Catalysis Methods

A Catalytic Langmuir Film as a Model for Heterogeneous and Homogeneous Catalytic Processes**

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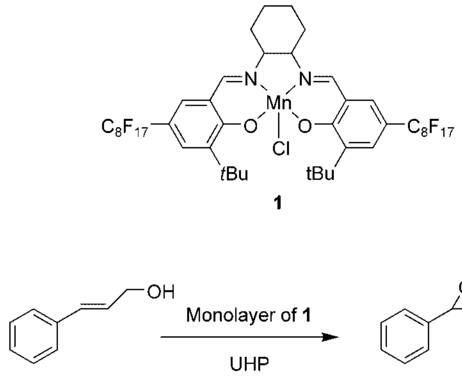
The design and optimization of new catalytic systems continue to inspire a tremendous amount of work due to the importance of catalysis in many scientific fields and especially in industry. In particular, development of recoverable catalysts,[1] for example, by immobilization of a homogeneous catalyst on a solid surface[2] or by means of surface organometallic chemistry,[3] offers interesting perspectives. Pseudohomogeneous systems such as dendritic catalysts have also been recently developed.[4] They exhibit many of the advantages of homogeneous catalysts, but also some of the benefits of heterogeneous catalysts (e.g., easy recovery after the reaction). Their well-controlled synthesis allows one to tune their chemical properties by adjusting their core and peripheral structure. In several cases, the dendrimer generation also has a strong influence on the reaction catalyzed by the dendrimer.[5,6] This is supposedly related to an increased density of external groups or to lesser accessibility to reactants.

Regardless of the type of catalytic system, it is difficult to perfectly control or characterize the density and orientation of the catalytic centers, as well as the accessibility of these centers to reactants. Yet the influence of these structural parameters on the catalytic properties is paramount. Therefore, there is a clear lack of a chemical system in which the orientation and density of the catalytic sites can be easily modified, so that the effect of those parameters on catalysis efficiency can be measured. We propose using the gas/water interface as a model for such catalytic processes. Indeed, the organization and molecular density in a monolayer at this interface are readily adjustable through compression of the layer and choice of amphiphilic compound. Chemical reactions (e.g., hydrolysis, polymerization) have indeed been performed in Langmuir films,[7–10] but in all cases the surfactants forming the monolayer were themselves the reactants. Langmuir films have also been used to organize molecular catalysts on a solid substrate to generate well-defined supported catalytic systems.[11–13] However, to our knowledge, no attempt has been made heretofore to form monolayers at the gas/water interface in which the Langmuir film is the catalyst.

We chose to study olefin epoxidation as a model reaction considering the scientific and industrial importance of this class of reaction. For this purpose, we selected a salen complex **1** bearing two fluorinated chains (Scheme 1) as a potential catalyst. Metal salen complexes are chemically robust, and their catalytic activity in epoxidation reactions is well documented for various substrates in many solvents.[14] Furthermore, fluorinated tails are well known for their ability to facilitate the formation of stable Langmuir films.[15] Finally, compound **1** is an efficient catalyst for the epoxidation of alkenes in bulk solution.[16] To assess the catalytic properties of a Langmuir film of **1** in such a reaction (Scheme 1), we chose as reactants a vinylic compound which is slightly soluble in water, namely, cinnamyl alcohol, and the urea/hydrogen peroxide complex (UHP) as an oxygen source for the oxidation, because of its stability and ease of handling.[17]



Scheme 1. Salen complex **1** and the chemical reaction studied in this work.

When spread at the gas/water interface, salen complex **1** formed stable monolayers up to its collapse at about 24 $\mathrm{mN\,m^{-1}}$ (Figure 1 and Table 1). Before the onset of the surface pressure (at about 183 $\mathrm{Å^2\,molecule^{-1}}$), Brewster-angle microscopy (BAM) demonstrated that the monolayer is in a biphasic state (inset of Figure 1) in which gaseous domains are in equilibrium with liquid domains. After the onset, the monolayer appeared quite homogeneous. The molecular area at collapse was around 115 Å^2, which is comparable to the average area of a salen complex with a conformation in which the average MnN_2O_2 plane is more or less perpendicular to the surface.[18] The monolayer of **1** was also transferred onto a calcium fluoride substrate in order to check its chemical

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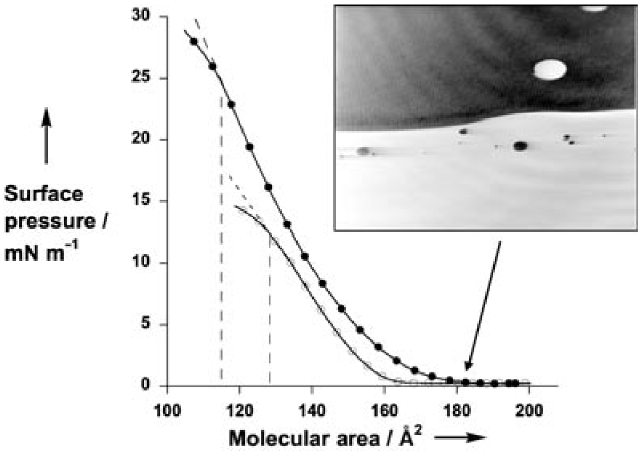

Figure 1. Compression isotherm of **1** at room temperature on pure water (●) and on a solution of UHP (5×10^{-5} mol L^{-1}) and cinnamyl alcohol (10^{-5} mol L^{-1}) (○). Inset: Typical morphology of the film observed by BAM at low surface pressure (dark domains: gaseous phase; light domains: liquid phase; real size: 430×536 μm^2).

Table 1: Analysis of the compression isotherms of **1** on various subphases at 20 °C.

Subphase solution	Surface pressure onset [Å^2]	Collapse area [Å^2]	Collapse surface pressure [mN m^{-1}]
pure water	183	115	24.4
cinnamyl alcohol[a]	189	119	22.5
UHP solution[b]	165	123	15.7
UHP and cinnamyl alcohol[c]	163	129	12.3

[a] Concentration: 10^{-5} mol L^{-1}. [b] Concentration: 5×10^{-5} mol L^{-1}. [c] Concentrations: 5×10^{-5} mol L^{-1} and 10^{-5} mol L^{-1}, respectively.

stability at the gas/water interface: the equivalence of the IR spectra of **1** in a KBr pellet and in the LB film proved the chemical integrity of the catalyst at the interface.

When cinnamyl alcohol was added to the subphase in a concentration of 10^{-5} mol L^{-1} (molar ratio catalyst/alkene close to 1/50), the isotherm was slightly shifted towards larger areas per molecule (Table 1). This may be related to some interaction or adsorption of cinnamyl alcohol molecules at the interface due to their partial lipophilic character. The effect of UHP (5×10^{-5} mol L^{-1}) was clearly stronger: the collapse pressure decreased to about 16 mN m^{-1}, and the monolayer was more dense at a given surface pressure. These changes suggest strong interactions between salen **1** and the oxidant and could be an indication of the formation of oxidized forms of **1**. Adding cinnamyl alcohol to this UHP solution did not induce any further important modification of the isotherm (Table 1).

When a solution of cinnamyl alcohol and UHP (10^{-5} and 5×10^{-5} mol L^{-1}, respectively) was kept for 18 h in the Langmuir trough without any monolayer spread at its interface, no oxidation of the cinnamyl alcohol could be detected by GC after extraction of the subphase with dichloromethane (see Experimental Section). To assess the effect of a monolayer of **1**, a shorter reaction time was used (typically 6 h) to limit any (undetected) bulk oxidation. After spreading and compression of the monolayer (if necessary), GC analysis demonstrated that some epoxide of the cinnamyl alcohol had formed in the subphase. The area of the epoxide peak (a few tenths of a per cent to a few per cent of the peak for unconverted cinnamyl alcohol) varied with compression of the monolayer (see below) and the reaction time. Preliminary experiments suggested a linear dependence of this peak area on time in the range 6–24 h. Thus, this oxidation was not an artefact due to the extraction/analysis process but was directly related to the Langmuir film.

Consequently, it can be stated that the monolayer of **1** plays the role of a catalytic surface for the epoxidation of cinnamyl alcohol dissolved in the subphase. Direct comparison of the kinetics in this system (without stirring) and in bulk solution is clearly difficult. Therefore, we concentrated on the relative effect of the compression of the Langmuir film on the reaction by measuring the area of the epoxide peak relative to the alkene peak (% A) in the GC chromatogram for different molecular areas of the catalyst at the interface. When the monolayer was compressed, the Langmuir film did not cover the whole surface of the subphase (which was, however, entirely recovered for the GC analysis). To take this experimental limitation into account, we assumed that the quantity of formed epoxide is proportional to the surface area S of the catalytic monolayer, and therefore we defined an apparent rate of reaction ρ [Eq. (1)],where τ is the reaction time. Figure 2 shows the experimental variation of the apparent rate with the molecular area of **1** in the monolayer.

$$\rho = \%\mathrm{A}\,(S\,\tau)^{-1} \qquad (1)$$

For low surface pressures and large molecular areas (greater than ca. 155–160 Å^2), the apparent rate increased slowly with compression of the film. For such low surface pressures, the monolayer was in a biphasic state. Compression of the Langmuir film leads only to changes in the proportions

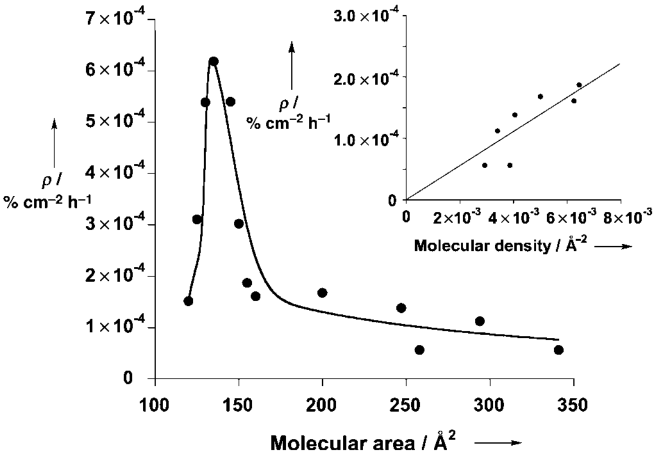

Figure 2. Apparent rate ρ of the catalyzed reaction (see text) versus the molecular area of catalyst **1** spread at the gas/water interface (the line is a guide to the eye). The inset plots ρ versus the molecular density for molecular areas larger than 155 Å^2 (linear fit).

of the liquid phase and the gaseous phase, but should not modify the organization within the liquid domains. Thus, the small increase in reactivity can not be ascribed to a change in the molecular orientation in the Langmuir film, but should be simply related to the variation of the average molecular density. Because the epoxidation of cinnamyl alcohol should be roughly first order in catalyst concentration, as was demonstrated in the bulk for indene,[19] we can assume that the reaction along the monolayer is also first-order in the average catalyst surface density. Therefore, the apparent rate of reaction should be proportional to the surface molecular density of **1**. Experimentally, this rate is indeed found to be reasonably proportional to the surface molecular density (i.e., the reciprocal molecular area) of **1** at the interface (inset in Figure 2).

When the monolayer was in a monophasic state (i.e., for molecular areas below ca. 160 Å^2), the apparent rate deviated strongly from the previous simple law, and the formation of epoxide was clearly enhanced. Contrary to the previous case, such a change can not be only related to the increase in the molecular density. Even if a definitive explanation of this higher catalytic activity can not be given at this stage of the study, one can propose a simple hypothesis. The increase in molecular density when the monolayer is compressed in its liquid phase can be achieved only by a reorientation of various chemical groups of **1**. In particular, the manganese salen complex should be less and less tilted versus the normal to the interface with increasing compression. Therefore, the access (ease and main relative orientation) of hydrogen peroxide or cinnamyl alcohol to the manganese center should depend on the mean molecular area of **1**. This effect alone may explain the observed change in the catalytic activity.[20]

For molecular areas below about 135 Å^2, the apparent rate ρ of the reaction was strongly decreased. Again, this may be due to changes in the orientation of the catalytic center. However, most probably, this is simply related to the slow collapse of the monolayer. Indeed, the collapse area at constant compression rate was found to be around 129 Å^2 molecule^{-1} (Table 1). Given that this value depends on the exact compression mode and that the collapse process is not abrupt (Figure 1), the observed change in reaction rate was more or less simultaneous with collapse of the monolayer. Such a process, which should lead to multilayer formation, decreases the number of catalyst molecules in close contact with the subphase, and this explains the experimental drop in catalytic activity.

These results demonstrate that the monolayer of **1** catalyzes the epoxidation of cinnamyl alcohol dissolved in the subphase with a rate strongly related to the molecular density and organization within the Langmuir film. For this particular catalyst/substrate pair, the highest efficiency is obtained for an average molecular area of about 140–145 Å^2. Further experiments will try to determine the molecular orientation within the monolayer and relate this to the molecular structure of the catalyst and the apparent rate of reaction. Finally, similar experiments will be performed with chiral salen complexes to check whether the architecture of the Langmuir film has any effect on the stereoselectivity of the epoxidation.

More generally, the present study proves that a soft and controllable interface like a Langmuir film is a powerful model of reactive surfaces and may help understand the reactivity in various heterogeneous and homogeneous catalytic systems.

Experimental Section

Amphiphilic complex **1** was prepared by metalation of the corresponding racemic salen ligand derived from *trans*-1,2-diaminocyclohexane by following a procedure previously described for the chiral analogue.[16] The crude compound was recrystallized from EtOH to give a brownish solid in 85% yield. UV/Vis (10^{-5} mol L^{-1}, CH_3OH): λ_{max} ($\lg\varepsilon$) = 235 (4.72), 405 nm (3.71). Elemental analysis (%) calcd for $C_{44}H_{34}ClF_{34}MnN_2O_2$ (1359.1): C 38.88, H 2.52, N 2.06; found: C 39.02, H 2.44, N 2.36.

All other compounds were obtained from Aldrich and used without further purification. The water of the subphase, purified by a Purite Select apparatus, had a resistivity higher than 16 MΩ cm. Chloroform (HPLC-grade from SDS) was the spreading solvent, and the solutions of the amphiphilic complex were kept at −18 °C between experiments to limit solvent evaporation.

Isotherms were obtained with a NIMA trough (type 601BAM) equipped with a Wilhelmy plate and maintained at 20 °C. The compression rate of the monolayer was close to 3 Å^2 molecule^{-1} min^{-1}. A BAM2plus from NFT was used for the Brewster-angle microscopy experiments.

The reactions were performed on a laboratory-made Langmuir–Blodgett trough (maximum available surface area ca. 1100 cm^2, volume of the subphase ca. 340 ± 40 mL including a ca. 30 mL dipping well) working at room temperature and under partial nitrogen atmosphere.[21] For the catalysis experiments, the subphase was an aqueous solution containing 5×10^{-5} mol L^{-1} of UHP and 10^{-5} mol L^{-1} of cinnamyl alcohol. Shortly after spreading, the monolayer was compressed (if necessary) at a rate of ca. 35 Å^2 molecule^{-1} min^{-1}, and the area per molecule was kept constant during the experiment. After 6 h, the whole subphase was recovered and extracted with ca. 20 mL of HPLC-grade dichloromethane. The solvent of the organic solution was evaporated under reduced pressure, and the residue was kept at −18 °C until GC analysis.

Built-up films were obtained by the vertical lifting method with a dipping speed set to 1 cm min^{-1}. Films (19 layers) were transferred from the gas/pure water interface onto optically polished calcium fluoride substrate (Y-type transfer with a transfer ratio of ca. 0.7 for a transfer pressure of 10 mN m^{-1}).

GC analysis was performed with a Varian Chrompack (CP-3800) apparatus equipped with an SGE nonpolar capillary column (BPX5 30 m × 0.25 mm) (injector temperature: 250 °C; splitless injection mode; carrier gas: helium at 1 mL min^{-1}; initial oven temperature: 30 °C, 2 min; rate 1: 15 °C min^{-1}; final temperature 1: 150 °C, 15 min; rate 2: 20 °C min^{-1}; final temperature 2: 250 °C, 2 min; detector temperature: 300 °C). The retention times were found to be ca. 12.5 min for the cinnamyl alcohol, and 13.6 min for the corresponding epoxide.

Infrared spectra were recorded on a Perkin Elmer FT 1760-X spectrometer. For spectra of the pristine powder of **1**, KBr pellets (containing ca 0.5 wt% of **1**) were used.

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