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Model for Enantioselective Hydrogenation of α-Ketoesters over Chirally Modified Platinum Revisited: Influence of α-Ketoester Conformation

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Interaction complexes between cinchonidine modifier and methyl pyruvate reactant proposed for the enantioselective hydrogenation over platinum catalysts have been calculated using *ab initio* methods. For *s-trans*-methyl pyruvate it was found that the complex yielding (*R*)-methyl lactate upon hydrogenation was more stable than the corresponding pro-(*S*) complex. The calculated energy difference of 1.8 kcal/mol corresponds to an enantiomeric excess of 92%, in good agreement with experiment. For the analogous complexes of *s-cis*-methyl pyruvate the energy difference is only 0.2 kcal/mol in favour of pro-(*R*), corresponding to 17% enantiomeric excess. Due to the larger dipole moment of the *s-cis* conformer of methyl pyruvate its hydrogen-bonded complexes with cinchonidine are considerably more stable than the corresponding *s-trans* complexes. However, the predicted low enantiomeric excess for the *s-cis* conformer is in contrast with experiment. Possible reasons for this behaviour are discussed. © 2000 Academic Press

Key Words: **enantioselective hydrogenation; α-ketoesters; mechanistic model; platinum; cinchona alkaloid; chiral modification; modifier–reactant interaction.**

INTRODUCTION

Enantioselective catalysis over chirally modified metals has gained considerable interest as one of the most promising heterogeneous catalytic routes for the transformation of prochiral substrates to chiral products. One of the most thoroughly investigated reactions is the enantioselective hydrogenation of α-ketoesters over platinum chirally modified by cinchona alkaloids, originally reported by Orito and co-workers (1, 2). The hydrogenation of ethyl or methyl pyruvate to (*R*)-ethyl or methyl lactate over cinchonidine (CD)-modified platinum, which affords more than 95% enantiomeric excess (ee) under optimised conditions, has served as the model reaction for several research groups. The most important parameters affecting ee have been identified and thoroughly studied and reviewed (3–5). In the search for the origin of enantiodifferentiation the systematic variation of the structure of the cinchonidine modifier revealed that the quinuclidine N is crucial, whereas the O–H group has only a marginal effect.

Despite the large body of available experimental data the mechanism of enantiodifferentiation is far from being completely resolved mainly due to the lack of direct information on the molecular level. Such information, although highly desirable, is very difficult to gain experimentally, owing to the complexity of the system and the need to obtain such information as close as possible to reaction conditions. First-principle calculations can equally yield molecular information. However, the many degrees of freedom involved and the size of the overall system, including α-ketoester, hydrogen, cinchonidine, platinum, and solvent, require that we make approximations in order for the calculations to become feasible and to rule out a completely unbiased treatment.

Several different models have been suggested for the enantiodifferentiating complex formed between α-ketoesters and cinchona alkaloids. Most of them have been discussed in recent reviews (4–6). Some years ago, our group proposed a model for enantiodifferentiation, which allowed us to predict the chirality of the main product by calculating the relative stability of the reactant–modifier complexes leading to (*R*)- and (*S*)-product, respectively (7). In the following these complexes will be termed pro-(*R*) and pro-(*S*), respectively. The model was successfully applied to different modifier–reactant pairs and served as a guide for the development of new modifiers (5). In this proposed model the relative abundance (i.e., the stability) of the reactive complexes on the surface, which would yield (*R*)- and (*S*)-product upon hydrogenation of methyl pyruvate, is proposed to represent the (*R*)- and (*S*)-product distribution. The directionality of approach of the hydrogen to the keto C of methyl pyruvate is crucial for enantiodifferentiation. The model assumes an approach from the surface side. Such a directionality of approach has recently been suggested for the hydrogenation of ethylene and acetylene on nickel (8). As an alternative to this thermodynamic control, dissimilar hydrogenation rates for the different reactant–modifier complexes could determine the enantiodifferentiation.

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This point has been discussed in the past but is yet unresolved (3, 9).

The model makes assumptions concerning the structure of the adsorbed reactant and modifier. Some of the assumptions have been addressed lately and it is the primary goal of this work to examine the proposed model for enantiodifferentiation in the light of these new findings.

PRESENT STATUS OF THE MODEL FOR ENANTIOSELECTIVE HYDROGENATION OF METHYL PYRUVATE

The model proposes 1 : 1 complexes between cinchonidine (CD) modifier, which is strongly anchored onto the platinum surface during the whole catalytic cycle, and α-ketoester reactant as the crucial entity for enantiodifferentiation. The two molecules interact via a hydrogen bond formed between the keto oxygen atom and the quinuclidine N, which is protonated in acidic media (10). For nonprotic solvents a half-hydrogenated state of the ketoester has been proposed to form a hydrogen bond with the quinuclidine N (5). In Fig. 1 such interaction complexes are depicted. Both CD and methyl pyruvate (MP) are assumed to be adsorbed via their π-system in a flat adsorption mode. Furthermore, CD is assumed to adopt conformation *open(3)*, where the quinuclidine N points away from the quinoline moiety. For methyl pyruvate *s-trans* conformation is assumed. For the calculations the platinum surface is not explicitly taken into account but the steric constraint imposed by the surface is considered by fixing the quinoline moiety of CD and the O=C–C=O part of MP in the same plane. In this way the complex, which would ultimately lead to the (*R*)-lactate upon hydrogenation from below the MP plane, is calculated to be more stable. Note that the model does not make any assumption concerning the local structure of the platinum surface and is equally valid for Pt(111), Pt(110), or any other relatively flat surface.

Since the model has been proposed some of the structural assumptions have been addressed. It has been shown that CD adopts the conformation *open(3)* in media which are favourable for enantiodifferentiation, i.e., in apolar or acidic solvents (11). Also the use of rigid cinchona modifiers, which have a fixed *open(3)* conformation, affords high enantiomeric excess (12). These findings justify the CD conformation used for the model calculations. As concerns the adsorption mode of CD, it has been shown that CD does not adsorb via the quinoline N (13), within the enantiodifferentiating complex, as for example found for the structurally related pyridine (14). The catalytic behaviour of CD and a synthetic variant, 2-phenyl-9-deoxy-10,11-dihydrocinchonidine, for which such an adsorption is prevented, is very similar (13). A recent ultrahigh-vacuum NEXAFS investigation shows that CD is adsorbed preferentially flat on Pt(111) (15). Although there is no direct spectroscopic *in situ* data available to date, an adsorption mode of CD via its quinoline π-system is most likely.

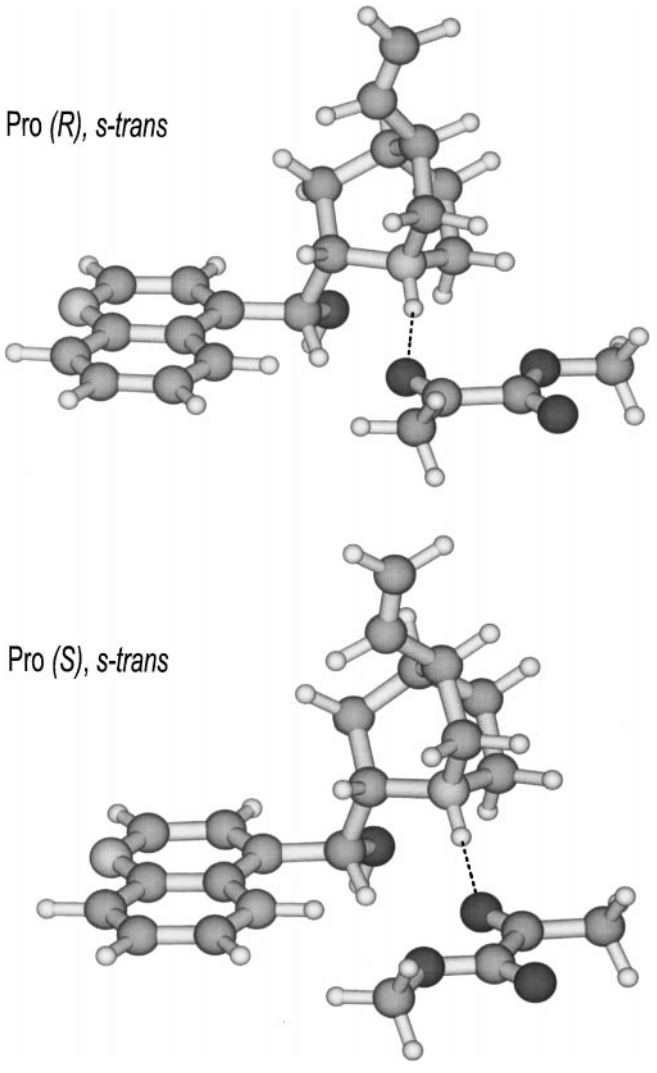

FIG. 1. Optimised structures of complexes between protonated cinchonidine (CDH^+) in its *open(3)* and methyl pyruvate (MP) in its *s-trans* conformation. During optimisation the quinoline moiety of cinchonidine and the O=C–C=O group of methyl pyruvate were kept coplanar. The calculations were performed at the Hartree–Fock level using a 6-31G(d,p) basis set. The top and bottom complex, respectively, would yield (*R*)- and (*S*)-methyl lactate, respectively, upon hydrogenation of methyl pyruvate from the bottom side (pro-(*R*) and pro-(*S*) complexes).

The adsorption mode of MP has recently also been addressed by several groups using different techniques. Infrared spectra on Ni(111) showed that MP interacts with the Ni surface via its O lone pairs, indicating that a *cis*-bidentate species oriented perpendicular to the surface is most stable (16). This is consistent with an ultraviolet photoemission (UP) study of ethyl pyruvate on Pt(111) under similar conditions, which showed that the O lone pairs are involved in the bonding to the surface (17). From angular-dependent

X-ray absorption near-edge structure (XANES) spectra on Pt(111) the mean tilt angle of the ethyl pyruvate molecular plane with respect to the surface was determined as 72°, confirming a perpendicular or tilted orientation (18). More importantly, when measured in a hydrogen atmosphere this mean tilt angle decreased to 58°, showing that ethyl pyruvate has a tendency to lie down under these conditions. This indicates that the adsorption mode of methyl or ethyl pyruvate is rather complicated. Further *in situ* information will be needed to reveal the influence of hydrogen, CD, and solvent on the adsorption of MP. From a catalytic point of view, the C=O group has to interact with the platinum surface during hydrogenation, in order to have access to activated hydrogen. This is only possible in a flat or nearly flat geometry, as proposed in the model.

For MP the *s-trans* conformation was considered in the model. In the gas phase *s-trans* is more stable than *s-cis* by about 1.1–1.6 kcal/mol (19, 20). However, the *s-cis* conformer has a considerably larger dipole moment than the *s-trans* (5.0 D vs 1.5 D) (19), for which the two polar carbonyl groups are oriented antiparallel. As has been shown, this results in a significant stabilization of *s-cis* relative to *s-trans* when increasing the solvent polarity (19). The relative stability of the *s-cis* and *s-trans* conformers of MP is likely to be affected by the platinum metal surface. Dipole–induced dipole interaction again favours the *s-cis* conformer due to its larger dipole moment. Indeed *s-cis* is the most abundant conformer of MP on Ni(111) under ultrahigh-vacuum conditions as indicated by a recent vibrational spectroscopic study (16).

Using the trimethyl ammonium ion as an example, it has furthermore been shown that N^+–H···O=C hydrogen-bonding interaction is stronger for the *s-cis* than for the *s-trans* conformer, thus stabilizing the former (19). An analogous type of hydrogen-bonding interaction is proposed in the model for enantiodifferentiation and therefore a similar stabilisation of the *s-cis* conformer is anticipated. Further support for the importance of the *s-cis* conformation stems from the enantioselective hydrogenation of ketopantolactone (21) and a cyclic imidoketone (22), which have a fixed *s-cis* conformation. These molecules can be hydrogenated with ee similar to that of MP.

Prompted by the several indications that the *s-cis* conformation of the α-ketoester reactant is stabilised with respect to *s-trans* by solvent, metal surface, and hydrogen-bonding interaction we revisited the model proposed for the enantioselective hydrogenation of α-ketoesters. Special attention was given to the influence of α-ketoester conformation.

CALCULATIONS

All calculations were performed using the Hartree–Fock (HF) method with a 6-31G(d,p) basis set as implemented in the GAUSSIAN94 suite of programs (23). No corrections were made for the basis set superposition error (BSSE). It has been shown recently that for hydrogen-bonded complexes calculated at the HF level using medium-sized basis sets such as 6-31G(d,p) the BSSE and the correlation correction to the binding energy cancel quite evenly (24). The calculations were restricted to protonated CD in its *open(3)* conformation.

To simulate the steric constraints imposed by the platinum surface the quinoline ring system of CD and the O=C–C=O group of EP were restricted to be coplanar. All other degrees of freedom were fully optimised to a gradient of less than 4.5×10^{-4} hartree/bohr. Different starting geometries were used for the geometry optimisations. In some calculations the influence of the solvent was investigated by using a self-consistent reaction field model (scipcm option in GAUSSIAN94) (23).

RESULTS

Figure 1 shows minimum energy structures of CDH^+–MP complexes, with MP in its *s-trans* conformation. The top and lower parts of Fig. 1 show the complexes, which would lead to (*R*)- and (*S*)-methyl lactate, respectively, upon hydrogenation from the platinum side, i.e., from below. The relative energies of these complexes are given in Table 1. The pro-(*R*) complex is more stable by about 1.8 kcal/mol. This finding is in accordance with force field and semiempirical calculations (7, 25, 26). The calculated energy difference corresponds to a relative abundance pro-(*R*)/pro-(*S*) of 96/4 at room temperature. When considering the solvent by surrounding the complexes shown in Fig. 1 by a dielectric medium with a relative permittivity of $\varepsilon_r = 20.7$ (moderately polar solvent) the energy difference reduces slightly to 1.5 kcal/mol. By relieving the constraint of coplanarity the two complexes shown in Fig. 1 relax by 1.2 and 2.5 kcal/mol, respectively, resulting in an energy difference of only 0.5 kcal/mol for the completely optimised structures.

TABLE 1

Relative Energies (kcal/mol) of Complexes between Protonated Cinchonidine (CDH^+) and Methyl Pyruvate (MP)

Complexes	ΔE (kcal/mol)	
	$\varepsilon_r = 1.0$	$\varepsilon_r = 20.7$
pro-(*R*)-CDH^+···*s-trans*-MP	0.0	0.0
pro-(*S*)-CDH^+···*s-trans*-MP	1.8	1.5
pro-(*R*)-CDH^+···*s-cis*-MP	−4.1	−1.0
pro-(*S*)-CDH^+···*s-cis*-MP	−3.9	−1.0

Note. The energies are given relative to the complex with methyl pyruvate in its *s-trans* conformation, which would give (*R*)-methyl lactate upon hydrogenation (pro-(*R*)-CDH^+···*s-trans*-MP). Values are given both for the gas phase ($\varepsilon_r = 1.0$) and for a solvent with relative permittivity of 20.7. The calculations were performed at the Hartree–Fock level using a 6-31G(d,p) basis set. Solvent effects were included via a self-consistent reaction field model.

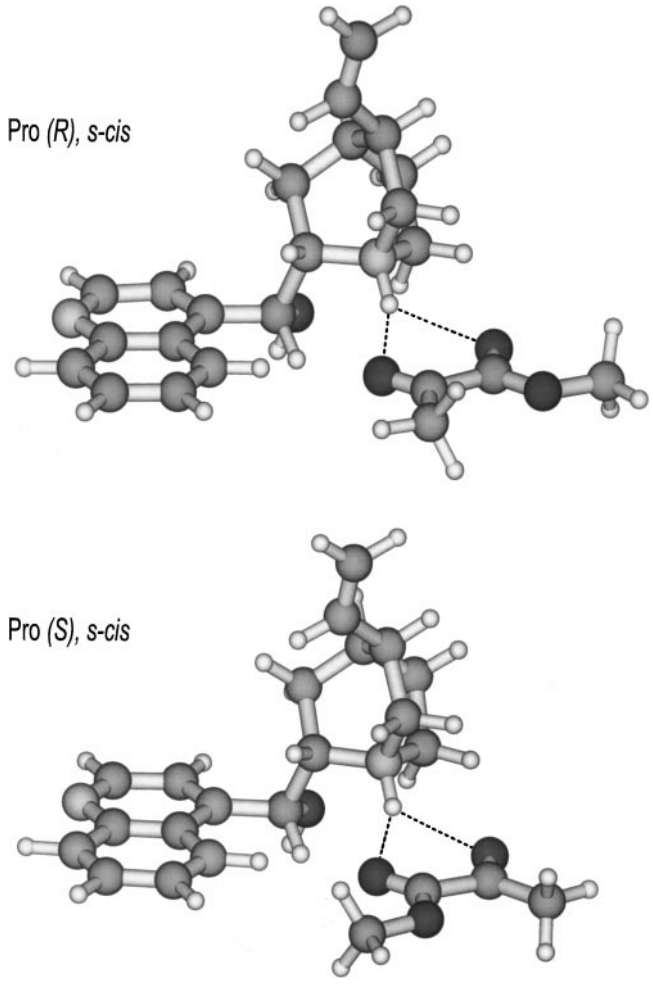

FIG. 2. Optimised structures of complexes between protonated cinchonidine in its *open(3)* and methyl pyruvate in its *s-cis* conformation. The procedure used for calculation was analogous to that described in Fig. 1. The top and bottom complex, respectively, would yield (*R*)- and (*S*)-methyl lactate, respectively, upon hydrogenation of methyl pyruvate from the bottom side (pro-(*R*) and pro-(*S*) complexes).

Figure 2 shows the pro-(*R*) and pro-(*S*) complexes between CDH^+ and MP in its *s-cis* conformation, which have not been considered in previous studies. As can be seen from Table 1, the complexes with *s-cis*-MP are considerably more stable than the complexes with *s-trans*-MP. Interestingly, the energy difference between the pro-(*R*) and pro-(*S*) complexes is only 0.2 kcal/mol. When considering the solvent, the energy difference completely vanishes and the stability of the *s-cis*-MP complexes is reduced with respect to that of the *s-trans*-MP complexes.

As can be seen in Fig. 2 the pro-(*R*) and pro-(*S*) complexes with *s-cis*-MP exhibit a bifurcated hydrogen bond with the N^+–H binding to the two carbonyl O atoms. In both cases the N^+–H···O distances are 2.18 and 2.4 Å. In the pro-(*R*) complex the distance to the keto carbonyl O is shorter, whereas in the pro-(*S*) complex the distance to the ester carbonyl O is shorter. On the other hand, for the complexes with *s-trans*-MP the N^+–H···O distance to the keto O is the shortest in both the pro-(*R*) and the pro-(*S*) complexes, amounting to 1.98 Å in both cases.

To investigate the rigidity of the complexes the potential energy along a coordinate *T* was calculated. *T* is defined as a translation of MP along the C–C bond as defined in Fig. 3, where the potential along *T* is shown for the pro-(*R*) CDH^+···*s-cis*-MP complex and for a trimethyl ammonium ion···*s-cis*-MP complex, for comparison. The coordinate zero point is defined as the minimum energy. The potential curves are quite flat, indicating high flexibility and large-amplitude motions at room temperature. At negative values for *T* the potential energy for the CDH^+···*s-cis*-MP complex strongly increases. This is due to repulsion between the keto O and the quinoline moiety. At $T = -1.25$ Å the distance between the keto O and the nearest quinoline H is only 1.83 Å. This repulsion is missing for the complex with the trimethyl ammonium ion.

In Fig. 4 the potential energy along *T* is compared for the pro-(*R*) and pro-(*S*) CDH^+···*s-cis*-MP complexes. Also given is the distance *r* between the quinuclidine proton and the keto O of MP. As can be seen, the potential energy along *T* is very similar for the two complexes, with a repulsive part at negative *T*. However, the distance *r* along *T* is different for the two complexes. For the two minimum energy structures, *r* is shorter for the pro-(*R*) complex. Also, the pro-(*R*) complex exhibits a smaller *r* on average. For the pro-(*S*) complex shorter *r* values are reached within the repulsive part of the potential along *T* and are thus less probable. Note that the local structure of the Pt surface could also contribute to the potential along *T*. However, the potential energy at strongly negative *T* would still be

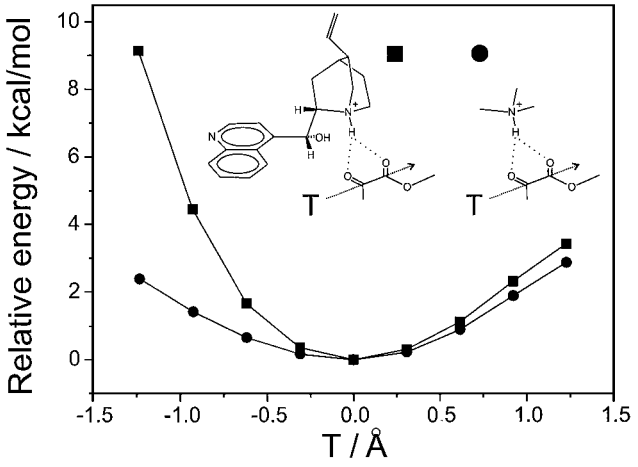

FIG. 3. Potential scan along a coordinate *T*, as defined in the figure for complexes between protonated cinchonidine and trimethyl ammonium ion, respectively, and *s-cis*-methyl pyruvate. The minimum energy structure corresponds to $T = 0$. The calculations were performed at the Hartree–Fock level using a 6-31G(d,p) basis set.

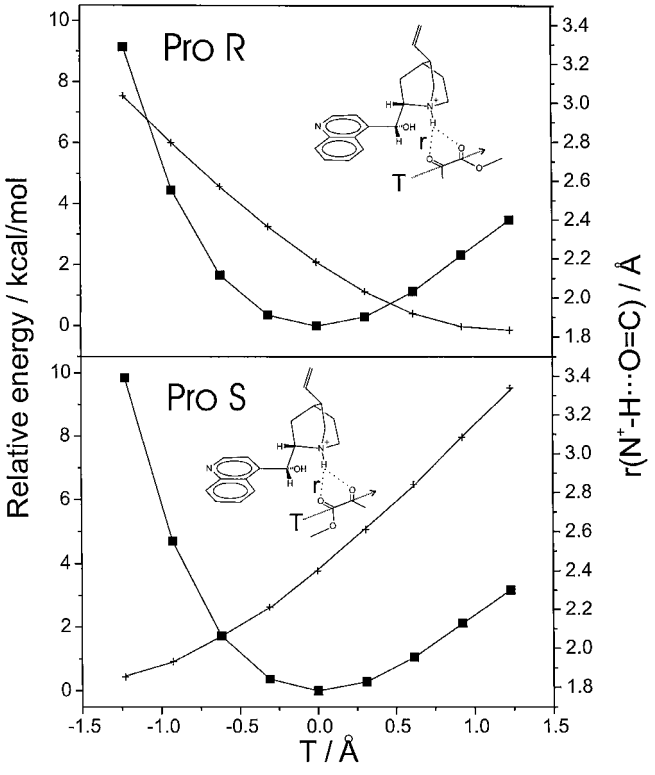

FIG. 4. Potential scan along a coordinate T as defined in the figure for complexes between protonated cinchonidine and *s-cis*-methyl pyruvate, which would yield (*R*)- and (*S*)-methyl lactate upon hydrogenation from the bottom side (pro-(*R*) and pro-(*S*) complexes). Also given is the distance between the proton at the quinuclidine N and the O atom of the methyl pyruvate keto group as a function of T. The minimum energy structure corresponds to $T = 0$. The calculations were performed at the Hartree–Fock level using a 6-31G(d,p) basis set.

dominated by the repulsion between the quinuclidine moiety and the keto O, leading to a shorter r for the pro-(*R*) complex on average.

DISCUSSION

Based on the model proposed for the enantioselective hydrogenation of α-ketoesters, as outlined above, the relative stability calculated for the pro-(*R*) and pro-(*S*) complexes between protonated CD and *s-trans*-MP (Fig. 1) would result in an ee of 92%, in close agreement with the reported 95% achieved in acetic acid (27). On the other hand, the analogous calculations for *s-cis*-MP (Fig. 2) would result in 17% ee only. This seems to indicate that the *s-trans* conformation of MP is more appropriate. However, the complexes with *s-cis*-MP are calculated to be more stable than the corresponding *s-trans* complexes and should therefore be more abundant. Following the argumentation of the proposed model the *s-cis* complexes would then largely determine ee, which is predicted to be small, in contrast with experiment. Hence the calculations seem to challenge the proposed model. Of course, the calculated relative energy might not be accurate enough to draw final conclusions. Also, explicit consideration of the metal surface and the solvent could alter the relative stability of the complexes. Nonetheless, the calculations support the importance of the *s-cis* conformer of MP, which is stabilised relative to *s-trans* upon interaction with CD. The metal surface, which is not explicitly treated in the present calculations, is also expected to affect the relative stability of the MP conformers. The larger dipole moment of *s-cis* leads to an enhanced dipole–induced dipole interaction on the metal surface and therefore a stabilisation of *s-cis* with respect to *s-trans*, as indicated by a vibrational spectroscopic study on Ni(111) (16).

An interesting issue is the question of the origin of the energy difference between the two complexes shown in Fig. 1, or rephrased: What is the origin of enantiodifferentiation within the frame of the proposed model? Complete optimisation of complexes between *s-trans*-ethyl pyruvate and the trimethyl ammonium ion shows that in the most favourable hydrogen-bonded structure the N^+–H points in between the two nearest O atoms of ethyl pyruvate with distances of 1.87 and 2.90 Å, respectively, to the keto and the ester carbonyl O, respectively (19). The pro-(*R*) complex (Fig. 1, top) comes close to this optimal arrangement with corresponding distances of 1.98 and 2.92 Å, respectively. On the other hand, the pro-(*S*) structure for *s-trans*-MP (Fig. 1, bottom) is quite different. The optimal N^+–H···O arrangement is prevented by repulsive interactions between the methyl group of MP and the nearest hydrogen of the quinoline moiety of CDH^+.

In this view of enantiodifferentiation the two crucial structural elements of the modifier are the quinuclidine N and the quinoline moiety. The first exhibits an attractive, and the second a repulsive interaction with MP. This two-point interaction is established only when the two groups have the "right" arrangement with respect to each other, as in conformation *open(3)* of CD. The chirality of the product is then determined by the relative arrangement of these two essential groups in space rather than simply the absolute configuration of CD at C8 or C9 (C9 is connected to the O–H group and C8 is the chiral C adjacent to C9). The absolute configuration at C8 and C9 "only" determines how probable such an arrangement is; i.e., it determines the stability of the various conformations of the modifier. Support for this view comes from the fact that CD, deoxycinchonidine (28), and (*R*)-2-(1-pyrrolidinyl)-1-(1-naphthyl)ethanol (29), a synthetic modifier with a structure similar to that of cinchonidine, show similar catalytic behaviours, although there is no common chiral center for all three modifiers. All afford considerable ee and result in the same absolute configuration of the hydrogenation product. In CD both C8 and C9 are chiral centers. In deoxycinchonidine C9 is nonchiral, whereas in (*R*)-2-(1-pyrrolidinyl)-1-(1-naphthyl)ethanol C8 is nonchiral. The common structural feature of the most stable conformer of

the three modifiers is a similar relative arrangement of the tertiary amine and the double ring anchoring group.

For the complexes between CDH^+ and *s-cis*-MP an analogous two-point interaction is established. Calculations of the complex between *s-cis*-ethyl pyruvate and the trimethyl ammonium ion showed that the optimal arrangement is a bifurcated hydrogen bond with the N^+–H proton interacting with the lone pairs of both carbonyl groups (19). The optimal distances between the proton and the keto and ester carbonyl O, respectively, were calculated as 2.04 and 2.20 Å, respectively. For the pro-(*R*) complex between CDH^+ and *s-cis*-MP (Fig. 2, top) the corresponding distances are calculated as 2.18 and 2.4 Å, respectively; i.e., the keto group is slightly closer to the proton, similar to what has been found for the optimal hydrogen-bonded arrangement. For the pro-(*S*) complex the distances are again 2.18 and 2.4 Å but in this case the keto group is farther away from the quinuclidine proton. This variance between the pro-(*R*) and pro-(*S*) complexes is reflected in the slight energy difference in favor of the pro-(*R*) complex. The origin is again the repulsive interaction between MP and the quinoline moiety, as shown in Fig. 4, which pushes the pro-(*S*) complex farther away from the optimal hydrogen-bonding arrangement than the pro-(*R*) complex. Because the potential is rather flat (Fig. 4), the energy difference is small.

The model calculations using the *s-cis* conformation of MP fail to predict a considerable energy difference between the pro-(*R*) and pro-(*S*) complexes. It is therefore obvious to ask whether enantioselectivity could be dictated by different hydrogenation rates of the pro-(*R*) and pro-(*S*) complexes, i.e., kinetically. At this point, we do not have microscopic information supporting this view. A possibility emerging from the above analysis is that the hydrogen bond formed between the N^+–H and the keto group, which is ultimately hydrogenated, influences the reaction rate. On thermal average the distance between the quinuclidine N and the keto O is considerably shorter for the pro-(*R*) complex (Fig. 4), which could lead to an enhanced rate of the pro-(*R*) with respect to the pro-(*S*) complex for the *s-cis* conformation. Similarly, the *s-trans* could be kinetically favoured over the *s-cis* complexes, since the quinuclidine N–keto O distance is shorter for the former.

Finally, it should be noted that the energetic considerations were made assuming that there is no effect of other coadsorbed species, such as solvent and product, on the MP–CD complexes. Coadsorbates are likely to affect the surface population of these complexes, leading to some uncertainty in the calculated relative stability versus surface coverage correlation.

CONCLUSIONS

Ab initio Hartree–Fock calculations of the intermolecular interaction between cinchonidine and methyl pyruvate relevant for enantioselective hydrogenation over modified platinum were performed. The calculations revealed the importance of the conformation of methyl pyruvate within the complex. For methyl pyruvate adopting the *s-trans* conformation the complex yielding (*R*)-methyl lactate upon hydrogenation is calculated to be more stable than the pro-(*S*) complex by 1.8 kcal/mol, corresponding to 92% enantiomeric excess, in full agreement with experiment. Upon changing the methyl pyruvate conformation to *s-cis*, the energy difference between the pro-(*R*) and pro-(*S*) complex decreases to 0.2 kcal/mol. In addition, the complexes with *s-cis*-methyl pyruvate are considerably more stable than the corresponding *s-trans* complexes. When including solvent effects, by applying a reaction field model, the energy differences between the various complexes generally decrease. The calculations furthermore suggest that the complexes are quite flexible and that the repulsion between methyl pyruvate and the anchoring group plays an important role for enantiodifferentiation. *s-cis*-Methyl pyruvate forms a bifurcated hydrogen bond to the quinuclidine H of protonated cinchonidine involving the O atoms of both carbonyl groups. On average, the hydrogen bond distance to the keto group is notably shorter for the pro-(*R*) complex, which could favour hydrogen addition to this complex in the case of *s-cis*-methyl pyruvate.

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