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Donor–acceptor interactions in the enantioselective hydrogenation of α-ketoesters

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Abstract

The origin of enantiodiscrimination in the hydrogenation of methyl pyruvate (MP) on cinchona alkaloid modified by Pt has been mainly ascribed to interactions between the modifier and the substrate. In the present work, the role of these substrate–modifier interactions on the stabilization of intermediate complexes is discussed on the basis of ab initio MP2/6-31G(d) and MP2/6-31G(d,p) calculations. The amines ammonia, trimethylamine and quinuclidine are employed as model for the cinchona alkaloid. Our results show that MP interacts with the amines via a donor–acceptor complex with a stabilization energy that increases from ammonia, to trimethylamine and to quinuclidine, being in the last case on the order of 4.0 kcal mol^{-1} after correction for BSSE and inclusion of solvent effects. NBO analysis of the interacting orbitals confirms the nitrogen lone pair of the amines as a donor and the antibonding $(C{=}O)^*$ orbital of the α-keto carbonyl as the acceptor. These results give support for experimental observations that interactions between the basic quinuclidine moiety of cinchonidine and the MP molecule may control the stereoselectivity of the catalytic process.
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Keywords: Heterogeneous catalysis; Enantioselective hydrogenation; Reaction mechanism; Ab initio calculations; Methyl pyruvate hydrogenation

1. Introduction

The heterogeneous asymmetric catalysis plays an important and crucial role in many chemical processes and has therefore become a growing and interesting field [1,2]. The enantioselective hydrogenation of α-ketoesters is one of the best-known examples of such processes [3–13]. The methyl pyruvate (MP, Fig. 1a), which can be converted to (*R*)- and (*S*)-methyl lactate with an enantioselectivity of up to 97% on alumina-supported platinum catalyst modified with (dihydro) cinchona alkaloids, has been widely used as a model compound [3–5,10,11]. No enantiodifferentiation is observed in the absence of the alkaloid. In recent years this reaction has been studied in considerable detail; its mechanism, however, is far from being completely resolved [6,11,14–16]. In special, there is a continuous discussion on the role of the chiral modifier in the induction of enantioselectivity and, therefore, on its interaction with the substrate and the metal surface [6,7,17,18]. Several models have been proposed for

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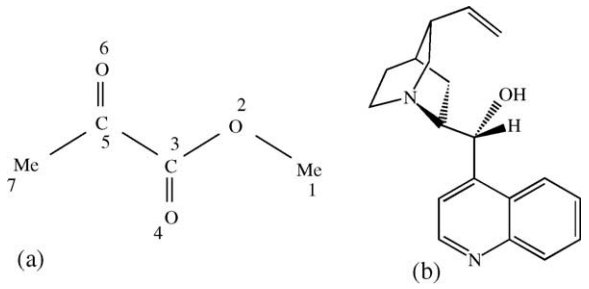

Fig. 1. (a) Methyl pyruvate (MP) and (b) cinchonidine.

the enantio-differentiating diastereomeric intermediate complexes, which, upon hydrogenation, lead to the (*R*)- or the (*S*)-methyl lactate [10], depending on the alkaloid present. Two basic proposals may be clearly identified. First, it has been suggested that the enantiodifferentiation occurs on a modified catalyst site [3,5,9]. On the other hand, it has also been suggested that the modifier and the substrate may form an initial complex which would than be hydrogenated on the metal surface [4,19,20]. Experimental evidence, however, more strongly supports the modified catalyst model [10]. In this model it is assumed that cinchonidine (Fig. 1b), the alkaloid inducing (*R*)-hydrogenation of MP, adsorbs on the platinum surface, forming active chiral sites. MP adsorbs reversibly on these modified sites, in two enantiomeric ways, leading to diastereomeric intermediates, which after hydrogenation afford preferentially the (*R*)-α-hydroxyester product.

In the modified catalyst mechanism, assuming that enantiodifferentiation takes place exclusively on the catalyst surface, significant interactions between modifier, substrate and the active metal surface are required [14,21]. There is clear evidence that cinchonidine adsorbs on the metal surface via the aromatic quinoline π system [16,18,22,23] forming the chiral site. MP adsorbs on these modified chiral sites either by the oxygen lone pairs [24,25] or the π-bonding of the C=O groups [26]. Hydrogen bond and donor–acceptor interactions between the modifier and selected functional groups of the substrate molecule control the adsorption mode of MP and facilitate the addition of hydrogen, thereby increasing the reactivity [8,9]. Formation of a complex between the modifier and the substrate in a 1:1 stoichiometry is a feature in this mechanism. This complex may be stabilized in different ways. Nucleophilic attraction of the electron rich nitrogen atom of the quinuclidine moiety to the carbonyl carbon of the keto group of pyruvate is one possibility. Similar attraction can also involve the C_9 oxygen of cinchonidine and the ester group of MP [21,27]. This would form a six-member ring arrangement that may control the stereochemistry. Interactions involving a half-hydrogenated substrate stabilized by hydrogen bonds have also been proposed [10,28].

In these and in other models [10], the description of the interactions which could provide face shielding (and acceleration effects) is well described, although in many cases qualitatively. Although participation of the metal surface in providing the chiral site where hydrogenation occurs has become evident [10], the interactions between the modifier and the substrate may also play a relevant role in the enantiodifferentiation process [14]. Therefore, a simple model providing the energetic origin of the interactions between substrate and modifier would decisively contribute to the elucidation of the mechanism of this reaction.

In the several models proposed, the main force stabilizing the potential diastereomeric intermediates involves some kind of donor–acceptor interactions between the electron rich nitrogen atom of the quinuclidine moiety of cinchonidine and the carbonyl carbons of the MP molecule. Therefore, calculations with model compounds that mimic the behaviour of this system should give relevant information on the nature of the donor–acceptor interactions supposed to be present in this case. In order to gain additional insight into the interactions between the substrate and the modifier, we present high level ab initio calculations to quantify the interactions between the methyl pyruvate molecule and the model systems ammonia, trimethylamine and quinuclidine. We intend to give quantitative indications of the role played by the cinchonidine-methyl pyruvate interactions to the stabilization of the intermediate complex. The NBO population analysis procedure [29] is employed to quantify the donor–acceptor interactions between methyl pyruvate and the model compounds. Previous calculations for the interaction between ammonia and formaldehyde [30] revealed that orbital superposition and dipole interactions may play some role in the stabilization of the intermediate complex, although at short intermolecular distances (below 3.4 Å) orbital superpositions clearly predominate.

2. Methods

The geometries reported in the present work were fully optimized at the MP2/6-31G(d,p) level [31]. Due to the size of the systems, for quinuclidine the 6-31G(d) basis set was used. The complexes were designed in order to favour the interaction between the basic nitrogen atom of the amines and the carbonyl carbons of MP. Methyl pyruvate was designed in both the s-*cis* and the s-*trans* conformations, which has been shown to be the two main conformers of methyl pyruvate [8,32]. The energy of interaction between the model systems and MP was determined as the difference between the energy of the complex and that of the individual molecules at infinite separation and was corrected for basis set superposition error (BSSE) using the method of counterpoise correction [33]. Population analysis for the interaction between the two subunities was done with the NBO method [29] at the MP2/6-31G(d,p) geometries (or MP2/6-31G(d) in the case of quinuclidine). In the NBO analysis we were specifically interested in the interaction between the nitrogen lone pair of the amines and the antibonding $(C{=}O)^*$ orbital of either the carbonyl or the carboxyl carbon–oxygen double bond. This interaction is given in terms of the second order perturbation interaction energy ($E^{(2)}$) between a donor (the nitrogen lone

Table 1
Stabilization energies (kcal mol^{-1}) for the interaction between MP and ammonia, trimethylamine (MP2/6-31G(d,p)) and quinuclidine (MP2/6-31G(d))

	s-*trans*		s-*cis*	
	Without correction for BSSE[a]	After correction for BSSE	Without correction for BSSE	After correction for BSSE
NH_3	6.70	3.29	7.28 (0.53)[b]	3.99
$N(CH_3)_3$	10.28	4.42	10.70 (0.69)	4.85
Quinuclidine	11.28	4.81	11.63 (0.78)	5.10

[a] Basis set superposition error corrected using the counterpoise method [33].
[b] In parenthesis are given the relative energies between the s-*trans* and the s-*cis* complexes.

pair) and an acceptor (the antibonding $(C{=}O)^*$ orbital) [29]. Solvent effects were simulated using the isodensity surface polarized continuum model (IPCM) [34]. This method analytically calculates the electric field and defines a cavity in the solvent based on the isosurface of the total electron density of the solute. The solvent effects are thus derived from the interaction of the potential isosurface with the dielectric continuum. Water was simulated using a dielectric constant $\varepsilon = 78.39$. For toluene a dielectric constant $\varepsilon = 2.38$ was used [35]. All calculations were done with the Gaussian 98W suite of molecular orbital program [36].

3. Results and discussion

The MP molecule may exist in two main conformations, the s-*cis* and the s-*trans* conformers, both of them having planar skeleton. In the gas phase, the s-*trans* conformer is more stable than the s-*cis* by 1.6 kcal mol^{-1} [32]. Both conformers were employed to study their interactions with the model amines.

Table 1 gives the stabilization energy for the interaction between the s-*trans* and the s-*cis* conformers of MP with ammonia, trimethylamine and quinuclidine. For all the three amines, the interaction with the s-*cis*conformer is stronger than with the s-*trans* conformer by about 0.3–0.7 kcal mol^{-1}. This preferential stabilization is, however, not high enough to make the complex with the s-*cis* conformer more stable. In general, the complex with the s-*trans* conformer is more stable by at least 0.5 kcal mol^{-1}. The stabilization energy steadily increases from ammonia, to trimethylamine and to quinuclidine, as a consequence of the increasing nucleophilicity of the amines [37]. For the stronger base quinuclidine, the interaction energy is on the order of 11.3 kcal mol^{-1} for the s-*trans* complex and 11.6 kcal mol^{-1} for the s-*cis* one. However, after correcting for BSSE these interaction energies are drastically reduced to about 5.0 kcal mol^{-1}. Although this interaction energy seems not to be the main origin of the forces responsible for the enantiodifferentiation process, it is high enough to bind the MP molecule in a specific orientation, therefore blocking up one side of MP, what may result in enantioselective hydrogenations [38,39].

In a previous work, we discussed the interaction between MP and ammonia in some detail [30]. Ammonia interacts with MP in an orientation almost perpendicular to the molecular plane of MP, nearly equidistant from both carbonyl carbons (Fig. 2). As shown before, this interaction is mainly due to orbital superposition between the lone pair of the amine and the antibonding $(C{=}O)^*$ orbital, which is mainly centered on the carbon atoms [30]. This interaction is quantified below on the basis of the NBO population analysis. The trimethylamine and quinuclidine molecules behave in a similar way, although with a small reduction in the N–C distances, as a consequence of the stronger interactions in the larger amines, as seen above.

The selected geometrical parameters given in Table 2, particularly the dihedral angle $N{-}C_3{-}C_5{-}O_6$ near to 90°, indicate that the amines are disposed almost perpendicularly to the molecular plane of MP, similarly to the results found elsewhere for the case of the interaction between ammonia and MP [30]. As indicated in Table 2, the nitrogen atom is almost equidistant from both the carbonyl and the carboxyl carbons, although always nearer to the carbonyl carbon. The N–C distances are about 2.6–3.0 Å. There is a small, although steady, reduction in the N–C distances from ammonia,

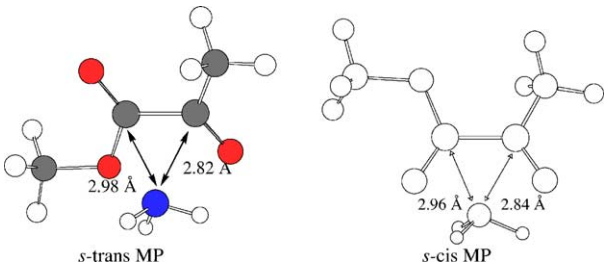

Fig. 2. Complexes between methyl pyruvate (MP) and ammonia.

Table 2
Selected geometrical parameters for the complexes between MP and the amines (distances $N{-}C_3$ and $N{-}C_5$ in Å, dihedral angle $N{-}C_3{-}C_5{-}O_6$ in °)

	s-*trans*			s-*cis*		
	$N{-}C_3$	$N{-}C_5$	$N{-}C_3{-}C_5{-}O_6$	$N{-}C_3$	$N{-}C_5$	$N{-}C_3{-}C_5{-}O_6$
NH_3	2.98	2.82	85.5	2.96	2.84	86.0
$N(CH_3)_3$	2.81	2.64	93.6	2.79	2.66	92.5
Quinuclidine	2.77	2.62	93.7	2.77	2.63	93.0

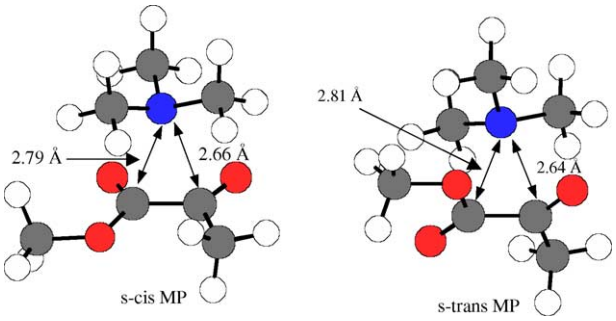

Fig. 3. Complexes between methyl pyruvate (MP) and trimethylamine.

to trimethylamine and to quinuclidine, probably due to the increased nucleophilicity of the larger amines (see also Figs. 3 and 4). There is not any significant difference between the N–C distances for the s-*trans* and the s-*cis* conformers.

In order to gain additional insight into the nature of the interaction between MP and the amines, we undertook a population analysis using the NBO method [29]. The NBO theory generates a basis set of orthogonalized and localized one- and two-center core, lone pair and bond orbitals, plus antibonding and Rydberg orbitals. The advantages of this approach is that it concentrates almost all the molecular energy and molecular charge within structures that mimic the traditional Lewis molecular pictures of strictly localized bonds. These Lewis structures are exclusively built up from core, lone pair and bond orbitals. The very small residual energetic and charge contributions in saturated systems are largely due to delocalized, non-covalent interactions between bonding and antibonding orbitals of the NBO approach. This non-covalent bonding–antibonding interaction gives the quantitative description of hyperconjugation [40]. In terms of the NBO approach this is expressed by means of the second-order perturbation interaction energy ($E^{(2)}$) involving neighboring orbitals. This energy represents the estimate of the off-diagonal NBO Fock matrix elements. The $E^{(2)}$ interaction involving the lone pair on the nitrogen atom as donor and the antibonding $(C{=}O)^*$ orbital as acceptor is of relevance in the present study.

In the context of the present work, we are especially interested in the interaction between the HOMO of the amines, the donor species, and the LUMO of MP, the acceptor species. According to NBO, the HOMO of the amines is formed by the lone pair of the nitrogen atom, which occupies an sp^x hybrid orbital with high p-character ($3.25 \leq x \leq 5.22$), mainly centered on the nitrogen atom. By its turn, the LUMO of MP is a delocalized antibonding orbital involving both carbonyls with higher density on the keto carbonyl bond.

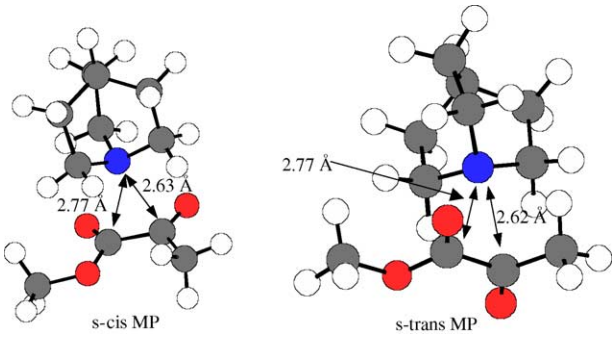

Fig. 4. Complexes between methyl pyruvate (MP) and quinuclidine.

Table 3
Second-order perturbation interaction energy ($E^{(2)}$, kcal mol^{-1}), for the interaction between the donor nitrogen lone pair and the acceptor antibonding $(C{=}O)^*$ orbitals

	s-*trans*		s-*cis*	
	$C_3{=}O_4$	$C_5{=}O_6$	$C_3{=}O_4$	$C_5{=}O_6$
NH_3	1.61	3.33	1.41	3.06
$N(CH_3)_3$	3.23	9.07	4.04	8.12
Quinuclidine	3.73	9.62	4.30	8.91

The $E^{(2)}$ interaction energy given in Table 3 indicates that the donor–acceptor interaction in the case of ammonia is rather small, increasing significantly in the case of trimethylamine and quinuclidine, where the donor–acceptor interaction is on the order of 10 kcal mol^{-1}. The difference in the interaction energy for the two carbonyl carbons is worth to note (Table 3). While the interaction with the keto group involves an energy about 9–10 kcal mol^{-1}, the corresponding interaction with the ester carbonyl is only on the order of 3–4 kcal mol^{-1}. This clearly reflects the higher electrophilicity of the carbonyl carbon, as compared to the carboxyl one. Note that, although the total interaction energy is higher for the s-*cis* conformers, this does not reflect in stronger donor–acceptor interactions, which is essentially of the same magnitude for the both conformers. Therefore, this should be dependent mainly on the distances and orientations of the two species. The intermolecular interaction calculated in the present case is on the same magnitude of intramolecular interactions associated to hyperconjugation that we have calculated elsewhere [40].

Additional information comes from the analysis of the occupancy of the orbitals involved in the interactions. The NBO analysis indicates that the occupancy of the lone pair at the complexed amines (Table 4) is significantly depleted when compared to the corresponding values in the isolated amines. There is also a correspondingly increase in the occupancy of the antibonding $(C{=}O)^*$ orbital of the keto carbonyl bond. The data in Table 4 show that while the occupancy of the

Table 4
Occupancies of relevant orbitals and charge densities in the amines—MP (s-*trans*) complexes as derived from the NBO analysis

	NH_3	$N(CH_3)_3$	Quinuclidine
Occupancy of n_N	1.982 (1.999)[a]	1.882 (1.911)	1.894 (1.927)
Occupancy of $(C_3{=}O_4)^*$	0.152 (0.161)	0.163	0.164
Occupancy of $(C_5{=}O_6)^*$	0.056 (0.047)	0.073	0.073
Charge density in the amines	0.016	0.041	0.042

[a] In parenthesis are given the occupancies in the isolated molecules.

Table 5
Stabilization energies (kcal mol^{-1}) for the interaction between MP and ammonia, trimethylamine (MP2/6-31G(d,p)) and quinuclidine (MP2/6-31G(d)) in toluene and water

	Toluene		Water	
	s-*trans*	s-*cis*	s-*trans*	s-*cis*
NH_3	5.25	5.62	3.51	3.90
$N(CH_3)_3$	9.54	9.86	8.78	9.42
Quinuclidine	10.75	10.72	10.37	11.01

antibonding (C=O)* orbital of the ester carbonyl bond is essentially the same in the complexes and in the isolated MP, the occupancy of the antibonding (C=O)* orbital of the keto carbonyl bond is somewhat bigger in the complexes than in isolated MP, mainly for the larger amines, trimethylamine and quinuclidine. This also reflects in the charge density of the MP moiety in the complexes, which is significantly negative, indicating a charge transfer from the amines to MP.

The results above indicate a clear stabilizing interaction between the amines and MP as result of orbital superposition between the HOMO of the amines and an antibonding (C=O)* orbital of MP. The strength of this interaction slightly increases on going from ammonia, to trimethylamine and to quinuclidine, being on the order of 5.0 kcal mol^{-1} in the last case (after correction from BSSE). The NBO decomposition procedure reveals that the main interactions involve the nitrogen lone pair as the donor orbital and (preferentially) the keto carbonyl antibonding (C=O)* orbital of MP, what results in high second-order perturbative interaction energy, lower occupancy of the nitrogen lone pair orbital upon complex formation and charge transfer from the amines to the MP.

Solvents have only negligible effects on the interaction energies discussed above, although with a clear general trend of destabilization of the intermediate complexes by the solvent in both the apolar (toluene) and the polar (water) solvent (Table 5). For the complex with ammonia, the destabilization is on the order of 1.5 kcal mol^{-1} in toluene, increasing to about 3.0 kcal mol^{-1} in water. For the complexes with trimethylamine and quinuclidine the destabilization is somewhat lower, on the order of 1.0 kcal mol^{-1} in both toluene and water. As expected, the effect of the solvent on the relative stability of these neutral species, as calculated using the continuum dielectric medium [34], is rather small, not enough to change in any significant way the relative stability of the complexes. It should be observed, however, that the reaction field model does not take into account the specific chemical interactions, resulting for example from the presence of a protic solvent. Only those non-specific interactions arising from polarization of the solvent due to the electrostatic potential of the solute and the back polarization of the solute due to the polarization of the solvent are considered in this methodology [34]. In a protic solvent, where the basic nitrogen atom of the amines may be protonated, more specific interactions, such as hydrogen bonding, may operate, since experimental evidence indicates that the reaction mechanism may be dependent on the solvent [16,41–44]. Work on protonated intermediates is in progress in our group.

4. Conclusions

The main goal of the present work was to quantify the energy of interaction between model amines and the MP molecule. We could show that in the intermediate complexes the amines act as a nucleophilic species to the keto carbonyl group of MP, with the nitrogen lone pair as the donor and the antibonding (C=O)* orbital of the keto carbonyl group acting as acceptor, according to the NBO analysis. In the complexes the nitrogen atom of the amines is almost equidistant from both carbonyl carbons, the interaction energy, however, is at least twice higher for the interaction with the keto carbonyl carbon than for the interaction with the carboxyl carbon, reflecting the higher electrophilicity of the first one. The total interaction energy between the amines and the MP molecule increases from ammonia, to methylamine to quinuclidine, as expected. After correction for basis set superposition error this energy is on the order of 4–5 kcal mol^{-1}. Solvent effects, as calculated with the IPCM methodology, tends to reduce this interaction energy, the reduction being larger for the smaller amines in the polar solvent. As a consequence, while for ammonia the interaction energy is reduced to less than 1 kcal mol^{-1}, for quinuclidine it still remains at least on the order of 4 kcal mol^{-1}. This low interaction energy is clearly much lower than the expected adsorption binding energies of either the modifier or the MP molecule on the metallic surface. Therefore, one should not expect previous formation of a complex between these species in the bulk medium before adsorption, mainly considering the low concentration of the modifier under experimental conditions. On the other hand, the interaction energies calculated in the present work may be large enough to stereoselectively bind the MP to the modifier, thereby blocking one face of MP and forming preferentially the intermediate complex which upon hydrogenation affords the (*R*)-α-hydrogenated product.

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