Asymmetric Sulfoxidation of Thioethers with Hydrogen Peroxide in Water Mediated by Platinum Chiral Catalyst

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Abstract: Easy stereoselective oxidation of prochiral aryl alkyl sulfides **2** to the corresponding sulfoxides can be achieved in water-surfactant medium with inexpensive hydrogen peroxide mediated by the chiral platinum diphosphine complex {[(*R*)-BINAP]Pt(μ-OH)}$_2$(BF$_4$)$_2$ (**1**). Remarkable key features of general interest are (i) easy isolation of the products from catalyst by simple diethyl ether/water-surfactant two phase separation, (ii) catalyst loading as low as 1% mol, (iii) good yields, sulfoxide **3** to sulfone **4** ratio up to 200:1 and enantioselectivities up to 88%, (iv) mild experimental conditions.

Keywords: asymmetric catalysis; oxidation; platinum; sulfoxides; surfactants; water chemistry

Introduction

In asymmetric catalysis, in addition to the classical targets such as high enantioselectivity and yield as well as easy procedures, the use of safe and environmentally friendly reagents and mild conditions are stringent requirements.[1–3] Last but not least, easy isolation of the enantioenriched product is also advisable. Other open challenges are the replacement of organic and especially chlorinated solvents with water[4,5] which, in many cases,[6–9] has been demonstrated to enhance selectivity and asymmetric induction compared to the same processes carried out in organic media.

To exploit the many advantages of water as reaction medium, like low cost, safety and environmental acceptability, the major handicap to be overcome is the generally low solubility of organic substrates (and of most metal complex catalysts) and their possible sensitivity to the acidity and nucleophilicity of this solvent. Among the different strategies employed to induce solubilization in water, besides the use of organic cosolvents, the employment of surfactants above the critical micellar concentration (CMC) plays a crucial role.[10] This approach has been applied to some asymmetric catalytic reactions such as hydrogenation.

In oxidation processes,[11,12] hydrogen peroxide is a highly appealing oxidant due to its low cost, high atom economy[13] and safe handling. Moreover, water is the only by-product of its reduction and this makes its use very attractive in the development of "green" oxidation processes.

We thus strived towards this goal by seeking an asymmetric catalytic oxidation system in water with hydrogen peroxide and, as a test reaction, we chose the asymmetric sulfoxidation of prochiral thioethers. Chiral sulfoxides find applications as important auxiliaries in asymmetric synthesis[14] and in the pharmaceutical industry.[15,16] Many catalytic processes have been developed for their preparation, usually based on catalysts comprising early transition metal complexes.[17] Only few of these processes are highly stereoselective towards a broad range of alkyl aryl and dialkyl thioethers, but they make use of stoichiometric amounts of chiral ligands.[18] Other systems are catalytic with loadings as low as 2% mol but employing alkyl or aryl hydroperoxides as primary oxidant which produce alcohols as by-products. Moreover, in most of these examples low temperatures were required, always in chlorinated solvents.[15] More recently, hydrogen peroxide has attracted the attention of many groups and it has been successfully employed as oxidant with good chemical yields and enantioselectivity[19] in catalytic sulfoxidation processes, but still in common organic chlorinated solvents.

Herein we report an easy to accomplish catalytic asymmetric sulfoxidation process (Scheme 1) in which the dimeric {[(*R*)-BINAP]Pt(μ-OH)}$_2$(BF$_4$)$_2$ complex (**1**)[20,21] with low loading activates 35% hydrogen peroxide in water-surfactant solutions towards aryl alkyl sulfides. To the best of our knowledge this is the first example of a catalytic asymmetric oxidation in water.[22]

Results and Discussion

The effect of different surfactants on the reaction (Scheme 1) is summarized in Table 1. If the reaction is

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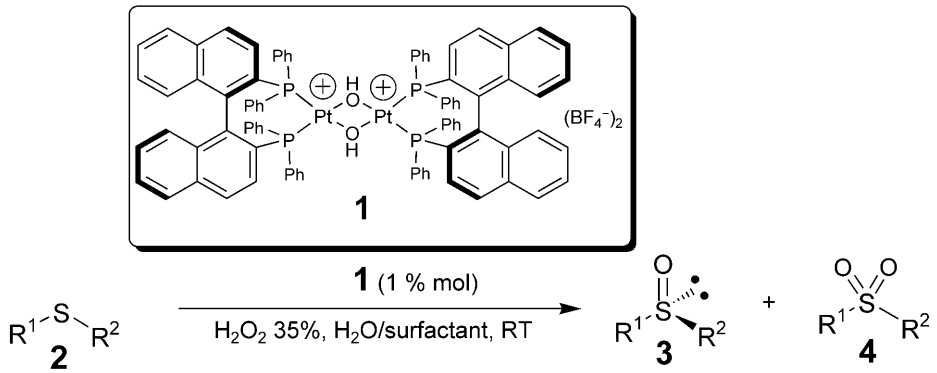


Scheme 1. {[(*R*)-BINAP]Pt(μ-OH)}$_2$(BF$_4$)$_2$ (**1**)-catalyzed asymmetric sulfoxidation of prochiral aryl alkyl sulfides **2** with hydrogen peroxide in water with surfactants.

carried out in dichloromethane (Table 1, entries 1 and 2), with a loading as low as 1% mol, a fast conversion with good chemical yields but rather low enantioselectivity is observed. When switching the reaction medium to water-surfactant, **1** is able to convert thioanisole (**2a**) into the corresponding sulfoxide **3a** with comparable yields, higher sulfoxide **3a** to sulfone **4a** ratio and better enantioselectivities,[23] depending on the type of surfactant used (Table 1, entries 5, 6, 7). Under the latter conditions the reactant-products mixture is separated from the catalyst by simple extraction with diethyl ether in which the catalyst itself is not soluble.

Cationic and neutral surfactants (Table 1, entries 3 and 4) led to low [**3**]/[**4**] ratios, as well as low yields in sulfoxide with no enantioselectivity. This behavior is likely due to low solubilization of the catalyst **1** by cationic and neutral micelles. On the contrary with anionic surfactants the bis-cationic catalyst **1** is much more soluble and, as a consequence, yields, [**3**]/[**4**] ratios and enantioselectivities increase ((Table 1, entries 5 to 7). Among the possible surfactants, sodium dodecyl sulfate (SDS) is responsible for the highest enantioselectivity and therefore the effect of its concentration was thoroughly investigated.

The action of the surfactant above its CMC is to solubilize in water the substrate and catalyst **1** (as demonstrated by the NMR spectra reported in Figure 1) thus allowing intimate contact between the two. If no surfactant is employed, the reaction is sluggish (one order of magnitude slower) and not stereoselective. Above 8 mM, SDS aggregates in water forming micelles, and up to 75 mM (Figure 2) an increase of the sulfoxide ee was observed.[24] When the SDS concentration was further increased to 300 mM an almost linear decrease of ee down to formation of racemic **3a** was observed.

Figure 2 shows also a concomitant influence of the SDS concentration on the initial rate of the reaction. The initial increase of activity due to a better catalyst

Table 1. Catalytic enantioselective oxidation of aryl methyl sulfides with hydrogen peroxide mediated by **1**.

Entry	R^1	R^2	Time [h]	Yield[a] [%]	[**3**]/[**4**] ratio	ee[b] [%]	Abs. Conf.[c]	Solvent
1	C_6H_5 (**2a**)	CH_3	8.5	99	80	16	*R*-(+)	CH_2Cl_2
2	*p*-NO_2-C_6H_4 (**2b**)	CH_3	24	41	25	26[d]	*R*-(+)	CH_2Cl_2
3	C_6H_5 (**2a**)	CH_3	24	16	31	5	*S*-(−)	H_2O–CTABr[e]
4	C_6H_5 (**2a**)	CH_3	24	20	56	0	–	H_2O-Triton-X100[f]
5	C_6H_5 (**2a**)	CH_3	24	85	>200	29	*R*-(+)	H_2O–$C_{12}H_{25}(C_6H_5)SO_3Na$[g]
6	C_6H_5 (**2a**)	CH_3	24	82	180	30	*R*-(+)	H_2O–$C_{12}H_{25}SO_3Na$[h]
7	C_6H_5 (**2a**)	CH_3	24	98	>200	40	*R*-(+)	H_2O–$C_{12}H_{25}SO_4Na$[i]

General conditions: substrate:H_2O_2:**1** = 100:100:1; [substrate] = 0.75 mmol, [H_2O_2] = 0.75 mmol, [**1**] = 0.0075 mmol, solvent 3 mL, room temperature in air.

[a] Yield in sulfoxide determined by GC (column HP-5).

[b] Enantiomeric excess determined by CSP-GC (column Lipodex-E).

[c] Absolute configuration determined by optical rotations and comparison of the retention orders with known literature data.

[d] Enantiomeric excess determined by integration of the ^{1}H NMR spectrum with (*R*)-BINOL at 253 K in $CDCl_3$.

[e] Cetyltrimethylammonium bromide (168 mM, 1 mM in micelles).

[f] Polyoxyethylene(10)isooctyl phenyl ether (150 mM, 1 mM in micelles).

[g] Sodium dodecylbenzenesulfonate (63 mM, 1 mM in micelles).

[h] Sodium dodecylsulfonate (58 mM, 1 mM in micelles).

[i] Sodium dodecyl sulfate SDS (75 mM, 1 mM in micelles).

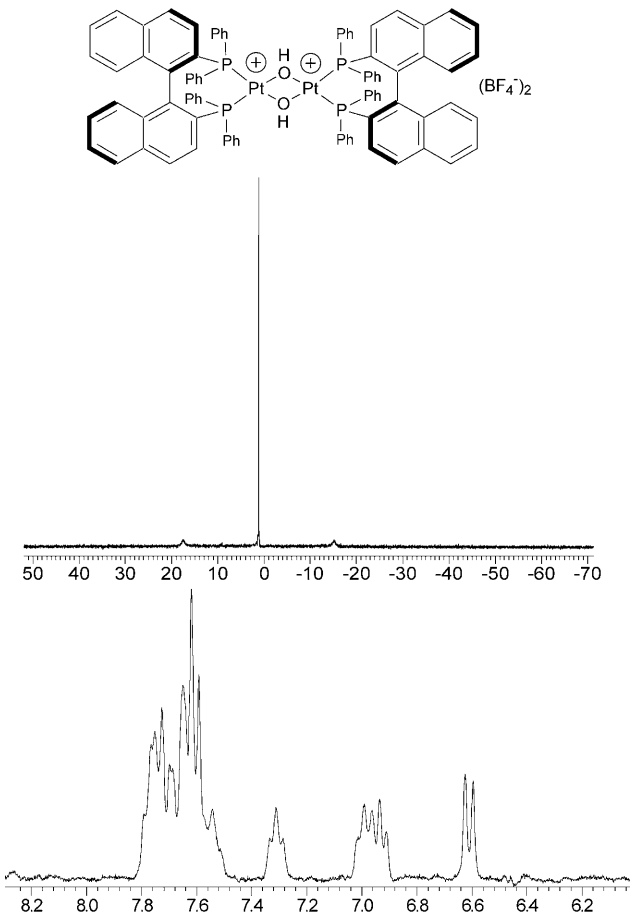


Figure 1. NMR spectra: $^{31}P\{^1H\}$ (*top*) and ^1H NMR spectra (*bottom*) of $\{[(R)\text{-BINAP}]Pt(\mu\text{-OH})\}_2(BF_4)_2$ (**1**). [**1**] = 2.5 mM, [SDS] = 75 mM in H_2O/D_2O (75/25).

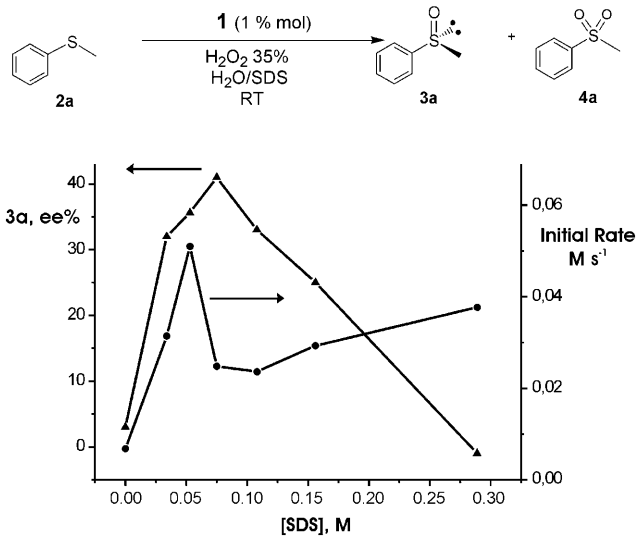


Figure 2. Effect of [SDS] on both enantiomeric excess (triangles) and initial rate (circles) for the asymmetric sulfoxidation of thioanisole (**2a**) with hydrogen peroxide [substrate **2a**:H_2O_2:**1** = 100:100:1; [**2a**] = 0.75 mmol, [H_2O_2] = 0.75 mmol, [**1**] = 0.0075 mmol, solvent water 3 mL, sodium dodecyl sulfate SDS (75 mM, 1 m M in micelles), room temperature].

and substrate solubilization is followed by a decrease down to a minimum corresponding to the highest enantioselectivity. This may be no coincidence as it is known that, in general, lower activities allow a better discrimination between the two diastereomeric transition states. Also the substrate to catalyst ratio (Table 2) appears to have an effect on the enantioselectivity (and on the [**3**]/[**4**] ratio) giving the maximum ee at an intermediate value, while the conversion remains unchanged.

This overall behavior seems to suggest that the micelle's average size[25] and the catalyst amount affect heavily both catalyst positioning and substrate approach to the active species. To further investigate this point and explore the synthetic scope of this oxidation procedure the catalytic enantioselective oxidation of different aryl alkyl sulfides with hydrogen peroxide in water-SDS solution catalyzed by **1** was studied (Table 3).

With solid substrates diethyl ether (generally used to extract the products) has to be employed from the beginning with the purpose of solubilizing the substrate and promoting catalyst-substrate interaction. Aqueous phase dissolves catalyst and oxidant, while the ether phase extracts the organic reagent and products.

Table 2. Catalytic enantioselective oxidation of thioanisole (**2a**) with hydrogen peroxide in water-SDS solution mediated by **1** at different molar ratios.

Entry	Yield[a] [%]	[**3**]/[**4**] ratio	ee[b] [%]	Abs. Conf.[c]	Molar ratios
1	98	>200	33	*R*-(+)	**2a**:H_2O_2:**1** = 50:50:1
2	98	>200	40	*R*-(+)	**2a**:H_2O_2:**1** = 100:100:1
3	99	115	34	*R*-(+)	**2a**:H_2O_2:**1** = 200:200:1
4	99	90	26	*R*-(+)	**2a**:H_2O_2:**1** = 1000:1000:1

General conditions: [**1**] = 0.0075 mmol, solvent water 3 mL, sodium dodecyl sulfate SDS (75 mM, 1 mM in micelles), room temperature in air , reaction time 24 h.

[a] Yield in sulfoxide determined by GC (column HP-5).

[b] Enantiomeric excess determined by CSP-GC (column Lipodex-E).

[c] Absolute configuration determined by optical rotations and comparison of the retention orders with known literature data.

Table 3. Catalytic enantioselective oxidation of aryl alkyl sulfides **2** with hydrogen peroxide in water-SDS solution mediated by **1**.

Entry	R^1	R^2	Time [h]	Yield[a] [%]	[**3**]/[**4**] ratio	ee[b] [%]	Abs. Conf.[c]
1	C_6H_5 (**2a**)	CH_3	24	98	>200	40	*R*-(+)
2	2-naphthyl (**2h**)	CH_3	24	99	32	34[d]	*R*-(+)
3	C_6H_5 (**2c**)	Bn	48	75	19	24[d]	n.d.
4	*p*-CH_3O–C_6H_4 (**2d**)	CH_3	24	96	97	22[d]	*R*-(+)
5	*p*-CH_3-C_6H_4 (**2e**)	CH_3	24	99	>200	31	*R*-(+)
6	*p*-Cl-C_6H_4 (**2f**)	CH_3	24	87	>200	48	*R*-(+)
7	*p*-CN-C_6H_4 (**2g**)	CH_3	48	68	21	63	*R*-(+)
8	*p*-NO_2-C_6H_4 (**2b**)	CH_3	48	63	90	88[d]	*R*-(+)

General conditions: substrate:H_2O_2:**1** = 100:100:1; [substrate] = 0.75 mmol, [H_2O_2] = 0.75 mmol, [**1**] = 0.0075 mmol, solvent water 3 mL, sodium dodecyl sulfate SDS (75 mM, 1 mM in micelles), room temperature in air.
[a] Yield in sulfoxide determined by GC (column HP-5).
[b] Enantiomeric excess determined by CSP-GC (column Lipodex-E).
[c] Absolute configuration determined by optical rotations and comparison of the retention orders with known literature data.
[d] Enantiomeric excess determined by integration of the ^{1}H NMR spectrum with (*R*)-BINOL at 253 K in $CDCl_3$.

The stereoselective oxidation is hardly sensitive to the steric hindrance between the thioether substituents R^1 and R^2 as observed by comparing **2a** and 2-methylsulfanylnaphthalene (**2 h**) (entries 1 and 2 in Table 3), while, as most other examples reported in the literature,[15] it does reflect the steric unbalance between R^1 and R^2 (entries 1 and 3 in Table 3). Additionally, it is much more affected by the electronic properties of the substrates (Table 3, entries 7 and 8 *versus* entry 1).

Decreasing the electron-donating properties of the substituents in the aryl moiety of aryl methyl sulfides (Table 3) causes both a decrease of yield, confirming the highly electrophilic oxidation character of the catalytic system, and a concomitant increase in the ee with the highest value (88%) observed with *p*-O_2N-C_6H_4-SCH_3 (**2b**). The selectivity of the process is very high, ranging from [**3**]/[**4**] ≥ 200 for electron-rich substrates, to 20 for electron-poor ones.

The Lewis acid character of the complex[26] favors racemization of the sulfoxides. This effect is more evident with the most electron-poor substrates which are known to be sensitive to acids.[18] For example, if the reaction with **2b** is carried out in dichloromethane solution (Table 1, entry 2), the initial 55% ee decreases to 26% after 24 h. This negative effect can be relieved in micellar media by employing diethyl ether in which **1** is not soluble. This allows us to extract the sulfoxides from the micelles, thus limiting the direct contact between catalyst and product and allowing isolation of the enantioenriched sulfoxide by simple two-phase separation. It has to be stressed once again that the higher initial stereoselectivity observed in aqueous media compared to dichloromethane is probably a consequence of the unique properties of water as solvent, in particular to its "hydrophobic effect"[6] that allows a closer contact between substrate and catalyst.

In order to get more insight into the stereoselective process, we explored the effect of the optical purity of the chiral diphosphine ligand on the product enantioselectivity, observing a remarkable positive non-linear effect (+)-NLE (Figure 3) which, according to the general principle suggested by Kagan,[27] supports the dimeric nature of the catalytically active species.

It is therefore likely that hydrogen peroxide is activated by substitution of the hydroxide bridging group of the catalyst to give a hydroperoxy species, with a bimetallic framework, with subsequent electrophilic oxidation of the substrates. This view, supported by the experimental evidence reported in Figure 3, seems peculiar for the present oxidation reaction and could be due to the specific medium employed. In fact, it contrasts with what is observed in dichloroethane solution with the same class

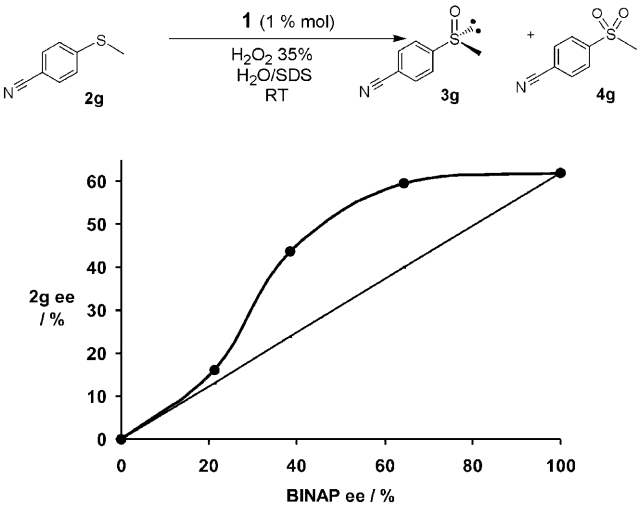


Figure 3. Positive non linear effect (+)-NLE for the oxidation of **2g** with hydrogen peroxide catalyzed by **1** in diethyl ether/water-SDS biphasic system {substrate **2g**:H_2O_2:**1** = 100:100:1; [**2g**] = 0.75 mmol, [H_2O_2] = 0.75 mmol, [**1**] = 0.0075 mmol, solvent water 3 mL, sodium dodecyl sulfate SDS (75 mM, 1 mM in micelles), room temperature}.

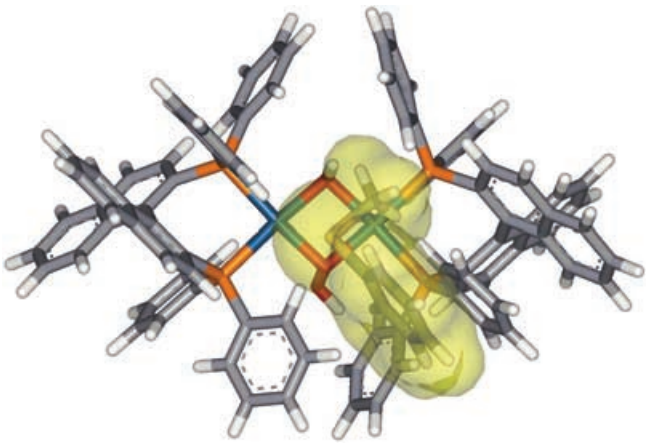


Figure 4. Postulated model for the approach of thioanisole (**2a**) to the dimeric hydroperoxo active species. In particular, it is worth noting the proximity between the aromatic groups of the substrate and the complex and between the peroxidic oxygen and the sulfur atom of the thioether.

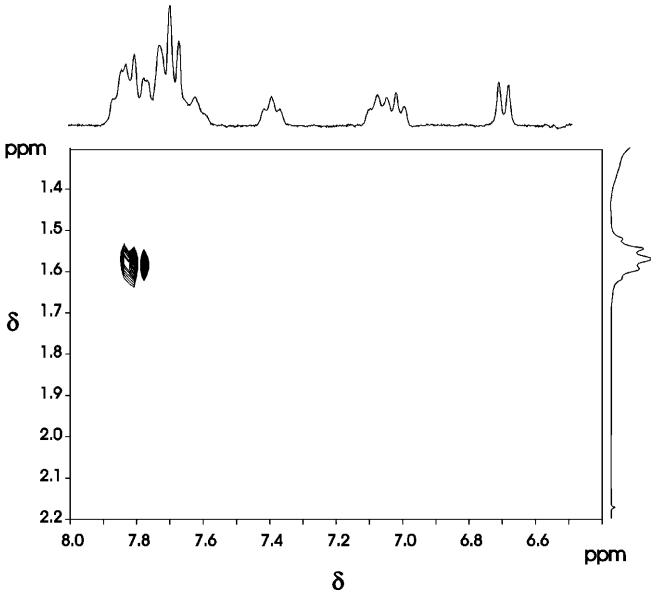


Figure 5. Portion of the 2D NOESY spectrum of {[(*R*)-BINAP]Pt(μ-OH)}$_2$(BF$_4$)$_2$ (**1**), [**1**] = 2.5 mM, [SDS] = 75 mM in H_2O/D_2O (75/25), showing the cross-peak between the catalyst and the second methylene of SDS.

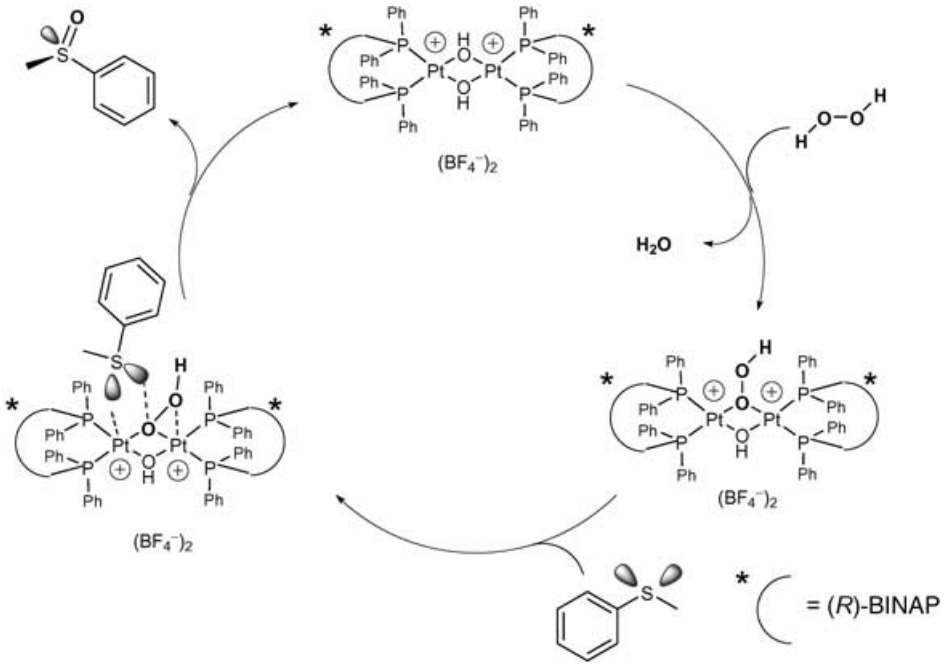
of complexes in the Baeyer–Villiger oxidation of ketones,[19] where the catalytically active species was recognized to be monomeric.

On the basis of the above observations, it is possible to propose a molecular model for the approach of the substrate to the catalyst like in Figure 4 in which the aromatic phenyl rings of (*R*)-BINAP present in the dimeric complex form a shallow pocket. Here the thioether can be accommodated driven by π–π interactions which are more pronounced for electron-withdrawing substituents on the substrate (see Table 3, entry 7 and 8, the highest enantioselectivity is observed with the most electron-poor substrates). The peroxidic oxygen is placed below the sulfur atom of the substrate which can attack the oxygen leading to the sulfoxide. This model accounts for the observed prevailing enantiomer in all cases tested.

The above observed modest effect on the ee found with either **2a** or **2 h**, seems to be an indication that the presence of both substrate and **1** inside a cavity such as a micelle is unlikely. In fact, as was found by Thomas and co-workers,[28] albeit for different enantioselective transformations, confining reactants and catalyst in the cavity of a zeolite results in strong steric effects. It may also be suggested that, the active species being bis-cationic, the latter is likely to interact with the micelle on the external part where the negatively charged sulfate groups are located. This is confirmed by a 2D-NOESY experiment (Figure 5) in which clear cross-peaks are detected between the naphthyl moiety of the dimeric catalyst and the second methylene of SDS (75 mM in H_2O/D_2O solution), suggesting the close proximity between the aromatic surfaces of the catalyst and the hydrocarbon chains of the surfactant, due to hydrophobic interactions. The approach of the substrate (from inside the micelle) to the catalyst (outside the micelle) may be mediated by channeling through the aliphatic chains of the aggregated surfactant in which the sulfide itself is dissolved. This view is also in general agreement with the micelle size effect reported in Figure 2.

The dimeric structure of the catalytically active species and the electrophilic nature of the oxidation suggest a possible catalytic cycle as reported in Scheme 2. The lower pK_a of hydrogen peroxide allows a facile acid-base reaction with exchange of the hydroxy bridging moiety with the hydroperoxidic anion.[29] Metal activation of the peroxy oxygen occurs, which is subsequently attacked by the sulfur atom of the thioanisole driven close to the complex by π–π and metal-sulfur coordination. This proposal is quite similar to the classical mechanism of electrophilic oxidation with hydroperoxides suggested by Sharpless[30] and Kagan[18a] many years ago. The neutral sulfoxide product is then released and the hydroxy bridging ligand is restored for the next catalytic cycle.

The synthetic methodology reported here represents a viable way for carrying out asymmetric sulfoxidation in water. Catalyst loading is low, yields and sulfoxide/sulfone selectivity are from good to excellent (no other products are formed) and, as was previously reported for other asymmetric transformations,[6–9] the aqueous medium allows a significant improvement in the asymmetric induction, compared to the use of organic solvents, although ees are from moderate to good, with only one case in the > 80% range. From this point of view, in the literature, catalysts capable of a better enantioselective performance do exist, but they invariably work in organic (chlorinated) solvents and require ei-



Scheme 2. Possible catalytic mechanistic cycle for the oxidation of aryl alkyl sulfides with hydrogen peroxide mediated by **1** in water-SDS.

ther a higher loading, or different oxidants, or low temperatures with consequent slow down of rates.[15]

So far, the synthetic scope of this protocol seems to be limited to alkyl aryl sulfides with a pronounced steric unbalance between the two substituents. This is relatively common and, indeed, catalysts capable of promoting the asymmetric oxidation of dialkyl or diaryl sulfides are only few and operate at the expenses of other important synthetic parameters.[18]

One major advantage of the present protocol is the possibility to use commercial hydrogen peroxide solutions as the oxidant, i.e., the most environmentally friendly peroxy oxidant one can think of.

The use of surfactants seems to be of quite general applicability, as micelles provide an interface that allows the catalyst (that is insoluble both in water and in diethyl ether) to contact the substrate and promote its oxidation. In doing so, they allow the use of water as the reaction medium also with "ordinary" transition metal catalysts, thereby avoiding the need to modify the catalyst with hydrophilic functional groups. Micelles also play a pivotal role in the approach between catalyst and substrate (depending on their size) that has a strong influence on the enantioselectivity of the system.

From a practical point of view, the possibility to separate the products from the catalyst and the exhausted oxidant by simple diethyl ether/water-SDS separation is also an important advantage. Products can be easily isolated by simple solvent evaporation and, in principle, the catalyst could be reutilized by simple addition of fresh substrate and oxidant. Unfortunately, the catalyst reported here is rather sensitive to hydrogen peroxide and hence, upon recycling, much of its activity and enantioselectivity are lost.

Conclusion

In summary, we have developed the first example of asymmetric catalytic sulfoxidation in water. Additional key features towards possible synthetic applications are (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 selectivities up to 200 and enantioselectivities up to 88%, (v) use of mild experimental conditions. Extension to a broader range of substrates, to the use of more oxidation-resistant catalysts and further investigation on the effect of surfactant on the catalytic activity are underway.

Experimental Section

General

Diethyl ether was freshly distilled prior to use and water was purified according to the milliQ technique. Hydrogen peroxide (35% Aldrich) as well as compounds **2a**, **2c**, **2d**, **2e**, **2f**, **2g**, **2b** (Aldrich) are commercial products and were used without further purification. ^{1}H NMR, and ^{31}P{^{1}H} NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 and

121.50 MHz, respectively. δ values in ppm are relative to $SiMe_4$ and 85% H_3PO_4. The 2D-NOESY experiment was acquired with a spectrum width of 10 ppm, a relaxation delay d_1 of 1 s, using 2 K data points in the t_2 dimension and 512 data points in the t_1 dimension, with subsequent weighting with the sine-bell function using 160 scans for each t_1 increment. The mixing time d_8 employed was 0.4 s. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector (gas carrier He). All reactions were monitored on a 25 m HP-5 capillary column. Enantiomeric excess was determined as reported in Tables 1 to 3.

Materials

Sulfide **2 h** was prepared by alkylation with methyl iodide of the corresponding 2-naphthalenethiol and purified by flash chromatography on silica. NMR spectroscopic data (^1H, ^{13}C NMR) and mass analysis are in agreement with literature data.[31] The chiral complex $\{[(R)\text{-BINAP}]Pt(\mu\text{-OH})\}_2(BF_4)_2$, was prepared following the procedure reported in the literature.[20]

Partially resolved **1** complexes employed for the non-linear effect study (NLE) were prepared starting from mixtures of $[(R)\text{-BINAP}]PtCl_2$ and $[(S)\text{-BINAP}]PtCl_2$.[20] The Pt precursors were dissolved in the proper enantiomeric ratio in wet acetone (25 mL) and dichloromethane (25 mL) at room temperature and treated with 2 equivalents per Pt atom of a standardized solution of $AgBF_4$ in acetone. The reaction mixture was stirred under nitrogen for 2 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with diethyl ether to give a pale yellow solid, which was filtered off and dried under vacuum; yield: 90–95%.

Oxidation Reactions

These were carried out in a 10-mL, round-bottomed flask equipped with a sidearm fitted with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer (700 rpm). Constant temperature (25 °C) was maintained by water circulation through an external jacket connected with a thermostat. The concentration of the commercial 35% H_2O_2 solution was checked iodometrically prior to use.

Typically, the proper amount of surfactant was dissolved in deionized water (3 mL), followed by catalyst **1** (13.8 mg 0.0075 mmol). After 10 min the substrate (0.75 mmol) was added [if solid with the aid of diethyl ether (3 mL)] and the mixture stirred for 10 minutes. To this 35% hydrogen peroxide was added in one portion (0.75 mmol) and the mixture stirred at room temperature. After 24 or 48 h diethyl ether (if not present from the beginning) was added to extract the product.

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