

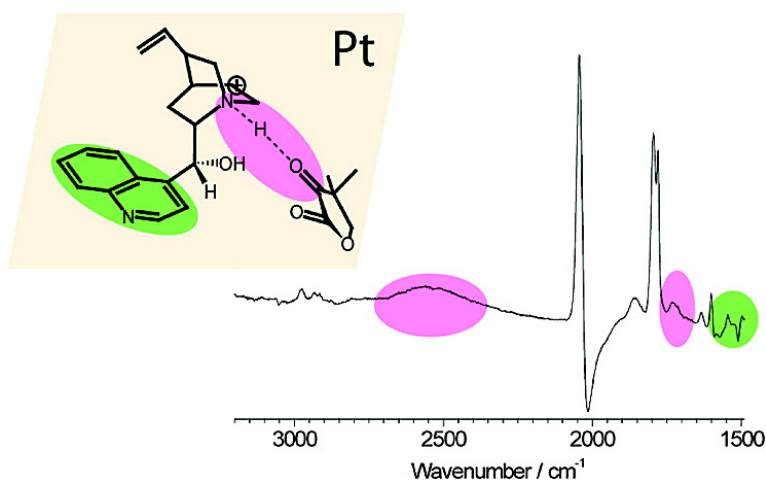
Communication

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## Interaction between Ketopantolactone and Chirally Modified Pt Investigated by Attenuated Total Reflection IR Concentration Modulation Spectroscopy

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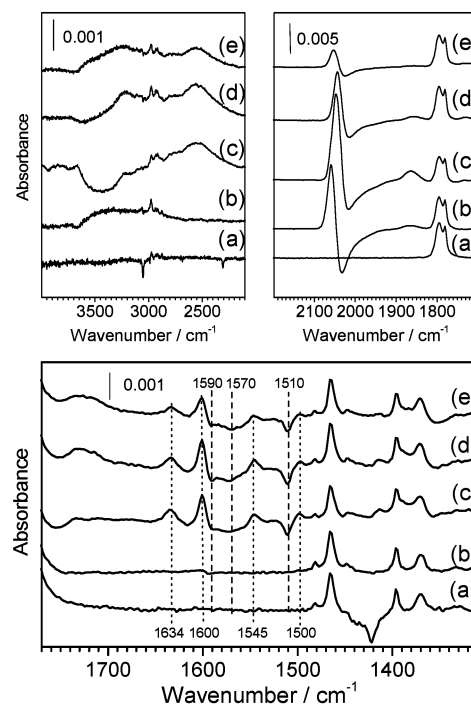
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The synthesis of optically pure compounds is an important challenge in the chemical industry, particularly in the areas of pharmaceuticals, agrochemicals, flavors, and fragrances.<sup>1</sup> A promising strategy is heterogeneous enantioselective catalysis, which combines chiral multiplication with the inherent practical advantages of a heterogeneous process. A simple although efficient way to transfer chiral information to the active catalyst surface is adsorption of one enantiomer of a handed molecule, called a chiral modifier. This approach is successfully applied for the enantioselective hydrogenation of functionalized ketones to the corresponding alcohols by Pt catalysts modified by cinchona alkaloids.<sup>2–4</sup> Despite the considerable effort and the numerous advances in its determination, the mechanism of this complex reaction is not considered to be completely understood.

We have recently studied the chiral modification of a Pt/Al<sub>2</sub>O<sub>3</sub> thin film by cinchonidine (CD) under hydrogenation conditions using attenuated total reflection (ATR) infrared spectroscopy.<sup>5,6</sup> At low solution concentration of CD, the latter tends to adsorb via its quinoline  $\pi$ -system. At higher concentration (and higher coverage), two tilted species were additionally observed. The general tendency of the quinoline moiety of cinchonidine to tilt at higher coverage was independently also proposed on the basis of reflection absorption infrared measurements on a Pt electrode.<sup>7</sup>

In this contribution, we report on the interaction of ketopantolactone (KPL) with modified Pt/Al<sub>2</sub>O<sub>3</sub>. KPL can be hydrogenated with high enantiomeric excess over chirally modified Pt<sup>8</sup> in a continuous fixed-bed flow reactor.<sup>9</sup> The same Pt/Al<sub>2</sub>O<sub>3</sub> thin film was used for the CD adsorption studies and characterized in detail elsewhere.<sup>10</sup> The strategy we followed was the combination of attenuated total reflection (ATR) and modulation excitation spectroscopy (MES) in a flow-through cell.<sup>11,12</sup> The KPL reactant concentration was periodically changed, and the response of the catalytic interface was followed by ATR. The key advantages of MES over conventional IR spectroscopy for revealing interactions at complex catalytic solid–liquid interfaces are the increase in sensitivity due to the phase-sensitive detection (PSD) of periodically varying signals and the high selectivity for species, which are affected by the stimulation. The KPL concentration modulation was achieved by periodically pumping two different solutions through the cell. One solution contained  $5 \times 10^{-4}$  mol/L CD, and the other contained  $5 \times 10^{-4}$  mol/L CD and  $5 \times 10^{-2}$  mol/L KPL. Both solutions were saturated with hydrogen as described in detail elsewhere.<sup>6</sup>

Figure 1 shows demodulated ATR spectra of KPL concentration modulation experiments with different samples. Spectrum a was recorded over a clean Ge internal reflection element (IRE). The observed bands correspond to dissolved KPL. Spectrum b was recorded over a Pt/Al<sub>2</sub>O<sub>3</sub> sample in the absence of CD. Spectra c–e represent different experiments in the presence of CD using



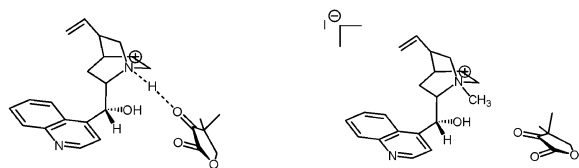
**Figure 1.** Demodulated ATR spectra of different concentration modulation experiments. The KPL concentration was modulated (modulation period  $T = 184$  s) between 0 and  $5 \times 10^{-2}$  mol/L in CH<sub>2</sub>Cl<sub>2</sub>. Spectrum a was recorded on a clean, uncoated Ge internal reflection element. Spectrum b was recorded on a Pt/Al<sub>2</sub>O<sub>3</sub> film in the absence of a modifier. Spectra c–e were recorded on a Pt/Al<sub>2</sub>O<sub>3</sub> film in the presence of CD ( $5 \times 10^{-4}$  mol/L). Before the modulation experiments were started (c–e), the Pt/Al<sub>2</sub>O<sub>3</sub> films were differently treated: (c) 30 min N<sub>2</sub> saturated CH<sub>2</sub>Cl<sub>2</sub> only; (d) pretreatment with 5 min H<sub>2</sub> saturated KPL solution; (e) directly contacted with modulation solutions.

different samples. Spectra c–e demonstrate the reproducibility of the experiments. Signals as small as 0.0001 au are significant. The bands observed in the spectra have different origins. The signals of dissolved KPL are easily identified by comparison with the spectrum of dissolved KPL (spectrum a in Figure 1).

The features in the demodulated spectra at about 2050 (positive) and 2020 cm<sup>-1</sup> (negative) are due to CO linearly bound to Pt, likely from some KPL decomposition. The integrated intensity of the two signals is identical for the experiments in the presence of CD. The signals arise due to a shift of the CO band to higher frequency upon admitting KPL. It can be concluded that the amount of CO on Pt does not increase during modulation and that the CO senses the changes on the Pt surface induced by the KPL concentration modulation.

In the spectral region of the quinoline ring vibrations of CD, several significant bands are observed as revealed in Figure 1 (bottom). Upon admitting KPL, negative bands are observed at 1510, 1590, and 1570 (broad) cm<sup>-1</sup>. We have demonstrated earlier

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**Figure 2.** Proposed model for CD–KPL interaction (left). This interaction is not possible for *N*-methyl CD (right).

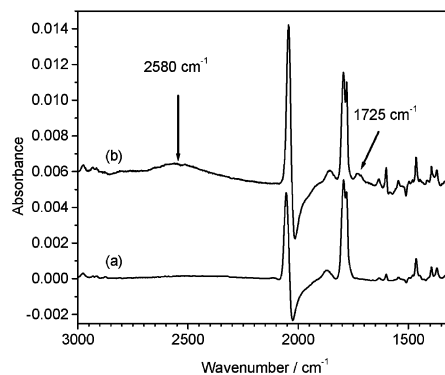
that the latter band does not belong to the same species as the bands at 1510 and 1590  $\text{cm}^{-1}$ , which were assigned to CD adsorbed by the quinoline N-lone pair. The band at 1570  $\text{cm}^{-1}$  was assigned to CD adsorbed via the quinoline  $\pi$ -system.<sup>6</sup> On the other hand, positive bands are observed at 1500, 1545, 1600, and 1634  $\text{cm}^{-1}$ . Very likely, at least some of these bands are associated with the quinoline ring of CD. The spectra reveal that the adsorbed CD is strongly affected by the KPL. One feasible interpretation is that the adsorption geometry is influenced by the KPL such that the CD spectrum is significantly changing.

A more striking feature of the spectrum and the most important finding is the broad band centered at about 2580  $\text{cm}^{-1}$ , which arises when both CD and KPL are present. The broadness of the band clearly indicates hydrogen bonding. Water at the interface can be excluded as its origin, because a comparison of spectra c–e in Figure 1 shows that the water present at the interface (signals at 3500–3000  $\text{cm}^{-1}$ ) is not correlated with the observed band at 2580 and those in the 1500–1600  $\text{cm}^{-1}$  spectral range.

The frequency of this band falls within the region where a  $\text{N}^+\text{---H}\cdots\text{O}$  hydrogen bond is expected to absorb.<sup>13</sup> The broadness of the band is consistent with such an interpretation. Furthermore, hydrogen bonding is expected to increase the intensity of a N–H stretching vibration. This observation is, to the best of our knowledge, the first direct spectroscopic indication of an interaction, such as the one depicted in Figure 2 (left), which was proposed some years ago to play an important role in the reactant–modifier interaction.<sup>14</sup> Because the experiments were conducted in the absence of acid and protic solvent, adsorbed hydrogen may act as the source of the hydrogen in the bridge.

An important experimental finding for  $\alpha$ -ketoester hydrogenation is the complete loss of enantiomeric excess by blocking the quinuclidine N of the modifier.<sup>15</sup> As proposed earlier, the involvement of the quinuclidine N in enantiodifferentiation, for example, through hydrogen bonding interaction as depicted in Figure 2 (left), could very well explain this finding.<sup>16</sup> To clarify whether the quinuclidine N plays a role for the spectroscopic observations made here, that is, the appearance of the 2580  $\text{cm}^{-1}$  band, *N*-methyl CD chloride was synthesized according to published procedures.<sup>17</sup> NMR spectroscopy validated the structure of the modifier and confirmed the high purity of the sample. When *N*-methyl CD chloride was adsorbed on the Pt/ $\text{Al}_2\text{O}_3$  sample, a spectrum was observed which was similar to that reported for adsorbed CD<sup>6</sup> with only minor frequency shifts of the quinoline ring modes (see Supporting Information), which indicates that both modifiers adsorb in a similar fashion.

Figure 3 shows a comparison of demodulated ATR spectra of KPL modulation experiments. Spectrum b was recorded in the presence of CD. For spectrum a, *N*-methyl CD chloride was used instead. Obviously the 2580  $\text{cm}^{-1}$  band is missing when *N*-methyl CD chloride is used as the modifier, which supports an interaction complex as shown in Figure 2 involving a  $\text{N---H}\cdots\text{O}$  hydrogen bond. Some changes in the spectral region where the quinoline ring modes absorb can also be observed in the *N*-methyl CD chloride experi-



**Figure 3.** Comparison between two KPL concentration modulation ATR experiments. The KPL concentration was modulated (modulation period  $T = 184$  s) between 0 and  $5 \times 10^{-2}$  mol/L in  $\text{CH}_2\text{Cl}_2$ . (a) *N*-Methyl CD was used as the modifier ( $5 \times 10^{-4}$  mol/L), (b) CD was used as the modifier ( $5 \times 10^{-4}$  mol/L).

ment. However, the bands are significantly weaker than in the case of CD and the negative band at 1570  $\text{cm}^{-1}$  seems to be missing. A further observation supports a  $\text{N---H}\cdots\text{O}$  interaction. The relatively broad band at 1725  $\text{cm}^{-1}$  observed in the experiments with CD but not in the absence of CD (Figure 1; Figure 3b, arrow) can be assigned to carbonyl stretching vibrations of KPL, shifted to lower frequencies due to hydrogen bonding. Figure 3 shows that this band is missing when *N*-methyl CD is used as the modifier.

In conclusion, the study provides support for a hydrogen-bonding interaction between CD modified Pt/ $\text{Al}_2\text{O}_3$  and ketopantolactone. The study furthermore indicates that the adsorption of the modifier is affected by its interaction with the reactant. This molecular level information from the catalytic solid–liquid interface could be obtained by the combination of ATR and modulation spectroscopy.

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**Supporting Information Available:** ATR spectra of adsorbed CD and *N*-methyl CD hydrochloride (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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