68. Singlet Oxygen and Superoxide: Experimental Differentiation and Analysis

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Summary

Superoxide produced by either pulse radiolysis or from KO_2 undergoes no reaction with furfuryl alcohol competitive to the corresponding *endo*-peroxide formation with singlet oxygen. Thus, furfuryl alcohol can be used as a specific chemical quencher of singlet oxygen.

Superoxide can be quantitatively analyzed by its electron transfer reaction with 1,4-benzoquinone.

The differentiation of the two activated species of oxygen has been realized in microemulsions. Singlet oxygen is known to penetrate the interfaces of surfactant aggregates and may be analyzed in the hydrophobic core by known methods. Charged surfaces on such aggregates, specially those formed by anionic surfactants, prevent the passage of superoxide and restrict its presence and the need for analysis to the bulk aqueous phase.

Hydrated electrons may penetrate the interface depending on the dose per pulse applied. 2,5-Di(*t*-butyl)-1,4-benzoquinone has been taken as an acceptor for electron transfer reactions within the hydrophobic core.

Introduction. – The formation of superoxide by electron transfer reaction of suitable donors with singlet oxygen has been evaluated for some time [1]. In the case of photochemical sensitization, it would, however, be difficult to conceive methods of analysis by which direct and indirect formation of superoxide (*Eqn. 1* and *2*, respectively) could be differentiated. A differentiation and separate analysis of singlet oxygen and superoxide would therefore certainly be of great importance in elucidating those mechanisms.

$$S \xrightarrow{h\nu} S^* \xrightarrow{^3O_2} S^{+\cdot} + O_2^{-\cdot} \qquad (1)$$

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$$\begin{array}{l} S \xrightarrow{h\nu} S^* \xrightarrow{^3O_2} S + {}^1O_2 \\ \qquad\qquad\qquad\quad \downarrow D(S) \\ \qquad\qquad\qquad\quad O_2^{-\cdot} + D^{+\cdot}(S^{+\cdot}) \end{array} \tag{2}$$

There are also several indications that rose-bengal-sensitized singlet-oxygen reactions might, depending on the experimental conditions, involve superoxide formation [2]. This may also be true for other singlet-oxygen sensitizers [3]. Polymer and silica-gel-bound insoluble singlet-oxygen sensitizers might even show an enhanced formation of superoxide due to a decrease of the oxidation potential of the chromophors, possible consequence of a strong interaction of the chromophors imposed by their high local concentration at the surface of the insoluble support and/or by structural effects of this support.

In dealing with such insoluble sensitizers, a true analysis of the efficiency of singlet-oxygen formation as well as of interfering secondary reactions, *e.g.* superoxide formation, is important.

Specificity of furfuryl alcohol as a singlet oxygen quencher. – Earlier investigations on the efficiency of singlet oxygen production by insoluble sensitizers have been carried out with furfuryl alcohol as the chemical quencher [4]. It has been shown that furfuryl alcohol can be used in a wide range of organic solvents as well as in water [5].

Assuming a concurrent superoxide production by the sensitizers used, we investigated the reactivity of furfuryl alcohol towards superoxide.

Water is certainly a suitable solvent for this study, and pulse radiolysis of phosphate-buffered HCOONa-solutions provides relatively high transient concentrations of superoxide (*Eqn. 3–9*)[4] [6].

$$H_2O \xrightarrow{e^-} e^-_{aq}, H^\cdot, OH^\cdot \tag{3}$$

$G_{e_{aq}} = 2.80$ [7]
$G_{OH^\cdot} = 2.80$ [7]
$G_{H^\cdot} = 0.60$ [7]

$$e^-_{aq} + O_2 \rightarrow O_2^{-\cdot} \tag{4}$$

$k_4 = 2.3 \times 10^{10}\ mol^{-1}\,l\,s^{-1}$ [6a]

$$H^\cdot + HCOO^- \rightarrow CO_2^{-\cdot} + H_2 \tag{5}$$

$$OH^\cdot + HCOO^- \rightarrow CO_2^{-\cdot} + H_2O \tag{6}$$

$k_6 = 2.5 \times 10^9\ mol^{-1}\,l\,s^{-1}$ [6a]

$$CO_2^{-\cdot} + O_2 \rightarrow CO_2 + O_2^{-\cdot} \tag{7}$$

$k_7 = 4.6 \times 10^9\ mol^{-1}\,l\,s^{-1}$ [6a]
$G_{O_2^{-\cdot}} = 6.20$

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[4]) G = number of specific species generated per 100 eV of energy deposited in H_2O.

Pulse radiolysis of water produces hydrated electrons, hydroxyl and hydrogen radicals *(Eqn. 3)*. For pulses of ≈3000 rads (radiation dose absorbed during one pulse, measured by dosimetry (see *Exper. Part*)) and the given G-values, the initial concentration of these different species should be $\approx 8.7 \times 10^{-6}$, 8.7×10^{-6} and 1.9×10^{-6} mol/l, respectively [8]. Addition of HCOONa (5×10^{-2} mol/l) to oxygen-saturated (1.25×10^{-3} mol/l [9]), phosphate-buffered[5]) solutions leads to a quantitative scavenging of the primary radicals of the water radiolysis (*Eqn. 5* and *6*) and to the formation of superoxide ($\varepsilon_{246} = 1970$ mol^{-1} l cm^{-1} [6g] [11], $[O_2^{-\cdot}]_{\text{initial}} \approx 1.9 \times 10^{-5}$ mol/l for pulses of ≈3000 rads) *(Eqn. 4–7)*.

Kinetic measurements based on the absorption of superoxide indicate that the rate of disappearance of $O_2^{-\cdot}$ depends on $[OH^\cdot]$ *(Eqn. 8)*. Halflives of $O_2^{-\cdot}$ calculated from second-order absorption decay curves increase from 6 to 23×10^{-3} s as [HCOONa] is varied from 5×10^{-3} to 5×10^{-2} mol/l. If *t*-BuOH (1 mol/l) is used as a scavenger of $OH^\cdot$-radicals *(Eqn. 9)* instead of formate ions, an initial concentration of $O_2^{-\cdot}$ of 9×10^{-6} mol/l has been determined with a halflife of $O_2^{-\cdot}$ of 2×10^{-2} s.

$$O_2^{-\cdot} + OH^\cdot \rightarrow O_2 + OH^- \tag{8}$$

$$OH^\cdot + CH_3C(CH_3)_2OH \rightarrow H_2O + {}^\cdot CH_2C(CH_3)_2OH \tag{9}$$

It has been shown that superoxide disappears in HCOONa-solutions primarily by a dismutation with its protonated species *(Eqn. 10)* [10b]. For pH-values where protonation *(Eqn. 11)* is negligible[5]) neither *Reaction 10* nor *Reaction 12*, the latter being very slow [6g] [10b], are of great importance.

$$O_2^{-\cdot} + HO_2^\cdot \xrightarrow{H_2O} H_2O_2 + O_2 + OH^- \tag{10}$$

$$O_2^{-\cdot} + H_3O^+ \rightleftharpoons HO_2^\cdot + H_2O \tag{11}$$

$$O_2^{-\cdot} + O_2^{-\cdot} \xrightarrow{H_2O} H_2O_2 + O_2 + OH^- \tag{12}$$

The observed dependence of the halflife of $O_2^{-\cdot}$ from $[OH^\cdot]$ is therefore due to *Reaction 8*, the rate constant of which (k_8) has been determined to be 1×10^{10} mol^{-1} l s^{-1} [11] and which must be taken into account for low formate- or *t*-BuOH-concentrations ($k_6 = 2.5 \times 10^9$ mol^{-1} l s^{-1} [6a], $k_9 = 5.2 \times 10^8$ mol^{-1} l s^{-1} [12]) and, thus, for inefficient scavenging conditions for $OH^\cdot$. Superoxide absorption and kinetics monitored under the above-mentioned conditions (phosphate buffer; 5×10^{-2} mol/l HCOONa or 1 mol/l *t*-BuOH) are not altered upon addition of up to 10^{-2} mol/l of furfuryl alcohol, indicating no major reaction of superoxide with the singlet-oxygen quencher [4]. Preparative experiments (2×10^{-3} mol/l of furfuryl alcohol) using repetitive pulses (350 mA, 3 MeV, 5×10^{-7} s, 500 pulses) or producing super-

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[5]) $pk(O_2^{-\cdot}/HO_2^\cdot) = 4.88$ [10a]; $pk(O_2^{-\cdot}/HO_2^\cdot) = 4.75$ [10b].

oxide from KO_2 in pyridine [13] do not yield even traces of reaction products. Reaction products are however observed when furfuryl alcohol is exposed to relatively high instantaneous concentrations of hydrated electrons or $OH^{\cdot}$-radicals.

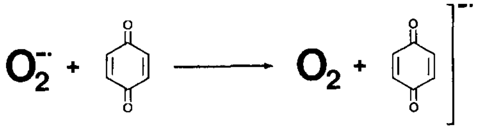
Phosphate buffered and Ar-saturated aqueous solutions of furfuryl alcohol (10^{-2} mol/l) containing 1 mol/l of *t*-BuOH exhibit a weak bleaching at 260 to 300 nm upon radiolysis (≈3000 rad). The resulting reduced optical density of the solution might be due to a partial and very inefficient hydrogenation of the substrate [14]. The reaction of $OH^{\cdot}$-radicals produced by radiolysis of phosphate-buffered aqueous solutions of furfuryl alcohol saturated with N_2O⁶) shows transients absorbing between 330 and 470 nm with a λ_{max} at 375 nm. According to earlier investigations on the radiolysis of aliphatic alcohols [15], hydrogen abstraction should take place in the α-position and the resulting allylic radical *(Eqn. 14)* absorbs at wavelengths >250 nm. The decay of the transient absorption follows second-order kinetics.

(14)

We deduce from those experiments that furfuryl alcohol does not react with superoxide or other electron-donating agents potentially present in photosensitized experiments. The reaction of furfuryl alcohol with singlet oxygen yields known products [5] which can be identified and quantitatively analyzed by established chromatographic methods. We could therefore readily detect any secondary products due to radical reactions and exclude them for the purpose of quantum yield determinations [16]. Thus, furfuryl alcohol is an efficient chemical quencher of singlet oxygen recommended for all quantitative experiments either where experimental conditions permit the isolation and detection of the specific products or where the kinetics of the oxygen uptake is of interest.

Rubrene-2,3,8,9-tetracarboxylic acid has been proposed as a specific singlet-oxygen quencher in neutral and basic aqueous solutions [17]. The substance has been used to prove the absence of any singlet-oxygen-forming decay mechanism of superoxide.

Superoxide analysis. – Aiming for a fast spectroscopic method for the detection and analysis of superoxide [6a–f] [9] [18], we selected the reduction of 1,4-benzoquinone *(Eqn. 15)* where the hydrophobicity of the oxidant can be modified without



(15)

changing drastically its oxidation potential [6a–f] [9] *(vide infra)*. The semiquinone radical anion absorbs in aqueous solutions at 430 nm (ε = 6100 mol⁻¹ l cm⁻¹ [9]). The electron transfer in phosphate-buffered, oxygen-saturated ([9]: 1.25×10^{-3} mol/l) aqueous solutions containing HCOONa (5×10^{-2} mol/l) and 1,4-benzo-

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[6] Under those conditions, *Reaction 13* takes place:

$$e^{-}_{aq} + N_2O \xrightarrow{H_2O} N_2 + 2\,OH^{\cdot} \qquad (13)$$

quinone (1.5×10^{-4} mol/l) is almost quantitative ($k_{15}=3.5\times10^{8}$ mol^{-1} l s^{-1} ([6e]: 7.8×10^{8} mol^{-1} l s^{-1}, initial concentration of semiquinone radical anion $\approx1.6\times10^{-5}$ mol/l for pulses of ≈3000 rad[7])). The semiquinone radical anion can also be produced by hydrated electrons *(Eqn. 16)* and by electron transfer from $CO_2^{-\cdot}$

(16)

(17)

(Eqn. 17). Having determined k_4 and k_{16} to be 2.3×10^{10} mol^{-1} l s^{-1} [6a] and 0.125 to 4.2×10^{10} mol^{-1} l s^{-1} [18] [19], respectively, and working under experimental conditions where $[O_2]/[1,4\text{-benzoquinone}]=8.2$, we assume that *Reaction 16* represents only a small fraction of the total semiquinone production *(Reactions 15–17)*.

To evaluate the importance of *Reaction 17* we repeated the experiment saturating the solution with N_2O[8]). Assuming again practically complete conversion for *Reactions 4–7, 15* and *17*, the two experiments with oxygen- or N_2O-saturated solutions should yield the same concentration of $O_2^{-\cdot}$ and $CO_2^{-\cdot}$, respectively, and, thus, of semiquinone radical anion ($G(O_2^{-\cdot})=G(CO_2^{-\cdot})=6.20$, pH 6.9). In fact, both experiments show the same concentration of reduced 1,4-benzoquinone. Consequently, the importance of *Reaction 17* has to be evaluated from known rate constants and concentrations of *Reactions 7* and *17*:

$$k_7=4.6\times10^{9}\ \text{mol}^{-1}\,\text{l}\,\text{s}^{-1}\ [6a],\ [1,4\text{-benzoquinone}]=1.5\times10^{-4}\ \text{mol/l}=[BQ]$$

$$k_{17}=6.6\times10^{9}\ \text{mol}^{-1}\,\text{l}\,\text{s}^{-1},\ [O_2]=1.25\times10^{-3}\ \text{mol/l}$$

$$\frac{k_{17}\,[BQ][CO_2^{-\cdot}]}{k_{17}\,[BQ][CO_2^{-\cdot}]+k_7\,[CO_2^{-\cdot}][O_2]}=0.15$$

In accordance to earlier reports [6a] [9], we could exclude a rapid transient depleting back reaction *(Eqn. 15)* for 1,4-benzoquinone. We assume a second-order decay of the semiquinone transient absorption with halflife measurements leading to rate constants of 1.7×10^{8} mol^{-1} l s^{-1} and 4.6×10^{8} mol^{-1} l s^{-1} for HCOONa- and *t*-BuOH-solution, respectively. The slightly faster decay in aqueous *t*-BuOH might be due to radical reactions in addition to the known dismutative processes [19].

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[7]) The electron transfer reaction *(Eqn. 15)* in phosphate-buffered, oxygen-saturated solution containing 1 mol/l of *t*-BuOH has also been reported [6a]. The experimentally observed optical density of the semiquinone radical anion corresponds to an initial concentration of 8.5×10^{-6} mol/l (1.23×10^{-4} mol/l of 1,4-benzoquinone, $k_{15}=8.2\times10^{8}$ mol^{-1} l s^{-1} ([17]: 9.6×10^{8} mol^{-1} l s^{-1})).

[8]) The $OH^{\cdot}$-radicals produced by *Reaction 13* are subsequently scavenged by the $HCOO^-$-ions *(Eqn. 6)*.

For the parallel analysis of singlet oxygen and superoxide, we had finally to demonstrate that there is no interference between the semiquinone radical anion and furfuryl alcohol as well as between singlet oxygen and 1,4-benzoquinone.

Concurrent superoxide trapping experiments using 1,4-benzoquinone (1.5×10^{-4} mol/l) and furfuryl alcohol in phosphate-buffered oxygen-saturated HCOONa-solutions (5×10^{-2} mol/l) show no appreciable effect on the absorbance and the kinetics of the semiquinone transient, until the concentration of furfuryl alcohol exceeds 10^{-2} mol/l. Although quencher concentrations $> 10^{-2}$ mol/l are of no practical use in our project, the almost total lack of formation ($\approx 3\%$) of the semiquinone transient absorption in presence of 5×10^{-1} mol/l of furfuryl alcohol without a significant change of its kinetics of disappearance is of fundamental interest. It means that furfuryl alcohol reacts at high concentrations with superoxide or with its precursors. If there would be a quenching of superoxide by furfuryl alcohol, the rate constant would be of the order of 10^3 and the reaction not detectable under normal conditions *(vide supra)*. Repeating those experiments where HCOONa has been replaced by *t*-BuOH, we observe a slower formation of the semiquinone radical anion, a small decrease of its concentration and a kinetics of disappearance of complex order as the concentration of furfuryl alcohol is increased up to 2×10^{-1} mol/l. Those reactions must be explained by additional reactions into which we have no further insight.

Probing the interference of singlet oxygen and 1,4-benzoquinone, thermal formation of singlet oxygen has been chosen to prevent the formation of any electronically excited species of the latter. Thus, 1,4-dimethylnaphthalene-*endo*-peroxide has been prepared photochemically, isolated and redispersed in aqueous solutions of 1,4-benzoquinone (10^{-3} mol/l). No products other than 1,4-benzoquinone and 1,4-dimethylnaphthalene have been isolated from those mixtures after heating up to 60°. Chemical quenching of singlet oxygen by 1,4-benzoquinone can therefore be excluded. A potential physical quenching of singlet oxygen by 1,4-benzoquinone should be observed in measuring the intensity of the singlet oxygen emission (1270 nm) as a function of the quencher concentration. The corresponding experiment reveals a rate constant far too low ($\approx 3 \times 10^3$ mol^{-1} l s^{-1}) as to be of any importance [20].

Differentiation in microemulsions. – Microheterogeneous systems containing ionic surfactants are known to reject ionic species of the same charge [21]. Since singlet oxygen passes through their interfaces [22], those systems could be used for the differentiation of singlet oxygen and superoxide, if the latter can be rejected. We used two different oil-in-water microemulsions (for their compositions, see *Exper. Part*) which have been chosen as microheterogeneous systems for their larger solubilizing capacity than that of usual aqueous surfactant solutions. Furthermore, *t*-BuOH could be used as a co-surfactant besides taking advantage of its ability to scavenge OH$^{\cdot}$-radicals.

Preliminary experiments with Ar-saturated cationic and anionic microemulsions show a lifetime of the hydrated electrons of the order of the pulse with 1.6×10^{-6} s which is slightly shorter than that measured in micellar systems [23]. The efficiency of penetration of hydrated electrons into the hydrophobic region of cationic and anionic microemulsions has been evaluated by comparing the reduction of a hydrophobic and a hydrophilic probe, respectively.

2,5-Di(*t*-butyl)-1,4-benzoquinone is totally insoluble in water and must be therefore a convenient hydrophobic probe. In solubilizing 2×10^{-4} mol/l of this $O_2^{\overline{\cdot}}$-scavenger in Ar-saturated microemulsions, no semiquinone radical anion is detected (analysis at $\lambda_{max} = 415$ nm) at doses < 5000 rad, indicating *i)* that no 2,5-di(*t*-butyl)-1,4-benzoquinone is located in the aqueous bulk phase and *ii)* that hydrated electrons cannot penetrate the interface. Furthermore, from those results, we deduce that this probe is indeed hydrophobic and localized far enough from the surface of the aggregate which could be reached by the hydrated electrons. Our data are also in accord with earlier experiments where no penetration of micellar interfaces was detected with pulses of 600 rad [24].

In contrast, we used 1,4-benzoquinone as a hydrophilic oxidant and we determined its location in analogy to an earlier published method [24] using pulses of 1500 rad. We compared the formation of the semiquinone radical anion in homogeneous aqueous solution *(vide supra)* and in cationic and anionic microemulsions, respectively, using the same concentration of 1,4-benzoquinone (1.5×10^{-4} mol/l). The results show that the semiquinone radical anion concentration is smaller by 20% in microemulsions[9]) as compared to the homogeneous solutions. The kinetics of its formation and decay remain similar within the limits of experimental error. Since hydrated electrons do not penetrate the interface of microheterogeneous systems under those conditions [24], we conclude that 80% of the 1,4-benzoquinone is located in the aqueous bulk phase of the microemulsions and/or at the surface of the aggregates.

However, if the experiments with 2,5-di(*t*-butyl)-1,4-benzoquinone are repeated with a radiation dose of ≈ 8500 rad, an efficiency of penetration of hydrated electrons of $\approx 60\%$ for anionic and of $\approx 70\%$ for cationic microemulsions is obtained. Those values are calculated assuming that the molecular extinction coefficients of the two scavengers (1,4-benzoquinone and 2,5-di(*t*-butyl)-1,4-benzoquinone) are approximately the same [9]. We think that the concentration of the radicals produced by the scavenging of $OH^{\cdot}$ by *t*-BuOH leads to a structural perturbation of the aggregate allowing the hydrated electrons to penetrate into the hydrophobic region and to reduce the hydrophobic scavenger to the observed extent.

Irradiating the same microemulsions now saturated with oxygen using pulses of ≈ 8500 rad should produce an initial concentration of $\approx 3 \times 10^{-5}$ mol/l of superoxide; experimentally determined concentrations vary from 2.5×10^{-5} mol/l for cationic to 3.4×10^{-5} mol/l for anionic microemulsions. Adding HCOONa (5×10^{-2} mol/l), the expected initial concentration of superoxide for pulses of ≈ 8500 rad can be estimated to be between 3.4 and 5.1×10^{-5} mol/l[10]).

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[9]) Those microemulsions do not contain cyclohexane.

[10]) $[O_2^{\overline{\cdot}}]_{initial} = 5.1 \times 10^{-5}$ mol/l, if only HCOONa and no *t*-BuOH would be used. Using both, *t*-BuOH (1 mol/l) and HCOONa (5×10^{-2} mol/l), we calculate that the scavenging of $OH^{\cdot}$-radicals by *Reaction 9* is ≈ 4 times faster than by *Reaction 6*. This leads to a minimum value of $[O_2^{\overline{\cdot}}]_{initial}$ of $\approx 3.4 \times 10^{-5}$ mol/l. The actual initial concentration is certainly greater because a large amount of *t*-BuOH is localized in the interface of the aggregates and is not available for this fast scavenging reaction.

In anionic microemulsions $[O_2^{-\cdot}]_{\text{initial}}$ has been measured to be 4.4×10^{-5} mol/l; the corresponding concentration in cationic microemulsions is $\approx 3 \times 10^{-5}$ mol/l. Initial semiquinone radical anion concentrations after adding both 1,4-benzoquinone (2.27×10^{-4} mol/l) and HCOONa to the microemulsion have been determined to be 1.9×10^{-5} mol/l for cationic and 2.2×10^{-5} mol/l for anionic microemulsions.

Taking into account the observed efficiency of *Reaction 15* of 85%, the initial concentration of the semiquinone radical anion should be 3.7×10^{-5} mol/l in anionic and 2.5×10^{-5} mol/l in cationic microemulsions. The reduced experimentally observed concentrations might be due *i)* to fast concurring reactions of superoxide and/or *ii)* to the partition of 1,4-benzoquinone between the bulk aqueous and the hydrophobic phases (assuming that superoxide cannot penetrate the interfaces, *vide infra*). Whereas the rate of formation of the semiquinone radical anion is similar to that in water, the second-order rate constant of the decay of superoxide in the absence of 1,4-benzoquinone is 4.4×10^7 mol^{-1}l s^{-1} in microemulsions and, thus, ≈ 10 times faster than in aqueous solution. It is easy to conceive that the efficiency of *Reaction 15* in microemulsions is not affected by this accelerated decay of superoxide.

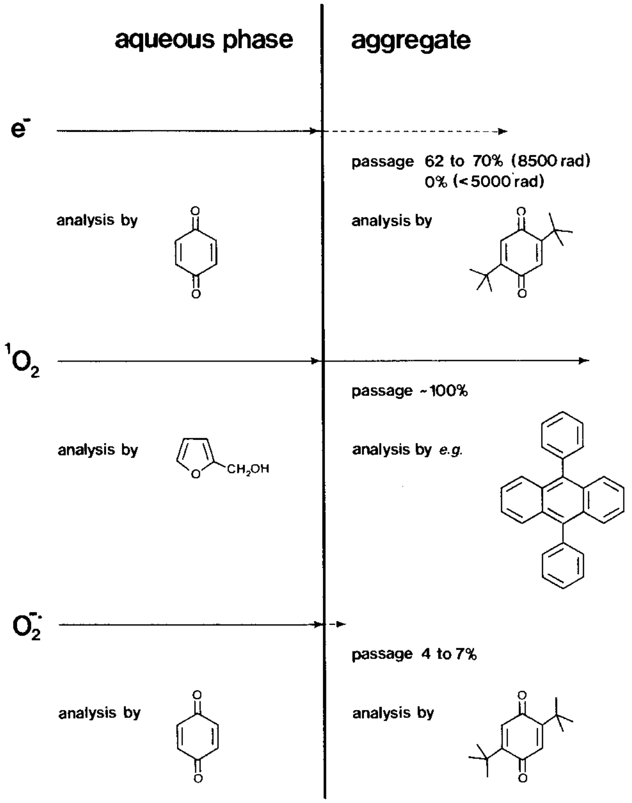

Fig. 1. *Separation of singlet oxygen from charged intermediates, as* e.g. *hydrated electrons or superoxide, at the interface of microemulsions containing ionic surfactants*

Consequently, the partition factor of 1,4-benzoquinone between the aqueous bulk and the hydrophobic phase can be calculated to be 0.75 in cationic and 0.60 in anionic microemulsions. In comparing these factors with the factor previously *(vide supra)* determined, the results of two different methods of analysis (reduction by hydrated electrons and by superoxide, respectively) yield slightly smaller values for the latter. This might be due to the fact that cyclohexane-containing microemulsions dissolve more 1,4-benzoquinone in their hydrophobic cores than those without cyclohexane. The even more reduced value for the anionic microemulsions might be explained by the repulsion of the superoxide radical anion not allowing its interaction with the benzoquinone located near the anionic surface of the aggregates.

It remains to show that superoxide cannot penetrate the interface of the aggregates. In fact, experiments using oxygen-saturated microemulsions containing 2,5-di(*t*-butyl)-1,4-benzoquinone (2.27×10^{-4} mol/l in anionic and 5.4×10^{-4} mol/l in cationic microemulsions, respectively) show very faint transient absorptions leading to an efficiency of penetration of 7% for the cationic microemulsion. No penetration can be observed for the anionic microemulsion.

Figure 1 summarizes our experiments in microemulsions: *i)* hydrated electrons are not observed to penetrate the interface of the aggregates for doses up to 5000 rad; at radiation doses of 8500 rad a corresponding efficiency of 60 to 70% depending on the charge of the aggregates surface is found; *ii)* superoxide cannot penetrate anionic microemulsions, and its efficiency of penetration of positively charged surfaces is limited to $\leqslant 7\%$ under the experimental conditions of these investigations.

Microemulsions, preferentially containing anionic surfactants, may, thus, be useful for the differentiation of superoxide and singlet oxygen: singlet oxygen, passing the interface, can be analyzed by a suitable trapping agent in the hydrophobic section of the microemulsion, whereas superoxide may be analyzed in the bulk aqueous phase.

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Experimental Part

Material. All solutions were prepared with triply distilled water buffered with potassium phosphates (pH = 6.9). 1,4-Benzoquinone *(Fluka)* was purified by vacuum sublimation; 2,5-di(*t*-butyl)-1,4-benzoquinone was a gift of Prof. *H. G. Cassidy* (Yale University). Furfuryl alcohol *(Fluka)* was purified by vacuum distillation; *t*-BuOH and HCOONa *(Fluka)* were used as supplied.

Pyridine *(Fluka, puriss.)* was distilled under Ar and kept over KOH. Dicyclohexyl-18-crown-6 *(Fluka)* was dried under vacuum before used. *Sensitox (Hydron Laboratories)*, 1,4-dimethylnaphthalene *(Fluka)* and isopentane *(Fluka, puriss.)* were used as supplied.

Microemulsions were prepared with triply distilled water, *t*-BuOH as co-surfactant, cyclohexane *(Fluka, puriss.)* and sodium dodecylsulfate (SLS) *(Merck)* or dodecyltrimethylammonium chloride (LTAC) *(Eastman)* as surfactants. SLS was recrystallized twice from dry EtOH *(Fluka, puriss.)*, LTAC from acetone *(Fluka, puriss.)*. No additional buffer was used in microemulsions, the measured pH-value being always close to 7.

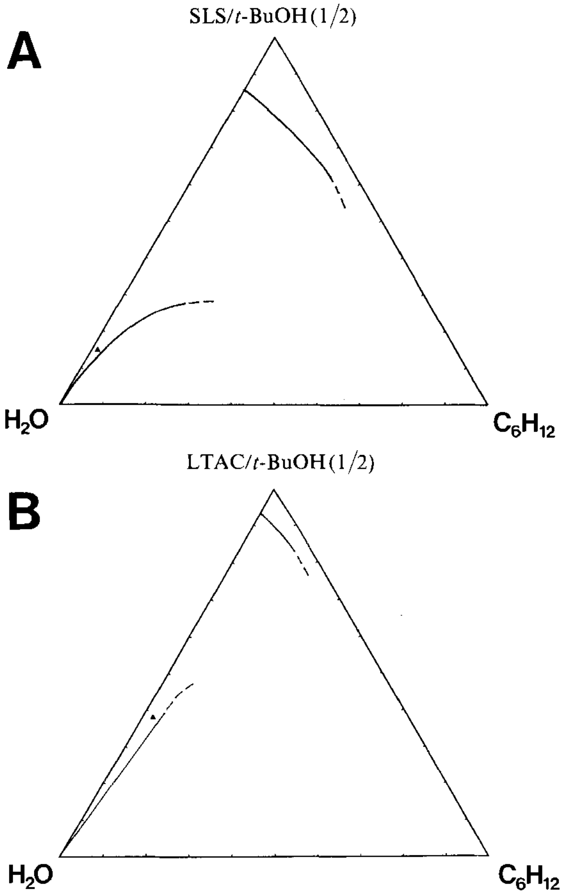

Fig. 2. *Pseudoternary phase diagrams of the microemulsion* **A** *containing* H_2O (84.1%), t-*BuOH* (9.6%), *SLS* (4.8%) *and cyclohexane* (1.5%) *and of the microemulsion* **B** *containing* H_2O (60.2%), t-*BuOH* (24.1%), *LTAC* (12.1%) *and cyclohexane* (3.6%)

Preparation of microemulsions. The two microemulsions used, **A** (containing SLS) and **B** (containing LTAC), are localized on the pseudoternary phase diagrams *(Fig. 2)*. The percentage of the different components is given in weight. The ratio surfactant/co-surfactant was taken as 0.5. The microemulsions were prepared by titrating a water/cyclohexane mixture just over the clearing point with a solution of surfactant and co-surfactant in water [25]. 1,4-Benzoquinone was dissolved directly in the microemulsions. In the case of 2,5-di(*t*-butyl)-1,4-benzoquinone, a corresponding cyclohexane solution was prepared and used to formulate the microemulsions.

Solutions and microemulsions were saturated with the appropriate gases by bubbling for 30 min. (O_2 for the production of $O_2^{-\cdot}$, Ar for e_{aq}^- and N_2O for $OH^\cdot$-radicals). With oxygen-saturated solutions, the oxygen concentration was taken as 1.25×10^{-3} mol/l [9]. All experiments were carried out at ambient temperature ($\approx 20°$).

Endo-*peroxide decomposition in presence of 1,4-benzoquinone. Sensitox* (5 g) were given to a solution of 1.6 g of 1,4-dimethylnaphthalene in 600 ml of isopentane. The suspension was placed in a reactor designed for photochemical reactions at deep temperatures *(DEMA)*, equipped with a dry ice condenser, cooled at – 15° and saturated with oxygen.

The well-stirred suspension was irradiated (*Philips HPK 125, Pyrex*, K_2CrO_4) for 4 h while maintaining its temperature at – 15° and a constant input of oxygen.

The suspension was filtered and the (*endo*-peroxide)-containing solution was concentrated by evaporating of about 300 ml of isopentane by a stream of N_2 passed trough while holding the temperature below 0°.

1,4-Benzoquinone (0.6 g) in 300 ml of H_2O was added to the remaining solution, and the isopentane was totally evaporated as indicated above. The aq. solution was allowed to warm up to 20° within 12 h, then heated consecutively to 40, 50, 60 and 70°.

Chromatographic analysis (TLC.) of the resulting suspension as well as of the $CHCl_3$-extracts did not show other substances than the substrates used.

Dissociation of potassium superoxide in presence of furfuryl alcohol. A solution of furfuryl alcohol (1 mmol) in dry pyridine (10 ml) was added to a mixture of powdered KO_2 (7 mmol) and dicyclohexyl-18-crown-6 (7 mmol) in 40 ml of pyridine under dry Ar. The resulting yellow mixture was protected from moisture with a Ca-drying tube and stirred during 24 h. No reaction was detected by chromatographic analysis (TLC. and GC.).

Irradiation conditions and dosimetry. A *van de Graaff* accelerator operating at 3 MeV with a beam current of 280–350 mA was used as the irradiation source. The dose per pulse changed from ≈ 1500 rad to ≈ 8500 rad as the pulse length was varied from 0.5 to 1.5×10^{-6} s. The electron beam was focalized on a quartz cell of 1 cm optical path length. Pulse-to-pulse fluctuations were monitored by charge collection; the reproducibility of the dose per pulse was better then 10%.

Dosimetry was carried out by measuring the optical absorption of $Fe(CN)_6^{3-}$ with a N_2O-saturated 10^{-3} mol/l $K_4Fe(CN)_6$-solution containing 2×10^{-5} mol/l of $K_3Fe(CN)_6$ to react with the H-atoms [6g]. The ferricyanide absorbance was measured at 400 nm where $\varepsilon = 980\ mol^{-1}l\ cm^{-1}$. The dose was calculated based on $G(Fe^{3+}) = 5.6 = (G(e_{aq}^-) + G(OH^{\cdot}))$.

Analysis. The electron pulse and the Xe-analyzing light are arranged in a crossed-beam manner intersecting in the quartz cell already described. Kinetic absorption spectrophotometry of the generated transients was implemented using a high-intensity monochromator *(Bausch & Lomb)* coupled with a *RCA 8480* photomultiplier and associated circuitry (overall risetime $< 5 \times 10^{-9}$ s). The electron signal from the photomultiplier was displayed on a *Tektronix* oscilloscope (7834, 400 MHz) and then photographed. Generally, we assume that our experimental error is $\approx 10\%$. GC./MS. combination *(Finningan 4000)* has been used for product analysis of preparative experiments (GC.: *OV 173Q*, 1 m, 120–240°, 10° min^{-1}).

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