

## CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICELLAR MEDIA AND MICROEMULSIONS IV: CONCENTRATION EFFECTS ON ISOPHORONE DIMERIZATION

REINE SAKELLARIOU-FARGUES, MARIE-THÉRÈSE MAURETTE,  
ESTHER OLIVEROS, MONIQUE RIVIÈRE and ARMAND LATTES

*Equipe de Recherche associée au CNRS 264, Université Paul Sabatier, 31062 Toulouse  
Cédex (France)*

(Received April 21, 1981)

### Summary

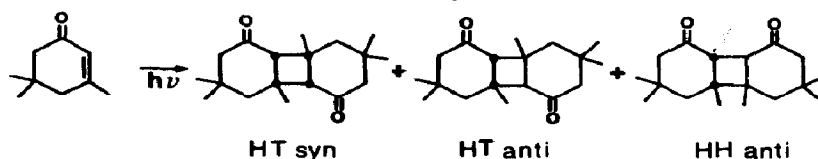
A study of concentration effects in isophorone photodimerization shows the importance not only of interfacial processes but also of selective extraction of the reactants and products. From this work, another feature can be pointed out: microemulsification is a general phenomenon and microemulsions containing a polar component as the "oil" can be prepared.

### 1. Introduction

Recent studies [1 - 3] concerning the photochemical reactivity in microemulsions have given an indication of the interest in using these media, which allow the effects of the polarity and of the bringing together and orienting of the substrate molecules to be combined.

In a preceding paper [2] we reported that isophorone dimerization is carried out more rapidly and with higher yields in micellar media and in microemulsions than in solvents. Furthermore the reaction presents a high regioselectivity. Similar results have recently been obtained with cyclopentenone in micellar media [4, 5].

In solvents, isophorone irradiation leads to the formation of three photodimers (HT, head to tail; HH, head to head):



Previous studies [6, 7] have shown that the dimerization rates are higher in polar and protic media than in apolar solvents. This effect is especially important for the HH isomer, the formation of which is clearly favoured by the solvent polarity (methanol, 80% HH; cyclohexane, 10% HH).

According to Chapman *et al.* [6], the photodimerization involves triplet states of isophorone. These researchers consider the possibility that two triplet species lead to the two observed dimers. No molecular association has been established for this reaction, in the ground state or in the excited state.

In microemulsions the quantity of HH isomer obtained is always substantial (50% - 90%). It should be noted that even when the continuous phase is cyclohexanic a minimum of 50% of HH regioisomer is obtained, although isophorone is soluble in cyclohexane but not in water.

In order to explain this phenomenon, we have put forward the assumption of a preferential reactivity of isophorone at the interface [2]. According to this interpretation, a variation in the ratio of HH and HT isomers can be expected for such a medium if the isophorone concentration is modified.

## 2. Experimental section

### 2.1. Materials

Sodium dodecylsulphate (SDS) (Prolabo) was recrystallized twice from absolute ethanol. 1-Butanol (Prolabo Normapur) and isophorone were distilled before use. Spectrograde cyclohexane (Merck) was used as received.

### 2.2. Preparation of the microemulsions

The determination of the isotropic area of the pseudoternary phase diagrams (Figs. 1 and 2) was accomplished by titration. Initial compositions

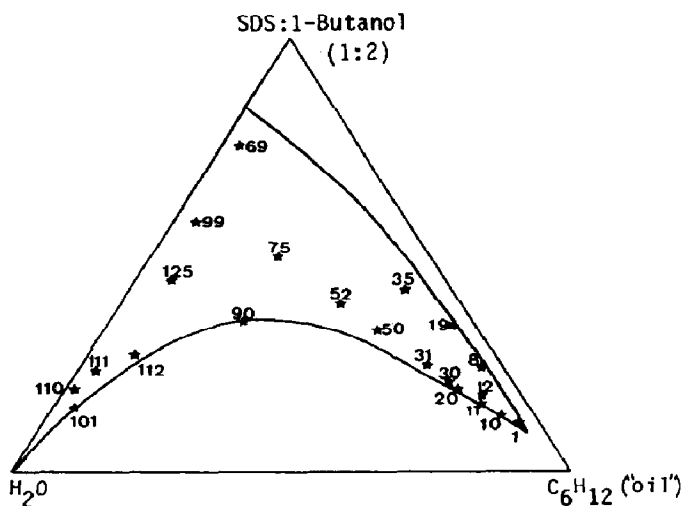


Fig. 1. Localization of microemulsions in the pseudoternary water-(SDS:1-butanol)-cyclohexane phase diagram.

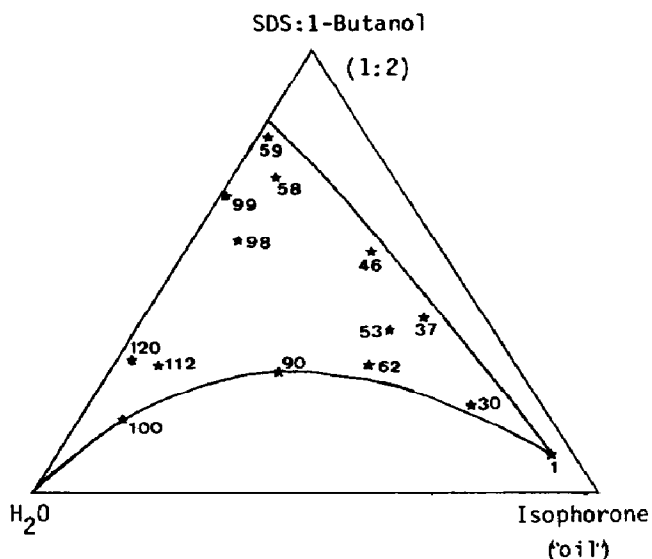


Fig. 2. Localization of microemulsions in the pseudoternary water-(SDS:1-butanol)-isophorone phase diagram.

of "oil" and water or of "oil", surfactant and cosurfactant (1:2) were titrated to the clearing point with homogeneous mixtures of SDS, butanol and water. All the microemulsions used in the photochemical experiments were prepared in the same way according to the compositions listed in Tables 1 and 2.

TABLE 1  
Composition of cyclohexanic microemulsions

Component	Microemulsion			
	12	31	101	125
Water	7.2	12.7	82.5	47.9
Cyclohexane	80.2	63.0	3.1	6.8
SDS	4.2	16.2	4.8	15.1
1-Butanol	8.4	8.1	9.6	30.2

TABLE 2  
Composition of microemulsions containing isophorone as "oil"

Component	Microemulsion									
	30	46	58	59	90	98	99	100	112	120
Water	10.9	12.5	17.1	16.8	43.1	34	32.9	76.8	65.2	68.3
Isophorone	69	32.6	8.8	2.2	29.9	8.7	1.7	6.85	6.9	2.3
SDS	6.7	18.3	24.7	27	9	19	21.8	5.45	9.3	9.8
1-Butanol	13.4	36.6	49.4	54	18	38.1	43.6	10.9	18.6	19.6

The microemulsions are numbered following isoconductivity lines starting from the water–oil area. Microemulsions having the same tens number are situated on approximately the same conductivity line [8].

### 2.3. Isophorone photolysis

The reaction mixtures were deaerated by bubbling nitrogen through for 30 min just prior to each run and were then irradiated in a Rayonet model RPR 100 photochemical reactor equipped with 16 RPR 2537 Å lamps.

### 2.4. Determination of the dimer yields

SDS was removed from the irradiated samples diluted with water by chromatography with an ion exchange resin (Amberlyst A 29). The non-ionic fraction, eluted with  $(\text{CH}_3)_2\text{CO}$  and  $\text{CHCl}_3$ , was then analysed by gas-liquid chromatography and nuclear magnetic resonance according to a previously described procedure [2]. Microemulsions containing known quantities of photodimers were treated in the same manner to check that the photodimer ratio was not modified during the process.

## 3. Results

### 3.1. Concentration effects

To confirm the hypothesis that there is a preferential reactivity of isophorone at the interface, it seemed interesting to study the variation in the ratio of HH and HT isomers as a function of the isophorone concentration in a microemulsion having a cyclohexanic continuous phase (Fig. 1, microemulsion 12).

As indicated in Table 3, an increase in the HH isomer yield is observed when the isophorone concentration increases from 0.025 M to 0.2 M; for higher concentrations the quantity of HH isomer remains constant.

TABLE 3

Solvent	Concentration	Yield of HT isomer <sup>a</sup> (%)	Yield of HH isomer <sup>a</sup> (%)
Cyclohexane	0.1 M	90	10
Methanol	0.1 M	20	80
Microemulsion 100	0.1 M	5	95
Microemulsion 99	0.1 M	10	90
Microemulsion 69	0.1 M	15	85
Microemulsion 46	0.1 M	15	85
Microemulsion 12	0.025 M	40	60
	0.1 M	30	70
	0.2 M	25	75
	0.4 M	25	75
	0.6 M	25	75

<sup>a</sup>After irradiation for 24 h at 254 nm.

These observations can be explained by the following facts.

(i) At the interface the HH dimerization rate is higher than the HT dimerization rate:

$$(v_{HH})_i \gg (v_{HT})_i$$

(ii) In cyclohexane the opposite phenomenon occurs:

$$(v'_{HH})_{\text{cyclohexane}} \ll (v'_{HT})_{\text{cyclohexane}}$$

(iii) At the interface the rate of HH isomer formation is much higher than the rate of HT formation in cyclohexane, probably because the rate constants are different but also because local concentration effects are important in the micelles:

$$(v_{HH})_i \gg (v_{HT})_{\text{cyclohexane}}$$

(iv) The photodimer produced at the interface does not remain in the micelle; it is then replaced by new isophorone molecules. Isophorone is consequently extracted in a continuous way from the cyclohexanic phase.

As long as the interface is not saturated, the concentration effect on the HH dimerization rate inside the micelle is preponderant and the yield of HH isomer increases with the isophorone concentration.

When the interface is saturated, the local isophorone concentration and consequently the HH dimerization rate are constant in the micelle. The rate of HT isomer formation increases then in the cyclohexanic phase, but this effect is balanced by the continuous extraction of isophorone towards the disperse phase. Thus the ratio of HH and HT isomers remains almost constant.

### 3.2. Microemulsions in which isophorone replaces the non-polar "oil"

During our study of the concentration effects, isophorone was found to be easily soluble in the microemulsions under investigation.

In microemulsion 12 (Fig. 1) it was possible to add up to 50 vol.% of isophorone and still to retain a transparent stable monophasic system. This led us to consider that isophorone could replace the hydrocarbon in microemulsions.

We therefore studied systems containing four compounds: water-(SDS: butanol (1:2))-isophorone. Several mixtures of these four compounds led to stable and transparent media, apparently monophasic. The phase diagram shown in Fig. 2 is quite similar to that for the cyclohexanic microemulsions in Fig. 1.

As this was the first time that a polar substance had been used as "oil", it was difficult to decide whether these systems were true microemulsions or cosolubilized systems.

However, for system 90 (Fig. 2), containing significant quantities of two non-miscible liquids (water, 43%, isophorone, 29.9%), it is unlikely that cosolubilization was attained just by adding small quantities of SDS and butanol. Furthermore, we checked, for this system, that the mixture (iso-

phorone–water–butanol) was heterogeneous and that the addition of SDS led immediately to a monophasic medium. Mixture 30 was tested in the same way. It is difficult to explain these facts except by an organization of the medium due to the surfactant.

The results obtained by irradiation of the systems containing isophorone as “oil” in comparison with those previously obtained for cyclohexanic microemulsions could give information on their structure.

Systems 30 to 120 (Fig. 2), in which isophorone is one of the constituents, were irradiated (254 nm) for 24 h. The results are listed in Table 4.

TABLE 4

<i>Solvent</i>	<i>Yield of HT isomer (%)</i>	<i>Yield of HH isomer (%)</i>
Isophorone:butanol (90:10)	40	60
Pure isophorone	60	40
Microemulsion 30	25	75
Microemulsion 46	15	85
Microemulsion 58	10	90
Microemulsion 59	10	90
Microemulsion 90	20	80
Microemulsion 98	10	90
Microemulsion 99	10	90
Microemulsion 100	25	75
Microemulsion 112	10	90
Microemulsion 120	10	90

For all the systems studied, the yield of HH isomer is much higher than that from pure isophorone or from isophorone–butanol mixtures. This shows that a significant quantity of isophorone reacts in a polar medium and probably also in a structured medium. In most cases, the results are in fact similar to those obtained in oil–water cyclohexanic microemulsions or in micellar media.

For system 30 (Fig. 2), in which the quantity of isophorone is substantial, we obtained the same result as in oil–water cyclohexanic microemulsions with an isophorone concentration superior to 0.2 M.

Systems 90 and 100 (Fig. 2) situated on the demixing curve have a particular behaviour. They are homogeneous before irradiation and become biphasic after isophorone photolysis, *i.e.* after the isophorone has partly disappeared, giving rise to the dimer. Water–(SDS:butanol)–cyclohexane microemulsions situated in the same area of the phase diagram behave in the same way when cyclohexane is removed by evaporation.

All these results are consistent with the existence of a microstructure for the water–(SDS:butanol)–isophorone medium.

#### 4. Conclusion

Two results must be singled out from this study.

(i) In microemulsions a phenomenon of continuous extraction of reactants and products occurs during photochemical processes. Owing to this, microemulsions are found to be interesting systems which allow high conversion rates and yields to be obtained.

(ii) The formation of a microemulsion is a general phenomenon which is not limited to surfactant-cosurfactant-water-hydrocarbon systems. Our work has shown that a polar component, isophorone, can replace the hydrocarbon.

#### References

- 1 I. Rico, M. T. Maurette, E. Oliveros, M. Rivière and A. Lattes, *Tetrahedron Lett.*, (48) (1978) 4795.
- 2 R. Fargues, M. T. Maurette, E. Oliveros, M. Rivière and A. Lattes, *Nouv. J. Chim.*, 3 (1979) 487.
- 3 I. Rico, M. T. Maurette, E. Oliveros, M. Rivière and A. Lattes, *Tetrahedron*, 36 (1980) 1779.
- 4 K. H. Lee and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, (11) (1979) 493.
- 5 K. H. Lee and P. de Mayo, *Photochem. Photobiol.*, 31 (1980) 311.
- 6 O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker and A. A. Griswold, *Rec. Chem. Prog.*, 28 (1967) 167.
- 7 R. E. Koning, G. J. Visser and A. Vos, *Recl. Trav. Chim. Pays-Bas*, 89 (1970) 920.
- 8 Ch. de Bourayne, E. Oliveros, M. T. Maurette, M. Rivière and A. Lattes, *Thesis 2373*, Toulouse; *C.R. Acad. Sci.*, to be published.