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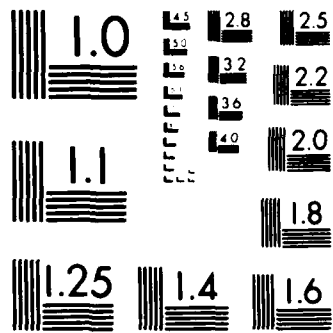
REACTIONS OF PORPHYRINS IN SURFACTANT ASSEMBLIES
MICROEMULSIONS AND IN SOLUTIONS(U) ROCHESTER UNIV NY
DEPT OF CHEMISTRY D G WHITTEN 25 JUN 87 ARO-20766 7-CH
DAG29-84-K-0011 F/G 7/3

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REACTIONS OF PORPHYRINS IN SURFACTANT ASSEMBLIES, MICROEMULSIONS
AND IN SOLUTIONS

FINAL REPORT

DAVID G. WHITTEN

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JUNE 25, 1987

U. S. ARMY RESEARCH OFFICE

CONTRACT/GRANT NUMBER: DAAG29-84-K-0011

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE		4 PERFORMING ORGANIZATION REPORT NUMBER(S)	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)		5 MONITORING ORGANIZATION REPORT NUMBER(S) ARO 20766.7-CH	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry	6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) University of Rochester Rochester, New York 14627		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-84-K-0011	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Reactions of Porphyrins in Surfactant Assemblies, Microemulsions and in Solutions.			
12 PERSONAL AUTHOR(S) David G. Whitten			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 12/1/83 TO 4/30/87	14. DATE OF REPORT (Year, Month, Day) 1987, June, 25	15. PAGE COUNT 3
16 SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		porphyrins, monolayers, reversed micelles, micelles, photochemistry, photooxidations, singlet oxygen, superoxide.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Our ARO-sponsored research has focused on three different areas, all of which center around photochemical reactions occurring in microheterogeneous media. The first area of investigation has been of photoisomerizations and related processes occurring in spread monolayer films at the air-water interface as well as in supported multilayer assemblies. Our studies in this area have demonstrated that reactivity in the spread films can be profoundly different from that occurring in solution. Moreover we have been able to investigate systematically specific factors such as the effect of film compression and the presence of various liquids such as water within or in contact with the film or assembly. A number of our findings in this area have been published and more publications will result from studies not yet completed. We have also studied extensively reactions occurring across an interface. Specifically we have examined photooxidations which are initiated from a light-absorbing sensitizer contained in a film or an assembly but have the chemical consequence of reaction of a (cont'd)			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

cont'd: (19)

solute either contained at a different site in the assembly or present in a contacting aqueous or mixed aqueous-organic solution. While we have found that these interface-spanning reactions can be quite efficient in certain cases, we have also investigated extensively environmental factors which can retard or eliminate them. Most of the reactions that we have investigated thus far originated by sensitization of singlet oxygen, a highly reactive but relatively short-lived reagent. Singlet oxygen has been found to migrate with relative ease through a number of different media, although we find that penetration of highly condensed or compressed films clearly retards the migration of the active oxygen, at least during its excited state lifetime. Although we have used a variety of light-absorbing molecules to initiate these reactions, most of our studies have focused on some synthetic porphyrins which absorb relatively strongly in the visible and near ultraviolet regions. These porphyrins have been specifically designed and synthesized due to their excellent film-forming abilities.

The synthetic porphyrins that we have used exist as various stereoisomers; the third part of our studies has been an investigation of the reactivities of these various stereoisomers of synthetic porphyrins at interfaces. We have been particularly interested in the relative ability of these porphyrins to be incorporated in or pass through an interface such as that formed when phospholipids are dispersed in water. We have found that the reactivity of different porphyrin stereoisomers at interfaces differs dramatically from that observed in solution. For example, we find the porphyrins are much stronger bases at anionic interfaces and undergo metal ion incorporation, in some cases, several orders of magnitude more rapidly than in solution. Preliminary results suggest that the different behavior of porphyrin stereoisomers can be largely associated to different differential orientation at charged interfaces. This should result in pronounced differences in the ability of the porphyrins to act as photosensitizers in a number of different photochemical reactions.

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