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CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICELLAR MEDIA AND MICROEMULSIONS

VII- EFFECT OF THE INTERFACE ON THE REACTIVITY OF EXCITED STATES

REINE SAKELLARIOU-FARGUES, MARIE-THERESE MAURETTE, ESTHER OLIVEROS
MONIQUE RIVIERE and ARMAND LATTES

Laboratoire des I.M.R.C.P., E.R.A. au C.N.R.S. n° 264, Université Paul
Sabatier - 31062 Toulouse Cedex - France

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Abstract - Study of the photodimerization of coumarin in micellar media and microemulsions shows that the orientation and the concentration of molecules in the interfacial film can favor reactions involving just one of the excited states (the singlet state in this case).

INTRODUCTION

Photocycloadditions of cyclenone moieties are important in many biological processes (photodimerization of DNA bases and of drugs like furocoumarins, photocycloaddition of such drugs with DNA bases, etc.).

The regioselectivity and stereoselectivity of these cycloadditions depend on the nature of the reaction medium. We were therefore interested to study such reactions in organized media which could mimic biological systems. Micellar solutions and microemulsions have been widely used as models for complex bioaggregates such as membranes and other cell organelles [1]. We had previously chosen [2] the photodimerization of isophorone to test these reaction media.

The preferential localization of isophorone at the solvent interface allows a combination of the effects of "proximity" and orientation of the substrate molecules, leading to particularly high yields and regioselectivities. However isophorone was dissolved by hydrocarbon solvents and the observed results were consistent with a competition between two reactions[3] :

- reaction at the interface leading to the H-H (head to head) dimer
- reaction in the hydrocarbon phase leading to the H-T (head to tail) dimer.

In order to circumvent this competitive reaction and observe a reaction occuring only at the interface, we decided to study the photodimerization of coumarin in organized media. This compound which is of biological interest, is neither soluble in water nor in cyclohexane, but is soluble in micellar media (solutions of sodium dodecyl sulfate : SDS) and in microemulsions (water-SDS/butanol (2/1)-cyclohexane). Coumarin is thereby localized at the interface.

Photodimerization of this compound presents another interesting feature. Depending on the nature of the solvent, two reaction mechanisms are possible, leading to two different stereoisomers [4,5,6,7].

The anti H-H dimer (II) is the only dimer formed in non polar solvents while both the syn (I) and the anti (II) dimers are obtained in polar solvents (fig. 1).

But even in polar solvents, high concentrations of coumarin are required to obtain a high syn/anti ratio (eg. I/II = 13 in a 0.3 M solution of coumarin in methanol)[6]. From a study of the reaction mechanism, it was deduced that the anti isomer resulted from the triplet state and that the syn isomer is generated from a singlet excimer [5].

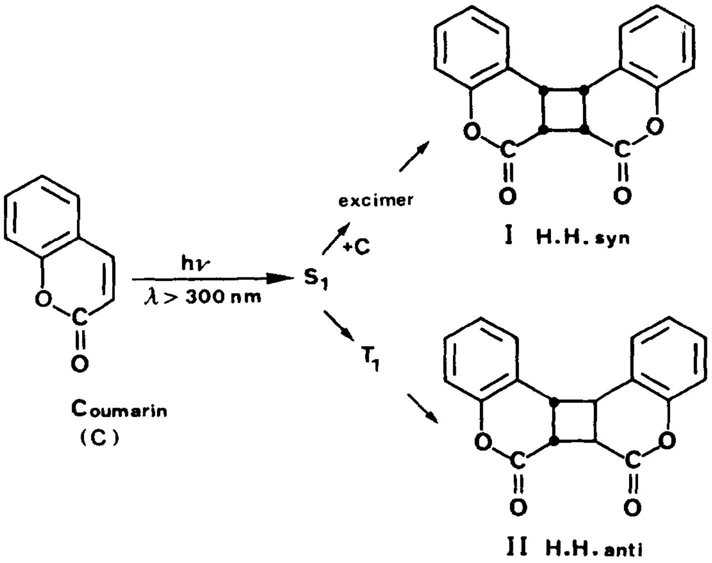

Figure 1

It was thought that the microstructure of the micellar medium or microemulsion would have an influence on the orientation of coumarin molecules in this photochemical reaction. In a recent paper, K. Muthuramu et al. [8] obtained satisfactory results using a micellar reaction medium : 21% of syn H-H dimer after 22 h irradiation in a 0.02 M aqueous solution of SDS. We have investigated such reactions in microemulsions, from both a mechanistic and preparative standpoint.

RESULTS AND DISCUSSION

Coumarin was photolyzed in an aqueous solution of SDS (5% by weight) and in several microemulsions (water-SDS/Butanol-cyclohexane). Microemulsions were chosen from different areas of the phase diagram (fig. 2, table 1).

The microemulsion structure depended on the proportions of its constituents. Typical normal or reversed "micelles" were only observed in microemulsions containing high concentrations of water or hydrocarbon. In the intermediate area, the structures of the aggregates and the continuous phase are not clearly established. In microemulsions 8, 10 and 41 the continuous phase was mainly cyclohexanic, while for microemulsions 101 it was aqueous. Microemulsions 69 and 90 were situated in the intermediate area.

The coumarin solutions were irradiated with 350 nm lamps at room temperature, and the reaction was followed by U.V. spectrometry. Decrease in absorption at 310 nm was used to measure the rate of coumarin conversion.

In organized media, irradiation led to the syn H-H dimer only (MP = 276°C in agreement with the results of Morrison et al. 6).

The yields of dimer I, calculated from the coumarin transformed, were over 90% in all cases. Analysis by ^1H NMR spectroscopy of the crude irradiated mixture indicated only small quantities of the anti H-H dimer (II) and/or its decomposition products ($<$ 5%).

Table II shows that, even with low concentrations (ten times lower than in ethanol) the yield of dimer I in micellar media and microemulsions were much higher than those obtained in ethanol.

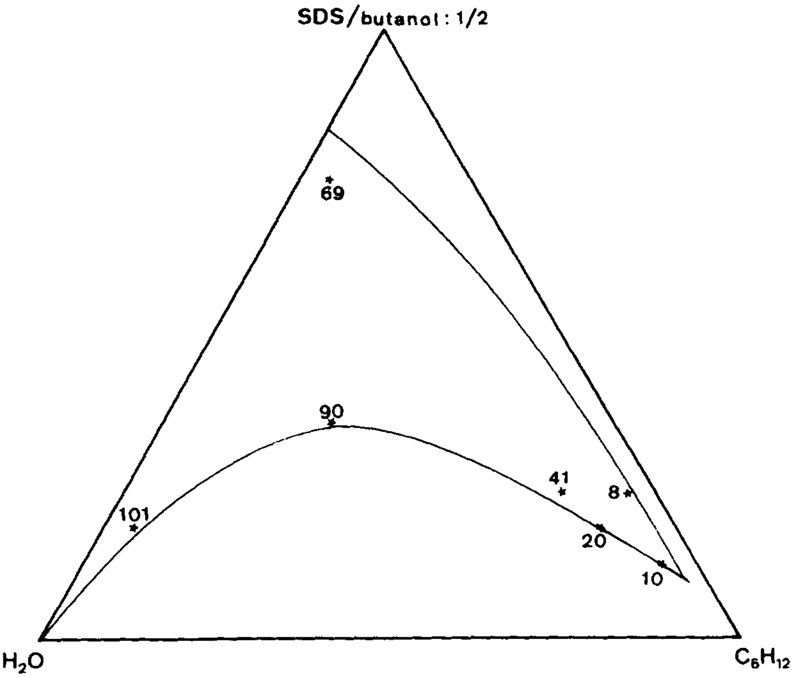

Figure 2

It appears therefore, that in micellar media and microemulsions, only one photoreaction takes place, namely, the formation of the H-H dimer I through the excited singlet state of coumarin.

We also noticed that this photoreaction was inhibited when the tubes were flushed with argon. This could be due to the same phenomenon as the CCl_4 effect described by Morrison (5) leading to a triplet reaction.

We conclude that the triplet reaction leading to dimer II does not take place in organized media. This probably results from the orientation of the coumarin molecules at the interface, only allowing formation of the syn dimer. Results on bis furocoumarin reactions [9] lend support to this explanation. The geometry of these molecules forces the syn cycloaddition.

These results show that the reaction in a microemulsion inhibits the triplet state reaction in coumarin photodimerization, and confirm the role played by interfacial organization in the reaction mechanism. Effects of the orientation and high local concentration of the substrate were thought to explain the reaction observed.

Table I : Composition of microemulsions (% in weight)

microemulsions constituents	8	10	20	41	69	90	101
H_2O	2,9%	5,2%	10,3%	13,1%	19,6%	40,0%	81,3%
cyclohexane	72,5%	82,2%	71,0%	62,3%	4,2%	24,3%	3,7%
SDS	8,2%	4,2%	6,2%	8,2%	25,4%	11,9%	5%
butanol-1	16,4%	8,4%	12,4%	16,4%	50,8%	23,8%	10%

Table II : Irradiation of coumarin in various media

Media	Concentrations	Irradiation time	% conversion (N_2)	% conversion (vacuum)
ethanol	0,3 M	120 h	25 %	
micellar solution	0,03 M	120 h	97 %	
microemulsion 8	0,034 M	120 h	60 %	
" 10	0,034 M	120 h	62 %	
" 10	0,034 M	85 h		92 %
microemulsion 20	0,034 M	120 h	65 %	
" "	0,034 M	190 h	83 %	
" "	0,034 M	85 h		92 %
microemulsion 41	0,034 M	120 h	59 %	
"	0,034 M	190 h	84 %	
"	0,034 M	85 h		85 %
microemulsion 69	0,034 M	120 h	75 %	
"	0,034 M	190 h	89 %	
microemulsion 90	0,034 M	120 h	60 %	
"	0,034 M	190 h	76 %	
microemulsion 101	0,034 M	120 h	89 %	

However K. Muthuramu et al. [10] using 7-alkoxy coumarins only observed the formation of syn H-T dimers in organic solvents and micellar media, with no orientation reversal. We suggest that the critical factor in these dimerizations is the enhancement of local concentration of substrate in both micellar and microemulsion systems.

REFERENCES

N.J. Turro, M. Grätzel and A.M. Braun, Angew. Chem. Intern. Ed., 19, 675 (1980)

[2] R. Fargues, E. Oliveros, M.T. Maurette, M. Rivière and A. Lattes, Nouveau Journal de Chimie 3 (7), 487 (1979)

[3] R. Fargues-Sakellariou, E. Oliveros, M.T. Maurette, M. Rivière and A. Lattes, J. Photochem. 18, 101 (1982)

[4] G.S. Hammond, C.A. Stout and A.A. Lamola, J. Amer. Chem. Soc., 86, 3103 (1964)

[5] F. Hoffman, P. Wells and H. Morrison, J. Org. Chem., 36 (1971)

[6] H. Morrison, H. Curtis and T. Mac Dowell, J. Amer. Chem. Soc., 88, 5415 (1966)

[7] G.O. Schenck, I. Von Wilucki and C.H. Krauch, Chem. Ber., 95, 1409 (1962)

[8] K. Muthuramu and V. Ramamurthy, J. Org. Chem. 47, 3976 (1982)

[9] J. Gervais and F.C. de Schryver, Photochem. and Photobiol., 21, 71 (1975)

[10] K. Muthuramu, N. Ramnath and V. Ramamurthy, J. Org. Chem., 48, 1872 (1983)