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REPORT DOCUMENTATION PAGE

1a.		1b. RESTRICTIVE MARKINGS

AD-A210 748

2a.	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b.	Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) R&D 5038-CH-01

DTIC ELECTE JUN 23 1989 S E

6a. NAME OF PERFORMING ORGANIZATION Institut de Chimie Physique	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION European Research Office USARDSG-UK

6c. ADDRESS (City, State, and ZIP Code) EPFL-Ecubiens CH-1015 Lausanne Switzerland	7b. ADDRESS (City, State, and ZIP Code) Box 65 FPO NY 09510-1500

8a. NAME OF FUNDING / SPONSORING ORGANIZATION European Research Office USARDSG-UK ARO-E	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAJA45-85-C-0026

8c. ADDRESS (City, State, and ZIP Code) Box 65 FPO NY 09510-1500	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO. 61102A	PROJECT NO. 1L161102BH5	TASK NO. ✓	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
(U) Enhanced Oxidation and Solovolysis reactions in Chemically inert Microheterogeneous Systems

12. PERSONAL AUTHOR(S)
Dr. A. Braun

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) May 89	15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
0704			
150603			Peroxide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The aim of the project has been to test the working hypothesis of an enhanced oxidative degradation of organic substrates solubilized in H_2O_2 containing microemulsions.

This work contains therefore three main topics:

1. The stability of H_2O_2 containing microemulsions and the research for a potential catalytic effect of its decomposition.
2. The qualitative and quantitative analysis of the intermediates of the H_2O_2 decomposition.
3. Kinetic investigations on the reactivity of these intermediates towards solubilized organic substrates and evaluation of the efficiencies of these oxidation reactions.

Both, the increased solubilization capability of microemulsions and an accelerated decomposition of H_2O_2 may be exploited for decontamination.

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☒ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert J. Campbell	22b. TELEPHONE (Include Area Code) 01-409-4423	22c. OFFICE SYMBOL AMXSN-UK-RC

19.
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In accord with the project submitted for the third year of contract, the work on the peroxide reactivity has been done in close collaboration with Dr. E. Oliveros (EPFL, Lausanne) and the group of Dres. M.-T. Maurette (Université Paul Sabatier, Toulouse).

ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS
IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

PD Dr. André M. BRAUN
Ecole Polytechnique Fédérale de Lausanne

DAJA45-85-C-0026, P00001

Final Report

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SUMMARY

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Both, the increased solubilization capability of microemulsions and an accelerated decomposition of H_2O_2 may be exploited for decontamination.

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STRATEGY

The general idea of this projects is based on extrapolated experience that organic substrates would be solubilized in faster rates and higher quantities by microheterogeneous systems (e.g. microemulsions) and on the working hypothesis that ionic microemulsions could be found which would show a catalytic effect on the rate of decomposition of rather large quantities of H_2O_2. The combined effects would lead to a enhanced rate of oxidative degradation of the solubilized organic substrate and could be exploited for decontamination purposes. Decontamination mixtures of this kind would also be less corrosive and might even be employed on skin.

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Solubilization studies should be undertaken with the organic substrates of interest. Aiming at a new system for decontamination, CWA's cannot be investigated in University research laboratories, and these investigations are thought to be taken up by the specialists of the US CRDC.

In our research work we planned to investigate first on the **stability of reactivity of H_2O_2 containing microemulsions** and to compare the kinetics of decomposition of H_2O_2 in those specific environments with the generally accepted reaction scheme. This work calls for a **reference kinetic investigation in water** and butanol/water mixtures. Hydroxyl radical being one of the reactive intermediates, **perfluorinated media** are of special interest, as they should remain practically inert in presence of

HO˙ and therefore should direct the reactivity of this intermediate towards the solubilized organic substrate. In a second part, the kinetics of **efficient reactions of the intermediates, peroxide anion, super-oxide anion and hydroxyl radicals**, should be determined, in order to evaluate the efficiency of this method of oxidative degradation.

STABILITY OF AQUEOUS H_2O_2

The decomposition of H_2O_2 has been observed by volumetric measurements of the produced oxygen and by titrimetric determination of the $[H_2O_2]$ remaining. From these measurements at constant temperature the autocatalytic characteristics of the decomposition could be determined (figure 1) and fitted to a calculated curve based on the generally accepted reaction scheme (scheme 1) [1]

From scheme 1 can be seen that the rate of decomposition depends on the concentration of deprotonated H_2O_2 ($[HOO^-]$), consequently, the rate of decomposition depends strongly on the pH of the solution (figure 1). The experimental results of this decomposition in aqueous solutions can be fitted in using the above mentioned models and the corresponding calculated rate constants. These calculated data have not yet been transmitted by Dr. Z. Haniotis, Basel, but will be added to this report as soon as possible. Investigations in H_2O at different pH serve as reference data for all kinetic experiments concerning the decomposition of H_2O_2 in butanol/water mixtures an in microemulsions.
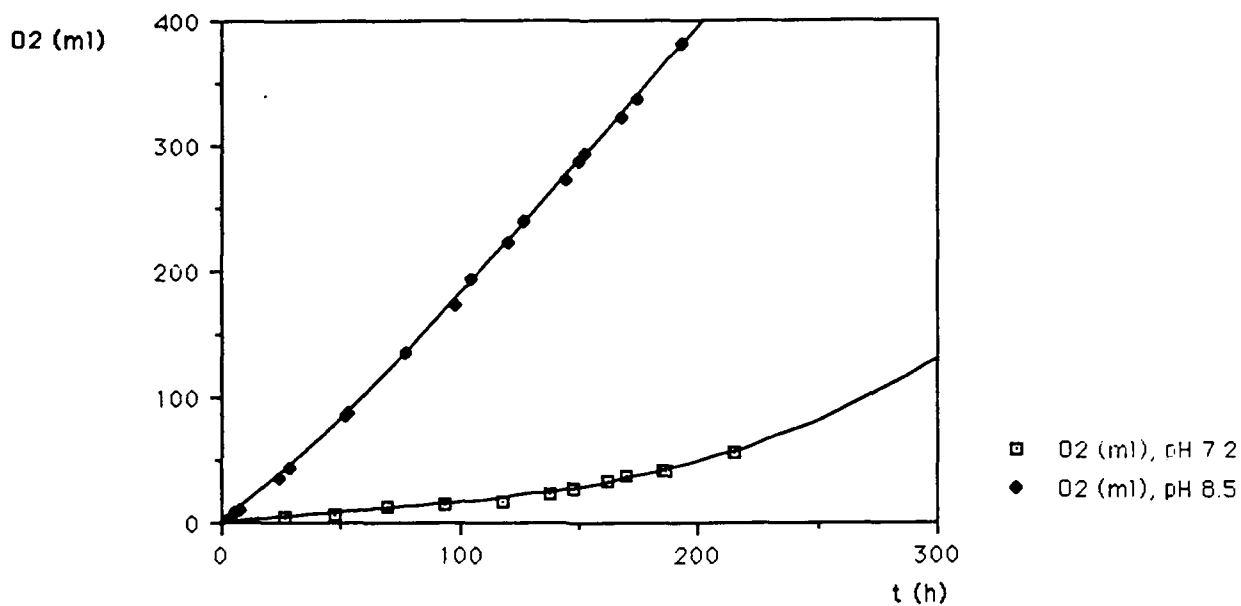
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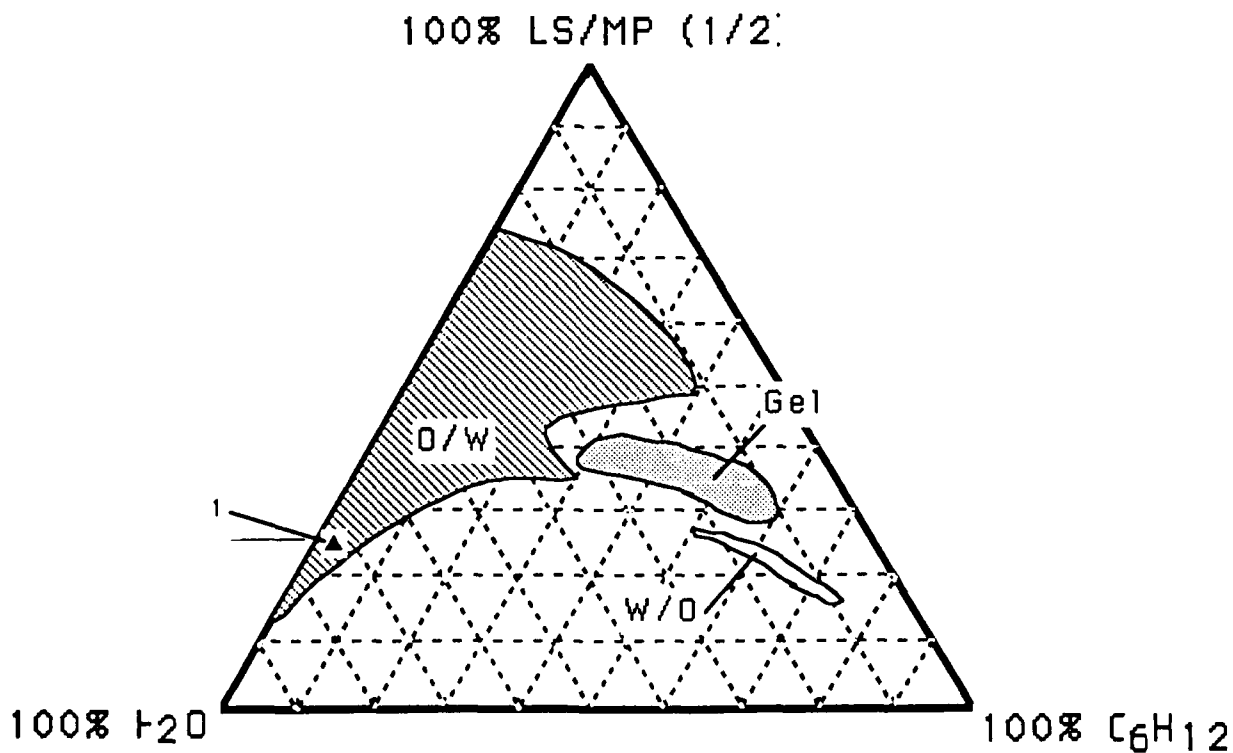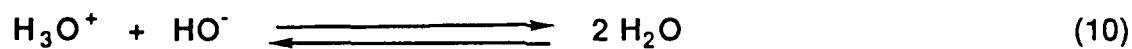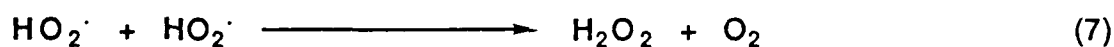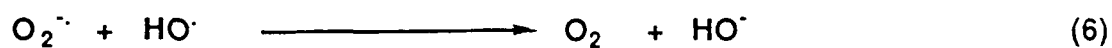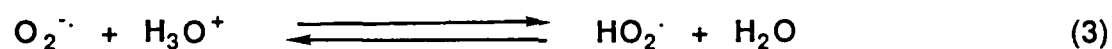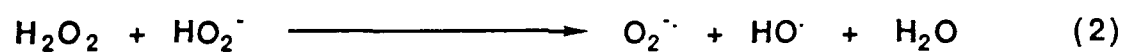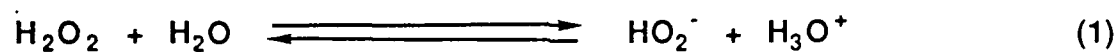Figure 1. – Decomposition of H_2O_2 in aqueous solution at different pH

Figure 2. – Pseudo ternary phase diagram of microemulsions containing sodium laurate/2-methyl-2-pentanol (1/2), cyclohexane and water as an example for all O/W microemulsions used in these investigations

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \qquad (1)$$

$$H_2O_2 + HO_2^- \longrightarrow O_2^{\cdot -} + HO^\cdot + H_2O \qquad (2)$$

$$O_2^{\cdot -} + H_3O^+ \rightleftharpoons HO_2^\cdot + H_2O \qquad (3)$$

$$O_2^{\cdot -} + HO_2^\cdot \longrightarrow O_2 + HO_2^- \qquad (4)$$

$$O_2^{\cdot -} + O_2^{\cdot -} + H_2O \longrightarrow O_2 + HO_2^- + HO^\cdot \qquad (5)$$

$$O_2^{\cdot -} + HO^\cdot \longrightarrow O_2 + HO^- \qquad (6)$$

$$HO_2^\cdot + HO_2^\cdot \longrightarrow H_2O_2 + O_2 \qquad (7)$$

$$HO^\cdot + H_2O_2 \longrightarrow HO_2^\cdot + H_2O \qquad (8)$$

$$HO^\cdot + HO^\cdot \longrightarrow H_2O_2 \qquad (9)$$

$$H_3O^+ + HO^- \rightleftharpoons 2\,H_2O \qquad (10)$$

$$HO_2^- + H_2O_2 \longrightarrow HO^\cdot + O_2 + H_2O \qquad (11)$$

Scheme 1. – Reaction scheme of the non-catalyzed decomposition of H_2O_2

STABILITY OF H_2O_2 CONTAINING MICROEMULSIONS

Microemulsions used in these investigation are of O/W type, and figure 2 shows their position on a pseudo ternary phase diagram, indicating their close to micellar characteristics.

The **rate of H_2O_2 decomposition** in microemulsions depends strongly on
1) the apparent pH of the medium,
2) on the cosurfactant used (figure 3)
3) and is faster in perfluorinated microemulsions (figure 4).

As shown in scheme 1, the rate of decomposition depends on $[HOO^-]$ and, hence on the pH of the reaction environment. If the apparent pH of the medium drops below 5, as found for microemulsions containing sodium lauryl sulfate (SLS) or benzyl-dimethyl-tetradecyl ammonium chloride (BMe_2TAC), the H_2O_2 containing microemulsions remain stable for months. Most reactive perhydrogenated microemulsions have been found with the components indicated in figure 2.

Differences in rate of decomposition found upon varying the cosurfactant in a perhydrogenated microemulsions have been more surprising (figure 3). A net acceleration of the decomposition of H_2O_2 is found in the microemulsion 2 containing 2-methyl 2-pentanol as a cosurfactant. The corresponding results cannot be explained with a variation of apparent pH, as all three microemulsions shown in figure 3 show the same apparent pH of 7.2 to 7.3.

The practically identical result of the H_2O_2 containing microemulsions with tert. butanol (t-BuOH) and 2-methyl pentanol (2MePOH), respectively, indicate that the reactivity of the cosurfactant with one of the intermediates of the H_2O_2 decomposition might be of importance. In fact, it is known that t-BuOH is a very efficient trap for $HO^.$ radicals, and there is no immediate reason why 2MePOH should be less reactive towards this intermediate. If $HO^.$ would be quenched more efficiently by those cosurfactants, reaction (6) and, hence, one of the O_2 producing steps would be less important. We could then explain the slower rate of H_2O_2 decomposition in comparison to the result found for the n-butanol (BuOH) containing microemulsion.

All microemulsions shown in figure 3 show faster rates of H_2O_2 decomposition than water. The enhancement would be even greater than pictured, if it would be based on the practically total inertness of H_2O towards H-abstraction by $HO^.$ radicals.

O2 (ml) H2O

legend:
- □ O2 (ml) H2O
- ◆ O2 (ml) t-BuOH
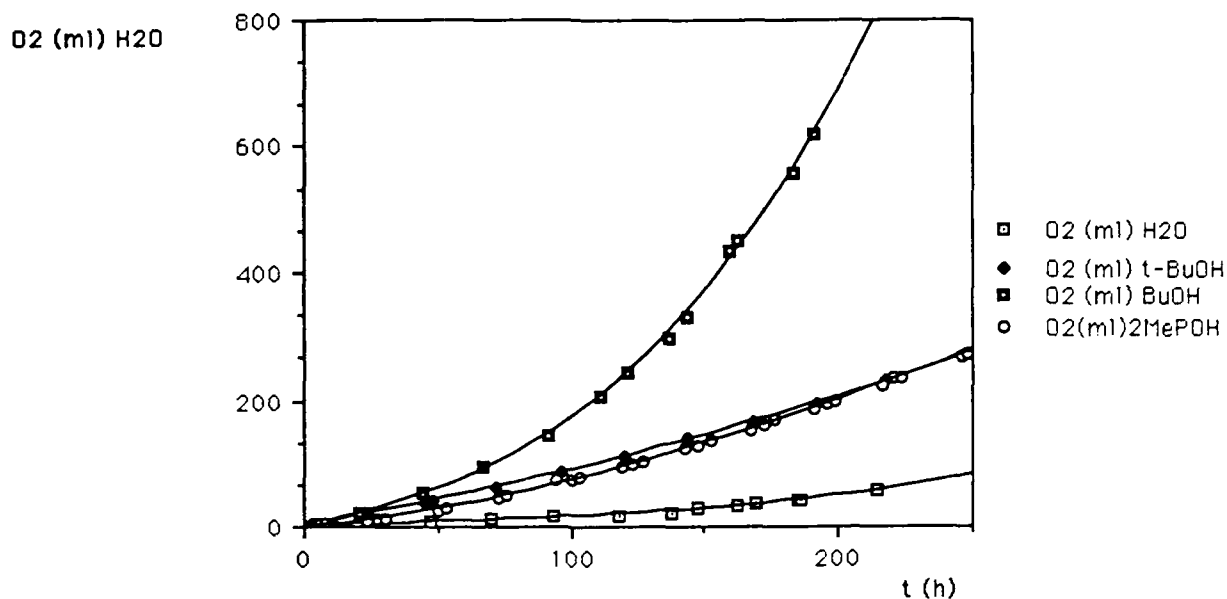- ▣ O2 (ml) BuOH
- ○ O2(ml)2MePOH

Figure 3. - O_2 Production from H_2O_2 decomposition in microemulsions containing different cosurfactants, pH: 7.2

The above working hypothesis concerning the reactivity of components of the microemulsions towards HO· radicals is certainly of main importance for the interpretation of the kinetic results of the H_2O_2 decomposition in perfluorinated media (figure 4). Since practically no H-abstraction can take place in these microemulsions, reaction (6) should be at maximum efficiency, and O_2 production should be at its maximum. In fact, perfluorinated microemulsions show the fastest rates of H_2O_2 decomposition at comparable pH values.

The above results show that microemulsions containing carboxylate, in particular, and tertiary alcohols exhibit catalytic effects on the decomposition of H_2O_2. On the other hand, microemulsions with low apparent pH, are practically inert and stabilize the dissolved H_2O_2.

REACTIVE INTERMEDIATES

Following reaction scheme 1 for the decomposition of H_2O_2, the intermediates are peroxide anion (HOO^-), superoxide anion ($O_2^{-\cdot}$) and hydroxyl radical ($HO^\cdot$). Hence, oxidative degradation of organic substrates involves at least one of the following fundamental reactions:

1) Nucleophilic addition or substitution by HOO^-

2) Nucleophilic addition or substitution by $O_2^{-\cdot}$

3) Electron transfer reaction with $O_2^{-\cdot}$ and/or $HO_2^\cdot$

4) Hydrogen abstraction by $HO^\cdot$

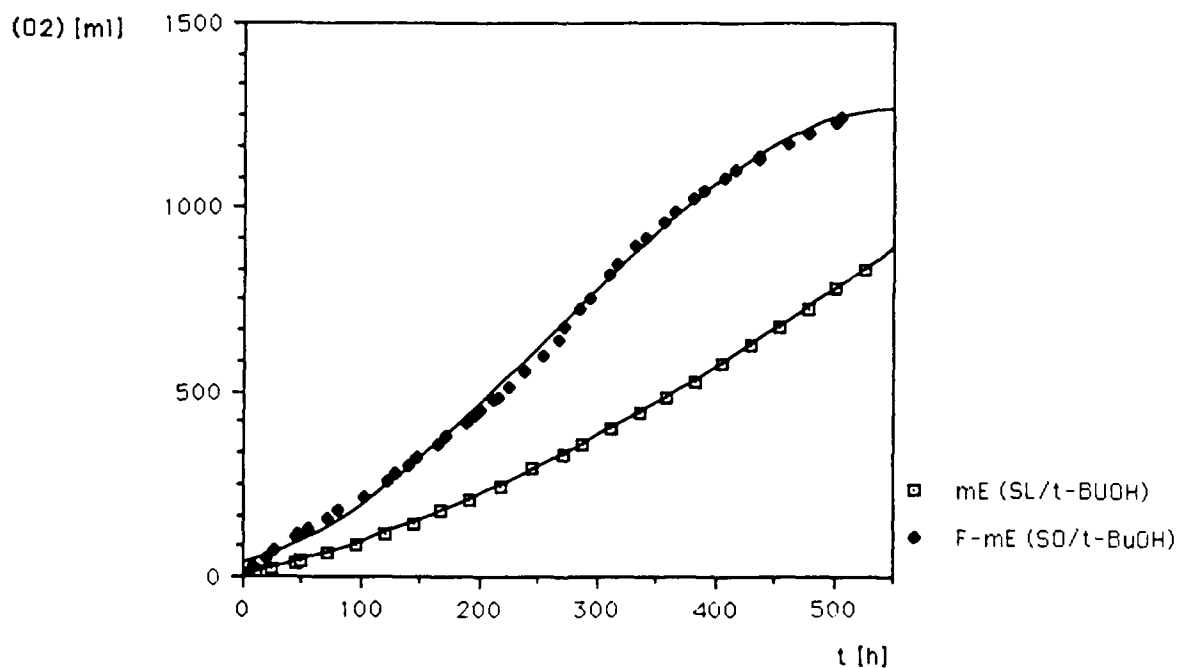5) Electron transfer reaction with $HO^\cdot$

Figure 4. – O_2 Production from H_2O_2 decomposition in a perfluorinated microemulsions (F-mE;SO: sodium perfluorooctanoate) compared to a reference result, pH: 7.2 (perhydrogenated microemulsion, s. figure 3)

PEROXIDE ANION

A second component of the accelerating effect of the laurate aggregates on the decomposition of H_2O_2 may be based on an enhanced deprotonation of H_2O_2 at the carboxylate interface (local pH). Consequently, specific reactions of the deprotonated form should also be enhanced.

1,4-Naphthoquinone (1,4-NQ) has been chosen as a specific reagent for a nucleophilic addition of HOO^- (scheme 2).

red coloured intermediate

H_2O_2, HO·

oxidation products
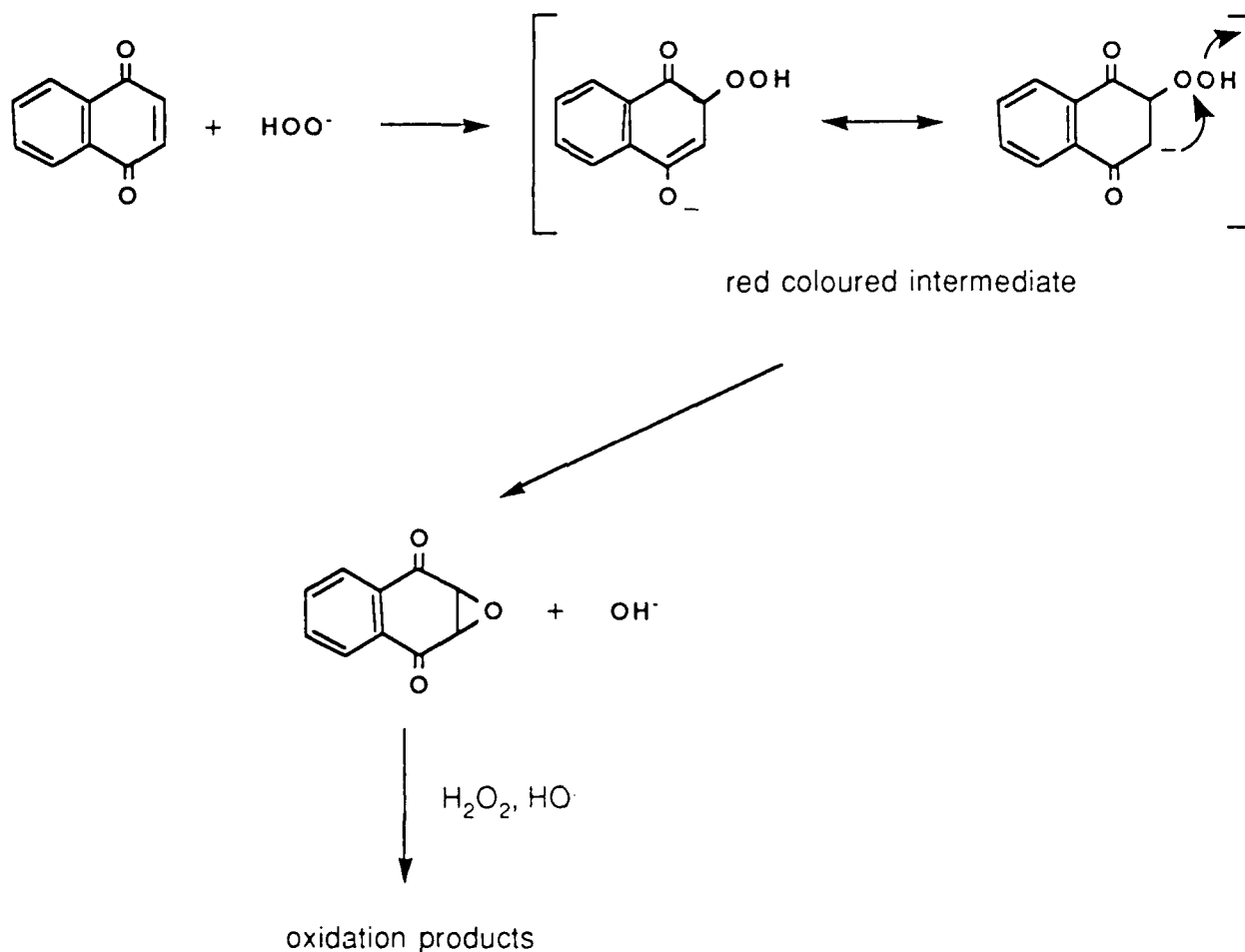
Scheme 2. - Sequence of reactions of peroxide anion (HOO^-) with 1,4-naphthoquinone (1,4-NQ)

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After having established the molecular absorption coefficients of 1,4-NQ in the different reaction media, the consumption of substrate and colored intermediate has been followed spectrophotometrically.

Taking $H_2O/t\text{-}BuOH$ as a reference media, the corresponding rate constant of nucleophilic addition producing the red-colored intermediate has been determined from experimental results as shown in figures 5 to be 2.6×10^{-7} s^{-1}.

The consumption of 1,4-NQ begins in pseudo first order, deviation from this linear plot towards a second order occurs after approx. 60% transformation. Considering the large excess concentration of H_2O_2, $[HOO^-]$ at pH = 3.6 is remaining practically constant during the observed reaction. Nevertheless, the measured $[1,4\text{-}NQ]_t$ fit a second order kinetics plot, the rate constant of which has been calculated to be 1.81×10^{-4} $l \cdot mol^{-1} \cdot s^{-1}$. Multiplication with $[1,4\text{-}NQ]_0$ yields a pseudo first order rate constant of 3.2×10^{-7} s^{-1} which compares favorably with the result found by the first order kinetic analysis.
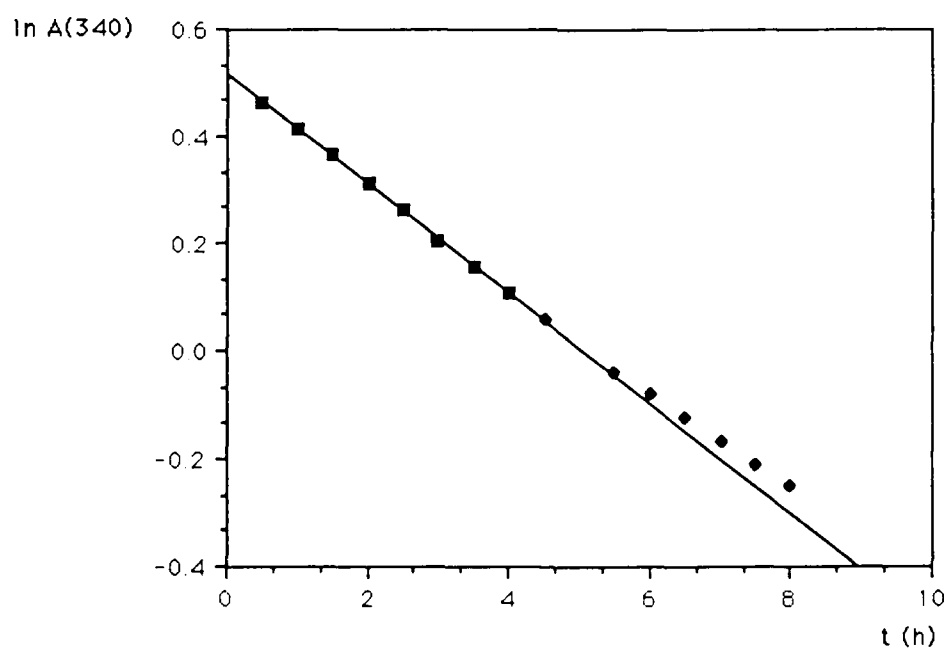

Figure 5. - Reaction of 1,4-NQ with HOO^- in $H_2O/t\text{-}BuOH$ at pH 3.6; 1,4-NQ consumption followed spectrophotometrically

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The given example may also serve in order to resume the spectrophoto-
metric experiments in which the production of the red-colored intermediate
has been followed.
Figure 6 shows the corresponding plot of $A_{460} = f(t)$, being entirely in accord
with the proposed scheme of reactions.

In accord with the above scheme of reactions (scheme 2), data as shown
in figure 6 could be used in order to calculate the rate constants of forma-
tion (k_1) and consumption (k_2) of the intermediate I, following the kinetic
laws of consecutive reactions:

$$NQ \xrightarrow{k_1} I \xrightarrow{k_2} P$$

The two rate constants k_1 and k_2 can be calculated in, first, determining k_1
using equation (12) and, second, in measuring t_{max} and placing the results in
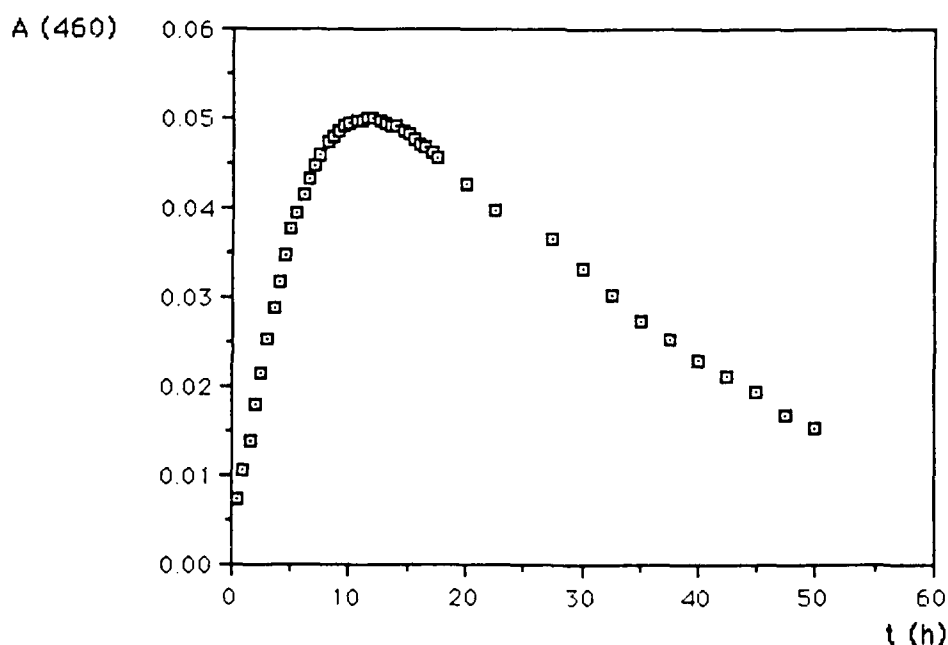equation (13) which is derived from equation (14).

Fig. 6. – Reaction of 1,4-NQ with HOO$^-$ in H_2O/t-BuOH at pH 3.6; the red-
colored intermediate followed spectrophotometrically

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$$[NQ] = [NQ]_0 \exp(-k_1 t) \tag{12}$$

$$t_{max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} \tag{13}$$

$$[I]t = [NQ]_0 \frac{k_1}{k_2 - k_1} \{\exp(-k_1 t) - \exp(-k_2 t)\} \tag{14}$$

These reference results for different pH are compiled in table 1

Table 1. – Rate constants of the reaction of 1,4-naphthoquinone (1,4-NQ) with H_2O_2 in H_2O/t-BuOH (65/35) at different pH

pH	k_1 $[s^{-1}]$	k_2 $[s^{-1}]$	t_{max} $[s]$
3.6	2.85×10^{-5}	1.84×10^{-5}	4.36×10^4
4.8	1.56×10^{-4}	8.00×10^{-5}	8.82×10^3
7.2	$> 2.5 \times 10^{-1}$ [b]	1.63×10^{-4}	$< 3.0 \times 10^1$ [a]

[a] minimum time required between dissolving 1,4-NQ and the first spectrophotometric measurement

[b] minimum value calculated from equation (13)

In fact, the nucleophilic addition reaction of HOO^- on 1,4-NQ at pH values of > 6 is becoming so fast, that we cannot follow any longer their consumption of the substrate figure 7). We fixed, therefore a minimum time for the first spectroscopic measurements and evaluated a minimum value of k_1 after experimental determination of k_2 at the end of the reaction.

After having established the reference values of k_1 and k_2, the same experiments could be carried out in microemulsions. The corresponding results are shown in table 2.

Our working hypothesis stipulates that the chromophoric system of the first intermediate is due to the resonance system (scheme 5). It should, hence, be possible to reach a similarly colored intermediate by dissolving 1,4-NQ in an alkaline aqueous solution. In fact, 1,4-NQ in aqueous NaOH at pH 11, yields a solution the absorption spectrum of which is similar to those
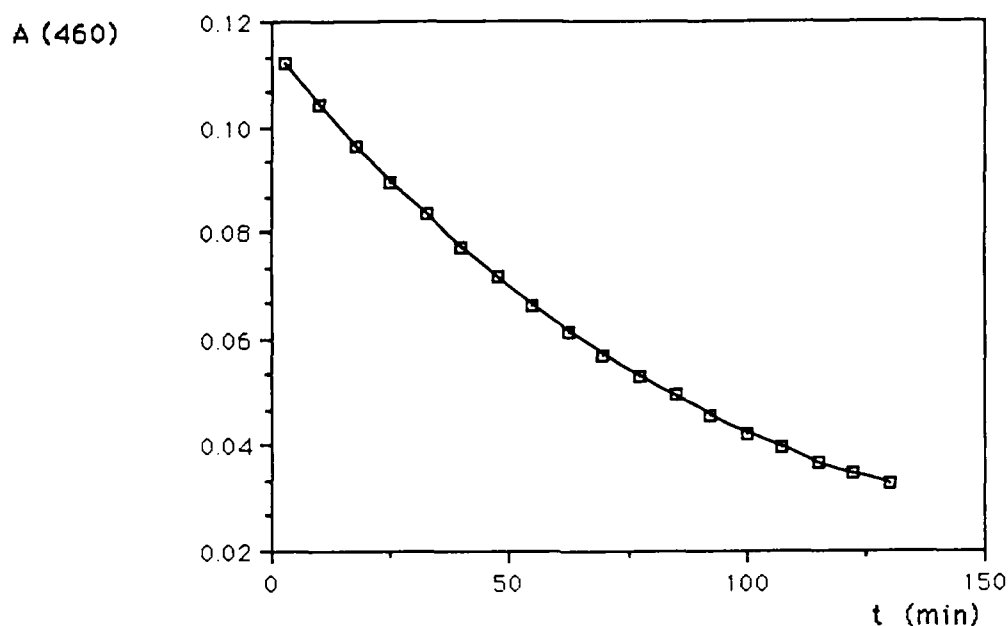
Figure 7. – Reaction of 1,4-NQ with HOO⁻ in H_2O/t-BuOH at pH 7.2; the red-colored intermediate followed spectrophotometrically

found in our investigations with H_2O_2. As expected, the nucleophilic attack of HO⁻ is by far less efficient than that of HOO⁻.

Apparent pH adjustments and spectrophotometric measurements in microheterogeneous systems are extremely difficult to achieve in a reproducible manner. The results (table 2) are, hence, affected with a limit of error which we would estimate to approx. 30%.

Under those conditions, we deduce from the data given in table 2, that the first step of the oxidative degradation of 1,4-NQ (nucleophilic addition of HOO⁻ and epoxidation of the intermediate, see scheme 2) is enhanced in SDS microemulsions by a factor of 4. The fact, that the epoxidation of the intermediate in the microheterogeneous system is slower as the pH is increased above 4, may be due to an integration and stabilization of the negatively charged intermediate into the interphase.

The substrate seems more protected when solubilized in positively charged aggregates; We cannot differentiate between a local pH effect near the interphase of these microheterogeneous systems, effecting the deprotonation of H_2O_2, and a in possible ionic binding between HOO⁻ and the positi

Table 2. - Rate constants of the reaction of 1,4-naphthoquinone (1,4-NQ) with H_2O_2 in different microemulsions at different apparent pH

| surfactant	pH	k_1 [s^{-1}]	k_2 [s^{-1}]	t_{max} [s]
---	3.6	2.85×10^{-5}	1.84×10^{-5}	4.36×10^4
SDS [a]	3.8	9×10^{-5}	7×10^{-5}	1.3×10^4
BMe_2TAC [b]	3.9	1×10^{-5}		
---	4.8	1.56×10^{-4}	8.00×10^{-5}	8.82×10^3
SDS	4.8	2×10^{-4}	6×10^{-5}	6.8×10^3
BMe_2TAC	4.8	3×10^{-4}		1.6×10^5
---	7.2	$> 2.5 \times 10^{-1}$	1.63×10^{-4}	$< 3.0 \times 10^1$
SDS	7.3	$> 2.5 \times 10^{-1}$	1×10^{-4}	$< 3.0 \times 10^1$
BMe_2TAC	7.3			1.6×10^4

[a] Sodium dodecyl sulfate

[b] Benzyl-dimethyl-tetradecyl ammonium chloride

vely charged aggregate, preventing a nucleophilic addition. The slow reactivity of the negatively charged intermediate these systems can be well explained by its stabilization by coulomb interactions with the positively charged Stern layer.

More details might be given in the report of the group of Drs. M.-T. Maurette and E. Oliveros in Toulouse who have done most of these experiments.

We have extended these studies to the more complex case of a hydroxy substituted naphthoquinone: 2-hydroxy 1,4-naphthoquinone (2-OH-1,4-NQ, lawsone). This substrate is easily deprotonated, yielding the same chromophore than the one produced by a nucleophilic addition of HOO^- (scheme 3).

Hydroxy substitution in position 2 should lead to slower rates of oxidative degradation upon exposure to H_2O_2 and HOO^-. This hypothesis is clearly shown with a relative limited series of data contained in table 3.

red coloured intermediates
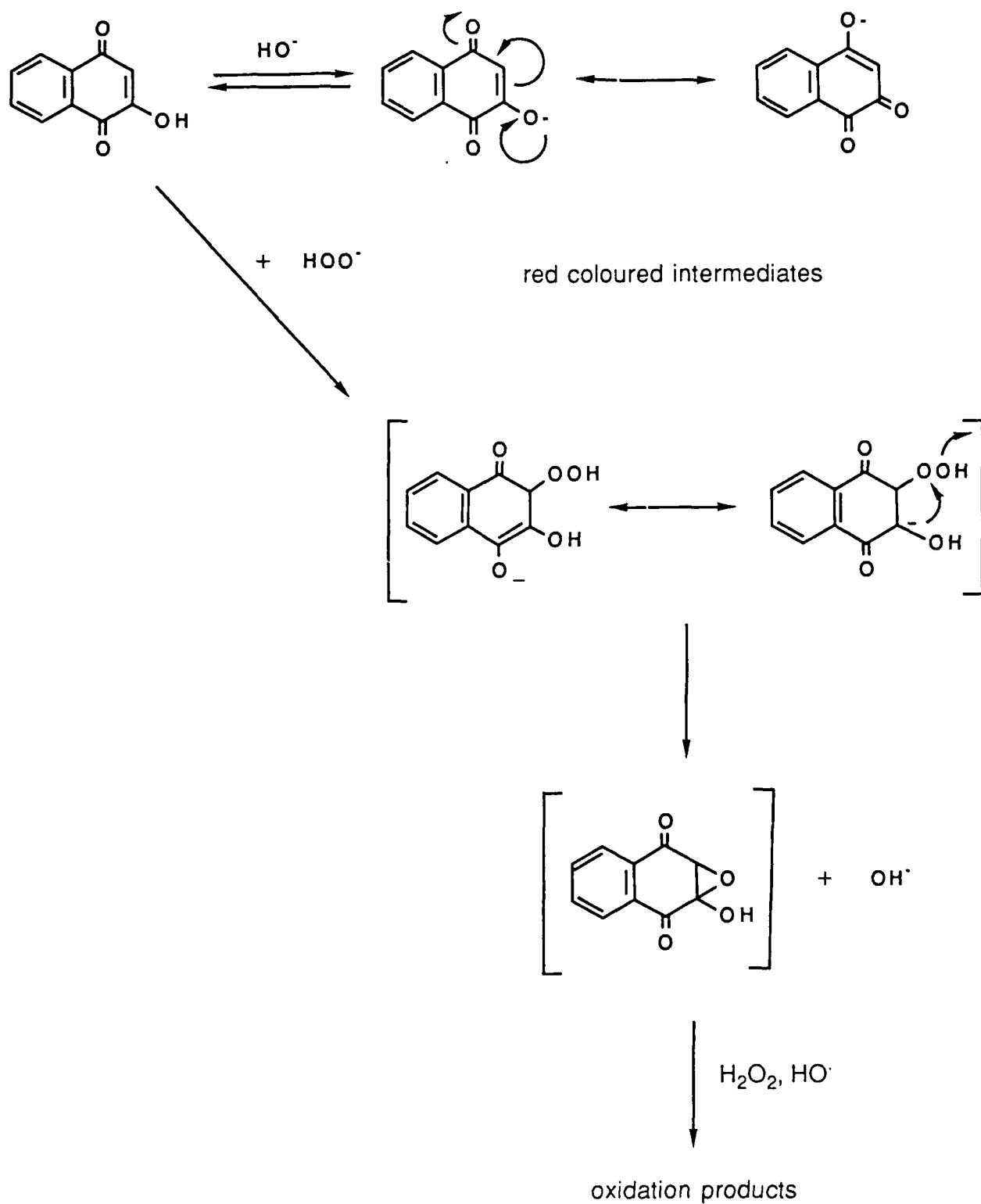
Scheme 3. – Sequence of reactions of peroxide anion (HOO⁻)with 2-hydroxy-1,4-naphthoquinone (2-OH-1,4-NQ)

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Table 3. – Rate constants of the reaction of 2-Hydroxy-1,4-naphthoquinone (2-OH-1,4-NQ) with H_2O_2 in different microemulsions at different apparent pH

1,4-NQ	surfactant	pH	k_1 [s⁻¹]	k_2 [s⁻¹]	t_{max} [s]
H	---	3.6	2.85×10^{-5}	1.84×10^{-5}	4.36×10^{4}
2-OH	---	3.6	1.6×10^{-6}	1.5×10^{-6}	2.0×10^{5}
H	SDS	3.8	9×10^{-5}	7×10^{-5}	1.3×10^{4}
2-OH	SDS	3.5	6.0×10^{4}	5.0×10^{-6}	5.4×10^{4}
H	BMe$_2$TAC	3.9	1×10^{-5}		
2-OH	BMe$_2$TAC	3.3	$> 2.5 \times 10^{-1}$	1.1×10^{-5}	$< 3.0 \times 10^{1}$
H	---	4.8	1.56×10^{-4}	8.00×10^{-5}	8.82×10^{3}
2-OH	---	4.8		4.6×10^{-6}	2.6×10^{4}
H	SDS	4.8	2×10^{-4}	6×10^{-5}	6.8×10^{3}
2-OH	SDS	4.8		1.8×10^{-5}	4.2×10^{3}
H	BMe$_2$TAC	4.8	3×10^{-4}		1.6×10^{5}
2-OH	BMe$_2$TAC	4.8	$> 2.5 \times 10^{-1}$		$< 3.0 \times 10^{1}$
H	---	7.2	$> 2.5 \times 10^{-1}$	1.63×10^{-4}	$< 3.0 \times 10^{1}$
2-OH	---	7.2	$> 2.5 \times 10^{-1}$	6.0×10^{-5}	$< 3.0 \times 10^{1}$
H	SDS	7.3	$> 2.5 \times 10^{-1}$	1×10^{-4}	$< 3.0 \times 10^{1}$
H	LS	7.4	$> 2.5 \times 10^{-1}$	5.7×10^{-5}	$< 3.0 \times 10^{1}$
2-OH	SDS	7.2	$> 2.5 \times 10^{-1}$	1.4×10^{-4}	$< 3.0 \times 10^{1}$
2-OH	LS	7.4	$> 2.5 \times 10^{-1}$	1.2×10^{-4}	$< 3.0 \times 10^{1}$
H	BMe$_2$TAC	7.3			1.6×10^{4}
2-OH	BMe$_2$TAC	7.2	$> 2.5 \times 10^{-1}$	4.3×10^{-5}	$< 3.0 \times 10^{1}$

All rate constants in table 3 have been calculated from experimental data measured from the depletion of either 2-OH-1,4-NQ or of the intermediate. In the latter case, absorbance measurements towards the end of the reaction are only taken in to account, where we assume that only minor concentrations of original substrate are present.

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The consumption of 2-OH-1,4-NQ is more difficult to observe spectrophotometrically, as the deprotonated form of the substrate and the intermediate of the epoxide formation show practically identical absorption bands. A specific analysis of this kinetics has been possible in measuring the absorbance at 360 nm (quinone function), until the spectrum shows a deviation from the isosbestic point (395 nm) observed at the beginning of the kinetic measurements.

It is interesting to note that, as far as the rate of the nucleophilic addition of HOO^- to the quinoid substrate is concerned, the anionic micro-emulsions containing SDS or LS show approximatively the same reactivity.

SUPEROXIDE ANION

H_2O_2 decomposition (scheme 1) is certainly not the method of choice for an investigation on the specific reactivity of superoxide anion in homogeneous and microheterogeneous media. The section on peroxide anion has clearly shown, that HOO^- would disturb the analysis of O_2^-, due to the facts that the nucleophilicity of the two intermediates is approximatively the same, that the reactivity of O_2^- as a radical is very weak in protic solvents and that the protonation/deprotonation equilibrium of superoxide anion at the pH values applied is shortening its lifetime.

We decided, therefore to investigate on the reactivity of superoxide anion in homogeneous and microheterogeneous media in generating O_2^- by pulse radiolysis. This method does not involve H_2O_2 or its deprotonated form other than by an eventual dismutation of O_2^- at reaction times far superior to those measured. On the other hand, the formation of HO radicals is efficiently quenched, either by the added sodium formate or by the cosurfactant, constituent of the microemulsion employed.

Under those experimental conditions [2], superoxide would react with naphthoquinone by two different paths of reaction, electron transfer (15) and nucleophilic addition (16).

If the consecutive reactions of the nucleophilic addition leading to the intermediate hydroperoxide are above a certain efficiency, the time dependent curve of the absorbance at 450 nm should show two superimposed decay curves: 1) a fast decay due to the retro transfer of the electron ((15) and (-15)), 2) a slower decay would indicate a depletion of the also red-colored intermediate of the nucleophilic addition.
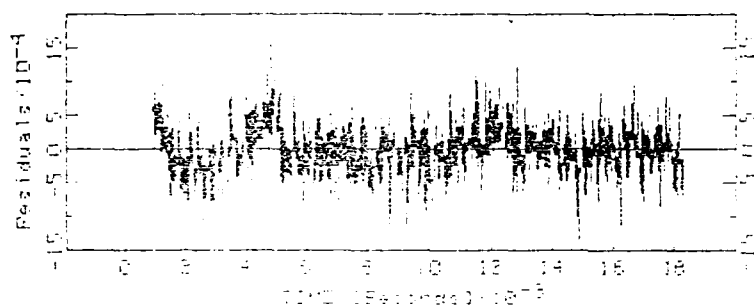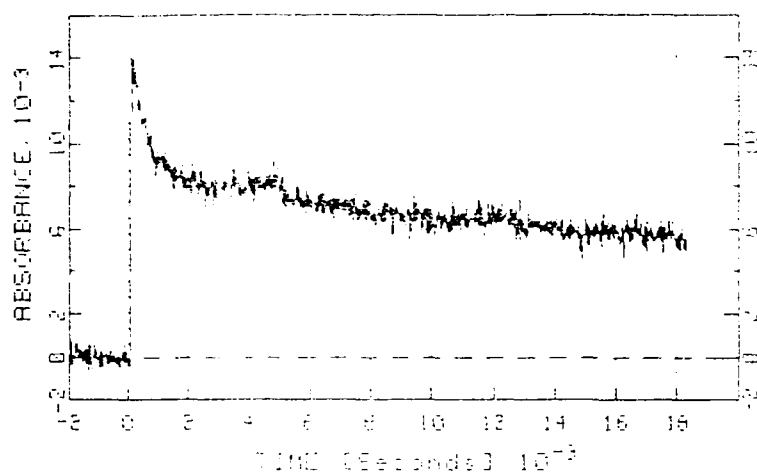
$$\text{(naphthoquinone)} + O_2^{\cdot -} \;\rightleftharpoons\; [\text{naphthoquinone}]^{+\cdot} + O_2 \qquad (15)$$

$$\text{(naphthoquinone)} + O_2^{\cdot -} \;\longrightarrow\;\longrightarrow\; \text{(2-OOH naphthoquinone radical)} \qquad (16)$$

$$\downarrow$$

oxidationproducts
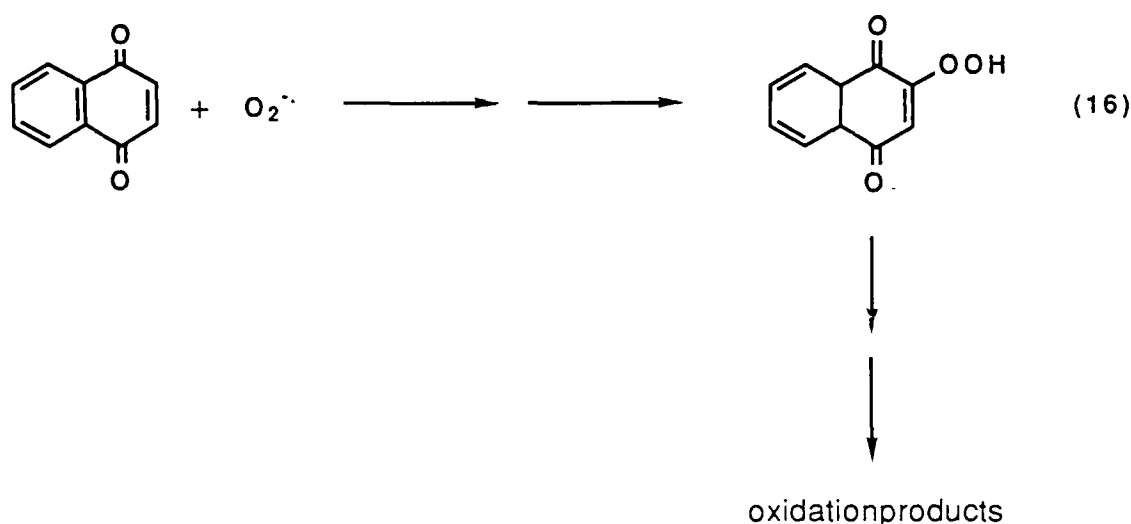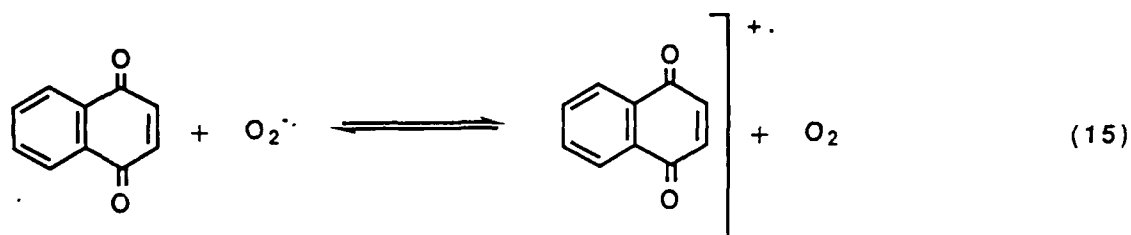
Scheme 4. – Modes of reaction of superoxide anion with naphthoquinone

Taking the example of 1,4-NQ dissolved in H_2O/tBuOH to which 5×10^{-2} M of sodium formate have been added, the time dependent absorbance after a pulse of 3 MeV shows in fact two superimposed decay curves which can be treated by (pseudo) first order kinetics (Figure 8).

The rate constants have been calculated to be $k_{15} = 1.8 \times 10^3$ s^{-1} and $k_{16} = 9.8 \times 10^1$ s^{-1}. Experiments without sodium formate show approximatively the same rate constant of electron transfer ($k_{15} = 1.2 \times 10^3$ s^{-1}) but an enhanced rate constant of 1,4-NQ consumption (4.8×10^2 s^{-1}), probably due to a reduction reaction of the non-trapped hydrogen atom. In the absence of any HO$^\cdot$ radical trapping agent, the rate constant of consumption of 1,4-NQ is found to be 8×10^3 s^{-1}, indicating a relative low reactivity of the substrate towards hydrogen abstraction. Under the latter conditions, the rate constant of electron transfer is found to be insignificantly enhanced ($k_{15} = 5.0 \times 10^3$ s^{-1}).
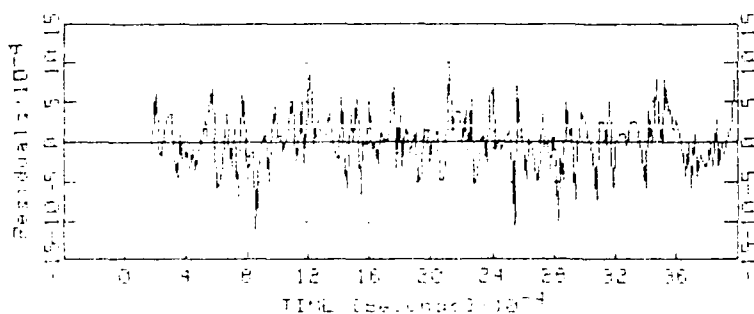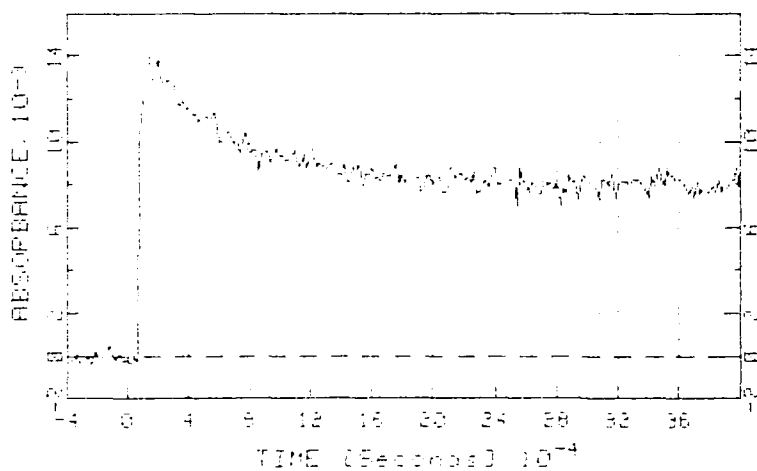
A supplement to this report will be added, as soon as the results of our experiments in microheterogeneous systems have been reproduced.

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Figure 8. – Absorbance (460 nm) after pulse radiolysis of 1,4-NQ in
$H_2O/tBuOH$ ([HCOONa] = 5 × 10^{-2} M. a) time scale: 10^{-3} s; b) time scale: 10^{-4} s

From the data shown above we can already deduce that the rate constant of the oxidative degradation induced by superoxide anion is by two to three orders of magnitude greater than the corresponding rate constant of the nucleophilic addition of HOO^-. However, at neutral pH, the steady state concentration of the latter is much larger, and we estimate the contribution of the superoxide anion reactions to the overall oxidative degradation for the substrates investigated as marginal.

HYDROXYL RADICAL

The investigations on the reactivity of the hydroxyl radical towards chosen organic and hydrophobic substrates could not be carried out due to a severe lack of time. The experiments which will involve perfluorinated as well as perhydrogenated microemulsions will be proposed in a second research proposal to ERO.

CONCLUSION

Under the present contract new perhydrogenated and perfluorinated microemulsions have been formulated and employed for investigations on the reactivity of the intermediates of the decomposition of H_2O_2 towards solubilized organic substrates.

Some anionic microemulsions have been found to accelerate the decomposition of H_2O_2. However, it is not clear at this moment, if these results can be related easily to the kinetic results of the nucleophilic addition of HOO^- and O_2^- initiating the oxidative degradation of the solubilized probe (1,4-naphthoquinone).

The rate of oxidative degradation depends strongly on the concentration of HOO^-, and best results have been found, again, in negatively charged microheterogeneous systems, th pH of which has been adjusted, in order to trigger the reaction. In applicatory work for new means of decontamination, this route is certainly worth to be followed. We estimate that the overall rate of oxidative degradation will be considerably enhanced by the reactivity of the $HO\cdot$ radical. Extrapolative work should, hence, make use of perfluorinated or partially fluorinated reactions systems.
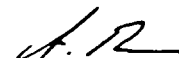
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FINANCIAL STATEMENT

As of May 31, 1989, SFR 105380.80 have been paid in salaries and chemicals leaving an uncovered balance of SFR 57427.35

Lausanne, May 31, 1989

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André M. Braun