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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN
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FEDERALE DE LAUSANNE (SWITZERLAND) A M BRAUN 13 JAN 87
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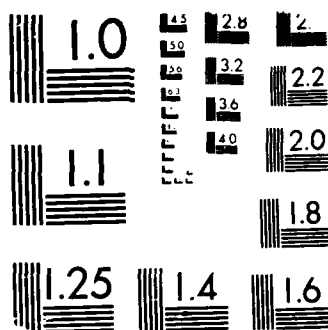
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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS
IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

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SUMMARY

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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.

Evaluation of rate constants and local concentrations of sensitizer and substrate 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.

For decontamination purposes, photochemically initiated singlet oxygen reactions may not be recommended due to the many efficient deactivating processes of singlet oxygen and of the triplet state of the sensitizer.

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SHORT TERM PROJECTS

Synthesis of 100g quantities of perfluoro 2-methyl pentanol and formulation of perfluorinated microemulsions containing this cosurfactant.

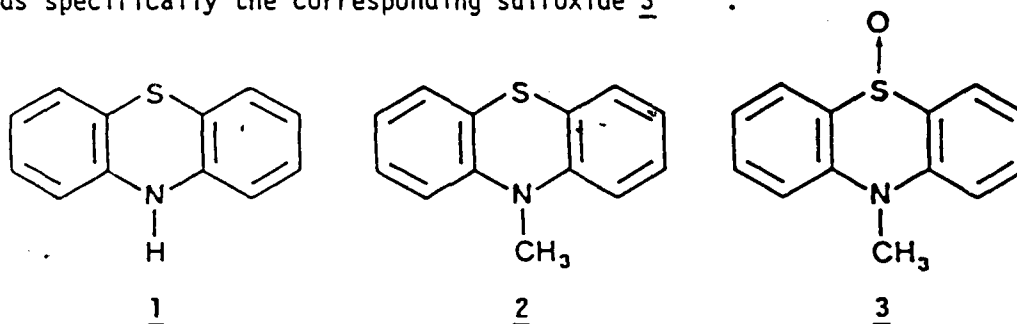
Kinetic investigations of the oxidation of hydrocarbons by hydroxyl radicals will be carried out in perfluorinated microemulsions, the reactive intermediate being produced by the decomposition of either hydrogen peroxide or sodium perborate.

CONCENTRATION EFFECTS ON THE SENSITIZED ~~PHOTO~~PHOTOOXIDATION OF N-METHYL PHENOTHIAZINE IN HOMOGENEOUS AND MICROHETEROGENEOUS MEDIA

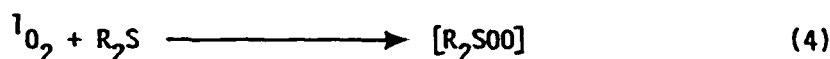
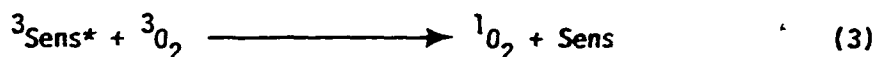
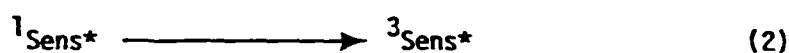
In applying microheterogeneous systems to chemical and photochemical reactions, some quite interesting effects have been observed, including rate and yield enhancements, variations in regioselectivity and stereoselectivity, enhanced charge separation and magnetic effects¹⁻¹⁰. Many of these observations can be interpreted by a high local substrate concentration, or, in general, by the preferential localization and/or accumulation of the substrate or reaction intermediate at a given site within the structural organization of the reaction environment.

For decontamination, microemulsions may show a net advantage with respect to micelles due to their greater capacity of solubilizing organic substrates.

Phenothiazine (1) derivatives have found many industrial applications as dyes, antioxidants and in pharmaceutical preparations¹¹. As already shown earlier, the sensitized photooxidation of N-methyl phenothiazine (MPT, 2) yields specifically the corresponding sulfoxide 3^{12,13}.

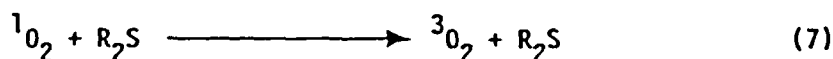
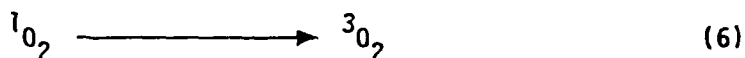


In this reaction, singlet oxygen, produced by a suitable sensitizer (reactions 1 to 3), reacts with ground state MPT (reaction 4). Starting from the mechanistic hypothesis of Foote and Peters^{14,15} for the sensitized photooxidation of organic sulfides (reactions 4 and 5), a higher local concentration of sulfide R_2S would enhance the rate of dismutation of the intermediate peroxy compound R_2SOO (reaction 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 its triplet quantum yield (Φ_{ISC})¹²,
- 2) the efficiency of the singlet oxygen production ($\Phi({}^1\text{O}_2)$) depends on this Φ_{ISC} , and on the concentration of oxygen assuming that reaction 3 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)^{16,17} and, again, on the concentration of the substrate (provided the compound is a more or less efficient physical quencher of singlet oxygen (reaction 7)).



For this investigation, the sensitized photooxidation of the phenothiazine moiety (NPT, 2) has been carried out in two types of microemulsions (O/W and W/O), as well as in methanol as a reference.

RESULTS

1. Apparent rate constants - Apparent rate constants of the rose bengal sensitized photooxidation of MPT have been measured 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 dodecyl 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 figure 1¹⁸.

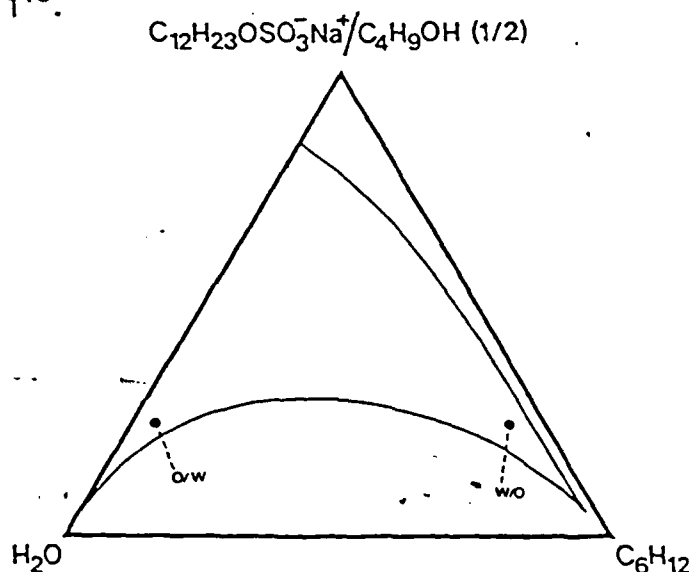


Figure 1 - Composition of the O/W and W/O microemulsions used as reaction media for the sensitized photooxidation of MPT. The pseudo-ternary phase diagram has been drawn in weight percent (Ref. 18).

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 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 3 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 2 and 3¹⁹. Figure 2 shows the kinetics of the formation of 3 in function of the reaction medium under similar experimental conditions as far as electronic excitation is concerned.

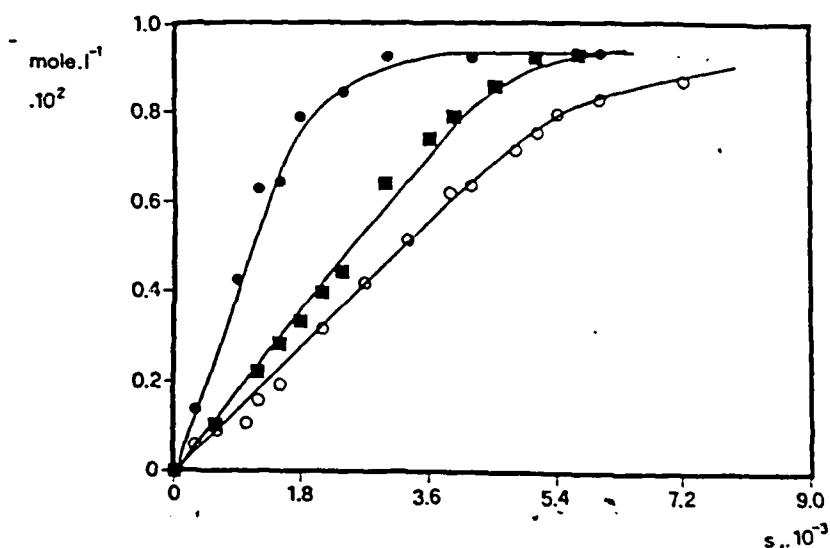


Figure 2 - Kinetics of product 3 formation upon sensitized photooxidation of N-methyl phenothiazine (MPT, 2) in methanol (■), O/W microemulsion (●) and W/O microemulsion (○); [MPT] = 0.01 mole/l

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 which are given in table 1.

Table 1 - Apparent rate constants and quantum yields of the sensitized photooxidation of N-methyl phenothiazine (MPT, 2) in different media; sensitizer: rose bengal

Medium	Sulfoxide formation k_{app} (mole.l ⁻¹ .s ⁻¹)	k_{rel}	Φ_{-O_2}
Methanol	$2.0(\pm 0.3) \times 10^{-6}$	1	$3.0(\pm 0.6) \times 10^{-1}$
O/W microemulsion	$4.5(\pm 0.5) \times 10^{-6}$	2.25	$7.0(\pm 1.5) \times 10^{-3}$
W/O microemulsion	$1.5(\pm 0.2) \times 10^{-6}$	0.75	$2.2(\pm 0.4) \times 10^{-3}$

The results show a rate enhancement of the sulfoxide 3 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 determination has been made by combined measurements of oxygen consumption in a closed system and actinometry, using a Clark oxygen electrode and an electronically integrating actinometer²⁰⁻²². Oxygen measurements have been made during the first 10% of oxygen consumption (diminution of [2] < 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 in methanol and in the O/W microemulsion. The quantum yield of oxygen consumption in the rose bengal sensitized photooxidation of MPT in methanol, Φ_{-O_2} , has been determined to be $3.0(\pm 0.6) \times 10^{-3}$.

The determination of quantum yields by this method requires the knowledge of the initial oxygen concentration in the reaction medium²³. Those concentrations are not known for the microemulsions used. However, the respective quantum yields can be evaluated from the relative rates of sulfoxide 3 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 $7.0(\pm 1.5) \times 10^{-3}$ and $2.2(\pm 0.4) \times 10^{-3}$, respectively (table 1).

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

$$\Delta n_{O_2} = \Phi_{-O_2} \cdot N_{abs} = \mathcal{K} \cdot (\Delta O_2\%) \cdot [O_2]_0 \cdot V / .100 \quad (8)$$

- 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)
 $\mathcal{K}$: 6.023×10^{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 $5.7(\pm 1.2) \times 10^{-4}$ mole.l⁻¹ of oxygen in the O/W microemulsion represent 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 (2.5×10^{-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 saturation²⁴ (6.9×10^{-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 ($\Phi(^1O_2)$) sensitized by rose bengal in methanolic solution has been determined by ways of quantitative chemical trapping using furane derivatives to be 0.76^{25,26}. 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, $k_6 = 10^5 \text{ s}^{-1}$ in methanol¹⁶) and by the substrate (reaction 7). The very low quantum yield of the sensitized photooxidation of MPT 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 earlier¹², 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 CD₃OD, using continuous excitation at 546 nm²⁷, for different concentrations of MPT reveals that the substrate is not only deactivating singlet oxygen but the triplet state of the sensitizer as well (figure 3).

The energy of $^3\text{MPT}^*$ has been estimated earlier to be 60 kcal.mole⁻¹^{12,28}, hence, energy transfer between $^3\text{Sens}^*$ and MPT is a very inefficient process. The quenching of rose bengal triplet has been confirmed by laser flash photolysis using degassed solutions of rose bengal and MPT in methanol, and further investigations in order to elucidate the mechanism of this deactivation process (e.g. reaction 9) are currently undertaken.



A fit for the non-linear Stern-Volmer curve can be developed in including

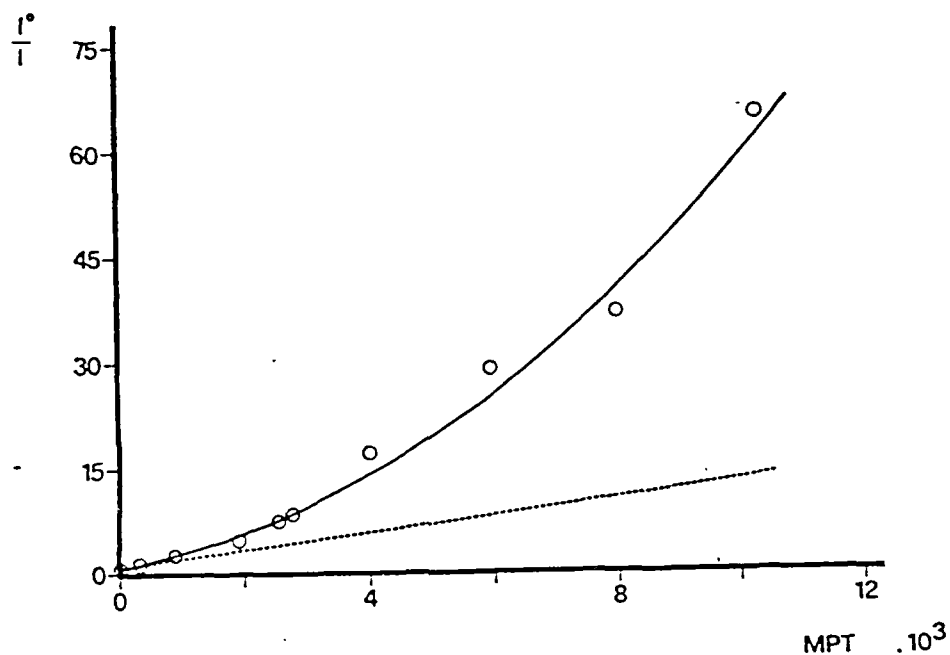
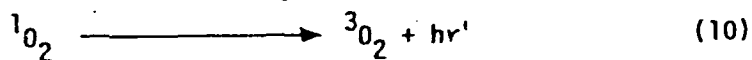


Figure 3 - Stern-Volmer plot of the quenching of the singlet oxygen luminescence (1270 nm) by MPT (2); sensitizer: rose bengal; solvent: CD_3OD

the quenching of $^3\text{Sens}^*$ by MPT (e.g. reaction 9) into the scheme of reactions. The quantum yield of the luminescence of singlet oxygen (reaction 10)



in the absence of MPT is defined as

$$\Phi_{10}^0 = \Phi^0(^1\text{O}_2) \cdot k_{10} / (k_{10} + k_6) \quad (11)$$

with

$$\Phi^0(^1\text{O}_2) = \Phi_{\text{ISC}} \cdot \eta_3^0 = 0.76^{25,26} \quad (12)$$

The quantum yield of intersystem crossing (Φ_{ISC}) has been determined to be 0.86 for rose bengal in ethanol²⁶, and we therefore calculate with an efficiency of energy transfer (reaction 3, φ_3^0) of 0.9.

In the presence of MPT

$$\Phi_{10} = \Phi_{ISC} \cdot \varphi_3 \cdot k_{10} / (k_{10} + k_6 + (k_4 + k_7)[MPT]) \quad (13)$$

In solution, k_{10} is negligible when compared to k_6 ²⁸, and the Stern-Volmer relation is given by

$$\Phi_{10}^0 / \Phi_{10} = \varphi_3^0 / \varphi_3 \cdot (1 + (k_4 + k_7)[MPT] / k_6) \quad (14)$$

where

$$\varphi_3^0 / \varphi_3 = (1 + (\varphi_3^0 \cdot k_9[MPT] / k_3[O_2])) \quad (15)$$

and, thus,

$$\begin{aligned} \Phi_{10}^0 / \Phi_{10} &= (1 + (\varphi_3^0 \cdot k_9 / k_3[O_2]) \cdot [MPT]) \cdot \\ &\cdot (1 + ((k_4 + k_7) / k_6) \cdot [MPT]) \end{aligned} \quad (16)$$

At very low concentrations of MPT, reaction 9 is inefficient compared to reaction 3, and $b (= \varphi_3^0 \cdot k_9 / k_3[O_2]) \cdot [MPT] \ll 1$. The resulting linear Stern-Volmer relation is represented in figure 3 by the tangent from $[MPT] = 0$ to up to $3.2 \times 10^{-4} \text{ mole.l}^{-1}$. From the slope $a (= (k_4 + k_7) / k_6)$ of this tangent, $(k_4 + k_7)$ is calculated to be $5.3(\pm 0.5) \times 10^6 \text{ l.mole}^{-1} \cdot \text{s}^{-1}$, knowing k_6 in CD_3OD ($4.4 \times 10^3 \text{ s}^{-1}$ ¹²). The best fit for equation 16 yields for b a value of $350 \pm 40 \text{ l.mole}^{-1}$ and, assuming the energy transfer (reaction 3) to be diffusion controlled ($k_3 = 1.2 \times 10^{10} \text{ l.mole}^{-1} \cdot \text{s}^{-1}$ in methanol) and $[O_2] = 2.05 \times 10^{-3} \text{ mole.l}^{-1}$, for k_9 a value of $9.5(\pm 1.0) \times 10^9 \text{ l.mole}^{-1} \cdot \text{s}^{-1}$.

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 favourably with earlier published values of 1.2×10^6 ¹³ and 2.9×10^6 ³⁰ $\text{l.mole}^{-1} \cdot \text{s}^{-1}$, calcu-

lated 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 $(k_4 + k_7)[\text{MPT}] = 5.3 \times 10^4 \text{ s}^{-1}$ is approximately two times slower than k_6 .

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

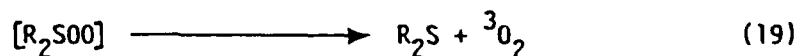
$$\Phi_{\text{OX}} = \Phi_{\text{R}_2\text{S}_{\text{OO}}} = \Phi(^1\text{O}_2) \cdot \varphi_4 \quad (17)$$

where

$$\varphi_4 = k_4[\text{R}_2\text{S}] / (k_6 + (k_4 + k_7)[\text{R}_2\text{S}]) \quad (18)$$

is the efficiency of the chemical reaction (reaction 4), we must take into account, for the particular case of MPT, that $\Phi_{\text{OX}} = f([\text{MPT}])$, because of reaction 9. Using the rate constants determined in the Stern-Volmer analysis, we find that under the given experimental conditions ($[\text{O}_2] = 2.05 \times 10^{-3}$ mole.l $^{-1}$, $[\text{MPT}] = 10^{-2}$ mole.l $^{-1}$), $\Phi(^1\text{O}_2)$ is reduced to 0.17. We may then calculate from the measured quantum yield (Φ_{OX}) the rate constant of the chemical reaction (k_4) to be $2.7(\pm 0.3) \times 10^5 \text{ l.mole}^{-1}.\text{s}^{-1}$, under the condition that all peroxo intermediates dismutate to the final product (reaction 5). We then obtain $k_7 = 5.0 \times 10^6 \text{ l.mole}^{-1}.\text{s}^{-1}$ 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).



In this case we may define

$$\Phi_{\text{R}_2\text{SO}} = 2 \Phi_{-\text{O}_2} = 2 \Phi(^1\text{O}_2) \cdot \varphi_4 \cdot \varphi_5 \quad (20)$$

where

$$\varphi_5 = 2 k_5 [R_2S] / (2 k_5 [R_2S] + k_{19}) \quad (21)$$

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.

Solubilization of MPT in a O/W microemulsion ($[MPT] = 10^{-2} \text{ mole.l}^{-1}$), 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 of $4 \times 10^{-2} \text{ mole.l}^{-1}$. 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 order 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 concentration¹⁷. From their plot, we take a rate constant of physical deactivation of $2 \times 10^5 \text{ s}^{-1}$ for $[SDS] = 0.28 \text{ mole.l}^{-1}$, 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 solvents¹⁶, in taking the above value for the aqueous pseudo-phase. From $\Phi_{-O_2} = 7.0(\pm 1.5) \times 10^{-3}$ (table 1), $[MPT] = 4 \times 10^{-2} \text{ mole.l}^{-1}$, $k_6 = 1.6 \times 10^5 \text{ s}^{-1}$ and choosing $k_7 = 5.0 \times 10^6 \text{ l.mole}^{-1}.\text{s}^{-1}$, the value calculated from our experiments in methanol, we estimate a k_4 of $8.4 \times 10^4 \text{ l.mole}^{-1}.\text{s}^{-1}$ in assuming no $^3\text{Sens}^*/\text{MPT}$ 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.

For the W/O microemulsion, we would estimate that the lifetime of singlet oxygen is comparable to that in cyclohexane and in 1-butanol ($2 \times 10^{-5} \text{ s}^{16}$), 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 production³¹. 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 conclusion, $^3\text{Sens}^*/\text{MPT}$ 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 a reaction between sensitizer and substrate (e.g. reaction 9) might be the efficiency determining factor.

Under field conditions, photochemically initiated singlet oxygen reactions seem rather inefficient for decontamination purposes: solubilized substrates of different kind might in fact increase the already high efficiency of singlet oxygen deactivating processes in water containing media. If this route of investigation should be pursued, high local sensitizer concentrations and sensitizer/substrate interactions have to be avoided.

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FINANCIAL STATEMENT

As of December 31, 1986, SFR 75794.40 have been paid in salaries leaving an uncovered balance of SFR 44905.15, since payment due June 30, 1986 has not yet been credited.

Lausanne, January 13, 1987


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André M. Braun

END

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