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Inversion of enantioselectivity in the hydrogenation of ketopantolactone on platinum modified by ether derivatives of cinchonidine

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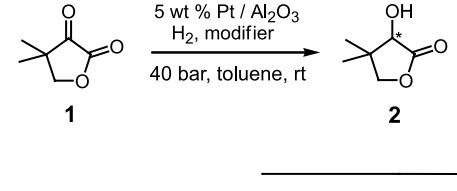
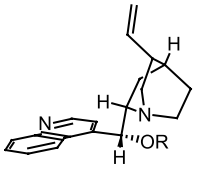
Abstract—Asymmetric hydrogenation of ketopantolactone was studied on a 5 wt% Pt/Al_2O_3 catalyst in the presence of cinchonidine and its *O*-methyl, -ethyl, -phenyl and -trimethylsilyl derivatives. Inversion of enantioselectivity with the latter two bulky substituents proved that in the enantiodifferentiating step cinchonidine adsorbs via the quinoline ring lying approximately parallel to the Pt surface. The striking nonlinear effect observed with cinchonidine–*O*-phenyl-cinchonidine mixtures is attributed to differences in the adsorption strength and geometry of the modifiers.

1. Introduction

The enantioselective hydrogenation of ketopantolactone **1** has been extensively investigated as one enantiomer of the product, (*R*)-(−)-pantolactone **2**, is an intermediate in the synthesis of pantothenic acid (vitamin B family) and a constituent of coenzyme A (Scheme 1).[1,2] Various rhodium(I) complexes have been tested in this reaction[3–7] that afforded up to 98.7% ee.[8] A heterogeneous catalyst, supported Pt chirally modified by cinchonidine (CD)[9–11] was less selective: the best ee was only 91.6% to (*R*)-**2**.[12] Practical advantages of the latter process are the extremely low CD/**1** molar ratio, only 4 ppm, and the high production rate achieved in a continuous flow fixed bed reactor (TOF = 1420 h^{-1}).[13]





modifier	R
CD	H
MeOCD	methyl
EtOCD	ethyl
TMSOCD	trimethylsilyl
PHOCD	phenyl

Scheme 1. Hydrogenation of ketopantolactone **1** to pantolactone **2** over chirally modified Pt/Al_2O_3 and the structure of ether derivatives of cinchonidine used as modifiers.

Supported by theoretical calculations, we proposed a model for the reactant–modifier interaction on the Pt surface involving a H-bond between CD and the half-hydrogenated state derived from **1** (Fig. 1).[10] However,

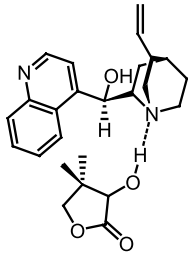


Figure 1. Top view of a calculated model for the CD-**1** interaction over the Pt surface, leading upon hydrogenation to (*R*)-**2**.[10] The π-bonded quinoline ring of CD and the two carbonyl groups of **1** lie approximately parallel to Pt.

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there is no direct evidence yet for the assumption implied to the model that **1** and the quinoline ring of CD are adsorbed parallel to the Pt surface during the enantiodifferentiating step. Various surface science techniques (NEXAFS,[14] STM,[15] XPS,[16] LEED,[17] SERS,[18] cyclic voltammetry,[19] IR[20–22]) and H/D exchange[23,24] clarified some important details of the adsorption of CD on Pt but none of these methods allowed a real in situ investigation, i.e. in the presence of the reactant. ATR-IR studies in H_2-saturated CH_2Cl_2 revealed three differently adsorbed species of CD: a π-bonded species, which adsorbed via the aromatic ring nearly parallel to the Pt surface and two species, in which the aromatic ring is tilted relative to the Pt surface.[20,21] The former adsorption geometry would correspond to the assumption depicted in Figure 1.

Here we used another approach to clarify the adsorption mode of CD and its interaction with **1** in the enantiodifferentiating complex: we synthesized some ether derivatives of CD (Scheme 1) and studied the influence of bulkiness of the functional group on the hydrogenation of **1**. If CD adsorbs via the quinoline ring lying approximately parallel to the Pt surface, the increasing steric hindrance in the ether derivatives should successively diminish the enantioselectivity, providing a truly in situ evidence for our model. This approach led us also to some other interesting observations, which will be reported below.

2. Catalytic hydrogenations with cinchonidine derivatives

At first we investigated the hydrogenation of **1** in toluene and THF over a 5 wt% Pt/Al_2O_3 catalyst (Fig. 2). In both solvents CD afforded somewhat higher ee's to (*R*)-**2** than MeOCD or EtOCD, though the efficiency

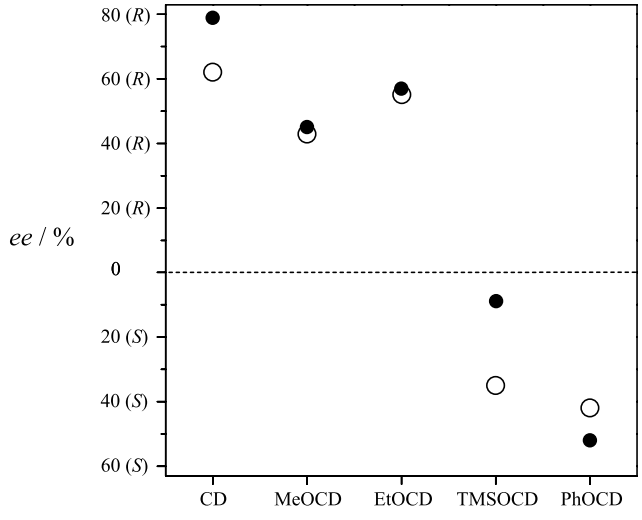

Figure 2. Enantioselectivities in the hydrogenation of **1** over a 5 wt% Pt/Al_2O_3 catalyst with two different solvents (● toluene; ○ THF) under standard reaction conditions. The structure of the modifiers is shown in Scheme 1.

of modifiers depended also on the pressure in the range 1–40 bar. The latter two modifiers possess small *O*-alkyl groups that do not substantially change the adsorption geometry, compared to CD. The reasonably good ee's achieved in these experiments support the assumption that the OH function of CD is not involved in the enantiodifferentiating step (Fig. 1). When using TMSOCD or PhOCD as modifiers, the opposite enantiomer formed in excess. The most striking effect was observed in toluene where CD afforded 79% ee to (*R*)-**2**, whereas modification with PhOCD resulted in 52% ee to (*S*)-**2**. Decreasing the temperature to 0°C (under otherwise standard conditions) improved the ee to 54.4% in the latter reaction.

Certainly, a complex between modifier and **1**, as depicted in Figure 1, cannot establish in the presence of the bulky trimethylsilyl and phenyl substituents in TMSOCD and PhOCD, respectively. In the original model calculated for the CD-**1** interaction, CD is bound via hydrogen bonding to the half-hydrogenated state derived from **1**.[10] Besides, a steric repulsion exerted by the quinoline ring ensures a fixed adsorption of **1** with dominantly one enantioface on the Pt surface. Introduction of the bulky trimethylsilyl or phenyl substituents changes dramatically the chiral pocket available for the adsorption of **1** over the Pt surface and leads to the favored adsorption of **1** on the opposite enantioface. A plausible explanation may be that TMSOCD and PhOCD do not adsorb via the quinoline ring being approximately parallel to the Pt surface (π-bonding) but rather in a tilted position (*N*-lone pair bonding). This change in the adsorption geometry should result in a considerably weaker adsorption of these modifiers compared to the adsorption of CD. Another possibility is that TMSOCD and PhOCD still adsorb with the quinoline ring approximately parallel to the Pt surface but the bulky phenyl and trimethylsilyl groups 'lying' on the surface change the adsorption mode of **1**.

3. Nonlinear behavior of modifier mixtures

To estimate the relative adsorption strength of the modifiers on Pt, the hydrogenation of **1** was carried out with mixtures of CD and PhOCD. A strong nonlinear behavior was observed as illustrated in Figure 3. The 'expected' or theoretical ee (dashed line) was calculated assuming that the molar ratios of the modifiers in solution and on the Pt surface are identical, and the reaction rates and ee's are linear combinations of those measured with CD and PhOCD alone. The average hydrogenation rates with the modifiers alone were similar: 183 and 140 mmol/h for CD and PhOCD, respectively. Nontheless, CD controlled the enantioselection in the whole range studied and even a modifier mixture containing only 0.7 mol% CD afforded 33% ee to (*R*)-**2**. This nonlinear effect is even more striking when considering that the purity of commercial CD was only 92% and contained 7% quinidine that alkaloid alone affords (*S*)-**2** in excess.

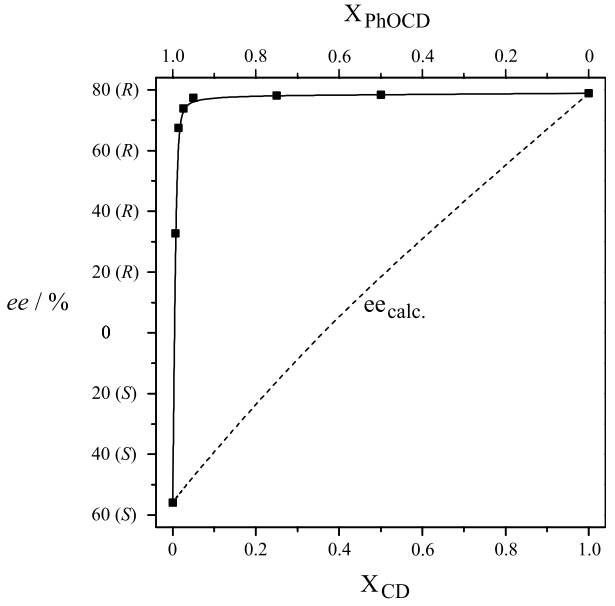

Figure 3. Hydrogenation of **1** over 5 wt% Pt/Al_2O_3 modified by CD-PhOCD mixtures; standard reaction conditions in toluene.

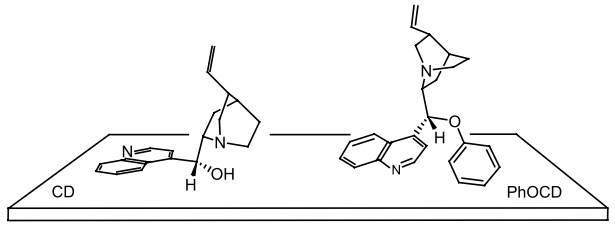

Figure 4. Schematic illustration of the adsorption of CD and PhOCD on an idealized flat Pt surface, showing the considerable steric hindrance by the phenyl group. The structure of PhOCD corresponds to the energetic minimum, as derived from preliminary calculations using Gaussian 98.

The well-known nonlinear effect has originally been described for homogeneous catalytic reactions carried out with enantiomerically impure ligands.[25,26] This interesting phenomenon has recently been extended to mixtures of two diastereomers and even to two chemically different chiral ligands in homogeneous catalysis,[27–31] and to similar but chemically different modifiers in heterogeneous catalysis.[32–37] The basic requirement for the extension is that the ligand or modifier pairs afford products of opposite configuration.

As mentioned in the introduction, ATR-IR studies of CD adsorption on Pt[20,21] allowed to select conditions nearest to those of catalytic hydrogenation. Based on this study we propose that the nonlinear behavior shown in Figure 3 is due to the different geometry and strength of the alkaloid modifier adsorption on Pt. CD adsorbs stronger than PhOCD. The quinoline ring of CD lying approximately parallel to the surface interacts strongly with Pt via π-bonding (Fig. 4). In contrast, PhOCD adopts a tilted position; it is anchored to Pt only weakly via the aromatic N atom and cannot efficiently compete with CD for the active Pt sites. It is very likely that some steric effects and electronic interactions also play a role though this contribution cannot be reliably estimated yet. This type of interactions has been thoroughly investigated in connection with the nonlinear effects (ligand association) in homogeneous catalysis.[25,26]

4. Conclusions

Hydrogenation of **1** over Pt modified by ether derivatives of CD provides strong support to our structural model for the enantiodifferentiating diastereomeric complex proposed earlier (Fig. 1).[10] Namely, the OH group of CD is not involved in the modifier-**1** interaction and in the modifier-**1** complex CD adsorbs approximately parallel to the metal surface via the quinoline ring (π-bonding). The hydrogen bonding between the quinuclidine N and the half-hydrogenated state of **1**, together with the steric hindrance by the quinoline ring, results in (*R*)-**2** as the dominant product. Replacing the OH group of CD by a bulky PhO or TMSO group prevents this adsorption mode of **1** and affords (*S*)-**2** as the major enantiomer. If the quinoline ring of CD would adopt a tilted position relative to the Pt surface during interaction with **1** (compare to Figs. 1 and 4), replacement of the OH group by the bulky PhO or TMSO groups should not significantly influence the adsorption of **1** and thus the stereochemical outcome of the hydrogenation reaction.

A practically and scientifically important consequence of the observed strong nonlinear effect is that only carefully purified cinchona derivatives provide genuine results concerning enantioselectivity. Trace amounts of CD can outperform the enantiodifferentiation of its derivatives, as demonstrated for PhOCD. This behavior is presumably more general and can be extended to other types of chiral modifiers in heterogeneous catalysis. Furthermore due care has to be taken when interpreting the behaviour of modifier mixtures screened by high-throughput methods.

5. Experimental

5.1. Synthesis of *O*-substituted cinchonidines

Melting points were determined using Büchi-545 automatic melting point apparatus. ^{1}H NMR spectra were recorded by Varian Unity Inova at 400 MHz in $CDCl_3$. All reactions were carried out under Ar. Starting materials were purchased from Aldrich and used without further purification. DMSO, DMF and THF were dried over molecular sieves before use.

5.2. O-Methyl-cinchonidine (MeOCD)

CD (10.0 g, 34 mmol) was added to a stirred suspension of NaH (2.1 g, 88 mmol) in dry DMF (50 ml) and the mixture was stirred for 30 min at rt, then 1 h at 50°C. The solution was cooled below 5°C and iodomethane

(2.2 ml, 15 mmol) was added. After 1 h stirring at 0–5°C the reaction mixture was diluted with water (150 ml) and extracted with EtOAc (2×100 ml). The combined organic layer was extracted with 2 M HCl, the aqueous solution was washed with hexane (50 ml) and the pH of the solution was adjusted to alkaline with solid $NaHCO_3$. After extraction with EtOAc (2×100 ml), the organic layer was dried over Na_2SO_4 and the solvent was evaporated to dryness (6.9 g white crystals, a mixture of MeOCD and starting CD). Pure product was obtained by chromatography on silica with hexane–acetone–TEA 40:18:1 followed by crystallization from hexane. Yield: 5.6 g (46%) white crystals. Mp 126.6–126.1°C; NMR ($CDCl_3$) 8.90 (d, 1H), 8.15 (d, 1H), 8.10 (d, 1H) 7.70 (t, 1H), 7.57 (t, 1H), 7.42 (d, 1H), 5.72 (m, 1H), 5.04 (d, 1H), 4.91–4.88 (m, 2H), 3.40–3.30 (m, 1H), 3.28 (s, 3H), 3.10–3.03 (m, 2H), 2.75–2.55 (m, 2H), 2.13–2.10 (m, 1H), 1.80–1.70 (m, 3H), 1.60–1.50 (m, 2H); MS ($M+H^+$) 309.

5.3. *O*-Ethyl-cinchonidine (EtOCD)

EtOCD was synthesized according to the recipe for MeOCD, but iodoethane was used instead of iodomethane. Yield: 55%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.90$ (d, 1H), 8.12 and 8.10 (two overlapping d, 2H) 7.72 (t, 1H), 7.60 (t, 1H), 7.52 (d, 1H), 5.75 (m, 1H), 5.17 (d, 1H), 4.97–4.86 (m, 2H), 3.43 (qa, 2H) and 3.41 (s, 1H), 3.15–3.05 (m, 2H), 2.75–2.57 (m, 2H), 2.30–2.22 (m, 1H), 1.85–1.75 (m, 3H), 1.65–1.55 (m, 2H), 1.25 (t, 3H); MS: 323 ($M+H^+$).

5.4. *O*-Trimethylsilyl-cinchonidine (TMSOCD)

TMSOCD was prepared according to a recent procedure.[38] CD (2.0 g, 6.7 mmol) and triethylamine (TEA, 0.81 g, 8.0 mmol) were dissolved in THF. The solution was cooled to 0–5°C and chlorotrimethylsilane (0.87 g, 8.0 mmol) dissolved in THF was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred at this temperature overnight, then at 60°C for 2 h. The mixture was poured to ice–water (~50 ml) and extracted with dichloromethane (2×50 ml), the combined organic layers were washed with water and brine, dried over Na_2SO_4 and evaporated to dryness. Column chromatography on silica with hexane–acetone–TEA 40:18:1 afforded a white crystalline material; yield: 1.2 g, 49%; mp 75.8–76.7°C; NMR ($CDCl_3$) 8.84 (d, 1H), 8.14 and 8.10 (two overlapping d, 2H) 7.71 (t, 1H), 7.56 (t, 1H), 7.48 (d, 1H), 5.71 (m, 1H), 5.60 (d, 1H), 4.92–4.87 (m, 2H), 3.40–3.30 (m, 1H), 3.10–3.00 (m, 2H), 2.75–2.55 (m, 2H), 2.10–2.10 (m, 1H), 1.80–1.70 (m, 3H), 1.60–1.50 (m, 2H), 0.1 (s, 9H); MS ($M+H^+$) 367.

5.5. *O*-Phenyl-cinchonidine (PhOCD)

This compound was prepared according to the literature procedure for the synthesis of dihydroquinidyl aryl ethers.[39] CD (2.2 g, 7.5 mmol) was dissolved in anhydrous DMSO (30 ml), NaH (0.40 g, 10 mmol) was added at room temperature and the mixture was stirred for 1 h. Then abs. pyridine (1.2 ml, 15 mmol) and CuI (1.45 g, 7.5 mmol) were added and stirred for 30 min. After addition of iodobenzene (0.85 ml, 7.5 mmol) the mixture was kept at 100°C for 72 h. After cooling to room temperature, water (25 ml), dichloromethane (50 ml), ethylenediaminetetraacetic acid (0.5 g), and finally cc. ammonia solution (5 ml) were added. The mixture was stirred at room temperature for 1 h, the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×15 ml). The combined organic layer was washed with 5% ammonia solution (5×25 ml) until the aqueous phase remained colorless, then water (25 ml) and solvent were evaporated in vacuo and the residue was dissolved in EtOAc (50 ml). It was extracted with 2 M HCl solution (50 ml), the acidic solution was washed with EtOAc (2×25 ml). Then the pH was set to alkaline with solid $NaHCO_3$ and extracted with EtOAc (2×30 ml). The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. Crude product was purified over silica using hexane–acetone–TEA 40:18:1 as eluent. After evaporation of the solvent the product was crystallized from hexane (0.6 g, 1.6 mmol, white crystals). Yield: 22%; mp 126.3–126.4°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.83$ (d, 1H), 8.20 (d, 1H), 8.19 (d, 1H) 7.78 (t, 1H), 7.57 (m, 1H), 7.62 (m, 1H), 7.10 (m, 2H), 6.88 (m, 1H), 6.78 (m, 2H), 6.08 (d, 1H), 5.73 (m, 1H), 4.98–4.82 (m, 2H), 3.40–3.30 (m, 1H), 3.28 (s, 2H), 2.75–2.55 (m, 2H), 2.13–2.10 (m, 1H), 1.80–1.70 (m, 3H), 1.60–1.50 (m, 2H); MS: 371 ($M+H^+$).

5.6. Catalytic hydrogenation

Tetrahydrofuran (THF, 99.5%, J. T. Baker) was dried over Na before use. Toluene (99.5%, J. T. Baker) and CD (92%, Fluka; impurities: 1% quinine, 7% quinidine, determined by HPLC at Fluka) were used as received.

A 5 wt% Pt/Al_2O_3 catalyst (Engelhard 4759) was prereduced in flowing H_2 for 60 min at 400°C, cooled to room temperature in H_2 in 30 min, and flushed with nitrogen. The pretreated catalyst was used on the same day. Hydrogenations were carried out at room temperature (ca. 20°C) in a stainless steel autoclave equipped with a 50 ml glass liner and a PTFE cover, and magnetic stirring (1000 rpm). Total pressure (40 bar) and hydrogen uptake were controlled by computerized constant-volume constant-pressure equipment (Büchi BPC 9901). In a standard procedure, 42 mg catalyst in 5 ml solvent was exposed to flowing H_2 for 2 min. Then 6.8 mol modifier or modifier mixture was added in 1 ml solvent. After a short preadsorption time of 1 min 236 mg (1.84 mmol) ketopantolactone **1** was added and the reaction was started. Conversion and enantioselectivity were determined by gas chromatography using a Chirasil-DEX CB column (Chrompack). No other product beside the two enantiomers of pantolactone **2** could be detected.

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