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First principles study of the conformations of cinchonidine on a Pt(111) surface

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Abstract

The conformations of cinchonidine (CD) adsorbed on a Pt(111) surface were studied using first-principles methods. Eight conformationally different adsorption states due to different degrees of rotation around the τ_1 and τ_2 degrees of freedom were identified and their possible role in the formation of chiral surface sites relevant to enantioselective hydrogenation investigated in light of the currently existing experimental evidence. Comparison of the conformational behavior of CD in solution and on platinum has revealed the effect of the metal surface on the internal mobility of the alkaloid. Although the study corroborates the outstanding role of the adsorbed Open(3) conformer suggested previously, the rich conformational flexibility observed on the platinum surface points to the possibility that other conformers of CD also may be involved in enantiodifferentiation. Closed conformations of CD are found to play an important role in the conformational equilibria on the surface due to their stability and are identified as precursors of the less stable, but presumably more active, open conformers. Although the open and closed conformers are closely related to the correspondent ones found in solution, surface species that are also adsorbed via quinuclidine moiety are characteristic of the metal–modifier interaction and should serve as precursors to catalytically active conformations.
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Keywords: Cinchonidine; Conformational analysis; Adsorption modes; Platinum; Enantioselective hydrogenation; DFT

1. Introduction

The asymmetric hydrogenation of ketones on cinchona alkaloid platinum catalyst is a promising route for the synthesis of enantiopure and enantioenriched alcohols [1–3]. The advantages, both technical and economic, of heterogeneous catalysis are well known and justify the intense interest in this versatile reaction system [4]. Although several proposals have been advanced concerning the reaction mechanism that leads to the observed selectivity of cinchona-modified platinum, this remains a matter of active debate [1,2]. At least one fact is almost universally accepted: that cinchonidine (CD) or another cinchona alkaloid or synthetic analog [5–8] generates chiral sites on the metal surface that are able to discriminate between the *re* and the *si* faces of a prochiral ketone. To open the door to predictive computations, any mechanistic model should be able to describe such sites to identify which prochiral face of a ketone best fits the interaction with the modifier. Given the conformational complexity of CD, we expect that several chiral sites can be generated on its adsorption on the metal. Using a first-principles approach is a particularly demanding task in this case because, even neglecting the effect of the solvent, it involves the computation of a three-component system characterized by the surface, the modifier, and the substrate. In particular, calculating the metal surface makes a first-principles approach a domain of nonstandard computations, because the large number of electrons of the metal can be treated only using highly parallel computer resources, and the necessary inclusion of relativistic effects becomes compelling [9]. A recent review analyzing the use of computer simulations in enantioselective heterogeneous catalysis concluded that predicting selectivities in such three-component systems demands computer resources beyond the scope of most computational chemists [11]. We have nevertheless attempted to address the problem using a stepwise approach, studying the chiral sites generated by the alkaloid on a platinum surface, temporarily reducing the problem to

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a two-component system. CD has a complex conformational behavior in solution that has been extensively studied both experimentally and computationally [12–15]. In most models the behavior in solution of the alkaloid has been extended to the metal surface, thereby neglecting conformational biases due to the interaction with the metal. Adsorption of the alkaloid on platinum has been studied both experimentally [16–20] and computationally [21–23], but a complete description of the adsorption modes and relative energies of the CD conformations on platinum is not yet available. In the present investigation, we analyzed the possibly complete set of conformations that CD can assume on Pt(111) using a large metal cluster approach for simulation of the surface. We report remarkable differences with respect to the conformational behavior in vacuum or in solution that can provide the basis for the observed selectivity of the catalyst.

2. Methods

2.1. Computational methods

The adsorption studies were performed using the platinum cluster shown in Fig. 1 formed by 38 platinum atoms. All of the cluster calculations were done using the Amsterdam Density Functional program package [24]. A frozen core approximation was used for the inner core of all atoms. The orbitals up to 1s were kept frozen for all second row elements, whereas the orbitals up to 4f were kept frozen for platinum. Decreasing the Pt frozen core to 4d (which implies the explicit calculation of 14 additional electrons per platinum atom) has been shown to increase the adsorption energy by only about 5 kJ/mol for the adsorption of benzene [25]. The importance of relativistic effects has been shown for calculations involving platinum [9,10]. The core was modeled using a relativistically corrected core potential created with the DIRAC utility in the ADF program. The DIRAC calculations imply the local density functional in its simple X-α approximation without any gradient corrections, but the fully relativistic Hamiltonian is used, including spin–orbit coupling. Relativistic scalar approximation (mass-velocity and Darwin corrections) was used for the Hamiltonian with the zero-order regular approximation (ZORA) method [26], which includes spin–orbit coupling in zero order. The first-order Pauli formalism [27] was shown to have theoretical deficiencies due to the behavior of the Pauli Hamiltonian at the nucleus, which led to variational collapse [28] for increasing basis set size. It was shown that the scalar relativistic correction could account for up to 70% of the total energy in the adsorption of carbon monoxide on platinum, and that also the calculated adsorption site was influenced by the use of a relativistic correction [9]. The ZORA formalism requires a special basis set that includes much steeper core-like functions implemented in the code. Within this basis set, the double-ζ (DZ) basis functions were used for platinum, and double-ζ plus polarization (DZP) basis functions were used for second-row elements. The local part of the exchange and correlation functional was modeled using a Vosko–Wilk–Nusair [29] parameterization of the electron gas. The nonlocal part of the functional was modeled using the Becke correction [30] for the exchange and the Perdew correction [31] for the correlation. Energies of surface conformers are reported as energy differences between the total electronic energy of the calculated structures (cluster plus adsorbed alkaloid) and the energy of a reference conformation [SC(1)], which was set to zero. Adsorption energies were calculated with respect to the Open(3) conformer of CD, using the following equation:

$$\Delta E_{\text{Ads.}} = E_{\text{Cluster+Adsorbate}} - E_{\text{Cluster}} - E_{\text{Free Molecule}},$$

where $E_{\text{Cluster+Adsorbate}}$ is the energy of the cluster with the molecule adsorbed, E_{Cluster} is the energy of the isolated cluster, and $E_{\text{Free Molecule}}$ is the energy of the free molecule. All calculations were run unrestricted. The bond distance for the platinum was fixed to the experimental value of 2.775 Å for bulk metal [32]. Molden [33] was used as graphical interface.

3. Results

The following description of the conformations of CD on platinum is based on the usual parameters (angles τ_1 and τ_2) used for defining the conformations of CD in vacuum and in solution [12–15]. As shown in Fig. 2, the angle τ_1 describes the rotation of the quinoline around the C(4′)–C(9) bond, whereas τ_2 describes the rotation of the quinuclidine moiety around the C(9)–C(8) bond. Here we define τ_1 and τ_2 by the dihedral angles C(8)–C(9)–C(4′)–C(4a′) and N–C(8)–C(9)–C(4′), respectively. The directions of rotation are also shown in Fig. 2, which defines the positive values for the angles. Throughout the paper, the rotations around the angles τ_1 and τ_2 are assumed to

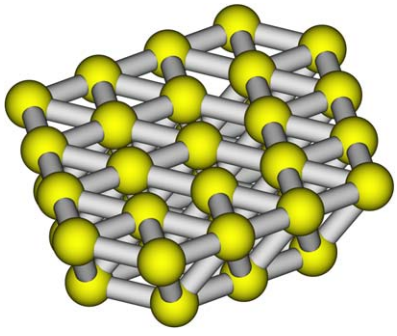

Fig. 1. The platinum 38 cluster used for simulation of a platinum surface.

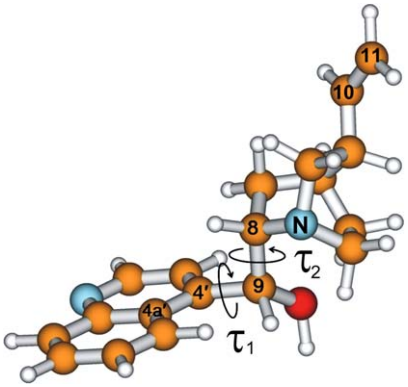

Fig. 2. Definition of the angles τ_1 and τ_2 used for the description of the conformational flexibility of cinchonidine.

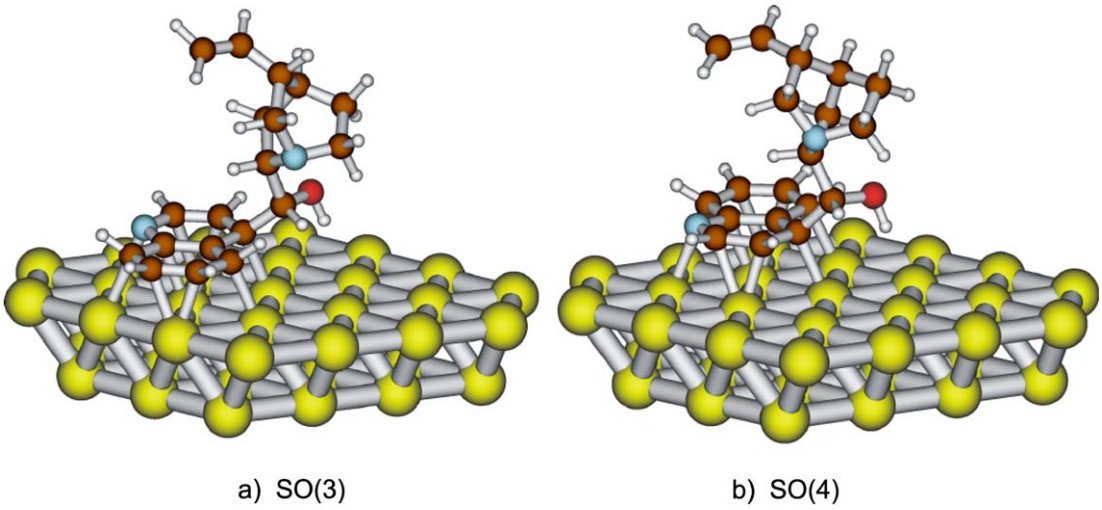

Fig. 3. (a) Surface Open(3) (SO(3)) and (b) Surface Open(4) (SO(4)) conformations of cinchonidine on a platinum surface.

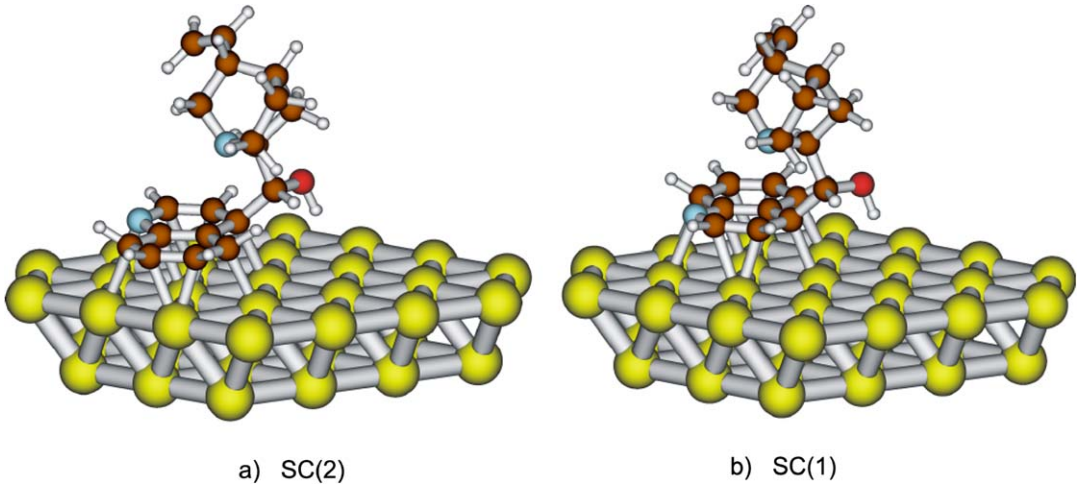

Fig. 4. (a) Surface Closed(2) (SC(2)) and (b) Surface Closed(1) (SC(1)) conformations of cinchonidine on a platinum surface.

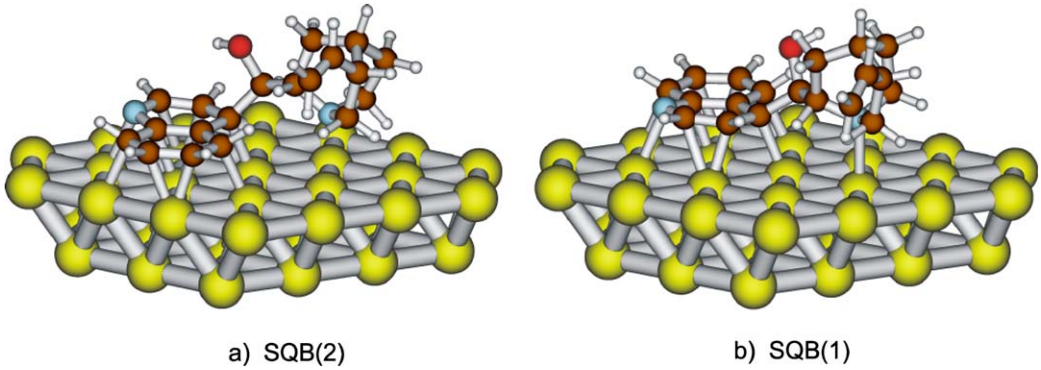

Fig. 5. (a) Surface Quinuclidine Bound(2) (SQB(2)) and (b) Surface Quinuclidine Bound(1) (SQB(1)) conformations of cinchonidine on a platinum surface.

be free at room temperature due to the sp_3 character of the carbon atoms C(8) and C(9), as already shown for CD in solution [13,15]. CD was adsorbed on the cluster via the quinoline ring, on a double-bridge site, analogously to benzene, for which it was shown that bridge sites are the most stable [25,34]. The angles τ_1 and τ_2 were set to values close to those found for the nonadsorbed molecule [12–15], and all degrees of freedom of the alkaloid were successively set free to optimize. All parameters describing the metal cluster were set instead as constant. Figs. 3–6 show the eight minimum energy conformations that were found, and Table 1 reports the relative energies, calculated with respect to the structure Surface Closed(1) [SC(1)], whose energy was taken as zero, and the values taken by the angles τ_1 and τ_2 at equilibrium. Note that the conformation in

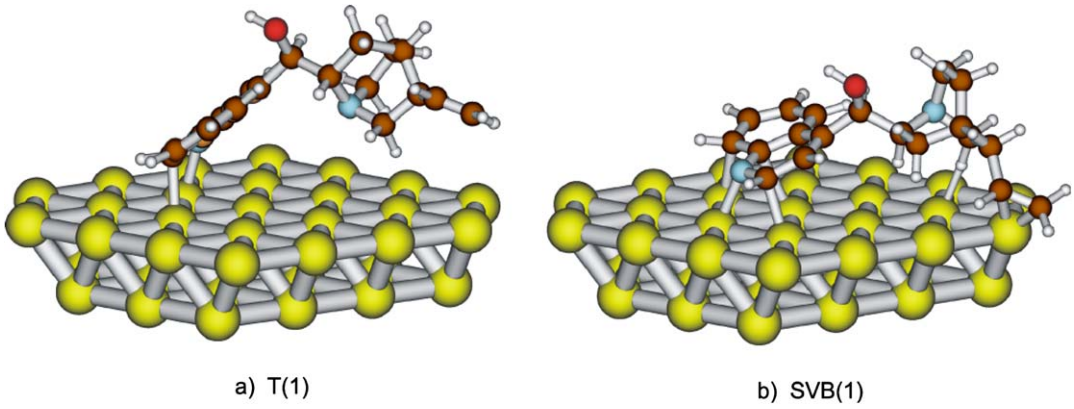

Fig. 6. (a) Tilted(1) (T(1)) and (b) Surface Vinyl Bound(1) (SVB(1)) conformations of cinchonidine on a platinum surface.

Table 1
Relative energies $\Delta E_{\text{el.}}$ calculated with respect to the energy of the structure SC(1) (set to zero), and values of the angles of rotation τ_1 and τ_2 for the surface conformations. Positive energy values stand for less stable structure than the reference. Note that the SVB(1) which is more stable than SC(1) is rapidly hydrogenated under reducing conditions [35]. Adsorption energies $E_{\text{Ads.}}$ were calculated with respect of the Open(3) conformer of CD. Energies in kcal/mol and angles in degrees. The full cartesian coordinates for the eight structures represented in Figs. 3–6 are available from the authors on request

	SO(3)	SO(4)	SC(1)	SC(2)	SQB(1)	SQB(2)	T(1)	SVB(1)
$\Delta E_{\text{el.}}$	1.7	3.9	0.0	0.5	0.2	6.6	24.6	−3.2
τ_1	58	300	302	69	120	310	287	110
τ_2	134	126	56	61	171	287	55	137
$E_{\text{Ads.}}$	31.3	29.6	33.0	32.5	32.8	26.4	12.0	40.2

Fig. 6b, Surface Vinyl Bound(1) [SVB(1)], is slightly more stable than the conformation chosen as the reference SC(1). We discuss this conformation separately from the others due to its instability under hydrogenation conditions. The conformations Surface Open(3) [SO(3)] and Surface Open(4) [SO(4)] depicted in Figs. 3a and 3b, are quite similar to the Open(3) and Open(4) found for the alkaloid in vacuum and in solution. The quinuclidine nitrogen points toward the metal, and the hydroxy group also interacts with the platinum. The major difference from the analogous conformations in solution is the rehybridization of C(4′) discussed in a previous paper [21], which nevertheless does not greatly affect the positions of the minima. The conformations SC(1) and Surface Closed(1) [SC(2)], shown in Figs. 4a and 4b, also closely resemble the closed conformations of the alkaloid in vacuum and in solution [12–15]. In this geometry, the tertiary nitrogen of the quinuclidine moiety points toward the anchoring group, whereas the other features are very similar to the open conformers. The conformations shown in Figs. 5a and 5b have no resemblance to those of the free alkaloid, because on adsorption, the rotation of the angle τ_1 allows the formation of a bond between the quinuclidine nitrogen and a platinum atom of the surface. In this case the contribution of the surface is fundamental, because it adds a constraint to both the surface mobility and the internal flexibility of the alkaloid. Such structures have been termed Surface Quinuclidine Bound(1) [SQB(1)] and Surface Quinuclidine Bound(2) [SQB(2)] [23]. They can be considered as generated by the SO(4) and SO(3) conformations, respectively, after rotation of τ_1. As already mentioned, the quinoline is adsorbed on bridge sites. The reason for this choice was that for benzene it was found that bridge adsorption sites are the most stable, followed by hollow sites [25,34]. To test conformational changes due to the site of adsorption of the quinoline moiety, CD was also adsorbed on hollow sites. The calculations showed that a shift of position brings CD back to the more favorable bridge sites, and eventually geometries identical to those of SQB(1) and SQB(2) were obtained. It had already been shown for benzene [25] that hollow sites act as transition states during surface diffusion and relax to bridge sites. The conformation in Fig. 6a has a tilted instead of a parallel adsorption mode of the quinoline moiety. It is in fact a Closed(1) conformation of the free alkaloid that interacts upside down compared with SC(1). The result is that quinoline is tilted with respect to the metal, and an additional interaction occurs through the quinuclidine skeleton. A T(2) conformation was not found, because when CD was adsorbed as Closed(2) upside down, the result was the structure shown in Fig. 6b. This structure was designated Surface Vinyl Bound(1) [SVB(1)], because it is bound via the vinyl moiety [C(10)–C(11)]. Although the energy value for this structure was the lowest, we discuss it separately, because the binding of the vinyl group is not stable under reducing conditions as those used for the hydrogenation reactions [35]. It is well known that the C–C double bond C(10)–C(11) is rapidly hydrogenated during hydrogenation, and that using dihydro-CD (i.e., CD with a saturated vinyl moiety) instead of CD does not alter the catalytic behavior [35]. Thus, SVB(1) is considered a transient species. When the vinyl moiety is saturated, the quinuclidine moiety will be detached and one of the previously described conformations generated. For this reason, the similar Surface Vinyl Bound(2) was not calculated, because this would add no new information concerning the formation of chiral sites on platinum. It should also be noted that a T(2) adsorption mode was not found, which is to be related to the kind of calculations performed, where a possible interaction with neighboring molecules was not considered. In the real system, the surface crowding of adsorbed species can hinder the occupation of metal sites and favor the presence of T(1) and T(2) surface conformations. The values of the angles τ_1 and τ_2 (Table 1) show that with the exception of the SQB(1) and SQB(2) conformations [and of SVB(1), which is considered apart], the

others are closely related to those of the alkaloid in vacuum and in solution [12–15]. Significant differences are nevertheless observed concerning the relative adsorption energies of the conformers. The closed conformations are more stable on the surface than the others, except for SQB(1). The tilted adsorption mode, on the other hand, is by far the less strongly bound and closely corresponds to the weakly bound species already observed via ATR-IR spectroscopy [16]. The different adsorption modes generate different chiral spaces on the surface sites adjacent to the alkaloid.

4. Discussion

4.1. Fractional coverages of the surface conformers

Computational study of the conformations of CD on platinum corroborates earlier results obtained by IR spectroscopy [16–19]. The species with a quinoline moiety adsorbed parallel to the metal are the most strongly adsorbed, whereas the species in which the quinoline ring is tilted with respect to the surface are less strongly adsorbed. Within the strongly adsorbed modes where only the quinuclidine moiety contributes to adsorption, the closed conformations are the most stable, whereas the two open conformations follow, but can be generated by the closed conformations by rotation of the angle τ_2. The adsorption modes in which the quinuclidine moiety also binds to the metal [SQB(1) and SQB(2)] can be generated from the open conformations through rotation of the angle τ_1. The mobility around the τ_1 and τ_2 angles for the strongly adsorbed conformers allows the definition of two groups of conformers: SC(1), SO(4), and SQB(1) and SC(2), SO(3), and SQB(2) (Scheme 1). The equilibria among SC(1), SO(4), and SQB(1) and among SC(2), SO(3), and SQB(2) depend only on internal rotations of τ_1 and τ_2, whereas equilibria among the species of the two groups must pass through a desorption–adsorption step and therefore must be slower, involving the desorption of a species strongly adsorbed to the metal. In the range where the adsorption of the alkaloid is irreversible, only the conformers belonging to each group convert one into the other by rotation around the τ_1 and τ_2 angles. Analysis of the relative energies within the two groups leads to fractional coverages of the conformers, as summarized in Table 2. In the first group, SC(1) and SQB(1) have almost identical energies, whereas SO(4) is relatively high in energy and should be less abundant compared with the other two. In other words, when adsorbing SC(1), CD should be either in a closed conformation or bound to the surface also via the quinuclidine moiety and present to only a minor extent as SO(4). In the second group, the contribution of the binding of quinuclidine to the surface is minor, because SQB(2) is of rather high energy compared with SC(2) and SO(3). Moreover, SC(2) and SO(3) are closer in energy (ca 1 kcal/mol) than are SC(1) and SO(4) (ca 4 kcal/mol). The relative abundance of the species of the two groups (as a total) is given by the smallest energy difference, that between SC(1) and SC(2). This results in a fractional coverage ratio of $\theta_{\text{group1}}/\theta_{\text{group2}} = 2.3$, meaning that, assuming thermodynamic equilibrium, species of group 1 are about twice as abundant than those of group 2.

$$\begin{array}{ccccc} (0.0) & & (3.9) & & (0.2) \\ \text{SC(1)} & \overset{\tau_2}{\rightleftharpoons} & \text{SO(4)} & \overset{\tau_1}{\rightleftharpoons} & \text{SQB(1)} \end{array}$$

$$\begin{array}{ccccc} (0.5) & & (1.7) & & (6.6) \\ \text{SC(2)} & \overset{\tau_2}{\rightleftharpoons} & \text{SO(3)} & \overset{\tau_1}{\rightleftharpoons} & \text{SQB(2)} \end{array}$$

Scheme 1. Two groups of conformers are in conformational equilibrium via rotation of the angles τ_1 and τ_2.

Table 2
Percentage coverages of conformers of group 1 and 2 that interconvert by rotation of the angles τ_1 and τ_2

Group 1	SC(1)	SO(4)	SQB(1)
	58%	1%	41%
Group 2	SC(2)	SO(3)	SQB(2)
	87%	13%	negligible

4.2. Relevance of the conformers in the mechanism of enantioselective hydrogenation

In the previous section we discussed the relative abundance of surface conformers of CD; however, most likely only some of these conformers are involved in the activated complex that leads to enantioselectivity. To discuss which conformations are most likely relevant for the formation of selective transition states, a view of the mechanistic hypotheses is necessary. Asymmetric hydrogenation occurs on the surface, on chiral sites generated by the adsorbed alkaloid. The likely most widely accepted model interprets the mechanism as being based on an interaction between the adsorbed alkaloid and adsorbed substrate through hydrogen bonding. In the case of α-ketoesters, this occurs between the protonated quinuclidine moiety of CD and the keto-carbonyl moiety of the ketoester [5]. It has recently been shown that protonation of CD by surface hydrogen can in principle also occur in aprotic solvents [23]. According to another model, the quinuclidine moiety acts as nucleophile to the keto-carbonyl, generating a zwitterion that can be catalytically reduced by the metal [36,37]. Another interpretation of the reaction mechanism considers the formation of a complex between the alkaloid and the substrate in the solvent and successive adsorption of this complex on the metal, where hydrogenation eventually occurs [38]. Within this so-called *shielding effect model*, the closed conformers are responsible for catalysis and adsorb upside down (after complexation to the substrate), blocking the substrate between the alkaloid and the metal.

If it is assumed that the ketone must be adsorbed to the metal to undergo hydrogenation (as in the first two models), and considering the crucial role of the quinuclidine nitrogen in selectivity [5], then the position of the tertiary amine (quinuclidine moiety) with respect to the surface is a critical feature. In particular, it should be close to the metal and free to react. This excludes the conformations SQB(1) and SQB(2), in which the tertiary nitrogen is blocked by a metal site. The SO(3) and SO(4) conformers are much better candidates, because the tertiary nitrogen points toward the surface, is unbound, and thus can interact via a hydrogen bond. In the closed conformers the quinuclidine nitrogen points toward the anchoring group and thus has no access the metal. To consider them catalytically

active, one should suppose that the reaction occurs above the anchoring group, which is unlikely. Therefore, they may be considered spectator species. Although the closed conformers may not be catalytically active, due to the equilibria mentioned in the previous paragraph, they can be considered precursors to the active conformations. Among the supposedly active species, SO(3) and SO(4), the former should be more abundant because of the lower relative energy and higher population within the internal conformational equilibrium in its group. The preceding considerations do not distinguish between the model in which the interaction occurs via a hydrogen bond and the model where the tertiary nitrogen acts as a nucleophile. Nevertheless, we briefly mention that the formation of zwitterionic species under the conditions used for this reaction has been disproved in a recent study [39], whereas spectroscopic evidence have been produced to support the hydrogen-bonding interaction [40]. Using the aforementioned criterion of the vicinity of the tertiary nitrogen to the metal, in principle the tilted conformations could be responsible for generating chiral pockets with the quinuclidine nitrogen in the proper position for interacting with an adsorbed keto-carbonyl group. Recent studies on the asymmetric hydrogenation of ketopantolactone show that ether derivatives of CD can cause inversion of the absolute configuration of the hydrogenation product pantolactone [41]. The inversion of the enantioselective properties of the surface seems to be connected to the change in the chiral sites generated by the O-substituted alkaloid on adsorption [42]. Examining the structures of the T(1) surface conformation reveals the striking finding that the hydroxy group at C(9) points in the opposite direction to that of the metal. It is evident that for these two conformations, an O-substituted alkaloid does not generate any change in the space near to the surface, where the quinuclidine nitrogen is located. This is a rather convincing argument against the role of tilted conformations in enantioselective hydrogenation. Using the same argument, the model proposed by Margitfalvi [38] to explain the mechanism of the asymmetric hydrogenation of α-ketoesters on cinchona modified platinum should be ruled out. According to this model, the T(1) and T(2) conformations are responsible for enantioselectivity; however, it is clear that O-substitution affects the chiral sites generated by the open surface conformations. In both SO(3) and SO(4) conformations, the ether substituent can interact with the surface (Fig. 3), and this can be correlated with the change in adsorption potential of the alkaloid shown for several O-substituted CDs [42]. Furthermore, binding of the O-substituent to metal sites in proximity to the quinuclidine nitrogen, where the reaction supposedly occurs, can allow for a different optimal fit of the substrate within the chiral pocket. This can account for the change in enantioselectivity observed when platinum is modified with CD ethers.

4.3. Comparison between the conformational behavior of CD in solution and on a platinum surface

The preceding discussion indicates that CD shows both differences and similarities in conformational behavior when in solution and when adsorbed on platinum. In both cases, the angles τ_1 and τ_2 determine the necessary internal mobility for populating the conformers, but on the surface the equilibrium between some of the conformers (belonging to what we have designated as groups 1 and 2) is mediated by a desorption step that allows conversion between the conformations of the two groups of conformers. In cases of irreversible adsorption, the conformer that is most present in the solution determines which of the two groups is most populated on the surface. It has been shown that the Open(3) conformer is the most populated in apolar solvents [15]; therefore, in such solvents group 2 conformers should be the most abundant on the surface. Only through equilibration should the conformers of group 1 prevail, with a relative abundance of about 2:1. This observation is of great interest, because it demonstrates the importance of studying the relative abundance of conformers in solution to determine the types of chiral sites present on the surface if an irreversible adsorption of the alkaloid is assumed. Another important difference between the conformations established in solution and on adsorption is that in apolar solvents (such as toluene, frequently used as solvent for enantioselective hydrogenation), the Open(3) conformer is the most abundant, whereas the closed conformers are more stable on platinum. Furthermore, as discussed previously, some conformations (and thus the conformational equilibria in which they take part) depend on the binding of the quinuclidine moiety to metal sites. In particular, within conformers belonging to group 1, the SQB(1) conformation is populated to a large extent, leaving only a minor fraction of SO(4) conformer at equilibrium. The role of the surface is also important for another reason. The closed conformations can be adsorbed on the platinum in two different modes: via the quinoline moiety, thus generating the Surface Closed conformations, or upside down, thus generating the tilted conformations [T(1) and T(2)]. But although we have demonstrated that the metal sites generated by the tilted adsorption modes are not compatible with the catalytic activity of the O-substituted CDs, such sites might not be irrelevant in all cases. It seems likely that tilted conformations are only precursors to strongly adsorbed species, but it is not clear whether they also might influence the dynamic behavior of the enantiodifferentiating process. In principle, at high surface coverages of the modifier, they might take part in the formation of a single enantiomer. The fractional coverage of tilted adsorption modes in fact increases with the surface concentration of the alkaloid, as it has been demonstrated by in situ ATR-IR spectroscopy [16], but their participation in catalysis and their role as spectators remain unclear, because the decreased enantioselectivity observed at high modifier concentrations might result either from displacement of active species or from generation of the opposite enantiomer. The conformation SVB(1) (Fig. 6b), as explained in the Results section, is considered apart from the others because of its transient character under reducing conditions. In this case, the surface sets a constraint that is rapidly removed by hydrogenation. Although explaining the experimental observation of the saturation of the vinyl moiety of CD [35], this adsorption mode is not considered to play any role in enantioselective hydrogenation on cinchona-modified platinum. Finally, it should be stated that the rich conformational behavior of adsorbed CD

may allow considerable geometric adaption of the chiral site to the substrate in an enantiodifferentiating 1:1 complex. In this light, it seems likely that, depending on the substrate, different adsorption states of the cinchona alkaloid may contribute to the enantiodifferentiating modifier–substrate complex.

5. Conclusion

Theoretical study of the conformations of CD on a platinum(111) surface has provided a more complete picture of the process of chiral modification of platinum. The relevant surface conformers have been calculated, together with their relative abundance and mechanism of interconversion that operates via the τ_1 and τ_2 angles. Analysis of the models proposed in the literature and comparison of the catalytic behavior of the system indicate that the surface open conformers are most likely involved in the formation of the enantiodifferentiating complex. The role of the surface in the conformational equilibria has also been analyzed to determine the differences between the conformational space of the alkaloid in solution and on platinum. The resulting fundamental picture of the possibilities of formation of chiral spaces due to the adsorption of CD on platinum should serve as a basis for ongoing investigation of the mechanism of this complex reaction system.

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