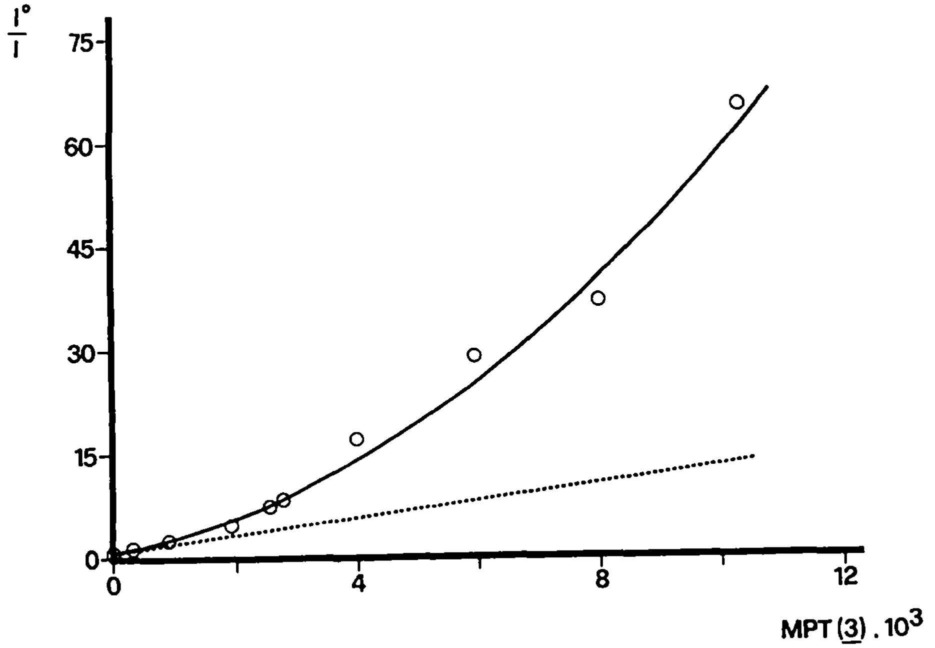

Figure 3 - Stern-Volmer plot of the quenching of the singlet oxygen luminescence (1270 nm) by MPT (3); sensitizer: rose bengal; solvent: CD_3OD

The energy of ^{3}MPT* has been estimated earlier to be ∿60 kcal.mole^{-1} [5,44], hence, energy transfer between ^{3}Sens* and MPT is a very inefficient process. The quenching of the rose bengal triplet has been confirmed by laser flash photolysis using degassed solutions of rose bengal and MPT (3) in methanol, and further inverstigations in order to elucidate the mechanism of this deactivation process (e.g. reaction 9) are currently undertaken.

$$^3\text{Sens}^* + \text{MPT} \longrightarrow \text{Sens}^{-\cdot} + \text{MPT}^{+\cdot} \qquad (9)$$

A fit for the non-linear Stern-Volmer curve can be developed in including the quenching of ^{3}Sens* by MPT (3) (e.g. reaction 9) into the scheme of reactions. The quantum yield of the luminescence of singlet oxygen (reaction 10)

$$^1O_2 \longrightarrow {}^3O_2 + h\nu' \qquad (10)$$

in the absence of MPT is defined as

$$\Phi^o_{10} = \Phi^o(^1O_2) \cdot \frac{k_{10}}{k_{10} + k_6} \qquad (11)$$

with

$$\Phi^{o}(^{1}O_{2}) = \Phi_{ISC} \cdot \varphi_{3}^{o} = 0.76 \text{ [41,42]} \qquad (12)$$

The quantum yield of intersystem crossing (Φ_{ISC}) has been determined to be 0.86 for rose bengal in ethanol[42], and we therefore calculate with an efficiency of energy transfer (reaction 3, φ_{3}^{o}) of 0.9.

In the presence of MPT (3)

$$\Phi_{10} = \Phi_{ISC} \cdot \varphi_{3} \cdot \frac{k_{10}}{k_{10} + k_{6} + (k_{4} + k_{7})[MPT]} \qquad (13)$$

In solution, k_{10} is negligible when compare to k_6[45], and the Stern-Volmer relation is given by

$$\frac{\Phi_{10}^{o}}{\Phi_{10}} = \frac{\varphi_{3}^{o}}{\varphi_{3}} \cdot \left(1 + \frac{(k_{4} + k_{7})[MPT]}{k_{6}}\right) \qquad (14)$$

where

$$\frac{\varphi_{3}^{o}}{\varphi_{3}} = \left(1 + \frac{\varphi_{3}^{o} \cdot k_{9}[MPT]}{k_{3}[O_{2}]}\right) \qquad (15)$$

and, thus,

$$\frac{\Phi_{10}^{o}}{\Phi_{10}} = \left(1 + \underbrace{\frac{\varphi_{3}^{o} \cdot k_{9}}{k_{3}[O_{2}]}}_{b} \cdot [MPT]\right) \cdot \left(1 + \underbrace{\frac{(k_{4} + k_{7})}{k_{6}}}_{a} \cdot [MPT]\right) \qquad (16)$$

At very low concentrations of MPT, reaction 9 is inefficient compared to reaction 3, and $b \cdot [MPT] \ll 1$. The resulting linear Stern-Volmer relation is represented in figure 3 by the tangent from $[MPT] = 0$ to up to 3.2×10^{-4} mole.l^{-1}. From the slope a of this tangent, $(k_4 + k_7)$ is calculated to be $5.3(\pm 0.5) \times 10^{6}$ l.mole^{-1}.s^{-1}, knowing k_6 in CD_3OD (4.4×10^{3} s^{-1} [5]). The best fit for equation 16 yields for b a value of 350 ± 40 l.mole^{-1} and, assuming the energy transfer (reaction 3) to be diffusion controlled ($k_3 = 1.2 \times 10^{10}$ l.mole^{-1}.s^{-1} in methanol) and $[O_2] = 2.05 \times 10^{-3}$ mole.l^{-1}, for k_9 a value of $9.5(\pm 1.0) \times 10^{9}$ l.mole^{-1}.s^{-1}.

The sum of the rate constants of chemical reaction (k_4) and of the quenching by the substrate (k_7), as determined in this work, compares favorably with earlier published values of 1.2×10^{6} [29] and 2.9×10^{6} [46] l.mole^{-1}.s^{-1}, calculated from photooxidation experiments in bromobenzene/methanol (2/1) and chloroform, respectively. For MPT concentrations as used in our experiments (10^{-2} mole . l^{-1}), the combined rate $(k_4 + k_7)[MPT] = 5.3 \times 10^{4}$ s^{-1} is approximately two times slower than k_6.

Defining the quantum yield of the sensitized photooxidation of a sulfide as

$$\Phi_{Ox} = \Phi_{R_{2}SOO} = \Phi(^{1}O_{2}) \cdot \varphi_{4} \qquad (17)$$

$$\text{where } \varphi_{4} = \frac{k_{4}[R_{2}S]}{k_{6} + (k_{4} + k_{7})[R_{2}S]} \qquad (18)$$

is the efficiency of the chemical reaction (reaction 4), we must take into account, for the particular case of MPT (3), that $\Phi_{Ox} = f([MPT])$, because of reaction 9. Using the rate constants determined in the Stern-Volmer analysis, we find that under the given experimental conditions ($[O_2] = 2.05 \times 10^{-3}$ mole.l^{-1}, $[MPT] = 10^{-2}$ mole.l^{-1}), $\Phi(^{1}O_{2})$ is reduced to 0.17. We may then calculate from the measured quantum yield (Φ_{-O_2}) the rate constant of the chemical reaction (k_4) to be 2.7(±0.3) x 10^5 l.mole^{-1}.s^{-1}, under the condition that all peroxo intermediates dismutate to the final product (reaction 5). We then obtain $k_7 = 5.0 \times 10^6$ l.mole^{-1}.s^{-1} which means that the rate of physical deactivation of singlet oxygen by MPT is about 18 times faster than the rate of the chemical reaction.

However, if dismutation (reaction 5) is not quantitative, dissociation of the peroxo intermediate (reaction 19) would lead to an alternative route of apparent physical deactivation of singlet oxygen by the substrate (reactions 4 + 19).

$$[R_2SOO] \longrightarrow R_2S + {}^3O_2 \qquad (19)$$

In this case we may define

$$\Phi_{R_2SO} = 2\,\Phi_{-O_2} = 2\,\Phi({}^1O_2)\cdot\varphi_4\cdot\varphi_5 \qquad (20)$$

where

$$\varphi_5 = \frac{2\,k_5[R_2S]}{2\,k_5[R_2S] + k_{19}} \qquad (21)$$

is the efficiency of dismutation. If $\varphi_5 < 1$, φ_4 increases and the calculated value of k_4 would be a minimum. In fact, if $\varphi_5 < 1$, this calculated value would represent the product ($k_4 \cdot \varphi_5$) which can be defined as the actual chemical reactivity of the phenothiazine moiety in the sensitized photooxidation.

Taking Φ_{-O_2} for MPT (3) in methanol as a reference, the formerly determined quantum yield of the sensitized photooxidation of the surfactant phenothiazine 5 ($\Phi_{-O_2} = 1.1(\pm 0.1) \times 10^{-1}$, with [5] = 10^{-2} mole.l^{-1}) is about 37 times higher. Dealing with a micellar solution, several of the efficiency determining factors would be rather at its disadvantage: possible aggregational effects of the sensitizer at the micellar interface would favour triplet deactivation[5], and the oxygen concentration in aqueous solutions is smaller. In addition, the lifetime of singlet oxygen in aqueous solution (4 x 10^{-6} s [32]) is about 4 times shorter than in methanol. The presence of 10^{-2} mole.l^{-1} of surfactant should not modify significantly this lifetime[33]. However, the structural organisation of the surfactant phenothiazine at [5] > CMC will lead to relatively high concentrations of the phenothiazine moiety in the micellar core, which in turn favour the relative efficiencies of reactions 4 and 7 and may prevent the quenching of the triplet state of the sensitizer by the phenothiazine moiety due to separation of sensitizer and substrate into two different pseudo phases. In fact, laser flash photolysis experiments show no appreciable reduction of the triplet lifetime of rose bengal upon addition of 5[47]. We may also assume that under those conditions dismutation is at its optimum efficiency.

From the already reported data on the aggregation of 5[34], we may estimate the micellar volume fraction of 10^{-2} mole.l^{-1} of 5 in water: the area required by one surfactant head group at the air/water interface and the aggregate number have been calculated to be S = 143 Å.molecule^{-1} and 4.2 x 10^3 molecules, respectively, leading to a micellar volume fraction of about 6 x 10^{-2}. This means that the local concentration of the phenothiazine moiety is about 17 times the macroscopic concentration of 5, i.e. 1.7 x 10^{-1} mole.l^{-1}. From the plot of $(\Phi_{-O_2})^{-1} = f([5]^{-1})$ derived from equation 22

$$\Phi_{-O_2}^{-1} = \frac{k_4 + k_7}{\Phi({}^1O_2)\cdot k_4} + \frac{k_6}{\Phi({}^1O_2)\cdot k_4}\cdot[5]^{-1} \qquad (22)$$

using the local concentration of 5 calculated above, we obtain an intercept of 4.1 and a slope of

0.64 mole.l^{-1}. With $k_6 = 2.5 \times 10^5$ s^{-1} and $\Phi(^1O_2) = 0.75$ in water, we then calculate k_4 to be 4.9×10^5 l.mole^{-1}.s^{-1} and k_7 to be 1.1×10^6 l.mole^{-1}.s^{-1}. A non-homogeneous distribution of the phenothiazine moiety is not critical for our calculation since randomization of singlet oxygen molecules is assured due to their relatively long lifetime. Within the limits of error of this evaluation, the rate of the physical deactivation of singlet oxygen by the phenothiazine moiety remains in the same order of magnitude when compared to k_7[MPT] in methanol.

The structural organisation in a O/W microemulsion is comparable to a micellar system. Solubilizing MPT (3) in a O/W microemulsion ([3] = 10^{-2} mole.l^{-1}), we may expect that the substrate is localized in the lipophilic dispersed pseudo-phase, MPT being practically insoluble in water. Given the composition of the O/W microemulsion used, we estimate a volume fraction of the lipophilic phase (micelles) of about 0.25: this would lead to an actual local concentration of MPT (3) of 4×10^{-2} mole.l^{-1}. The experimentally determined k_{app} and, consequently, the calculated Φ_{-O_2} are in fact higher than the respective values in methanol and could be consistent with the argument of a higher local concentration.

In oder to calculate k_4 under the conditions of the O/W microemulsion, we must evaluate k_6. Lee and Rodgers have measured the rate constant of the physical deactivation of singlet oxygen in micellar solutions of SDS in function of the surfactant concentration[33]. From their plot, we take a rate constant of physical deactivation of 2×10^5 s^{-1} for [SDS] = 0.28 mole.l^{-1}, the actual surfactant concentration in the O/W microemulsion. The corresponding k_6 in the O/W microemulsion is then calculated from the composition of the microemulsion and the rate constants of the physical deactivation of singlet oxygen by the pure solvents[32], in taking the above value for the aqueous pseudo-phase. From $\Phi_{-O_2} = 7.0(\pm 1.5) \times 10^{-3}$ (table 1), [3] = 4×10^{-2} mole.l^{-1}, $k_6 = 1.6 \times 10^5$ s^{-1} and chosing $k_7 = 5.0 \times 10^6$ l.mole^{-1}.s^{-1}, the value calculated from our experiments in methanol, we estimate a k_4 of 8.4×10^4 l.mole^{-1}.s^{-1} in assuming no ^{3}Sens/MPT interaction and, hence, $\Phi(^1O_2) = 0.75$. It is, however, significant, that an evaluation of $\Phi(^1O_2)$ on the basis of the data obtained in methanol yields a strongly reduced value of 0.24 indicating that quenching processes like reaction 9 may occur in O/W microemulsions with high efficiency.

The rate constant of chemical reaction (k_4) calculated from the experiment with the micelles of 5 is 4.9×10^5 l.mole^{-1}.s^{-1}, hence, about 2 times higher than the rate constant calculated from the experiment with MPT (3) in methanol and about 6 times higher than the one found for the O/W microemulsion. A simple evaluation based on those rate constants and using equation 17 reveals that the experimentally determined quantum yield $\Phi_{-O_2} = 1.1 \times 10^{-1}$ (table 1) cannot be reached in a O/W microemulsion by increasing the macroscopic substrate concentration. The observed enhancement must therefore be linked specifically to the functionalized surfactant and might be due to the aggregation of the phenothiazine moiety[34].

For the W/O microemulsion, we would estimate that the lifetime of singlet oxygen is comparable to that in cyclohexane and in 1-butanol (2×10^{-5} s[32]), an argument in favour of a higher quantum yield of photooxidation when compared to the result of our experiments in methanol. However, the experimentally determined k_{app} and, consequently, the calculated Φ_{-O_2} ($2.2(\pm 0.4) \times 10^{-3}$, table 1) are smaller than the corresponding values in methanol. The enhancing factors seem to be compensated by a decrease of $\Phi(^1O_2)$. Several authors have shown that aggregation of sensitizer molecules leads to a decrease of the efficiency of singlet oxygen production[48]. This argument may well apply to the present case, since rose bengal is dissolved in the water pools of the W/O microemulsion and, hence, its actual local concentration will be higher than the macroscopic concentration by at least a factor of 4. In addition, quenching of the triplet state of the sensitizer is likely to occur at the interface.

In conclusion, two factors might be responsible for the relatively high Φ_{-O_2} in micelles of the surfactant phenothiazine 5: 1) high local concentration of the phenothiazine moiety and 2) the absence of a deactivation of ^{3}Sens* by this phenothiazine moiety, due to an efficient separation of sensitizer and substrate in two different pseudo-phases. In contrast, ^{3}Sens/MPT interaction (e.g. reaction 9) is under the given experimental conditions the most efficient process among the different reactions taking place during the sensitized photooxidation of MPT in methanol. The interfaces of the two microemulsions used contain large concentrations of cosurfactant (1-butanol) which can solubilize sensitizer as well as substrate, hence, favouring this route of deactivation. The comparable Φ_{-O_2} in all three media (methanol, O/W and W/O microemulsions) may well indicate that the energy transfer between sensitizer and substrate might be the efficiency determining factor.

Sensitizer aggregates and their effect on energy and electron transfer reactions remain in the center of our investigations[49].

EXPERIMENTAL PART

Materials - 10-methyl phenothiazine (MPT, 3) has been prepared from phenothiazine (1, Fluka) (Ref. 50); the isolated product having been recrystallized from ethanol under argon (m.p. 99.5^{0}C). 10-methyl phenothiazine-9-oxide (4) has been synhtesized by sensitized photooxidation of 3 and recrystallized from water/5% ethanol (m.p. 185-7^{0}C). Sodium 12-(10'-phenothiazinyl)dodecyl-1-sulfonate (PTDS, 5) has been used as prepared and purified (Ref. 34). Sodium dodecyl sulfate (SDS, Merck, p.a.) has been recrystallized from absolute ethanol. Ethanol, 1-butanol, cyclohexane, methanol (all Fluka puriss.) and rose bengal (Fluka, Standard für Mikroskopie) have been used as purchased. Tridistilled water has been used for the preparation of the microemulsions ; perdeuterated methanol (99.5%) from Ciba-Geigy Ltd.

Microemulsions - The compositions of the microemulsions used are, in weight percent:
O/W microemulsion: 8% SDS, 16% 1-butanol, 4% cyclohexane, 72% water
W/O microemulsion: 8% SDS, 16% 1-butanol, 69% cyclohexane, 7% water
The microemulsions are localized on the pseudo-ternary phase diagram given in figure 1. Thay have been prepared by simply mixing the four components.

Methods - Apparent rate constant measurements - Sensitized photooxidations gave been carried out in a DEMA 13/12 Solidex glass reactor containing 135 ml of solution or microemulsion. In all experiments, concentrations of 0.01 mole/l of MPT (3) and of 0.00005 mole/l of rose bengal have been used, and the reaction mixtures have been permanently saturated with air and kept at 16^{0}C. The light of a Philips HPK 125 lamp has been filtered by a circulating and cooled solution of potassium chromate and 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate (Ref. 40). At various irradiation times, samples (0.5 ml) have been taken and, after dilution by a factor 100, analyzed spectrophotometrically for their concentration of sulfoxide 4. Table 2 shows the molar absorption coefficients (ε) determined at 343 nm and used for the calculation of [4].

Table 4 - Molar absorption coefficients of 3 and 4 determined at 343 nm (ε_{343}, l/mole.cm) in different media

	methanol	O/W micromeulsion	W/O microemulsion
3	960 ± 15	910 ± 15	890 ± 10
4	6230 ± 180	5560 ± 110	5570 ± 110

A Shimadzu UV 260 spectrophotometer has been used for all spectrophotometric analysis. Each series of experiments has been repeated at least twice in order to check reproducibility, and the reported data are average values from the different experiments.

Quantum yield determinations - The oxygen consumption (ΔO_2% < 10%) during irradiation has been determined by following the decrease of the oxygen concentration by means of a Clark electrode inserted into a 22.3 cm^3 sample cell kept without gas bubbles during the time of the experiment. The temperature of the sample has been maintained at 23^{0}C, and the liquide has been rapidly stirred. In all experiments, total absorption of the incident momochromatic light (546 nm) has been assured in using a concentration of rose bengal of 0.00005 mole/l; $[3]_0$ = 0.01 mole/l as in the apparent rate measurements. The number of absorbed photons has been determined from the voltage difference measured on a pair of bolometers and integrated during the time of irradiation, after calibration with chemical actinomters[36-38].

Singlet oxygen luminescence - A fluorescence cell containing the sample is placed on an optical bench and irradiated with the monochromatic light of a 1000 W Hg/Xe lamp. The chopped emitted light is filtered (\$270 ± 20 nm) and measured by means of a Ge-detector (Judson-IR), the corresponding voltage amplified appropriately.

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