ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS
IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

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DAJA45-85-C-0026, P00001

Fifth Interim Report
January - September 1987

The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. The report is intended only for the internal management use of the Contractor and the U.S. Government.
SUMMARY

In the second year of contract, the following parts of the original project have been accomplished:

1. Model calculations of the kinetics of the decomposition of \( \text{H}_2\text{O}_2 \) in \( \text{H}_2\text{O} \) and fitting of the model of sequence and rates of reactions to the experimental results.

2. Synthesis of perfluoro 2-methyl-2-propanol

3. Formulation of microemulsions containing totally perfluorinated components:
   - sodium perfluorocaprylate
   - perfluoro n-hexane
   - perfluoro 2-methyl-2-pentanol or perfluoro t-butanol
   - water

SHORT TERM PROJECTS

The projects for the third year of contract have already been transmitted (1). The work will be done in close collaboration with Dres. M.-T. Maurette and E. Oliveros (Université Paul Sabatier, Toulouse).

MECHANISM OF \( \text{H}_2\text{O}_2 \) DECOMPOSITION.
MODEL CALCULATIONS AND KINETIC EXPERIMENTS

After having accomplished an extensive investigation on the kinetics of \( \text{H}_2\text{O}_2 \) decomposition in \( \text{H}_2\text{O} \) and in perhydrogenated four components microemulsions (s. Final Report, 1986) we began in this second year of contract to study some sequences of reactions which may be of importance for the observed decomposition of \( \text{H}_2\text{O}_2 \) and which could be fitted to the experimental kinetic results in using rate constants independently determined.
The general scheme of reactions comprises:

\[ \begin{align*}
H_2O_2 + H_2O & \rightarrow HO_2^- + H_3O^+ \\ (1) \\
H_2O_2 + HO_2^- & \rightarrow OH^- + O_2^- + H_2O \\ (2) \\
O_2^- + H_3O^+ & \rightarrow HO_2^- + H_2O \\ (3) \\
O_2^- + HO_2^- & \rightarrow O_2 + HO_2^- \\ (4) \\
O_2^- + O_2^- + H_2O & \rightarrow O_2 + HO_2^- + HO^- \\ (5) \\
O_2^- + HO^- & \rightarrow O_2 + HO^- \\ (6) \\
HO_2^- + HO_2^- & \rightarrow H_2O_2 + O_2 \\ (7) \\
HO^- + H_2O_2 & \rightarrow HO_2^- + H_2O \\ (8) \\
HO^- + HO^- & \rightarrow H_2O_2 \\ (9) \\
2 H_2O & \rightarrow HO^- + H_3O^+ \\ (10) \\
\end{align*} \]

The rate and equilibrium constants have been taken as determined and published independently by different authors\textsuperscript{3-9}:

\[ \begin{align*}
K_1 &= 2.4 \times 10^{-12} M^3 \\
k_2 &= 8.6 \times 10^{-6} M^{-1} s^{-1} \textsuperscript{3} \\
k_3 &= 4.7 \times 10^{10} M^{-1} s^{-1} \textsuperscript{4} \\
K_3 &= 1.49 \times 10^{-5} M^4 \\
k_4 &= 8.5 \times 10^7 M^{-1} s^{-1} \textsuperscript{5} \\
k_5 &= 6 M^{-1} s^{-1} \textsuperscript{6} \\
\end{align*} \]
\[ k_6 = 1 \times 10^{10} \text{M}^{-1} \text{s}^{-1} 6 \]
\[ k_7 = 8.5 \times 10^5 \text{M}^{-1} \text{s}^{-1} 7 \]
\[ k_8 = 2.65 \times 10^7 \text{M}^{-1} \text{s}^{-1} 8 \]
\[ k_9 = 5.5 \times 10^9 \text{M}^{-1} \text{s}^{-1} 9 \]
\[ k_{10} = 1.3 \times 10^{11} \text{M}^{-1} \text{s}^{-1} 10 \]

The fitting to our experimental results (o) is shown in figures 1 and 2. The model fits in fact excellently yielding only slight changes for \( k_1 \) and \( k_5 \), as well as a major variation on \( k_3 \) which has to be taken as a first order rate constant (7.0 x 10^5 s^{-1}).

A complete fitting requires some experiments with times of reaction between 700 and 1000 h in order to confirm the acceleration of the reaction, as predicted by the model (figures 1 and 2). These experiments are currently undertaken in an appropriately stabilized equipment. The results already obtained confirm qualitatively the shape of the calculated curves.

**SYNTHESIS OF PERFLUORINATED 2-METHYL-2-PENTANOL**

Perfluoro 2-methyl-2-pentanol has been prepared using and optimizing the procedure of K.V. Scherer, Jr et al.\(^\text{11}\): 

\[ \text{CF}_3\text{CF}_2\text{CF}=\text{C(CF}_3\text{)}_2 \xrightarrow{\text{KF, N}_2\text{O}_4, \text{DMA}} \text{CF}_3\text{CF}_2\text{CF}_2\text{C(CF}_3\text{)}_2\text{NO} \] (11)

\[ \text{CF}_3\text{CF}_2\text{CF}_2\text{C(CF}_3\text{)}_2\text{NO} \xrightarrow{\text{O}_2} \]
\[ \text{CF}_3\text{-CF}_2\text{-CF}_2\text{-C(CF}_3)_2\text{ONO} \quad (12) \]

\[ \text{CF}_3\text{-CF}_2\text{-CF}_2\text{-C(CF}_3)_2\text{ONO} \xrightarrow{\text{H}_2\text{O}} \]

\[ \text{CF}_3\text{-CF}_2\text{-CF}_2\text{-C(CF}_3)_2\text{OH} \quad (13) \]

The synthesis is currently undertaken on a level of 50 g of substrate in order to prepare sufficient material for the planned kinetic experiments.

**FORMULATION OF NEW MICROEMULSIONS CONTAINING THREE PERFLUORINATED COMPONENTS AND WATER**

Following the procedure already published\(^1,2\), three new pseudo-ternary phase diagrams have been established concerning the following formulations:

- sodium perfluorocaprylate/perfluoro 2-methyl-2-pentanol (1/1), perfluoro n-hexane, water (figure 3)
- sodium perfluorocaprylate/perfluoro 2-methyl-2-pentanol (1/2), perfluoro n-hexane, water (figure 4)
- sodium perfluorocaprylate/perfluoro t-butanol (1/2), perfluoro n-hexane, water (figure 5)

**CONCLUSION**

The results of the work made possible through this contract provide the basis for:
- the confirmation of the observed carboxylate catalyzed decomposition of \(\text{H}_2\text{O}_2\) in perfluorinated microemulsions,
- the determination of \(\text{OH}\) radical recombination in a chemically inert environment.
- the application of perfluorinated microheterogeneous media for oxidation reactions and efficiency determinations with respect to aqueous and perhydrogenated microheterogeneous media.

REFERENCES

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3 S. Rinaudo, thesis, Université de Haute Alsace, Mulhouse, 1985


9 J. Rabani, S.O. Nielsen, J. Phys. Chem. 73, 3736 (1969)

10 Z. Haniotis, Ciba-Geigy AG, Basel, private communication


FINANCIAL STATEMENT

As of August 30, 1987, SFR 57534.30 have been paid in salaries and chemicals leaving an uncovered balance of SFR 34766.50 since the last payment due June 30, 1987 has not yet been credited.

Lausanne, October 24, 1987

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Figure 1. - Decomposition of H$_2$O$_2$ in H$_2$O (pH 7.2)
Volumetric Measurements of oxygen evolution and fitted curve of reaction model
Figure 2. - Decomposition of $H_2O_2$ in $H_2O$ (pH 7.2)
Manganometric Measurements of $H_2O_2$ and fitted curve of reaction model
Figure 3. - Pseudo ternary phase diagram of a mixture of sodium perfluorocaprylate/perfluoro 2-methyl-2-pentanol (1/1), perfluoro n-hexane and water
Figure 4. - Pseudo ternary phase diagram of a mixture of sodium perfluoro-caprylate/perfluoro 2-methyl-2-pentanol (1/2), perfluoro n-hexane and water.
Figure 5. - Pseudo ternary phase diagram of a mixture of sodium perfluorocaprylate/perfluorot-butanol (1/2), perfluoro n-hexane and water.