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Monolayers of Salen Derivatives as Catalytic Planes for Alkene Oxidation in Water

Andrea Pasc-Banu,[a] Claudia Sugisaki,[a] Thierry Gharsa,[a] Jean-Daniel Marty,[a] Ignacio Gascon,[a] Michael Krämer,[a] Gianluca Pozzi,[b] Bernard Desbat,[c] Silvio Quici,[b] Isabelle Rico-Lattes,[a] and Christophe Mingotaud*[a]

Abstract: Monolayers at the gas/water interface have been used as an adjustable catalytic system in which the molecular density may be modified. Mn^{III}–salen complexes bearing perfluoroalkyl substituents have been organized as a Langmuir film on an aqueous subphase containing a urea/hydrogen peroxide adduct (UHP, the oxidant) and cinnamyl alcohol (the substrate). The catalytic activity of the monolayer for the epoxidation of the alkene dissolved in water has been demonstrated and the reaction kinetic investigated. For a constant area per molecule of catalyst, the reaction rate exhibits first-order dependence on oxidant concentration and zero-order dependence on alkene concentration, in agreement with the reaction orders reported for Mn^{III}–salen-catalyzed epoxidation reactions carried out in solution. Furthermore, kinetic experiments suggest an enhanced activity of the catalysts assembled in a Langmuir film relative to that observed in bulk reaction. Finally, varying the molecular density of the catalyst at the gas/water interface highlights an important dependence of the catalytic activity of the layer with the mean molecular area. A strong increase of the catalytic properties of the monolayer was observed for a mean molecular area of 140–145 Å^2, an increase which was supposedly related to a modification of the Mn^{III}–salen complex orientation at the interface upon compression. This hypothesis was supported by PM-IRRAS (polarization modulation infrared reflection adsorption spectroscopy) experiments performed in situ on the monolayer. Such results demonstrate that a soft and adjustable molecular system like a Langmuir film can be used to better understand the reactivity in various heterogeneous and/or pseudohomogeneous (such as those based on dendrimers) catalytic systems.

Keywords: epoxidation · heterogeneous catalysis · Langmuir film · manganese · monolayers · N,O ligands

Introduction

The organization and confinement of molecular catalysts may considerably modify their properties, as clearly demonstrated in various systems, in particular in the case of dendrimeric catalysts. Indeed, a strong influence of the generation number of the dendrimer has been observed on reactions occurring at the dendrimer surface. One example is the enantioselective reduction of a prochiral ketone by $NaBH_4$ in presence of chiral amphiphilic dendrimers prepared from polyamidoamine (PAMAM) and D-gluconolactone.[1] Cooperative effects have been also reported for dendrimeric Co–salen complexes, which exhibit enhanced catalytic activity in the hydrolytic kinetic resolution of terminal epoxides tuned by the generation number.[2] The peculiar effects observed in these two examples suggest that proper molecular orientation and density of the catalytic centers at the dendrimer/solution interface are crucial. In the burgeoning field of supported molecular catalysts, similar questions arise concern-

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[a] Dr. A. Pasc-Banu, Dr. C. Sugisaki, T. Gharsa, Dr. J.-D. Marty,
Dr. I. Gascon, Dr. M. Krämer, Dr. I. Rico-Lattes, Dr. C. Mingotaud
Laboratoire des Interactions Moléculaires et
Réactivité Chimique et Photochimique
CNRS UMR 5623, Université Paul Sabatier
118 route de Narbonne, 31062 Toulouse Cedex 4 (France)
Fax: (+33) 561-558-155
E-mail: cmingo@chimie.ups-tlse.fr.

[b] Dr. G. Pozzi, Dr. S. Quici
CNR-Istituto di Scienze e Tecnologie Molecolari
via Camillo Golgi, 19, 20133 Milano (Italy)

[c] Dr. B. Desbat
LPCM, CNRS UMR 5803, Université de Bordeaux I
Bât. A12, 33405 Talence cedex (France)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Analytical and spectral characterization data of compounds **1**, **2** and **3**. IR spectra of **3** in bulk and LB films. Analysis of the compression isotherm of **3** with various UHP concentrations. Comparison between the experimental rate of epoxidation and the one expected following a linear dependency of the rate with the molecular density.

ing the influence of the local organization of the active species on the macroscopic catalytic properties. Whatever the strategy used to immobilize the catalytic center on an organic or inorganic solid support may be,[3–6] it is often difficult to point out the influence of the molecular architecture on chemical activity, because of the lack of homogeneity of the modified surface of the solid support. Therefore, development of model systems in which the molecular catalytic centers are organized with a well-defined molecular density and mean orientation with respect to the normal of a surface is highly desirable. To this end, the generation of Langmuir–Blodgett films from appropriately modified molecular catalysts has been proposed. Manganese[7] or iron[8] porphyrins as well as rhodium complexes of 4,4′-dialkylbipyridines[9] have been thus structured on a solid substrate leading to well-defined, supported catalytic systems. Those studies provided new insights on the major influence of molecular architecture on the catalytic activity. In addition, we recently suggested that a monolayer of a fluorous Mn^{III}–salen complex at the fluid gas/liquid interface was able to catalyze a chemical reaction and that the compression state of the film modified the efficiency of the catalytic process.[10] In this paper, we demonstrate that such a film catalyzes the epoxidation of a particular alkene dissolved in the subphase. The reaction follows kinetic behavior similar to that observed in bulk, but the activity of the catalyst in the organized system is appreciably enhanced. Furthermore, we show that the effect of the compressed state of the monolayer on its catalytic activity can be explained in terms of change in the catalyst orientation during the compression. This modification in the organization was demonstrated by PM-IRRAS (polarization modulation infrared reflection adsorption spectroscopy) experiments performed at the gas/water interface.

Experimental Section

Materials: Urea/hydrogen peroxide adduct (UHP) and cinnamyl alcohol were obtained from Aldrich and were used without further purification. Water for the subphase was purified by a Purite Select apparatus and had a resistivity higher than 16 MΩ cm. Chloroform used as spreading solvent was HPLC grade from SDS. Synthesis of the amphiphilic catalyst **3** was carried out as described in a previous publication.[10] The amphiphilic complexes **1** and **2** were prepared by metalation of the corresponding racemic salen ligands derived from *trans*-1,2,-diaminocyclohexane, following a procedure described previously for enantiopure analogues.[11] Details are given as Supporting Information. (*E*)-3-Pheny1–2,3-epoxypropan-l-ol was prepared as described in the literature.[12]

Methods: The amphiphile solutions 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 speed 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 reaction experiments were performed on a Langmuir–Blodgett laboratory-made trough (maximum available surface 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.[13] For the catalysis experiments, the subphase was an aqueous solution containing UHP (typical concentration 5×10^{-5} mol L^{-1}) and cinnamyl alcohol (typical concentration 10^{-5} mol L^{-1}). Shortly after spreading, the monolayer was compressed (if necessary) with a speed of about 35 Å^2 molecule^{-1} min^{-1} to increase the molecular density to the desired value. Then, the area per molecule was kept constant during the experiment. After 6 h, the whole subphase was recovered and extracted with approximately 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.

GC analyses for Langmuir experiments were performed with a Varian Chrompack (CP-3800) apparatus equipped with a 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 250 °C, 2 min; detector (FID) temperature: 300 °C). The retention times were found to be about 12.5 min for the cinnamyl alcohol and 13.6 min for the corresponding epoxide. The calibration for such analyses was performed by injection of solutions containing a known concentration of cinnamyl alcohol or its epoxide as well as an external reference (1,4-dichlorobenzene).

For kinetic experiments in bulk, GC analyses were performed on an Agilent 6850 instrument (column: HP-1 100 % dimethylpolysiloxane 30 m × 320 mm × 0.25 mm) (injector temperature = 150 °C; splitless injection mode; carrier gas: Helium at 1 mL min^{-1}; detector (FID) temperature = 280 °C).

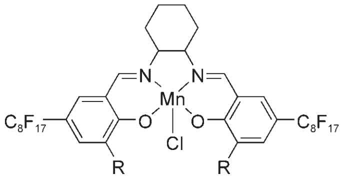
Built-up films were obtained by the vertical lifting method with a dipping speed set to 1 cm min^{-1}. Films (19 layers) were transferred from the gas/pure water interface onto optically polished calcium fluoride substrate (Y type transfer with a transfer ratio of ca. 0.7 for a transfer pressure of 10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

Infrared spectra were recorded on a Perkin Elmer FT 1760-X spectrometer. For spectra of the pristine powder of **3**, KBr pellets (containing ca. 0.5 wt % of **3**) were used.

PM-IRRAS measurements: The PM-IRRAS (polarization modulation infrared reflection adsorption spectroscopy) experimental set-up has been described previously.[14,15] It is based on the fast modulation of the incident IR beam between parallel (p) and perpendicular (s) polarizations. The processing of the intensity of the reflected beam leads to the differential reflectivity spectrum $\Delta R/R = (R_p - R_s)/(R_p + R_s)$. In the case of the water substrate, the calculated spectra were then divided by those of the subphase (normalized PMIRRAS spectra) to remove the contribution of the liquid water absorption. The spectra were collected by a Nexus 870 spectrometer working with an 8 cm^{-1} resolution (two levels of zero-filling) and equipped with a liquid-nitrogen-cooled HgCdTe detector (SAT). Those measurements were performed on a Teflon Langmuir trough from Nima, equipped with a Wilhelmy balance and a plate made of Whatman paper for the surface pressure measurement.

Results and Discussion

Selection of the catalyst: Metal–salen complexes were chosen as target compounds because they are versatile catalysts in a variety of chemical transformation.[16] Despite the fact that their properties in solution have been widely investigated, limited amount of data is available concerning the behavior of such compounds at the gas/water interface. To select a suitable complex for the generation of Langmuir films, three Mn^{III}–salen derivatives with different hydrophilic–hydrophobic balances were examined. These complexes are characterized by the presence of perfluoroalkyl chains, a structural feature that should facilitate the formation of stable Langmuir films,[17] and were easily synthesized by a modification of a literature procedure.[11] Compound **1** formed Langmuir films with an onset of the surface pressure



1 R = H
2 R = C_8F_{17}
3 R = *t*Bu

found for about 102 Å^{2}molecule^{-1} and a slow collapse at 18 mN m^{-1}. However, the stability of the monolayer versus time was poor, especially for surface pressure higher than 6 mN m^{-1}. This instability was not compatible with the goal of the study for which well-defined molecular density at the interface was required. Generally, stability may be increased by means of longer hydrophobic tails or by increasing the number of such groups. Therefore, compound **2** was spread at the gas/water interface. Langmuir films of this compound exhibit enhanced stability versus time and have a collapse point at 14 mN m^{-1} and approximately 98 Å^{2}molecule^{-1}. Unfortunately, Brewster angle microscopy (BAM) demonstrated that those Langmuir films were formed by the coexistence of monolayer with thicker "crystallites". Hydrophobic interactions between molecules of **2** were thus too high and were stabilizing three-dimensional aggregates of compound **2** at the gas/water interface. This not purely bidimensional system was therefore also not suitable for further investigations. Intermediate hydrophobicity between compounds **1** and **2** was then attempted by selecting compound **3**. The compression isotherm of this salen derivative showed an increase of the surface pressure for an area close to 180 Å^{2}molecule^{-1} on pure water and a collapse which appeared at about 24 mN m^{-1} and approximately 115 Å^{2}molecule^{-1}. This last value 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 was quite stable versus time and the BAM experiments demonstrated that the Langmuir film was homogeneous, with a gaseous/liquid phase transition at zero surface pressure (see insert of Figure 1). Chemical stability of compound **3** at the gas/water interface was also confirmed by comparison of the IR spectrum of the pristine compound with that of multilayers obtained by transfer of the Langmuir onto a solid substrate (see Supporting Information). Compound **3** was therefore selected as potential catalyst in Langmuir film.

Selection of the substrate and the oxidant: Several vinyl and allyl compounds were initially selected as potential reactants. For example, *trans*-stilbene was first tested. Its poor solubility in water was sufficient for its use as a reactant. However, various experiments demonstrated that uncatalyzed oxidation of stilbene occurred without any monolayer. Therefore, a less reactive (and more soluble) vinyl molecule, that is, cinnamyl alcohol, was chosen. No spontaneous oxidation was detected for this compound. Concerning the oxidant, a large panel of compounds was also available.[19–22] We reasoned that a mild oxidant endowed with high solubility and stability in water would be preferable. Therefore, the 1:1 adduct between urea and hydrogen peroxide, noted UHP, (in which the hydrogen peroxide is bound to urea by hydrogen bonding[23]) was chosen, in particular because of its stability and easiness to handle.[24]

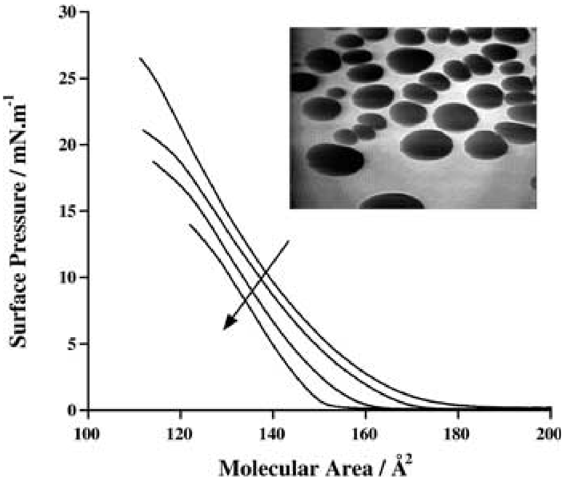


Figure 1. Compression isotherms of **3** on UHP solution of various concentrations (0 mol L^{-1}, 1.25×10^{-5} mol L^{-1}, 5×10^{-5} mol L^{-1}, and 10^{-4} mol L^{-1}) at 20 °C. The arrow indicates the evolution for increasing concentrations of UHP. Insert: typical image of the monolayer obtained at zero surface pressure by Brewster angle microscopy (real size of the image: 430×536 μm^2).

Effect of the substrate and the oxidant on the surface properties of the catalyst: The effect of the substrate and the oxidant dissolved in the subphase was then investigated. Increasing the concentration of UHP (in the range 0 to 10^{-4} mol L^{-1}) induced a destabilization of the monolayer and led to steeper compression isotherms (see Figure 1). Indeed, on increasing the UHP concentration up to 10^{-4} mol L^{-1}, the collapse pressure decreased from 24.4 to 12.7 mN m^{-1} (the corresponding molecular area increased only slightly from 115 to ca 125 Å^2) and the onset shifted from 183 without UHP to about 153 Å^2. These results point toward an interaction between the hydrogen peroxide coming from UHP and the monolayer (i.e., either oxidation of compound **3**) and/or (partial) adsorption of urea along the surface. The destabilization of the monolayer clearly limits the range of UHP concentration that one could use for the catalytic experiments.

Similar experiments were carried out with increasing concentration of cinnamyl alcohol in the subphase (see Figure 2). For a 10^{-5} mol L^{-1} concentration, the compression isotherm of **3** was just slightly shifted toward larger areas. No destabilization of the monolayer was observed. Increasing the concentration (up to 5×10^{-5} mol L^{-1}) did not induce further modifications in the isotherms. Such a change may be related to a slight adsorption of cinnamyl alcohol along the monolayer.

Therefore, a monolayer consisting of **3** could be used on a subphase containing UHP (concentration up to ca

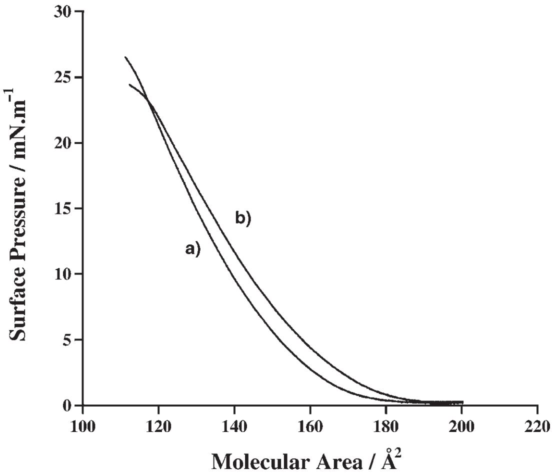


Figure 2. Compression isotherms of **3** at 20 °C on a) pure water and b) an aqueous solution of cinnamyl alcohol (10^{-5} mol L^{-1}).

10^{-4} mol L^{-1}) and cinnamyl alcohol for catalytic experiments. Typical experiments were performed with a solution of cinnamyl alcohol and UHP (10^{-5} and 5×10^{-5} mol L^{-1}, respectively) in as the subphase. Kept for 18 h in the Langmuir trough without any monolayer spread at its interface, no oxidation of cinnamyl alcohol could be detected by gas chromatography (GC) after extraction of the subphase with dichloromethane. To limit any (undetected) bulk oxidation, a shorter reaction time (6 h) was used in order to assess the catalytic effect of a monolayer of Mn^{III}–salen **3**. Thus, after spreading and compression (if needed), the monolayer was kept at constant molecular area during 6 h. The whole subphase was recovered and extracted with dichloromethane to be quickly analyzed by GC. Chromatograms demonstrated that some epoxide of cinnamyl alcohol was formed in the subphase in the presence of the monolayer. To assess this catalytic effect of the monolayer, a GC calibration curve was obtained in order to quantify the area of the epoxide peak (a few tenths to few percents of the area of the peak associated to the unreacted cinnamyl alcohol). The influence of three experimental parameters (concentration of UHP, concentration of cinnamyl alcohol, and mean molecular area of the catalyst) on the outcome of the reaction was then investigated.

Effect of substrate and oxidant concentrations on the reaction: Various concentrations of cinnamyl alcohol were used in the range 2.5×10^{-6} to 10^{-5} mol L^{-1} for a constant concentration of UHP (10^{-5} mol L^{-1}). The area per catalyst of **3** was kept constant (ca. 150 Å^2), as well as the total surface of the catalytic monolayer (774 cm^2). Under such conditions, the percentage of epoxide recovered after 6 h was more or less constant and found to be around 5.0 ± 0.6 %. This suggested that the kinetics of the reaction was independent of the concentration of the substrate. Kinetic studies have shown that the rate of the epoxidation of indene catalyzed by Mn^{III}–salen complexes is zero-order for the substrate both under aqueous/organic biphasic conditions[25] and in homogeneous organic solution,[26] with aqueous NaOCl or UHP as primary oxidants. Even if those bulk experiments were performed with a cocatalyst (e.g., an *N*-oxide or ammonium acetate which bind to the catalytic center) and for much higher concentrations of different reactants, it is reasonable to assume that the behavior found with the Langmuir film is similar to that described in solution. In contrast, a clear dependence of the reaction rate with the concentration of the oxidant UHP was observed in the Langmuir trough. As shown in Figure 3, increasing the concentration of UHP (up to 10^{-4} mol L^{-1}, concentration of cinnamyl alcohol maintained at 10^{-5} mol L^{-1}, molecular area of **3** at 150 Å^2, total surface of the catalytic monolayer: 774 cm^2) resulted in an increase in the percentage of recovered epoxide. This linear dependency is consistent with the results of kinetic experiments in solution, which demonstrated that the epoxidation kinetics is first-order with respect to the UHP concentration.[26]

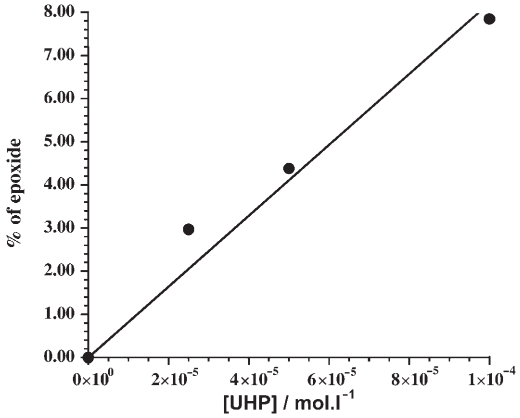


Figure 3. Molar percentage of epoxide recovered from the subphase after 6 h of reaction for various concentrations of the UHP oxidant. For all these experiments, the total surface of the monolayer was 774 cm^2, the molecular area of **3** was maintained at about 150 Å^2 and the cinnamyl alcohol concentration was 10^{-5} mol L^{-1}.

Effect of the molecular density of the catalyst on the reaction: Kinetic investigations in bulk have also shown that the epoxidation of indene is first-order with respect to the catalyst concentration. This should correspond, in our experiment, to a linear dependence of the reaction rate on the molecular density of the catalyst at the interface. To check this hypothesis, we measured the percentage of epoxide formed depending on the mean molecular area of the catalyst, but keeping the surface pressure to zero. In this case, the monolayer should be maintained in the biphasic gaseous/liquid state. Any change in the mean molecular area should modify the ratio between the surface occupied by the liquid phase and that occupied by the gaseous phase, but should not induce any structural or orientational change in the two phases. If one neglects the catalytic activity due to the gaseous domains (in which the molecular density is very low), the rate of epoxidation should therefore be proportional to the molecular density of the catalyst **3**. However, experimentally, the whole subphase was recovered and analyzed by GC, but the surface of the subphase was only partially covered by the catalytic monolayer (because of the compression necessary to modify the molecular density). To take into account such an experimental limitation, we defined an apparent rate of reaction per unit of monolayer surface as the molar percentage of epoxide recovered after a given time of reaction (evaluated after calibration of the GC, see Experimental Section) divided by the product of the time of reaction and the surface of the catalytic monolayer expressed in cm^2 of the monolayer. Figure 4 shows the plot of this apparent rate of reaction versus the mean molecular density of the catalyst along the interface. Within the experimental error, a linear dependency between the rate and the density was found, as expected. Finally, experiments performed at zero surface pressure and for a mean molecular area of 254 Å^2 for various reaction times suggested a linear increase of the epoxide percentage with the reaction time (see Supporting Information). Because the extent of the reaction was low in all our experiments, this linear dependency is in agreement with the bulk kinetic experiments. All those results indicate that the catalytic process at the gas/water interface is kinetically similar to that in bulk in which the catalyst oxidation is the rate-determining step.[25,26] Therefore, a comparison between reaction rate constants for the process in bulk and in the organized system is possible. In bulk, in which the reaction rate can be expressed as k_0^{bulk}[UHP][catalyst], values of k_0^{bulk} of 0.7–1.7 $\text{M}^{-1}\,\text{min}^{-1}$ depending on the Mn^{III}–salen complex can be estimated from literature data for the epoxidation of indene by UHP at 2 °C in a 1:1 dichloromethane/methanol mixture.[26] Analogously, kinetic investigation of the epoxidation of cinnamyl alcohol performed at 20 °C with UHP and catalyst **3** in 1:1 dichloromethane/methanol (see Supporting Information), but in the absence of a cocatalyst to better fit conditions used for the Langmuir film experiments, led to an estimated k_0^{bulk} constant of 0.2–0.3 $\text{M}^{-1}\,\text{min}^{-1}$. The rate constant for the organized system can be estimated assuming the number of moles of catalyst spread at the interface divided by the total volume of the subphase as the catalyst concentration. A value of $k_0^{\text{monolayer}}$ of about 50–100 $\text{M}^{-1}\,\text{min}^{-1}$ was thus calculated from the data previously obtained in the Langmuir film experiments. Such a rough estimation shows nonetheless that the catalytic process is much more efficient in the monolayer than in solution. This might be related to the adsorption of the oxidant along the interface (the increase in the local concentration inducing a faster reaction than expected). However, other examples of catalytic Langmuir–Blodgett films (i.e., on solid supports) have also shown better catalytic efficiency of those thin films with respect to the similar reaction in solution.[7,9] In those systems as well as in ours, the particular orientation adopted by the catalytic center along the interface might explain this higher catalytic efficiency.

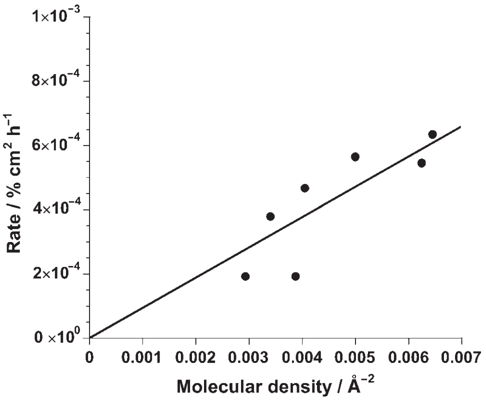


Figure 4. Evolution of the apparent rate of epoxidation (see text) with the molecular density of **3** at the gas/water interface and at zero surface pressure. The cinnamyl alcohol and UHP concentrations were 10^{-5} and 5×10^{-5} mol L^{-1}, respectively.

The previous measurements were performed at zero surface pressure and without any expected change in the molecular organization in the liquid phase of the monolayer. It was therefore interesting to probe the catalytic effect of the monolayer for higher surface pressures and for a monolayer in a monophasic state. Figure 5 shows the plot of the molar percentage of recovered epoxide versus the mean molecular area of the catalyst **3** spread at the gas/water interface. For large areas (above ca. 160 Å^2), the slight increase of the percentage of epoxide for higher molecular density corresponds to the linear dependency of the rate of reaction with the molecular density, as discussed above. For smaller areas, the formation of epoxide appeared to be strongly enhanced. A two–threefold increase in the percentage of epoxide was observed when the monolayer was compressed resulting in an

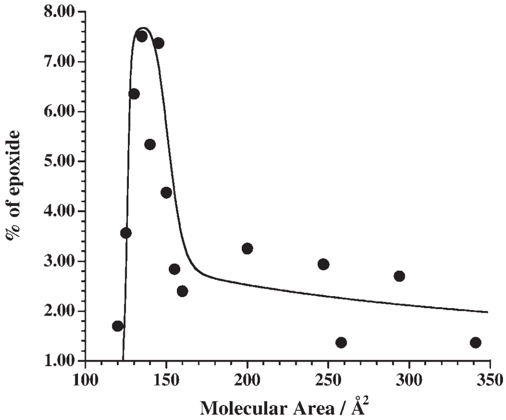


Figure 5. Molar percentage of epoxide recovered from the subphase after 6 h of reaction for various areas per molecule of **3**. The spread quantity of **3** was around $7.7\pm0.3\times10^{-8}$ mol for the experiments corresponding to mean molecular areas below 160 Å^2. The cinnamyl alcohol and UHP concentrations were 10^{-5} and 5×10^{-5} mol L^{-1}, respectively. The plotted line visualizes the dependence of the area per molecule on the catalytic activity.

area per molecule of up to about 140 Å^2. Reaction rates defined as the percentage of epoxide formed per h and per cm^2 of catalytic monolayer were also calculated taking into account the decrease of the surface of the catalytic monolayer with the compression. Comparison with reaction rates expected on the basis of the simple law deduced from data obtained at zero surface pressure confirmed the enhanced catalytic activity of the monolayer for those specific molecular area of catalyst (see Supporting Information). This striking effect of the compressed state of **3** on its catalytic activity demonstrated the importance to build model systems based on a controllable interface. Again, multiple causes, such as adsorption of the oxidant along the interface, cooperative effects similar to those observed in the ring-opening of epoxides catalyzed by dendrimeric Co^{III}–salen complexes,[2] and the effect of the surface pressure might be invoked. However, we believe that the primary reason of the observed phenomenon is the modification of the catalyst orientation with the compression. In particular, the average MnN_2O_2 plane of **3** should be less and less tilted with respect to the normal of the interface with increasing compression. This should modify the access (easiness and main relative orientation) either of the oxidant or of cinnamyl alcohol to the manganese center. To check this hypothesis, we performed PM-IRRAS measurements at the gas/water interface in order to probe the molecular orientation of catalyst **3** upon varying on the state of compression of the monolayer. Indeed, this technique, which combines Fourier transform IR reflection spectroscopy with fast modulation of the polarization of the incident beam, is sensitive to the molecular orientation relative to the interface. Transition moments parallel (or perpendicular) to the interface give upwards (or downwards) oriented bands. Figure 6 shows typical spectra obtained for a monolayer of **3** spread on pure water for various mean molecular areas. The weakness of the recorded absorbance was due to the low density of the catalyst (compared to the classical amphiphilic molecules such as fatty acids). However, several interesting features of those spectra were clearly observed. When the monolayer was compressed, bands at about 1150 and 1205 cm^{-1} increased in intensity. Simultaneously, a negative band appeared around 1255 cm^{-1}. Those peaks corresponded to those recorded for the catalyst in a KBr pellet (at 1150, 1208, and 1248 cm^{-1}). They were associated to the fluorinated tails,[27] and more precisely to $\nu_s(CF_2)$ and $\delta(CF_2)$, $\delta(CCC)$ and $\nu(CC)$, and $\nu_a(CF_2)$ and $r(CF_2)$, respectively. Since the bands around 1208 and 1248 cm^{-1} were broad and overlapping, we concentrated our analysis on the band at 1150 cm^{-1}, which is assigned to an E_1 symmetry and a dipole moment perpendicular to the main axis of the fluorinated tail.[27,28] To analyze the change in intensity of this band with the concentration, we calculated its normalized intensity defined as the product of the molecular area of the catalyst by its PM-IRRAS absorbance. This calculation considers the increase of the intensity due to the change in the molecular density with the compression.[29] Figure 7 (top) shows the evolution of the normalized intensity at 1150 cm^{-1} with the mean molecular area of **3** spread on pure water. The increase of the normalized intensity of this band demonstrated that the fluorinated tail had a different orientation at low and high surface pressures. Indeed, the normalized intensity of this degenerated E_1 band should be proportional to $\cos^2(\alpha)+\cos(76°)$, in which α is the mean tilt angle of the tail with respect to the normal of the interface.[14,15] Therefore, the IR data suggest-

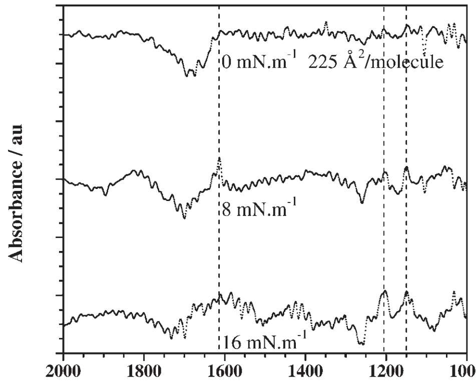


Figure 6. PM-IRRAS spectra of a monolayer of catalyst **3** spread on pure water.

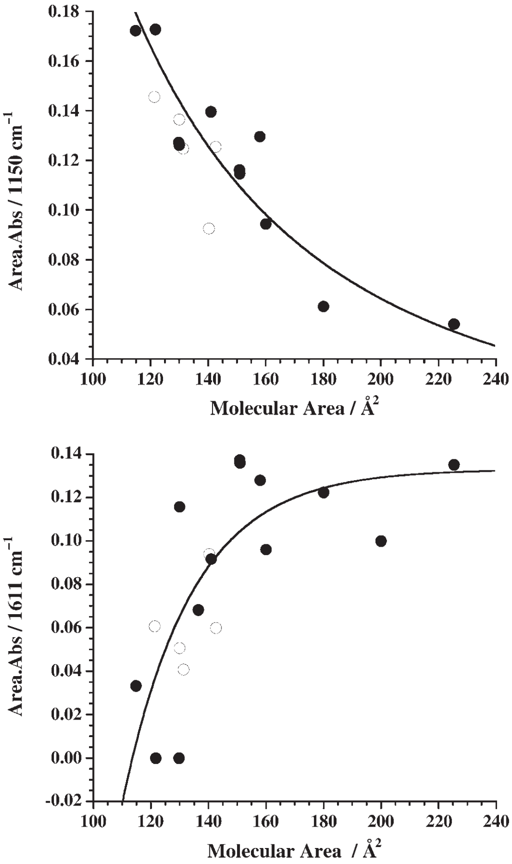


Figure 7. Normalized absorbance of the PM-IRRAS peaks at 1150 (top) and 1611 cm^{-1} (bottom) for a monolayer of **3** spread on pure water (full circles) or a 5×10^{-5} mol L^{-1} UHP subphase (open circles). The lines are plotted to improve the visualization of the results.

ed that this tilt angle decreased during the compression. If one assumed a vertical position of those chains at the collapse, the previous curve led to an evaluation of the mean tilt angle at low surface pressure in the liquid phase of approximately 60°. This result is in agreement with the increase in the monolayer thickness during the compression, which was deduced from the evolution of the relative reflectivity of the Langmuir film measured by BAM.[30] The PM-IRRAS measurements performed on a 5×10^{-5} M UHP subphase showed similar behavior compared to pure water (see Figure 7, top).

Another interesting feature of those IR spectra was the presence of a band at $1615\,cm^{-1}$ (sometimes with a shoulder at $1625\,cm^{-1}$ observable in some of the recorded spectra). This band clearly corresponded to the peak recorded for **3** dispersed in a KBr pellet at $1613\,cm^{-1}$ with a shoulder at $1622\,cm^{-1}$. It was assigned to stretching vibrations of the CN bond with some contributions of vibrations of the phenyl rings and CO group chelating the metal atom.[31,32] The transition moment corresponding to this band should lie within the average MnN_2O_2 plane of **3** (even though its exact orientation within this plane is unknown). It may therefore be used as a probe of the orientation of the catalytic center. The evolution of the normalized intensity of this peak versus the compression of the monolayer was found to be quite different relative to that associated with the fluorinated tails. As shown in Figure 7 (bottom), this intensity was more or less constant for large areas per molecule, but decreased strongly for higher molecular densities. This decrease was already suggested by the fact that the band vanished for high surface pressure in the PM-IRRAS spectrum of the layer (see Figure 6). Because this band should not be degenerate, its intensity should be proportional to $\sin^2(\beta)-\sin^2(38°)$, in which β is the mean tilt angle with respect to the normal of the interface of the transition moment associated to the IR peak.[14,15] Therefore, the IR data suggested that compression below 160 $Å^2$ induced a decrease of the angle β, which may finally reach the magic angle of PM-IRRAS (38°) for high surface pressure. As before, results obtained on a $5\times10^{-5}\,mol\,L^{-1}$ UHP subphase were quite similar (see Figure 7). This result demonstrated that the catalytic center of **3** has different orientations at low and high surface pressures as suggested by the catalytic experiments.

Finally, concerning these data, a strong decrease of the recovered percentage of epoxide (or of the apparent reaction rate) was found for areas smaller than about 130 $Å^2$. Such a drop in the catalysis efficiency may be related to an increasing difficulty for the reactant to reach the catalytic centers; however, it may also just be related to the slow collapse of the monolayer as suggested by Figure 1.

All these results point to the large influence of the organization of catalysts on their activities and demonstrate that a soft interface, such as the gas/water interface, can be a useful model to better understand supported molecular catalysis. Further experiments are currently in progress to evaluate the influence of the molecular structure of the catalyst on its orientation along the gas/water interface and the consequence on its catalytic activity. In the case of chiral Mn^{III}–salen complexes, the effect of the orientation and that of the molecular packing on the stereoselectivity of the epoxidation will be also analyzed.

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