

## Part VI

### Supramolecular Catalysis in Water

## 31

### Metal Catalysis in Micellar Media

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#### 31.1 Introduction

The use of micellar media is receiving increasing attention in transition metal catalysis for a number of reasons involving both practical and fundamental issues, such as the possibility to get rid of large amounts of organic solvents as reaction media and simplify work-up operations involved in product isolation, thus resulting in a significant improvement from the point of view of environmental acceptability. This is an important motivation from a practical point of view and in the perspective of possible industrial applications. Equally important are some extra advantages imparted by micelles, some of them hardly predictable when this field started being systematically explored. These include remarkable reaction rate acceleration, substrate, and product selectivities, all depending on the choice of the appropriate surfactant. These effects are basically due to the weak, yet very effective, supramolecular interactions between catalyst, substrate, and surfactant, occurring inside the confined nano space present in a micelle [1, 2]. These features are typical of the behavior observed in biological systems and more specifically in enzymes, which are an unlimited source of inspiration, so that micellar catalysis with transition metals can be viewed also as a bridge between traditional homogeneous catalysis and enzymatic catalysis.

The field has been reviewed a few times over the years [3–6] and has been particularly successful thanks to the use of neutral designer surfactants [7] introduced by the work of Lipshutz et al. [8], with which some remarkable results have been obtained in a series of classical C–C forming reactions (Heck, Stille, Suzuki–Miyaura, etc.) involved in the synthesis of active pharmaceutical ingredients. The interest in this area stemmed mainly from the seminal work of Engberts reported some 30 years ago [9], but it was not before 2004 that systematic evaluation of micellar systems for transition metal catalysis started being investigated.

When we stepped in the field we had been working in catalytic oxidations with hydrogen peroxide for about 25 years, dealing with two-phase systems made of water (for hydrogen peroxide) and an immiscible organic solvent (generally 1,2-dichloroethane [DCE] or dichloromethane [DCM]) to dissolve both catalysts and substrates, observing that much better results in terms of activity and selectivity could be achieved with respect to single phase systems using, e.g. THF to dissolve all reaction ingredients. At that time we were mainly interested in finding an easy way to separate soluble catalysts from the reaction medium, this being our main motivation to test micellar media, with the idea of confining the catalyst inside the micelle dispersed in water, then extracting the products with a water immiscible solvent at the end of the reaction. Since the beginning we opted to use commercially available surfactants for a number of reasons: (i) the easy availability of a wide range of cationic, anionic, zwitterionic, and neutral surfactants with different chemical composition; (ii) their generally low cost; and (iii) their already wide use in industry (albeit for different purposes) that will eventually pave the way in case of possible practical applications. Also the choice of the transition metal is critical because it must withstand the presence of water without being inactivated. This excludes early transition metals. On the other hand, simple ions (e.g.  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ) may be good to mimic biochemical reactions, but they behave as simple Lewis acids catalysts and do not possess the kaleidoscope of properties exhibited by organometallic complexes. Looking for the appropriate class of catalysts, the choice is therefore limited mainly to noble metal complexes because many of them do not suffer from inactivation by water.

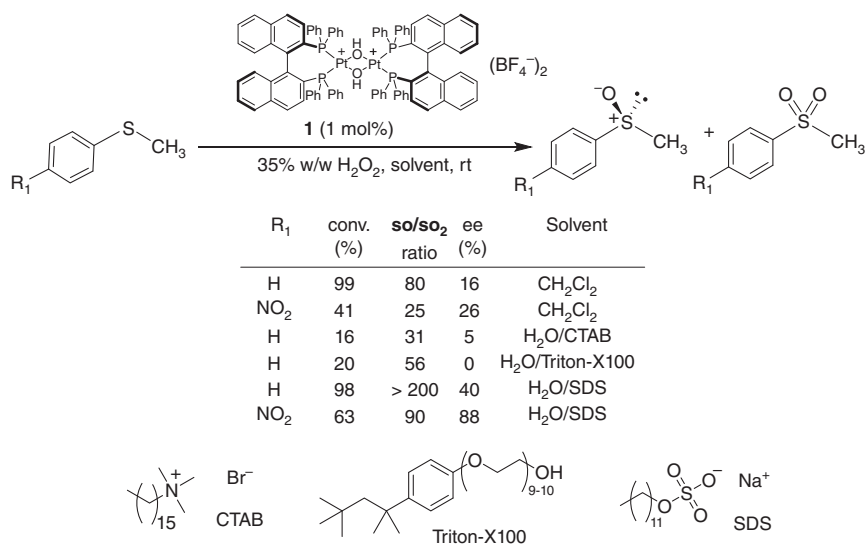
## 31.2 Oxidation Reactions

Our first bet in micellar catalysis was in enantioselective oxidation for several reasons: (i) because it is involved in the synthesis of important drugs like, e.g. the proton pump inhibitor Esomeprazole, the anticancer Taxol, or the anti-HIV Indinavir and (ii) because it allows one to check the effects of the reaction medium on reactivity and on whole array of selectivities (chemo-, regio-, enantio-), all at the same time.

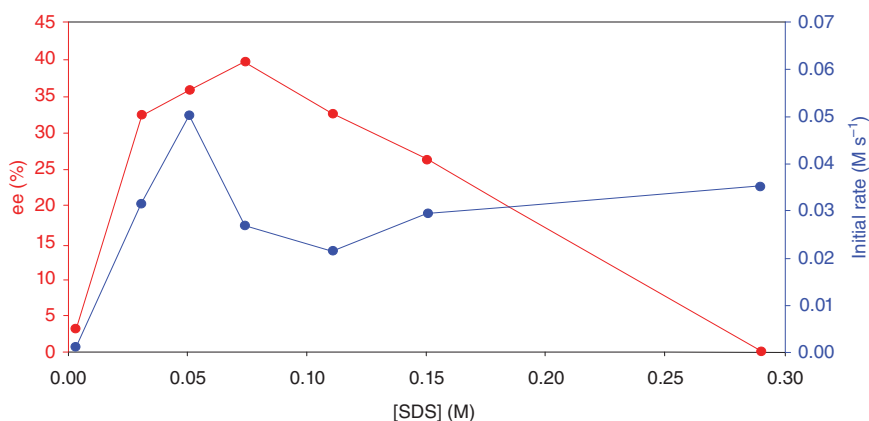
Our initial tests were in the sulfoxidation of different thioanisoles with hydrogen peroxide using the cationic dimeric Pt complex **1** as catalyst [10]. Some representative data are shown in Figure 31.1.

As shown, the choice of the appropriate surfactant is crucial (anionic in this case) to improve both reactivity as well as the sulfoxide/sulfone ratio and the enantioselectivity of the former. Another important point was the optimization of the surfactant concentration described in Figure 31.2 because this has a dramatic effect on both the activity (initial rate) and the enantioselectivity. This is an operation that must be done with any micellar system.

Key features observed were (i) easy isolation of the products from the catalyst by simple diethyl ether/water SDS two phase separation, (ii) use of green and inexpensive hydrogen peroxide as oxidant, (iii) catalyst loading as low as 1 mol%, (iv) good yields, sulfoxide/sulfone ratios larger than 200, and enantioselectivities up to 88%, and (v) use of mild experimental conditions.



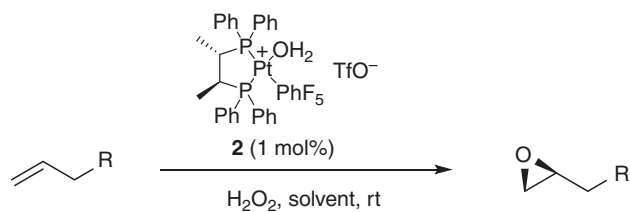
**Figure 31.1** Stereoselective oxidation of thioanisoles in different micellar media with **1**.



**Figure 31.2** Effect of SDS concentration on the initial rate and ee in the sulfoxidation of thioanisole with **1**.

Similar results were found also in the enantioselective epoxidation of terminal alkenes [11] still using hydrogen peroxide and a cationic Pt complex **2** as the catalyst (see some data in Figure 31.3). In this case, a neutral surfactant proved to be the best choice. It was also possible to separate and recycle the Pt<sup>II</sup> catalyst for at least three times without loss of activity and enantioselectivity.

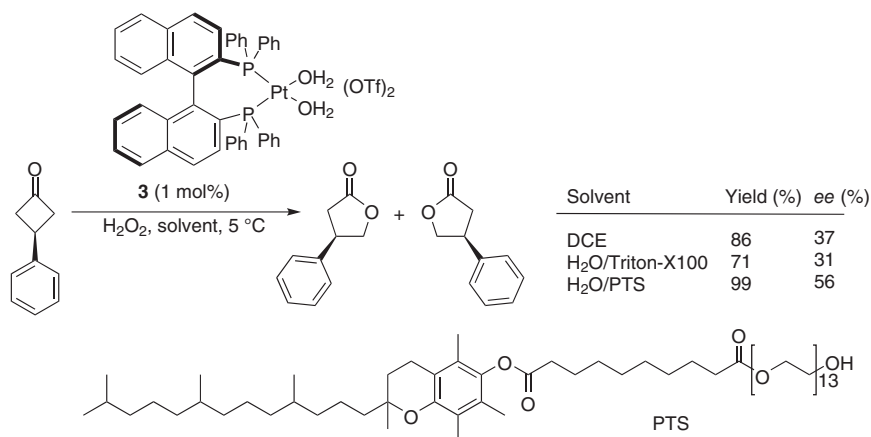
However, it was in the Baeyer–Villiger oxidation of ketones that some surprising results were observed. Our initial attempts involved bis-cationic Pt complexes as catalysts in the desymmetrization of meso cyclic ketones [12]. In the case of 4-substituted cyclohexanones, the use of SDS in water as the reaction medium compared to DCE allowed significant amplification of the enantioselectivity but at the



R = *n*-(C<sub>3</sub>H<sub>7</sub>), *n*-(C<sub>5</sub>H<sub>11</sub>), *n*-(C<sub>9</sub>H<sub>19</sub>), *iso*Pr, *iso*Bu, 3,4-(MeO)<sub>2</sub>Ph

R	Solvent	Yield (%)	ee (%)
<i>iso</i> Pr	ClCH <sub>2</sub> CH <sub>2</sub> Cl	56	58
<i>iso</i> Pr	H <sub>2</sub> O/Triton-X100	51	84

**Figure 31.3** The enantioselective epoxidation of 4-methyl-1-pentene with **2**: comparison between the use of an organic solvent and a micellar medium.

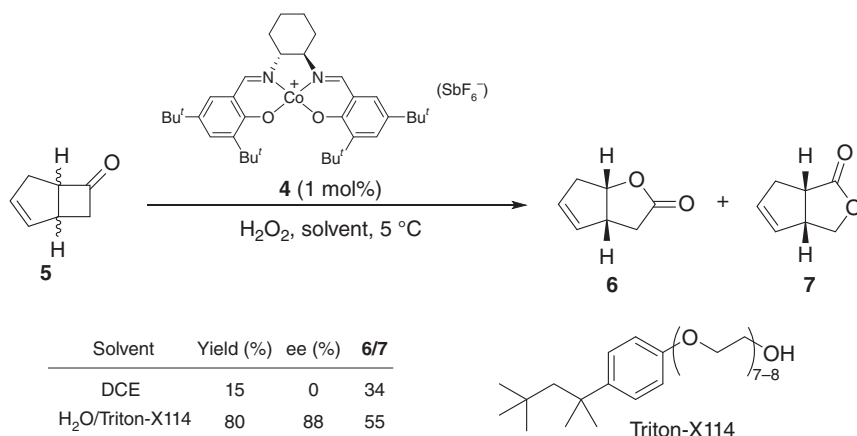


**Figure 31.4** Effect of the surfactant in the asymmetric Baeyer–Villiger oxidation of *meso*-3-phenyl-cyclobutanone in micellar media with **3**.

expense of a much lower product yield, whereas with 3-substituted cyclobutanones (Figure 31.4) a neutral surfactant like PTS in water showed both an improvement in product yield and a much better asymmetric amplification.

However, the most striking effect on a catalytic reaction due to the supramolecular interactions induced by micelles was observed in the Baeyer–Villiger oxidation of a substituted cyclobutanone (Figure 31.5) [13]. The Co<sup>III</sup> catalyst **4** used is commercially available and virtually useless in this reaction if tested in DCE, but once dissolved in water with the aid of the neutral surfactant Triton-X114, good catalytic activity, high regioselectivity, and a jump in enantioselectivity were observed. All that is simply due to the reaction occurring inside the micelles.

Overall, the use of surfactants in the oxidation reactions studied implies the partition of all reaction components (substrate, oxidant, and catalyst) between the micelle, bulk water, and the interphase between the two. Moreover, the lipophilicity of all species is crucial to rationalize their positioning in the micellar system,



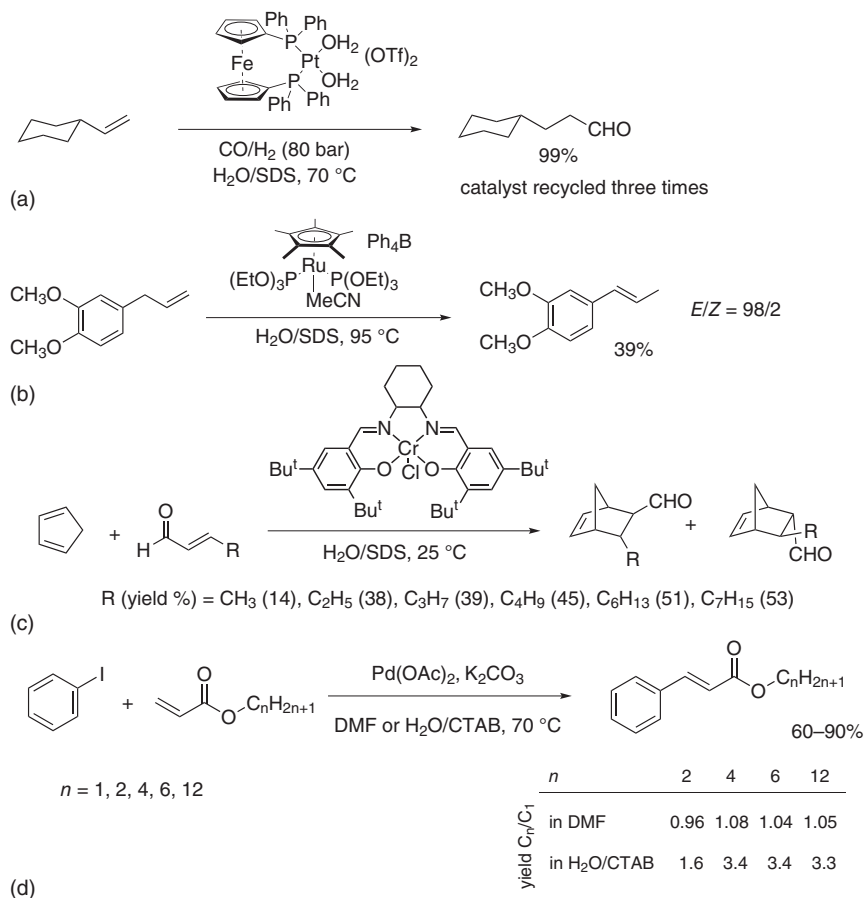
**Figure 31.5** Striking effect on the activity and the enantioselectivity due to the micellar medium in the Baeyer–Villiger oxidation of a substituted cyclobutanone catalyzed by a Co<sup>III</sup> catalyst **4**.

and as a general observation, more hydrophilic substrates gave better results in neutral surfactants, whereas anionic micelles were preferred for more lipophilic substrates. Analogously, a general increase in enantioselectivity was observed for more apolar substrates in water–surfactant medium compared with reaction in chlorinated solvent. The supramolecular control exerted by the micelle on the conformation/configuration of the catalyst–substrate adduct is not possible in common organic solvents, because simple solvation leads to a lower order of the molecules around the catalyst. A similar principle is observed in several enzymes, in which the binding of substrates and their juxtaposition in the hydrophobic active site is driven by the hydrophobic effect.

### 31.3 C–C and C–X Bond Forming Reactions

The use of micellar media was extended to a variety of catalyzed C–C and C–heteroatom bond forming reactions. The first category includes hydroformylation [14], C=C double bond isomerization [15], Diels–Alder reaction [16], and Heck coupling [17]. A summary of the essential results obtained in these catalytic processes is shown in Figure 31.6.

In hydroformylation (Figure 31.6a), the micellar system containing a bis-cationic Pt catalyst modified with a large-bite angle diphosphine shows catalytic activity comparable, and in some cases better, than traditional Pt–Sn systems, with excellent linear to branched selectivities that can rival with the best Rh catalysts. The catalytic system can be successfully applied to a large range of substrates characterized by terminal or internal cis double bonds and even with the latter high selectivities to the most desired linear aldehydes is observed thanks to a prior isomerization process. The catalyst can be recycled up to four times employing 1 mol% as the catalyst loading with only a modest decrease in activity and no effect on selectivity.

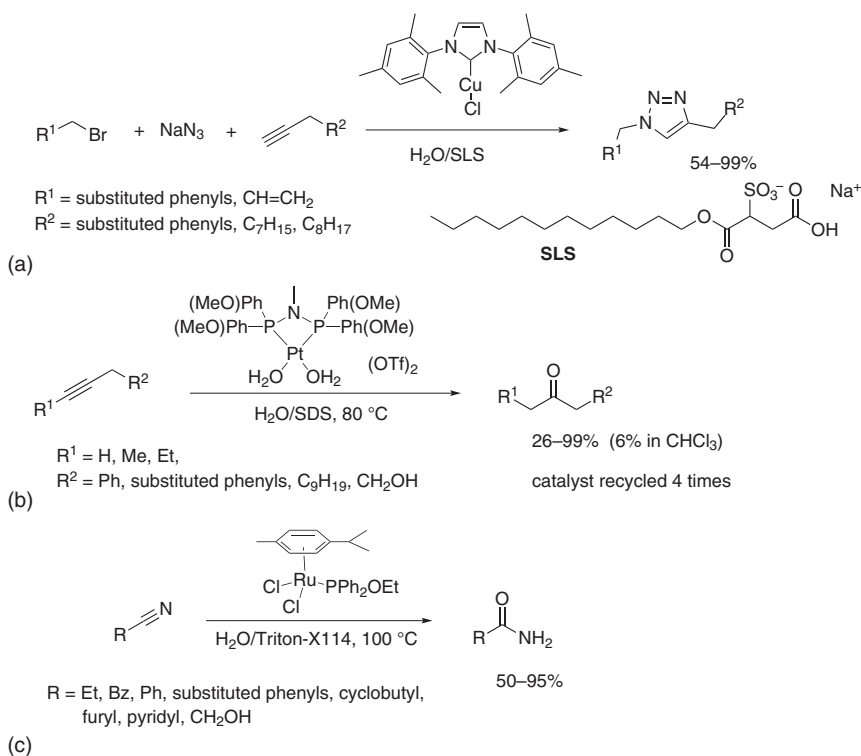


**Figure 31.6** An overview of the results obtained in hydroformylation (a), C=C double bond isomerization (b), Diels–Alder reaction (c), and Heck coupling (d) in catalytic experiments carried out under micellar conditions.

In isomerization (Figure 31.6b), a cationic Ru complex in water/SDS was applied to a series of allylbenzenes that are precursors to fragrances showing excellent E-isomer selectivity and overall good performance with respect to the use of organic solvents. The latter was retained even when the reaction was scaled up to substrate in gram quantities.

In the Diels–Alder reaction (Figure 31.6c) between cyclopentadiene and a series of  $\alpha,\beta$ -unsaturated aldehydes bearing aliphatic chains of variable length, a  $\text{Cr}^{\text{III}}(\text{salen})\text{Cl}$  catalyst embedded into a  $\text{H}_2\text{O}/\text{SDS}$  supramolecular aggregate can display substrate selectivity. It was observed that while in  $\text{CHCl}_3$  there is virtually no difference in yields when using the variable length dienophiles in competitive experiments, in the micellar system an up to 3.5 increase in activity in favor of longer substrates compared to the shorter ones was observed.

A similar effect was observed in the Pd-mediated Heck coupling between iodoaryl substrates and linear acrylic esters in water (Figure 31.6d) to yield cinnamyl



**Figure 31.7** An overview of the results obtained in the synthesis of 1,2,3 triazoles (a), the hydration of alkynes (b), and the hydration of nitriles (c).

esters of different length. Here some competitive experiments were carried out by reacting methyl acrylate ( $C_1$ ) and longer length  $n$ -alkyl acrylates ( $C_n$ ) in pairs and taking the ratio in yields between  $C_n$  and  $C_1$  as a parameter to evaluate substrate selectivity. While no difference was observed operating in DMF as the solvent, in water/cetyltrimethylammonium bromide longer acrylates give much better yields in cinnamyl esters with respect to shorter ones.

In the latter examples for Diels–Alder and Heck reactions, the selection rule is imparted by the hydrophobic effect that forces the more lipophilic substrates to migrate inside the micelle and get in contact with the catalyst. The results obtained underline the importance of hydrophobic interactions and mimic the behavior observed with natural catalysts such as enzymes. Substrate selectivity has often been observed in confined spaces such as molecular capsules [1, 2], but only rarely in micellar media.

The C–X bond forming reactions studied were the following: the synthesis of 1,2,3-triazoles [18], the hydration of alkynes [19], and the hydration of nitriles [20]. A summary of the main features is reported in Figure 31.7.

A very simple and efficient regioselective multicomponent synthesis of 1,4-disubstituted 1,2,3-triazoles starting from organic bromides, sodium azide, and alkynes catalyzed by 1 mol% of a  $\text{Cu}^{\text{I}}$  catalyst modified with a substituted



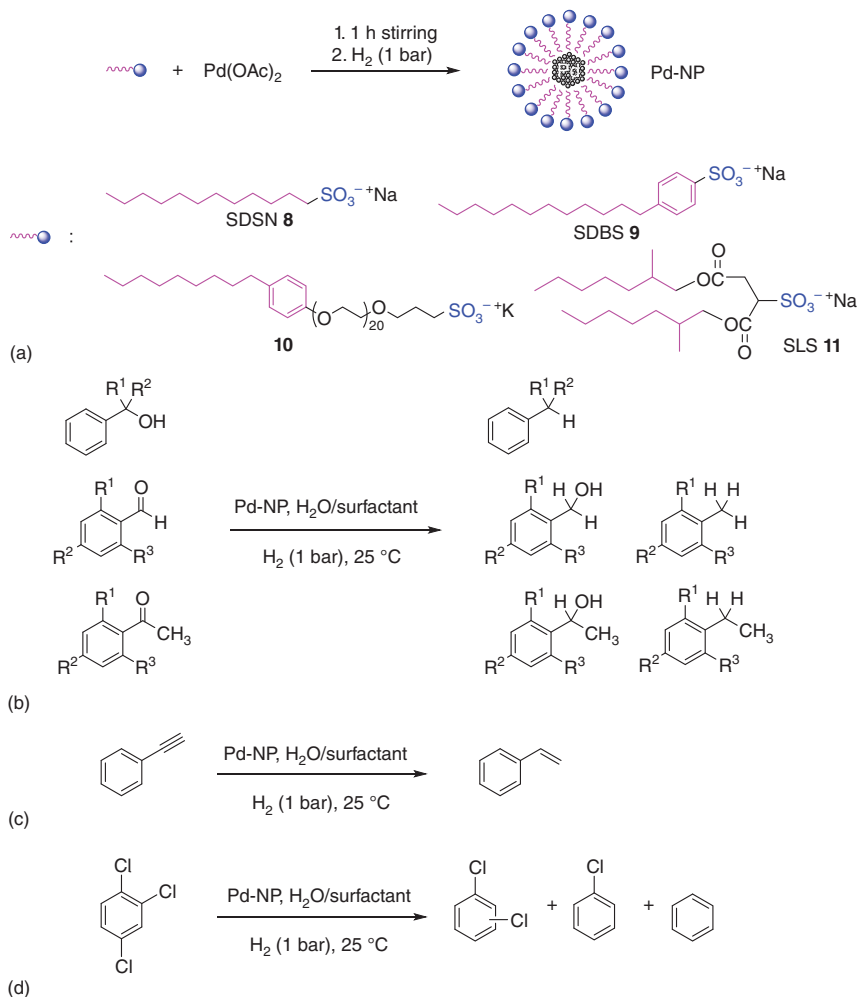
imidazole-2-ylidene ligand was accomplished in one pot, operating in water at room temperature and in the presence of surfactants (Figure 31.7a). The micellar medium obtained by the addition of commercially available SLS or TPGS-750-M surfactants in water favors the *in situ* formation of the organic azide, thus avoiding its separate synthesis and storage. The micellar medium is also responsible for the consecutive positive interaction between the organic azide and the alkyne mediated by the organometallic Cu<sup>I</sup> catalyst. This system could be applied to a wide range of combinations of organic bromides and alkynes, obtaining overall more than 20 different 1,2,3-triazoles in high yields. In one case, the reaction was scaled up to 2 mmol of product. The triazole products could be easily isolated by means of simple extraction with ethyl acetate. The multicomponent reaction can be carried out in a greener way and is competitive in terms of yields and selectivities with respect to an isolated organic azide, thus avoiding the manipulation of these noxious chemicals and with the advantage of carrying out the whole procedure in one pot.

Alkyne hydration was achieved thanks to a new class of monomeric bis-cationic Pt complexes bearing a series of small bite angle diphosphinamine PNP ligands operating in water under micellar conditions selectively yielding the corresponding ketones (Figure 31.7b). The micellar medium enables a large improvement in catalytic activity compared to the reaction performed in homogeneous binary solvent mixtures like acetone-water, dioxane-water, or biphasic 1 : 1 CHCl<sub>3</sub>/water. The specific role played by the micellar aqueous medium is to favor the formation of catalytically active Pt<sup>II</sup> species bearing  $\sigma$ -vinyl moieties, while in organic media with water the reaction stops at forming the  $\pi$ -coordinated alkyne species. The strong interaction between the bis-cationic catalyst and the anionic micelles allows catalyst recycling for four times without significant loss of catalytic activity. The Pt<sup>II</sup> catalytic system remains confined in the aqueous phase, while the product was isolated by extraction with hexane.

Efficient nitrile hydration to the corresponding amide derivatives was observed in water using poorly soluble [RuCl<sub>2</sub>( $\eta^6$ -arene)(PR<sub>3</sub>)] catalysts with the aid of surfactants to ensure substrate and catalyst solubilization, thus enabling a ligand effect study on catalytic activity (Figure 31.7c). Neutral surfactants showed the best catalytic activity, probably because they do not interfere (as charged species do) with ligand exchange on the catalyst, allowing high amide yields with a large variety of nitrile substrates. In this case, micellar media enabled the screening of common monophosphine ligands, like in classical organometallic chemistry studies, and it was observed that neither electron-rich nor electron-poor phosphines ensured high catalytic activity, but rather an appropriate balance of steric and electronic features is required. In general, with respect to the use of intrinsically water soluble catalysts, the micellar approach can, in principle, be applied to exploit libraries of existing catalysts for libraries of reactions without the need to synthesize specific water-soluble catalysts for each reaction.

## 31.4 Metal Nanoparticles in Micellar Media

The micellar media approach to catalysis was not limited to organometallic catalysts, and we tested also a facile and inexpensive method for the preparation of Pd nanoparticles (Pd-NP) in water stabilized by anionic sulfonated surfactants as shown in Figure 31.8 [21]. These were obtained by stirring aqueous solutions of  $\text{Pd}(\text{OAc})_2$  with commercial anionic surfactants **8–11** and further treating under hydrogen atmosphere for variable amounts of time (Figure 31.8a). The Pd-NPs



**Figure 31.8** Preparation of Pd nanoparticles with different sulfonated anionic surfactants **8–11** and their reactivity in a series of hydrogenation reactions.

showed similar size range and distribution but different morphologies as a function of the nature of the surfactant employed as well as its concentration and experimental conditions.

The aqueous Pd nanoparticle solutions were tested in the selective hydrogenolysis of aryl-alcohols, leading to complete conversion to the deoxygenated products even in the absence of strong Brønsted acids as well as in the hydrogenation of aromatic aldehydes and ketones (Figure 31.8b). Their activity and selectivity could be modulated by choosing the appropriate surfactant; thus, with **10** the hydrogenation of benzaldehyde and other aromatic derivatives showed a very high chemoselectivity toward the formation of the corresponding benzyl alcohols, whereas Pd/C as a comparison was more difficult to control, causing the formation of deoxygenation reaction products. Similarly, with sodium dodecylsulfonate **8** and with sodium lauryl sulfosuccinate **11** complete hydrogenolysis was observed and deoxygenation of secondary and tertiary alcohols could be achieved with quantitative conversion.

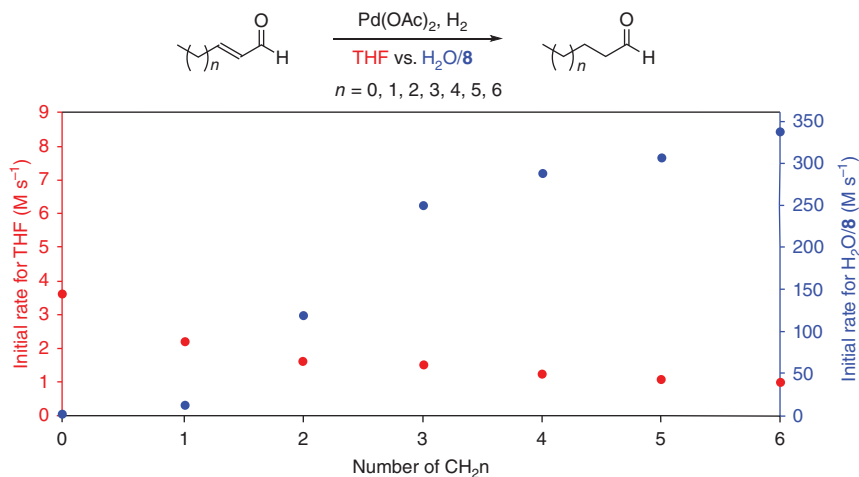
Surfactant sodium dodecylbenzene sulfonate **9** gave a catalytic system with controlled activity in the semi-hydrogenation reactions of alkynes to alkenes (Figure 31.8c) with a particular affinity for compounds containing aromatic rings, probably due to  $\pi$ - $\pi$  supramolecular interactions between the surfactant and the substrates.

To demonstrate the generality of the catalytic system developed in water, we studied also the application of these systems to the decomposition of hazardous chlorinated aromatic compounds directly in water (Figure 31.8d). With this purpose, the catalytic activity of Pd-NP stabilized by the sulfonated anionic surfactant **10** was checked in the reaction of 1,2,4-trichlorobenzene. Pd-NP could convert quantitatively the substrate under mild conditions in water, and recycling of the catalytic system was possible without detrimental effects on its activity and selectivity.

In this system, the role of the surfactant is crucial to ensure the necessary stability to Pd-NP under the catalytic conditions applied. In spite of the fact that the reaction environment is always the same (water, surfactant, and hydrogen), the type of substrate analyzed in the individual cases can completely change the stability of the metal system; for example, surfactant **9** leads to Pd metal precipitation with aldehydes while giving the best catalyst with acetylenes. In some cases, the delicate balance between catalytic activity and stability can be quite significant as in the case of the hydro-dechlorination reaction with surfactant **10** that can even be recycled.

In all these reactions, criteria like particle size/particle distribution were poorly helpful to rationalize catalytic activity and selectivity; rather, intriguing and somehow unpredictable “ligand” effect by the different surfactants capping the Pd-NP could be invoked to explain, at least in part, the sometimes large differences in activity observed. What is interesting is also that a benchmark catalyst like Pd/C can often be surpassed in activity and/or selectivity in the reactions tested by simply switching to the appropriate cheap and commercially available surfactant, thereby providing an easy to use, flexible, and practical catalytic system capable of efficiently addressing a variety of synthetically significant hydrogenation reactions.

Pd-NP stabilized by **8** showed also a remarkable example of substrate selectivity in the selective hydrogenation of a series of  $\alpha,\beta$ -unsaturated aldehydes (Figure 31.9)



**Figure 31.9** Substrate selectivity in the hydrogenation of a series of  $\alpha,\beta$ -unsaturated aldehydes catalyzed by Pd metal in different media.

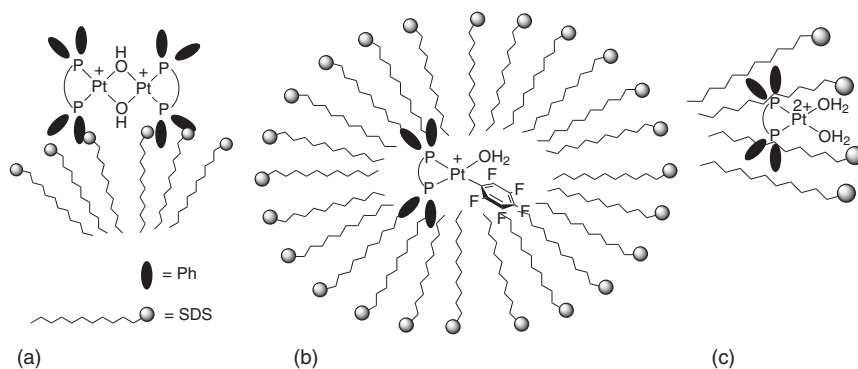
[22]. The Pd metal catalyst was generated either by treating a THF solution of  $\text{Pd(OAc)}_2$  with hydrogen or as in Figure 31.8 in water containing **8**. A competitive experiment was performed in both reaction media by feeding seven  $\alpha,\beta$ -unsaturated aldehydes from  $\text{C}_4$  to  $\text{C}_{10}$  all together into the catalytic system. Substrate selectivity was determined by calculating the relative initial rates for all aldehydes with respect to the slowest one. As shown in Figure 31.9, in THF the relative rates decreased from  $\text{C}_4$  to  $\text{C}_{10}$  with a maximum selectivity factor of 3.6 for the shortest aldehyde. When the same experiment was carried out in the micellar medium, not only the trend was reversed, but the substrate selectivity showed a 330-fold increase on going from  $\text{C}_4$  to  $\text{C}_{10}$ .

Here again the selection rule corresponds to the affinity between the aldehyde and the micelles generated by **8**. These competitive experiments demonstrate that this driving force can greatly amplify selection issues even in simple systems like the present ones as shown by the large preference for longer lipophilic substrates that outperform the shorter more hydrophilic ones by a factor of two orders of magnitude.

## 31.5 Catalyst Surfactant Interactions

In conclusion, commercial surfactants can be profitably exploited for carrying out in water a variety of catalytic reactions using well-known transition metal complexes already optimized in traditional homogeneous catalysis for working in organic solvents. The advantages of micellar media are the following:

- They drastically reduce the use of large amounts of organic solvents that in the industrial practice can be recycled only to a minor extent.
- They improve the separation and recycling of the catalyst. Although this is not always possible, we have observed that it depends on catalyst robustness, on the



**Figure 31.10** Positioning of cationic (diphosphine)Pt complexes in SDS micelles in different oxidation reactions with hydrogen peroxide: sulfoxidation (a), epoxidation (b), Baeyer–Villiger oxidation (c).

nature of the organic solvent used for extraction, on the hydrophobic nature of reaction products, and on the nature of the surfactant. From our experience, ionic surfactants tend to favor separation.

- They increase catalytic activity, partly because of an increase in concentration inside the micelle by an order of magnitude with respect to an organic solution and partly because of the interactions between the micelle and the transition state of the reaction in the micelle confined space.

The latter argument is crucial also for selectivity and has not been adequately addressed in the literature at least for micellar catalysis. In studying catalytic oxidation reactions, we have observed that, even with a very simple surfactant like sodium dodecyl sulfate, quite similar cationic  $\text{Pt}^{\text{II}}$  complexes exhibit different positioning (Figure 31.10) inside the surfactant, driven essentially by the gradient of polarity present in the micelle on going from the hydrophilic surface to the hydrophobic core. This nano environment influences differently the steric and electronic requirements necessary to stabilize the transition state of the catalyzed reaction, thus affecting both the activity and selectivity.

The extent of this stabilization can be easily evaluated from the ee in the case of enantioselective reactions and can be very high. For example in the Baeyer–Villiger oxidation shown in Figure 31.5, there is no difference in energy between the diastereomeric transition states when working in DCE (ee = 0%), while in water/Triton-X114, the two diastereomeric transition states differ by  $-6.82 \text{ kJ mol}^{-1}$  (ee = 88%), a large discrimination effect solely due to the interactions with the micelle.

From an industrial point of view, all together these factors imply a drastic decrease in the E-factor associated with the individual reactions, an improvement of yields in the desired product, milder reaction conditions, ease in catalyst and products separation, a decrease in energy consumption, a shortening of operation times, and eventually a cut in production costs.

## Acknowledgments

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