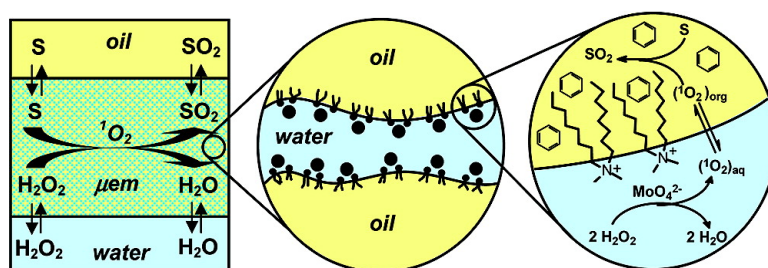


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## Oxidation in Three-Liquid-Phase Microemulsion Systems Using “Balanced Catalytic Surfactants”

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Microemulsions ( $\mu\text{em}$ ) are thermodynamically stable submicron dispersions of two immiscible liquids stabilized by a surfactant monolayer.<sup>1</sup> They are used as reaction media in organic synthesis to overcome the incompatibility between hydrophilic reagents and hydrophobic substrates.<sup>2</sup> The considerable increase ( $\sim 10^5$  times) of the oil–water interfacial area and the compartmentalization of reactants often provide a significant rate enhancement and better selectivity compared to the routine Phase-Transfer Catalysis (PTC) or to cosolubilization in polar solvents.<sup>3,4</sup> Single-phase water-in-oil microemulsions have been applied to the peroxidation of fragile organic compounds by singlet oxygen,  $^1\text{O}_2$  ( $^1\Delta_g$ ), chemically generated by the  $\text{H}_2\text{O}_2/\text{Na}_2\text{MoO}_4$  catalytic system.<sup>4</sup> These microemulsions suffer two main drawbacks: (i) lengthy recovery of products because of the high concentration of amphiphiles ( $\approx 20\%$ ); (ii) demixing after addition of a certain amount of  $\text{H}_2\text{O}_2$ . Two-phase microemulsion systems with an excess oil phase require lower amounts of surfactant ( $\sim 5\%$ ) and allow easier workups, but they are still sensitive to dilution by water arising from  $\text{H}_2\text{O}_2$  disproportionation.<sup>5</sup>

This work describes the concept of “Balanced Catalytic Surfactants” (BCSs) giving three-liquid-phase systems that overcome all these drawbacks. The catalyst ( $\text{MoO}_4^{2-}$ ) is electrostatically bound to a cationic surfactant moiety leading to a “catalytic surfactant” (CS). Cetyltrimethylammonium bicarbonate may be considered as a CS since it catalyzes the micellar oxidation of aryl sulfides by  $\text{H}_2\text{O}_2$ .<sup>6</sup> Furthermore, a CS is named “balanced” if it spontaneously forms a three-liquid-phase system when mixed with an appropriate organic solvent and water. Several types of nonionic surfactants possess this uncommon feature,<sup>7</sup> whereas most ionic surfactants require a cosurfactant and an electrolyte to give a three-phase system. Only a few double-tailed ionic surfactants behave as balanced surfactants.<sup>8,9</sup>

A series of CSs suitable for dark singlet oxygenation has been prepared by coupling  $\text{MoO}_4^{2-}$  with single-chain  $[\text{C}_n\text{N}(\text{C}_1)_3]^+$  and double-tailed  $[(\text{C}_n)_2\text{N}(\text{C}_1)_2]^+$  ammonium groups. The latter provide BCSs which play the role of surfactant, cosurfactant, and catalyst simultaneously, leading to a three-liquid-phase system with only three constituents (Figure 1). In this medium,  $\text{MoO}_4^{2-}$  is specifically localized at the water–oil interface of the middle-phase microemulsion. The hydrophobic substrate partitions between the microemulsion and the excess oil phase, whereas  $\text{H}_2\text{O}_2$  partitions between the microemulsion and the excess water phase. The generation of  $^1\text{O}_2$  exclusively takes place in the aqueous microdomains of the middle-phase microemulsion. As the typical size of these microdomains (ca. 10 nm) is much smaller than the mean travel distance of  $^1\text{O}_2$  in water (ca. 200 nm), this small uncharged and rather hydrophobic excited molecule diffuses freely through the charged interfacial film to the organic compartments where it reacts with the substrate S. In this process, the upper oil and the lower aqueous excess phases can be regarded as reservoirs for

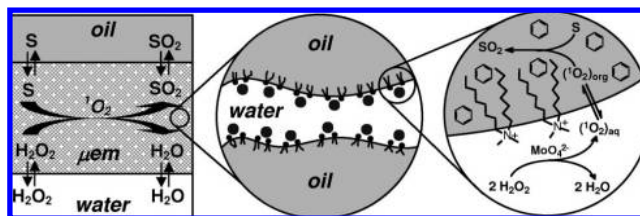


Figure 1. Dark singlet oxygenation of a substrate S in a three-liquid-phase microemulsion ( $\mu\text{em}$ ) system based on  $[(\text{C}_8)_2\text{N}(\text{C}_1)_2]_2\text{MoO}_4$ .

Table 1. Microemulsion Systems as a Function of Catalytic Surfactants,  $[(\text{C}_n)_2\text{N}(\text{C}_1)_2]_2\text{MoO}_4$ , and Oil Hydrophobicity at 25 °C (Composition is Water/Oil = 1/1 (v/v) and 5 wt % CS)<sup>a</sup>

n	C <sub>6</sub> H <sub>6</sub> or AcOPr	Xylene or AcO <i>t</i> -Bu	Pentane	Octane
8	W III			
9		W III		W I
10		W II	W III	
12				W III

<sup>a</sup> WI, WII, WIII refer to the Winsor systems, i.e. to microemulsions in equilibrium with oil, aqueous, or both excess phases respectively.<sup>5,12</sup>

the reagents and the products. Under stirring, oxidation products are continuously extracted from the microemulsion to the organic phase and the water arising from disproportionated  $\text{H}_2\text{O}_2$  is expelled in the aqueous excess phase without destabilizing the microemulsion (Figure 1). At completion of the reaction, stirring is stopped and the three phases separate within a few seconds.

A balanced three-phase microemulsion system is formed when the interfacial film between oil and water is flexible and has a zero mean curvature.<sup>10</sup> To fulfill this condition, the interfacial packing parameter  $p = v/al$ , where  $v$ ,  $a$ ,  $l$  are the alkyl chain volume swollen with oil, the headgroup area, and the alkyl chain length respectively, must be equal to 1.  $p$  is related to the structure of the surfactant in solution and to the ability of the oil to penetrate the interfacial film.<sup>11</sup> Single-chain ammonium molybdates  $[\text{C}_n\text{N}(\text{C}_1)_3]_2\text{MoO}_4$  ( $n = 12, 14, 16$ ) do not behave as BCSs ( $p \ll 1$ ) since they do not form three-phase systems without electrolytes, the anion of which would exchange with molybdate ions. To increase  $p$  and to obtain a flexible interfacial film without cosurfactant, double-tailed CSs  $[(\text{C}_n)_2\text{N}(\text{C}_1)_2]_2\text{MoO}_4$  ( $n = 8, 9, 10, 12$ ) were prepared and turned out to be balanced in the presence of water and an appropriate oil. The range of experimentally effective chain lengths, i.e. the values of  $n$  providing three-phase systems at room temperature, lies between 8 and 12 carbons. The ternary systems based on these CSs have been investigated with various oils of increasing hydrophobicity (Table 1).

The three-phase microemulsion system based on one of the BCSs ( $n = 8$ ) was applied to the peroxidation of three substrates reacting according to a [4 + 2] cycloaddition, the most specific reaction of  $^1\text{O}_2$ . Rubrene, **1**, which is very hydrophobic, bulky, and poorly

**Table 2.** Peroxidation of Rubrene **1** (0.02 mol L<sup>-1</sup>) by the H<sub>2</sub>O<sub>2</sub>/X<sub>2</sub>MoO<sub>4</sub> Systems (X = Na<sup>+</sup> or (C<sub>8</sub>)<sub>n</sub>N(C<sub>1</sub>)<sub>m</sub>)<sup>a</sup>

	Ref <sup>b</sup>	PTC <sub>1</sub> <sup>b</sup>	PTC <sub>2</sub> <sup>b</sup>	μem <sup>c</sup>	BCS <sup>d</sup>
[H <sub>2</sub> O <sub>2</sub> ] mol L <sup>-1</sup>	13	13	0.61	0.080	0.092
Δt (h)	60	60	15	0.5	0.5
yield (%) <sup>e</sup>	10	13	>98	>98	>98
trapping (%) <sup>f</sup>	0.3	0.4	6.5	50	45

<sup>a</sup> For all experiments, *T* = 25 °C, water/benzene = 1/1 (v/v), [MoO<sub>4</sub><sup>2-</sup>] = 0.014 mol L<sup>-1</sup> (see Supporting Information). <sup>b</sup> Biphasic systems: PTC/Na<sub>2</sub>MoO<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub>O with no PTC (entry ref), with (C<sub>4</sub>)<sub>4</sub>NBr (entry PTC<sub>1</sub>) or with (C<sub>8</sub>)<sub>4</sub>NBr (entry PTC<sub>2</sub>). <sup>c</sup> Single-phase microemulsion: sodium dodecyl sulfate (SDS)/BuOH/Na<sub>2</sub>MoO<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub>O. <sup>d</sup> Three-phase system: [(C<sub>8</sub>)<sub>2</sub>-N(C<sub>1</sub>)<sub>2</sub>]<sub>2</sub>MoO<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub>O. <sup>e</sup> Yield (%) = 100 × [oxidation product]/[rubrene]. <sup>f</sup> Trapping (%) = 100 × [oxidation product]/0.5 × [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>.



soluble in most organic solvents, was first used as a model for the comparison with PTC and single-phase microemulsion (Table 2). Benzene was used as the oil since it is the sole solvent which solubilizes **1** while providing the Winsor III system.

When the reaction is performed in a sodium molybdate/water/benzene system (entry Ref), most (>99%) of the generated <sup>1</sup>O<sub>2</sub> is wasted through deactivation by water molecules before reaching the organic phase since the aqueous droplets formed during stirring are millimetric, i.e. much larger than the mean travel distance of <sup>1</sup>O<sub>2</sub> in water. No improvement is observed in the presence of the hydrophilic PTC<sub>1</sub> since (C<sub>4</sub>)<sub>4</sub>N<sup>+</sup> and MoO<sub>4</sub><sup>2-</sup> mainly lie in the aqueous phase (entry PTC<sub>1</sub>). When the hydrophobic (C<sub>8</sub>)<sub>4</sub>NBr is used (entry PTC<sub>2</sub>), the complete conversion of rubrene can be reached but with a large excess of H<sub>2</sub>O<sub>2</sub> (~15 times). Actually, (C<sub>8</sub>)<sub>4</sub>NBr is mainly localized in the organic phase and is able to convey ~56% of the intermediate peroxomolybdates into the benzene phase where the peroxidation reaction takes place.<sup>13</sup> As reported previously,<sup>4</sup> the single-phase microemulsion based on SDS (entry μem) is very efficient but has the drawbacks discussed above. The three-phase system obtained with the “balanced catalytic surfactant” (entry BCS) was found to be as efficient but much more convenient since only 1 wt % of amphiphile (BCS) was used instead of 30 wt % of (SDS + BuOH) in the single-phase microemulsion. Moreover, the product is readily recovered almost completely from the excess oil phase, whereas the BCS remains in the very small middle-phase μem which can be reused.

Benzene can readily be replaced by more environmentally acceptable solvents such as *tert*-butyl acetate, which also provides a three-phase μem when all reactants are present in the reaction medium. The system [(C<sub>8</sub>)<sub>2</sub>N(C<sub>1</sub>)<sub>2</sub>]<sub>2</sub>MoO<sub>4</sub>/AcO*t*-Bu/H<sub>2</sub>O was thus applied to the preparative peroxidation (0.5 mol L<sup>-1</sup>) of α-terpinene **2** (Table 3). In contrast with rubrene, this reactive substrate is very soluble in common organic solvents. Such reaction conditions demonstrate the catalytic nature of the BCS (molar ratio **2**/BCS = 7/1) and the reusability of the μem since, after complete conversion of **2** into ascaridole, the replacement of the excess oil phase containing the oxidation product by a fresh oil phase containing a new batch of **2** (0.5 mol L<sup>-1</sup>) leads to the same reaction efficiency.

Finally, the stability of the three-phase microemulsion system against water dilution was demonstrated with the preparative oxidation (0.1 mol L<sup>-1</sup>) of a poorly reactive substrate, 1,4,5-trimethylnaphtalene **3** (*k<sub>r</sub>* + *k<sub>q</sub>* = 9 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> in the μem), which requires larger amounts of aqueous H<sub>2</sub>O<sub>2</sub> (3.2 mol L<sup>-1</sup>) for complete conversion (>98%) into the 1,4-endoperoxide. **3** was

**Table 3.** Peroxidation (>98%) of Substrates **2** and **3** in Three-Phase Systems Based on Water/Oil = 1/1 (v/v) and [(C<sub>8</sub>)<sub>2</sub>N(C<sub>1</sub>)<sub>2</sub>]<sub>2</sub>MoO<sub>4</sub> = 75 mmol/kg (see Supporting Information)

Substrates	( <i>k<sub>r</sub></i> + <i>k<sub>q</sub></i> ) <sup>a</sup> (10 <sup>5</sup> M <sup>-1</sup> .s <sup>-1</sup> )	[substrate] (mol L <sup>-1</sup> )	Δt (h)	[H <sub>2</sub> O <sub>2</sub> ] (mol L <sup>-1</sup> )
 <b>2</b> <sup>b</sup>	450	0.5	3.0	1.25
 <b>3</b>	9.0	0.1	33	3.2

<sup>a</sup> Overall rate constants as determined by laser flash photolysis in microemulsion with sodium tetraphenylporphine sulfonate (TPPS) as sensitizer. <sup>b</sup> *T* = 25 °C. <sup>c</sup> *T* = 10 °C.

peroxidized at 10 °C in order to limit the thermolysis of the endoperoxide (*t*<sub>1/2</sub> = 290 h at 25 °C).<sup>14</sup>

Balanced three-phase microemulsion systems based on water, an appropriate organic solvent, and a balanced catalytic surfactant combine both distinct advantages of PTC (simplicity, fast phase separation, easy workup) and microemulsions (huge water–oil interface, compartmentalization of reactants in nanometric reactors). The catalytic surfactants developed in the present work are suitable for dark singlet oxygenation of organic substrates, but the concept can be extended to many other reactions involving both hydrophilic reactants and hydrophobic substrates.

**Supporting Information Available:** Preparation of catalytic surfactants; characterization of the three-liquid-phase systems; peroxidations of rubrene **1**, α-terpinene **2**, and 1,4,5-trimethylnaphtalene **3**; procedure for the recovery of products; recyclability of the microemulsion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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