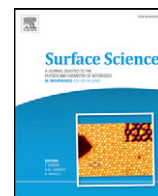




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Dependence of the adsorption of chiral compounds on their enantiomeric composition

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ABSTRACT

The adsorption of two different chiral molecules on platinum surfaces has been explored as a function of enantiomeric composition. In the first case, the saturation monolayers obtained by the adsorption of 1-(naphthyl) ethylamine (NEA) from CCl_4 solutions were characterized in situ by reflection–absorption infrared spectroscopy (RAIRS). It was found that racemic mixtures yield different IR spectra than those obtained from enantiopure monolayers, a behavior that was interpreted as the result of the formation of racemate pairs via hydrogen bonding at the amine moiety also responsible for bonding to the surface. NEA adsorption under these conditions is reversible and can be modified by subsequent exposures to solutions of different chiral compositions, but that appears to take place only via changes in the relative fractions of enantiopure versus racemic domains on the surface; no other enantiomeric ratios are apparent in the IR data. The second study focused on the uptake of propylene oxide (PO) on Pt(111) under ultrahigh vacuum (UHV) conditions. In that case, racemic monolayers show densities up to ~20% lower than those obtained with one single enantiomer. This can be explained by kinetic arguments, since data from isothermal molecular-beam experiments indicated that the PO sticking coefficient depends on the chirality of the incoming PO molecules relative to that of the neighboring adsorbed PO species. Monte Carlo simulations could reproduce the experimental data by assuming adsorbate-assisted adsorption and enantiospecific adsorption geometries for molecules impinging on sites adjacent to previously adsorbed surface species.

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1. Introduction

Chemical chirality is ubiquitous in nature, and central to the biochemistry of life. In our desire to control certain aspects of that biochemistry, as is the case in the development of pharmaceuticals or agro-products, for instance, we need to be able to exert control on the chirality and enantioselectivity of the chemicals involved. As a consequence, there is a great interest in finding ways to synthesize chiral compounds and in separating their individual enantiomers. Much chemistry has been advanced toward this goal in solution, but much less is known and understood about the chemistry of chiral compounds on surfaces [1–3].

The adsorption of chiral molecules on metal surfaces has received some attention from the surface-science community in recent years. Many chiral molecules have been shown to adopt complex ordered adsorption patterns on single-crystal surfaces depending on their total coverage and on the enantiocomposition of the adsorbed mixture. Interesting symmetry breaking has been reported in some cases, induced either by chiral seeding [4–6] or via amplification of small imbalances

in enantiomeric composition [7–9]. These observations may have significant implications for the design of schemes for the enantiopurification of chiral compounds via preferential crystallization [10].

The use of small amounts of chiral molecules has also been evaluated as a way to bestow enantioselectivity to heterogeneous catalysts, typically to hydrogenation catalysts based on transition metals [11–13]. The best, and basically only, examples of such imparting of enantioselectivity on catalysts via the addition of chiral modifiers are those with tartaric acid on nickel-based catalysts [14] and with cinchona alkaloids on platinum-based catalysts [15,16], in which a C=O double bond in a prochiral molecule is hydrogenated to yield the chiral product. In the latter case, it is believed that the structure of the modifier provides a chiral pocket for complexation with the reactant, which may possibly occur via strong interactions such as hydrogen bonding [17]. That is assumed to be followed by adsorption of the reactant–modifier complex on the surface of the catalyst in a particular geometry and by the consequent biasing of the hydrogenation step toward one of the two possible enantiomeric products [18,19]. With tartaric acid as the chiral modifier, on the other hand, this one-to-one reactant–modifier complexation may not be sufficient, and enantioselectivity may require more extended supramolecular structures. In fact, supramolecular chiral templating of surfaces has also been proven possible with small chiral adsorbates by chiral titration experiments with a second probing molecule, typically

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propylene oxide [20–24]. In that case, the argument has been that surface chiral pockets may result from specific geometrical arrangements of the adsorbates on the substrate. Typically, no additional forces are at play, but in some cases strong intermolecular interactions such as hydrogen bonding may be required as well [25].

Our knowledge on the adsorption of chiral molecules by themselves is still quite limited. As indicated above, chiral resolution based on crystallization forces has been identified in ordered systems, and strong intermolecular interactions such as hydrogen bonding have also been observed in heterochiral systems on surfaces. Yet, the role of those properties on the formation of chiral monolayers of adsorbates is poorly understood. Here we report on two different systems where the adsorption of chiral molecules varies depending on their enantiocomposition. For both 1-(1-naphthyl)ethylamine (NEA) [23] and propylene oxide (PO) [26] on platinum surfaces, different adsorption modes and/or coverages have been observed with enantiopure versus racemic mixtures. The reasons behind these differences seem to be several, but do not appear to require the involvement of long-range order, and, at least in the case of PO, do not include strong intermolecular interactions either. Below, we expand on the results from these studies.

2. Experimental details

Two types of experiments are reported here, carried out with two different instruments. The study on the adsorption of 1-(1-naphthyl)ethylamine (NEA; Sigma-Aldrich, >99% purity) was performed by using a reflection-absorption infrared spectroscopy (RAIRS) cell designed for in situ studies of adsorption from solution [27] where a thin liquid film of the solution of interest is trapped between a polished polycrystalline Pt disk and a transparent trapezoidal CaF₂ prism used as the optical element to guide the IR beam in and out of the system. The Pt disk was cleaned in situ before each experiment by electrochemical oxidation–reduction cycles in 0.1 M KClO₄ for 1 h. The reported spectra correspond to differences between data obtained with p- and s-polarized light to discriminate between adsorbed species (which show up only in the p-polarized data) and molecules in solution (visible in both p- and s-polarized spectra), after ratioing against the equivalent p–s background data obtained with the pure solvent. All the reported spectra correspond to averages from 256 scans, taken with 4 cm⁻¹ resolution. Deionized water, used as a solvent, was purified in house; all other solvents (CCl₄, toluene, ethanol, acetone) were purchased from Sigma-Aldrich and used as received.

The second set of experiments, on the adsorption of propylene oxide (S-, R-, and Rac-PO; Sigma-Aldrich, 99% purity; 98 D atom % in Rac-PO-d₆) on a Pt(111) single-crystal surface, was performed in a ultrahigh-vacuum (UHV) instrument equipped with a UTI mass spectrometer, placed at the back of the chamber and interfaced to a personal computer, which was employed for gas identification and detection and for temperature-programmed desorption (TPD) and isothermal molecular-beam kinetic measurements (for which an effusive collimated beam was also used) [28,29]. The surface of the Pt sample was cleaned before each experiment by a combination of ion sputtering and O₂ treatments. Linear heating rates of 10 K/s were used for the TPD experiments by using a homemade temperature controller, and constant fixed temperatures were set for the molecular beam uptakes. Exposures in these experiments are reported in units of Langmuirs (1 L = 1 × 10⁻⁶ Torr s), with pressures measured by using a nude ion gauge (not corrected for ion gauge sensitivity factors).

Density functional theory (DFT) calculations (Fig. 1) were carried out for the assignment of the infrared absorption frequencies in the NEA IR absorption spectra by using the B3LYP method and the 6–311 + G(2d, p) basis set [30]. The Monte Carlo simulations carried out for the second system were performed using a home-written routine in Matlab, using “L” shaped molecules surrounded by a one-lattice-space frame to prevent adsorption of molecules directly touching each other, and two separate intrinsic sticking probabilities (S₀) for adsorption on empty

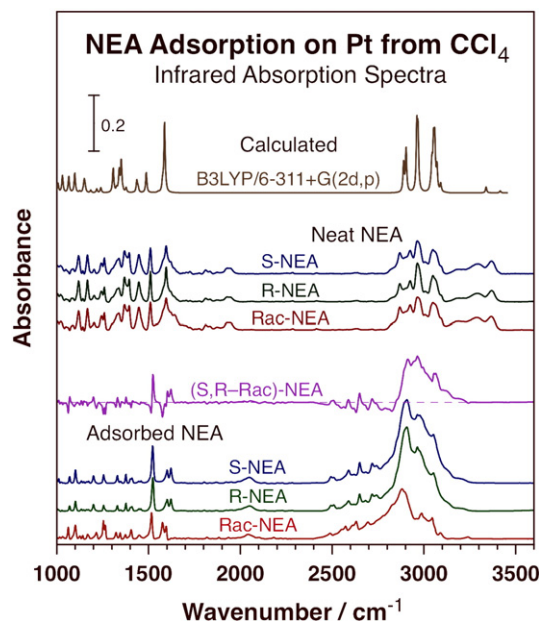


Fig. 1. Bottom four traces: In-situ reflection-absorption infrared spectra (RAIRS) for S-, R-, and racemic-1-(1-naphthyl)ethylamine (NEA) adsorbed onto a polished polycrystalline platinum surface from 500 μM CCl₄ solutions at room temperature, and the differential spectra obtained by subtracting the trace for the Rac-NEA from an average of the S- and R-NEA data. To notice here are the differences between the trace for the racemic mixture and those for the enantiopure layers (highlighted in the differential trace), in particular in the 1500–1700 cm⁻¹ region. Next three traces from bottom: Equivalent transmission IR spectra for the same S-, R-, and Rac-NEA but in neat liquid form. No differences are seen in those cases. Top trace: Calculated IR spectrum for NEA, obtained by using the B3LYP method and the 6–311 + G(2d,p) basis set.

versus occupied sites [26]. Specific adsorption geometries were also defined for the incoming molecules hitting on adsorbates depending on their relative handedness (S–S or R–R versus S–R or R–S) [26].

3. NEA adsorption onto a Pt surface from solution

Our first study was carried out with 1-(1-naphthyl)ethylamine (NEA). This is a relatively simple chiral molecule that nicely represents the chiral modifying chemistry of cinchona alkaloids in catalysis. NEA possesses the main functionalities required for the formation of one-to-one reactant–modifier complexes in such systems, namely, an aromatic ring and an amine group near a chiral center [23,31–33], and has also shown to be able to add some enantioselectivity to the catalytic hydrogenation of α-ketoesters [34–36]. Several surface-science studies have focused on the adsorption of NEA on Pt and Pd surfaces [23,37–40], but, to the best of our knowledge, there have been no comparative studies on the adsorption of NEA as a function of the relative amounts of R- versus S-enantiomers on the surface. This is the behavior that we discuss below.

The bottom four traces of Fig. 1 correspond to RAIRS data from saturated layers of S-, R-, and racemic- (Rac-) NEA adsorbed on a polycrystalline Pt surface, and to the difference between the average of the S- and R-NEA spectra minus the trace for the Rac-NEA. These spectra were obtained in situ upon adsorption from 500 μM NEA solutions in a CCl₄ solvent. The data for the S- and R-NEA enantiomers are, within experimental error, identical, but those obtained with Rac-NEA show a number of distinct features not seen with the enantiopure layers (highlighted in the differential spectrum), indicating a potential difference in pairwise interactions between molecules of the same versus different chirality on the surface. Perhaps the most noticeable difference is in the pair of peaks detected around 1600 cm⁻¹: with the enantiopure layers two features are centered around 1600 and 1622 cm⁻¹, whereas the racemic mixture shows those at 1575 and 1597 cm⁻¹. Other changes in the 1000–1700 cm⁻¹ (molecular deformations) frequency range

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