Coadsorption of cinchona alkaloids on supported palladium: nonlinear effects in asymmetric hydrogenation and resistance of alkaloids against hydrogenation

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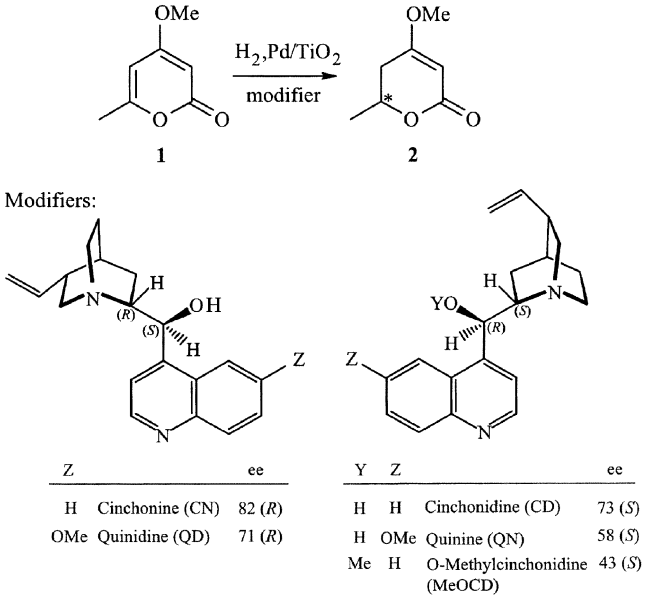
The transient behavior of the adsorption of cinchona alkaloid modifiers on Pd/TiO_2 has been investigated *in situ* during the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone (**1**). Modifier mixtures consisting of pairs of alkaloids that alone afford the opposite enantiomers in comparable excess were applied to probe the adsorption behavior and possible nonlinear phenomena. Complementary information has been gathered from an indirect UV–vis study of the adsorption and hydrogenation of cinchonidine and quinidine on Pd/TiO_2. The striking nonlinear behavior of cinchonidine–quinidine and cinchonine–quinine pairs in the hydrogenation of **1**, and in the competitive saturation of the quinoline rings of the alkaloids, is attributed to differences in the adsorption strength and geometry of the alkaloids. The results are in good agreement with our former mechanistic model assuming that the quinoline ring of cinchona alkaloid and **1** adsorb parallel to the Pd surface during the enantiodifferentiating step.

KEY WORDS: asymmetric; hydrogenation; cinchona alkaloids; adsorption; Pd/TiO_2; 4-methoxy-6-methyl-2-pyrone.

1. Introduction

Chirally modified metals afford over 90% enantiomeric excess (ee) in the hydrogenation of various functionalized ketones and olefins, and the performance of these solid catalysts is in some reactions comparable to that of sophisticated homogeneous chiral metal complexes [1–5]. The mechanistic understanding of heterogeneous enantioselective catalysis, however, lags behind the synthetic development. The major reason for this discrepancy is the well-known difficulty in studying the adsorption and interaction of reactant and modifier on the metal surface under reaction conditions.

Various physicochemical methods have been applied for the investigation of the adsorption of pyruvate esters [6–9] and cinchonidine (CD, scheme 1) [10–15] on Pt and Pd. Particularly valuable are those methods that allow the study of adsorption at the solid–liquid interface. Cyclic voltammetry in an aqueous acidic solution revealed that adsorption of doubly protonated CD on polycrystalline Pt is irreversible and the coverage strongly depends on the structure of the metal [16]. ATR-IR spectroscopy indicated the existence of three different surface species of CD over Pt/Al_2O_3 and Pd/TiO_2 [17–19]. In the latter case measurements were carried out under conditions very close to those of enantioselective hydrogenations (in the presence of hydrogen and an organic solvent).



Scheme 1. Hydrogenation of 4-methoxy-6-methyl-2-pyrone (**1**) over chirally modified 5 wt% Pd/TiO_2 and the structure of cinchona alkaloids used as modifiers.

Another approach for *in situ* investigation of modifier adsorption is the application of pairs of modifiers for chiral induction [20–23]. With this strategy, recently we have observed a remarkable nonlinear behavior of cinchona alkaloids in the enantioselective hydrogenation of ethyl pyruvate on Pt and 4-methoxy-6-methyl-2-pyrone (**1**, scheme 1) on Pd [24,25]. For example, in the presence of equimolar amounts of quinidine (QD) and

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CD the latter dominated the reaction and (*R*)-lactate formed with close to 90% ee, though QD alone provided higher than 90% ee to (*S*)-lactate. This nonlinear effect was attributed to differences in the adsorption strength and geometry of the alkaloids.

The nonlinear effect of enantiomerically impure ligands in homogeneous catalysis has been a topic of great interest [26–29]. In the past few years it has been shown that the concept can be extended to pseudo-enantiomeric or diastereomeric catalysts, such as the derivatives of cinchona alkaloids QD and quinine (QN), or even to two different ligands giving products of opposite configuration [30–34].

In the present paper we discuss the nonlinear behavior of cinchona alkaloid pairs in the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone (**1**) on Pd/TiO_2. The study provides further support to the crucial role of the adsorption strength and geometry of alkaloids in enantioselection and in resistance against self-hydrogenation.

2. Experimental

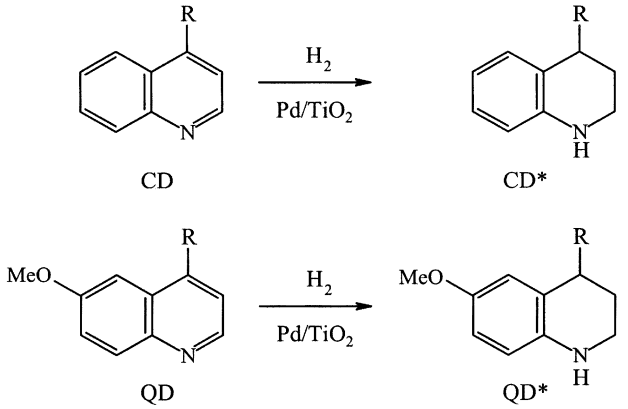
Most of the solvents and 1-hexene (99.8%, Fluka) were of analytical grade and used as received. Tetrahydrofuran was distilled over potassium before use. The commercially available cinchona alkaloids contained a high proportion of impurities (for the abbreviations, see scheme 1): CD (92%; impurities: 1% QN, 7% QD, determined by HPLC, amounts given by Fluka), CN (85%; impurity: 15% 10,11-dihydro-CN, determined by HPLC, Fluka), QD (>90%; impurity: <10% 10,11-dihydro-QD, determined by HPLC, Fluka), and QN (>95%; impurity: <5% 10,11-dihydro-QN, determined by HPLC, Fluka).

4-Methoxy-6-methyl-2-pyrone (**1**) was synthesized according to a former procedure [35] and characterized by NMR. Prior to use, small portions were purified by sublimation in vacuum followed by repeated crystallization from hexane. MeOCD was prepared according to a known method [36] and its structure was confirmed by elementary analysis, and ^1H and ^{13}C NMR spectroscopy.

A 5 wt% Pd/TiO_2 sample (metal dispersion: 0.18, determined by H_2 chemisorption) was prepared as follows. $PdCl_2$ (0.97 g) was dissolved in 10 ml water and 1 ml concentrated HCl. TiO_2 (11.16 g) (P25, Degussa, 55 m^2/g) was added to the solution and the pH was set to 10 by dropping an aqueous Na_2CO_3 solution to the stirred slurry at room temperature. After centrifugation the catalyst was washed to neutral and dried at 80 °C in vacuum for 24 h. Small portions of the dry catalyst were reduced in a H_2 flow at room temperature for 30 min and stored in air until use.

The hydrogenation reactions were carried out in a magnetically stirred 100 ml glass reactor. In a standard procedure, 20 mg catalyst was prereduced in 10 ml 2-propanol in flowing H_2 for 5 min at 1 bar and room temperature. Then 3.4 μmol modifier was added in 1 ml 2-propanol. The reaction was started 5 min later by introducing 50 mg (0.35 mmol) reactant in 1 ml 2-propanol. In the transient experiments an additional modifier (3.4 μmol) in 1 ml 2-propanol was injected into the reaction mixture after 30 min reaction time. The conversion and enantiomeric excess ($ee = |R(\%) - S(\%)|$) were determined by a HP 6890 gas chromatograph using a Chirasil-DEX CB column (Chrompack). The actual or incremental ee was calculated as $\Delta ee = (ee_1 \cdot y_1 - ee_2 \cdot y_2)/(y_1 - y_2)$, where y represents the yield to the dihydropyrone **2**, and subscript 2 refers to a sample subsequent to sample 1. The (initial) reation rates were calculated from the conversion of **1** in the first 30 min.

UV–vis measurements were used to determine the amount of CD and QD remaining in solution after pre-adsorption (and hydrogenation of the quinoline ring) on the catalyst in the presence of hydrogen at atmospheric pressure. Measurements were performed in transmission mode on a CARY 400 spectrophotometer using a 1 cm path length quartz cuvette. Spectra are given in relative absorbance units with neat solvent serving as the reference. Pretreatment of the catalyst or support before measurement was the same as described for the hydrogenation of **1**. The individual concentration and the relative amount of modifiers remaining in solution after filtering off the catalyst was determined as follows. A synthetic curve, generated by linear combination of the reference spectra of individual alkaloids, was substrated from a measured spectrum. This process was accepted when the difference between the measured and synthesized spectra did not exhibit typical absorption bands of CD and QD as, for example, at 315 nm for CD and 332 nm for QD. The difference spectrum, however, showed broad bands at around 305 and 318 nm, which belong to modifiers CD* and QD*, respectively, possessing a partially hydrogenated quinoline ring system (scheme 2). The latter bands were found in all



Scheme 2. Major products in the hydrogenation of cinchonidine (CD) and quinidine (QD) over 5 wt% Pd/TiO_2 in 2-propanol.

experiments where the catalyst and modifier were treated with hydrogen. Since these bands were much broader than the characteristic features of CD and QD at 300–350 nm, its presence does not hinder quantification of CD and QD in solution. NMR and UV–vis measurements indicated that CD* and QD* were the dominant products in the hydrogenation of CD and QD, respectively, under the conditions applied here. A test with CD–QD mixtures of known concentrations revealed that the reliability of the method is high: the relative error is estimated to be less than 2%. More details can be found in an earlier publication [25].

3. Results

3.1. Transient behavior of pyrone hydrogenation with alkaloid pairs as modifiers

In a preliminary report [24] we have shown a striking nonlinear effect in the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone (**1**) when applying mixtures of CD and QD. Here we used a different strategy based on transient experiments. We started the reaction in the presence of an alkaloid and after 30 min an equimolar amount of a second alkaloid was injected that alone affords the opposite enantiomer of **2**. An example is shown in figure 1. The hydrogenation of **1** was started with Pd/TiO_2 modified by QD, which provided (*R*)-**2** in excess. Addition of one equivalent CD, which alone gives (*S*)-**2** as the major product, resulted in an immediate decrease of ee and reaction rate. The time-dependent changes of the calculated incremental ee (Δee) demonstrate that CD took over the control of enantioselection within 2–3 min after its addition. Apparently, an equivalent amount of CD rapidly replaced QD on the Pd surface. In the control experiment the hydrogenation of **1** was started in the presence of CD and QD was added after 30 min. In this case the enantioselectivity and reaction rate were not affected by the added modifier, indicating that QD is inferior to CD in the competition for interaction with the reactant during enantioselection.

These two experiments were repeated under the same conditions but CN and QN were used as modifiers (figure 2). Injection of QN did not influence the hydrogenation of **1** over CN-modified Pd/TiO_2, which alkaloid favored the formation of (*R*)-**2** in excess. In the reverse case, addition of CN to a reaction running over the Pd/TiO_2–QN system induced an immediate shift in reaction rate (not shown) and ee. Here again, the apparent exchange of QN by CN on the metal surface was complete within 2–3 min (as indicated by the rapid shift in Δee) and the dominant modifier CN controlled the reaction.

From the transient experiments shown in figures 1 and 2 we can deduce that those cinchona alkaloids that possess a methoxy group at the quinoline ring (QD, QN) are less effective in the competition than the corresponding alkaloids without this functional group (CD, CN).

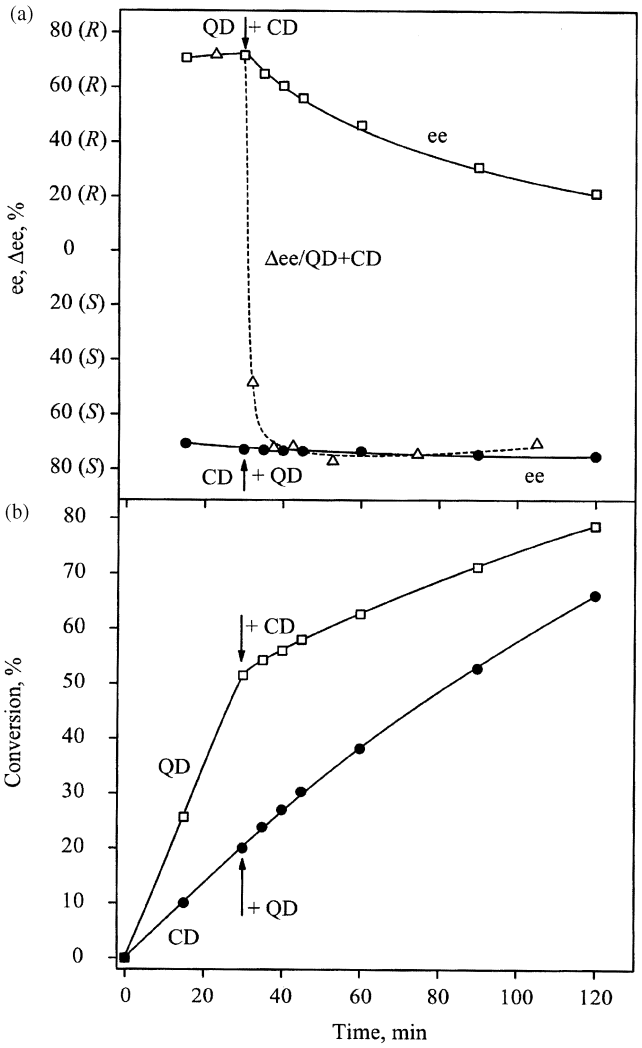


Figure 1. Transient behavior of the hydrogenation of **1** induced by the addition of one molar equivalent QD or CD to the reaction mixture containing CD or QD, respectively. (a) Enantiomeric excess (ee) and incremental ee (Δee) *versus* time; (b) conversion *versus* time. Standard conditions, second modifier added after 30 min reaction time.

When the pseudo-enantiomers QD and QN, or CN and CD, were applied as modifiers, domination of one of the modifiers was much less pronounced (figure 3). These alkaloid pairs possess the same aromatic ring system, either a quinoline or a 6′-methoxy-quinoline moiety. In all four experiments Δee values of 20–25% to (*R*)-**2** were achieved at the end of the reaction. That is, CN and QD always dominated the enantioselective hydrogenation over CD and QN, respectively, independent of the order of addition. Another interesting point is that the changes in Δee were relatively slow and 40 to 60 min were necessary to reach the approximate final Δee characteristic of the equimolar mixture of the modifiers.

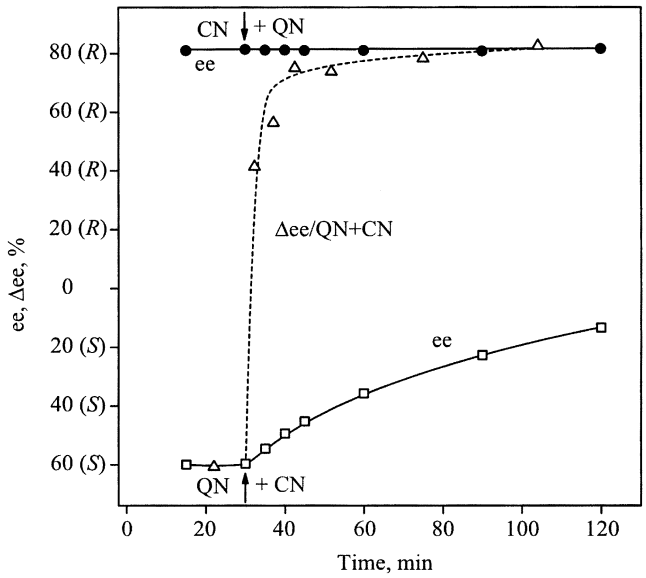


Figure 2. Changes in ee and incremental ee (Δee) in the hydrogenation of **1** induced by the addition of one molar equivalent QN or CN to the reaction mixture containing CN or QN, respectively. Standard conditions, second modifier added after 30 min reaction time.

The transient experiments were completed with hydrogenations using MeOCD, and either CN or QD as competing modifier. This simple derivative of CD (scheme 1) showed an intermediate behavior: it was dominant against QD but inferior to CN. Unfortunately, an unambiguous interpretation of the results concerning the role of 9-OH group in CN is not possible as it is not yet clear whether the OH group is involved in the reactant–modifier interaction [4,37].

Figure 4 illustrates the order of domination of the five modifiers used in the hydrogenation of **1**. When

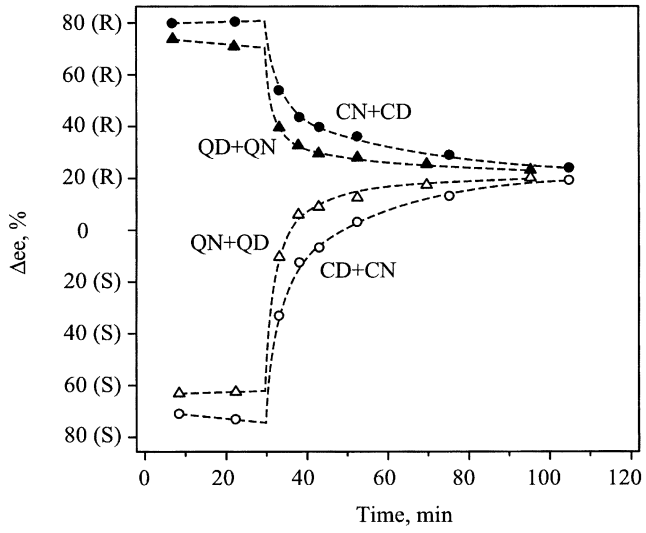


Figure 3. Transient behavior of the hydrogenation of **1** with pseudo-enantiomeric cinchona alkaloids. Changes in incremental ee (Δee) induced by the addition of one molar equivalent QD or CN to reactions that were started with QN and CD, respectively (open symbols); or the reverse cases (filled symbols). Standard conditions, second modifier added after 30 min reaction time.

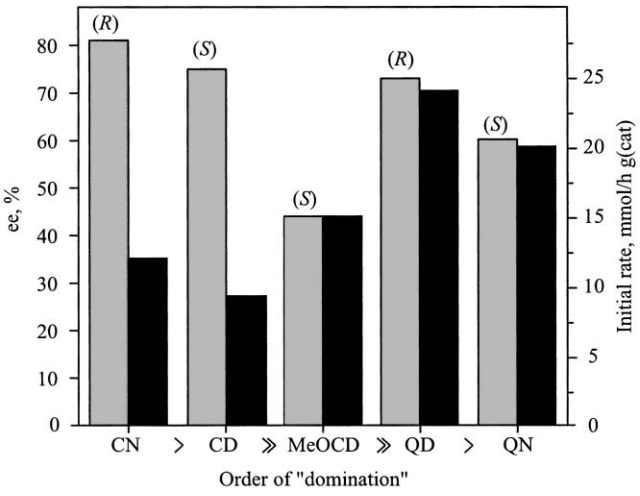


Figure 4. The order of "domination" of chiral modifiers in the hydrogenation of **1** over Pd/TiO_2. The initial reaction rate (black) and ee (gray) were determined under standard conditions.

comparing the pseudo-enantiomers CD and CN, or QD and QN, the dominant modifier alone affords higher ee and initial rate. In these cases the relatively small nonlinear effect shown in figure 3 should partly be attributed to the higher efficiency of CN and QD in the enantioselective hydrogenation of **1** [24]. For example, when CD–CN mixtures were used, the ee calculated by linear combination of the individual rates and ee values was 10% and the experimentally observed ee was 27%. In contrast, the situation is the opposite when modifiers with different anchoring moieties (quinoline or 6′-methoxy-quinoline) are compared. For example, CD is dominant over QD though the latter modifier affords a similar ee and more than twice as high an initial reaction rate as CD alone.

3.2. UV–vis study of the competitive adsorption and hydrogenation of CD and QD

The catalytic experiments were completed with UV–vis spectroscopic analysis in the presence of hydrogen [25]. The 6′-methoxy group in QD and QN has a strong influence on the electronic structure of the quinoline ring system that is the chromophore moiety of the molecules. Besides, (partial) hydrogenation of the quinoline ring (scheme 2) is sensitively detected, allowing the study of the competitive adsorption and hydrogenation of CD and QD, or CN and QN, alkaloid pairs. To increase the sensitivity of this indirect spectroscopic method, the catalyst/modifier ratio was doubled compared to that applied in the hydrogenation of **1** under standard conditions (figure 1).

Figure 5 illustrates the competitive adsorption of CD and QD on the 5 wt% Pd/TiO_2 catalyst in hydrogen at 1 bar. The curves represent the amounts of alkaloids and their hydrogenation products in solution, relative to the initial amount of each alkaloid. In these model studies

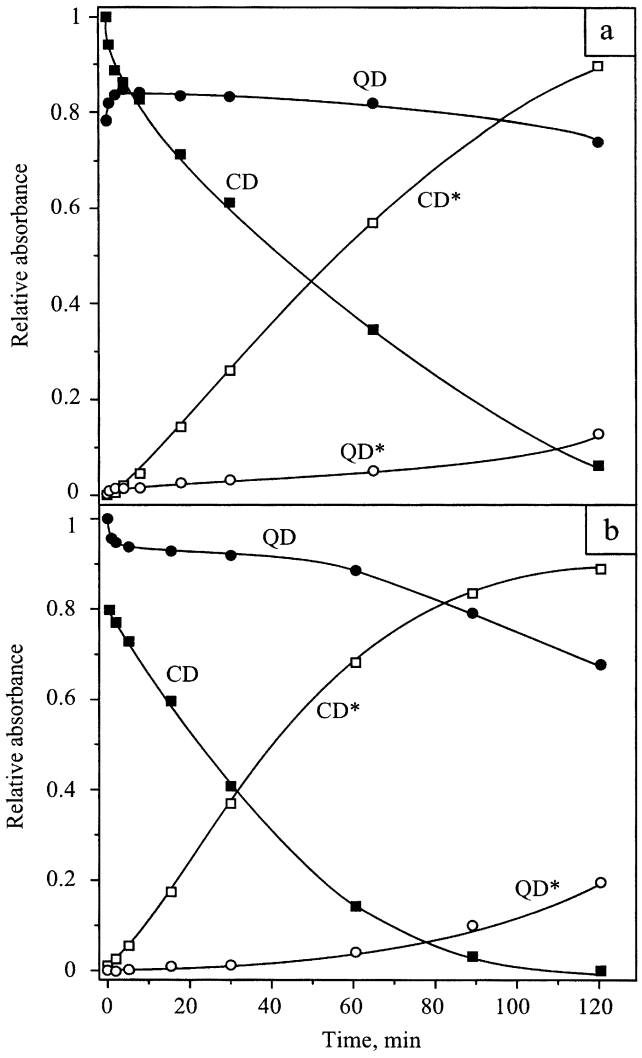


Figure 5. Adsorption and hydrogenation of CD–QD mixtures on 5 wt% Pd/TiO_2 at 1 bar and room temperature. Catalyst (40 mg) in 19 ml 2-propanol is modified by 3.4 μmol QD (a) or CD (b) and after 1 min one molar equivalent CD (a) or QD (b) is added in 1 ml 2-propanol; addition of the second modifier is considered as the zero time.

at first QD was contacted with Pd/TiO_2 (modifier/$Pd_s = 1$) in 2-propanol. After 1 min an equimolar amount of CD in 2-propanol was added and stirring continued (figure 5(a)). Before addition of CD, 23% of the original amount of QD adsorbed on the catalyst, as indicated by the lower relative absorbance of QD remaining in solution (starting point of the curve). Due to the very short contact time with the catalyst, hydrogenation of the aromatic moiety of the modifier was negligible at this point. Addition of CD resulted in the desorption of only a few percent QD in the following 2 min. Then the QD concentration remained almost constant in solution for more than 60 min and only small amounts of the hydrogenation product (QD*) were detected in solution. In contrast, CD disappeared rapidly from solution as the quinoline ring was hydrogenated. In the first 60 min the ratio of the rate of formation of CD* and QD* was about 11. Hydrogenation of QD accelerated only after CD was mainly converted. Note that according to NMR analysis CD* and QD* were the major hydrogenation products but small amounts of other products could also be detected. Hydrogenation of the vinyl group of the alkaloids is not considered here, as this functional group has no significant influence on the reaction rate and ee, and is also not detectable by UV–vis analysis.

The control experiment under the same conditions but with reverse order of modifier addition resulted in an initial adsorption of 20% of CD on the catalyst (figure 5(b)). An immediate desorption of CD after addition of QD was not observed, though about 5% of QD adsorbed on the catalyst in the following 2 min. It is probable that the small amount of CD desorbed was covered by the fast hydrogenation of the quinoline ring. The initial rate of hydrogenation of the aromatic moiety of QD was about the same as in the former experiment (figure 5(a)) but the hydrogenation rate of CD was 50% higher here, resulting in a ratio of the initial hydrogenation rates of 16. Hydrogenation of QD accelerated only when the conversion of CD exceeded 80%.

In order to minimize the disturbing effect of the hydrogenation of the quinoline ring, the experiment shown in figure 5(a) was repeated in a 5% H_2–Ar atmosphere. The low hydrogen concentration was necessary to keep the metal surface in a reduced state. In this experiment hydrogenation of CD was very slow, as expected, and hydrogenation of QD was not detectable in the first 2 h. Addition of CD induced desorption of about one-third of preadsorbed QD, confirming the partial replacement of the inferior modifier by the dominant modifier.

The individual hydrogenation rates of CD and QD are shown in figure 6. The decay of the UV–vis absorbance relative to the initial values reveals that the presence of

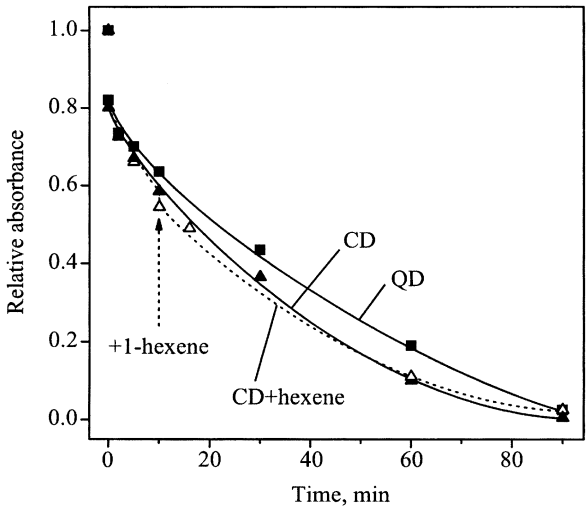


Figure 6. Conversion of CD and QD on a 5 wt% Pd/TiO_2 catalyst in the presence of hydrogen and, alternatively, also 1-hexene as a model reactant. The hydrogenation reactions are followed by UV–vis spectroscopy. Conditions: 1 bar and room temperature, 40 mg 5 wt% Pd/TiO_2, 20 ml 2-propanol, 3.4 μmol modifier. Addition of 2 ml 1-hexene after 10 min hydrogenation of CD (open symbols, dashed line).

the 6′-methoxy function in QD has only a minor effect on the stability of the aromatic ring. The difference in the initial rates was less than 25% and after about 90 min both modifiers were completely converted. A comparison with figure 5(b) reveals that hydrogenation of CD alone was as fast as in the presence of QD, *i.e.* saturation of the aromatic ring of CD is barely affected by the addition of QD. In contrast, hydrogenation of QD is strongly suppressed by addition of the dominant modifier CD.

A limitation of the experiments shown in figure 5 is that the adsorption of alkaloids was studied in the presence of hydrogen but in the absence of the reactant **1**. Unfortunately, UV–vis analysis of the alkaloids and their hydrogenation products was not possible in the presence of **1**. To clarify the possible distorting effect of a large excess of reactant, 1-hexene was used as a model reactant that does not disturb the UV–vis analysis. The curves in figure 6 show that the influence of 1-hexene on the hydrogenation of CD was minor despite the high 1-hexene/CD molar ratio of 9400.

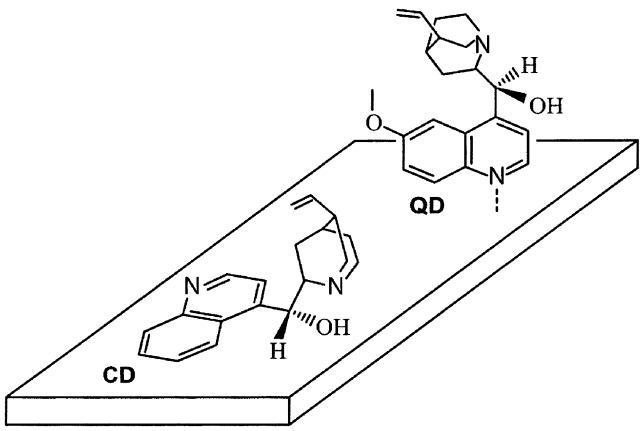


Figure 7. Adsorption of the dominant modifier cinchonidine (CD) via its quinoline ring lying approximately parallel to the Pd surface and that of the inferior modifier quinidine (QD) via the 6′-methoxy-quinoline ring being in a tilted position relative to the surface of Pd.

4. Discussion

The transient behavior observed in the hydrogenation of **1** with pairs of cinchona alkaloids indicates that the alkaloid, which does not possess a methoxy function in the quinoline ring system (CD, CN), rapidly replaces the other alkaloid (QD, QN) in the reactant–modifier interaction on the Pd surface. The replacement is demonstrated by the instantaneous shift of the actual or incremental ee in figures 1 and 2 after addition of the dominant modifier. The kinetic analysis indicated that the dominance of CD or CN cannot be traced to kinetic effects. A feasible explanation for this phenomenon is the difference in adsorption strength and geometry of the alkaloids on Pd.

The observations support our recent interpretation for the nonlinear behavior of cinchona alkaloid pairs [24,25], which is based on a series of ATR-IR studies of CD adsorption on Pt and Pd in organic medium in the presence of hydrogen [17–19]. Shortly, CD can adopt a position in which the quinoline ring lies approximately parallel to the metal surface (strong adsorption via π-bonding), or the aromatic moiety may be in a tilted position (more weakly adsorbed). We assume [24] that in the enantiodifferentiating step of the hydrogenation of **1** the dominant modifier adsorbs mainly via the quinoline ring being approximately parallel to the Pd surface. The inferior modifier, QD, adsorbs more weakly adopting a tilted position (figure 7) that is unfavorable for enantiodifferentiation, or even partly desorbs from the Pd surface. The former fraction of the inferior modifier represents a spectator species on the Pd surface that barely influences the enantioselection. This interpretation is in good agreement with the probable mechanism of the enantioselective hydrogenation of substituted pyrones [37–39]. We assume that both the reactant and the quinoline ring of the cinchona alkaloid modifier adsorb parallel to the metal surface during the enantiodifferentiating step.

The above explanation for the nonlinear behavior of cinchona alkaloid pairs in the hydrogenation of **1** is corroborated by the competitive hydrogenation of CD and QD under similar reaction conditions (figure 5). Saturation of the quinoline ring of CD or QD, when only one alkaloid was present, occurred with similar rates but in equimolar mixtures the rate of CD hydrogenation was higher by a factor of 11–16. According to the above model, in equimolar mixtures the quinoline ring of CD (dominant modifier) lies approximately parallel to the Pd surface and its hydrogenation is expected to remain unaffected by the presence of QD. In contrast, hydrogenation of the quinoline ring of the inferior modifier QD is strongly suppressed in QD–CD mixtures, as hydrogen uptake by the quinoline ring being in a tilted position relative to the Pd surface is strongly hindered.

When the diastereomeric pairs CD–CN or QD–QN were applied in the hydrogenation of **1**, the replacement of one alkaloid by the other was relatively slow, leading to slow changes in the enantiomer distribution (figure 3). The likely explanation is that in these alkaloid pairs the driving force for replacement, the difference in adsorption free energy, is small.

5. Conclusions

The striking nonlinear behavior of cinchona alkaloid pairs in the enantioselective hydrogenation of the methoxypyrone **1** and the competitive hydrogenation of the quinoline rings of the alkaloids on Pd are attributed to differences in the adsorption strength and geometry

of the alkaloids. The more strongly adsorbing alkaloid is enriched on the surface and, more importantly, it adsorbs via the quinoline ring lying approximately parallel to the metal surface. This ''dominant'' alkaloid is the efficient modifier of Pd in the enantioselective hydrogenation of **1** and its quinoline ring is hydrogenated relatively fast. The more weakly adsorbing alkaloid adopts a position in which the quinoline ring is tilted relative to the Pd surface. This position hinders the saturation of the quinoline ring and also the effective reactant–modifier interaction resulting in enantioselection.

The present data, together with some recent catalytic and spectroscopic studies, reveal an apparently similar adsorption behavior of cinchona alkaloids on Pt and Pd. This agreement is astonishing in the light of the strikingly different application range and efficiency of Pt–cinchona and Pd–cinchona catalyst systems in the hydrogenation of functionalized ketones and olefins, and requires further clarification.

Acknowledgment

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