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Enantioselective hydrogenation of ethyl pyruvate catalysed by cinchonine-modified Pt/Al_2O_3: tilted adsorption geometry of cinchonine

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The enantioselective hydrogenation of ethyl pyruvate (EtPy) was studied on Pt-alumina catalyst modified by cinchonine (CN) and for comparison by cinchonidine (CD) in toluene and in AcOH. The effects of the modifiers concentration on the reaction rate and the enantioselectivity were examined. Using the Engelhard 4759 catalyst under mild experimental conditions (room temperature, hydrogen pressure 1 bar) in the case of CN (*S*)-ethyl lactate (EtLt) formed in excess (ee) (in AcOH $ee_{max} \sim 88\%$; in toluene $ee_{max} \sim 72\%$). In the case of CD (*R*)-EtLt formed in excess (in AcOH $ee_{max} \sim 93\%$; in toluene $ee_{max} \sim 84\%$). The results of H–D exchange measurements and results of modifier mixtures suggest that the compounds responsible for chiral induction are different intermediates, which structure depends mostly on the acidic or non-acidic nature of the hydrogenation medium. The proposed structure of intermediate responsible for enantioselection is an 1:1 CN– or CD–EtPy surface complex in which the quinoline skeleton of CD approximately parallel on the Pt surface while the quinoline plane of CN being tilted relative to the Pt surface under identical experimental conditions.

KEY WORDS: chiral hydrogenation; Pt-alumina; cinchonine; ethyl pyruvate; ESI-MS-MS; intermediate; conformation; solvent effect; tilted adsorption.

1. Introduction

The increasing demand for chiral compounds has called for the development of an ever-increasing number of asymmetric syntheses [1–4], which in turn depend on readily available chiral auxiliaries [5]. In most cases, even catalytic amounts of these compounds enable chiral induction. Certain plant-derived cinchona alkaloids, namely cinchonidine (CD), quinine (Q) and their diastereoisomers (or pseudoenantiomers), cinchonine (CN) and quinidine (QD) are utilized as chiral auxiliaries in a wide range of different asymmetric syntheses [6,7]. The diastereomer pairs of CD–CN and Q–QD differ in the configuration of carbon atoms C8 and C9 (figure 1).

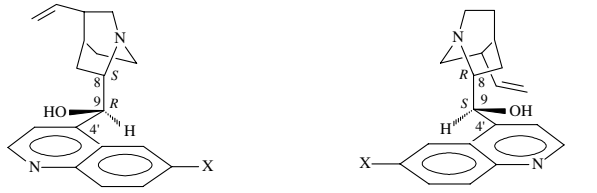
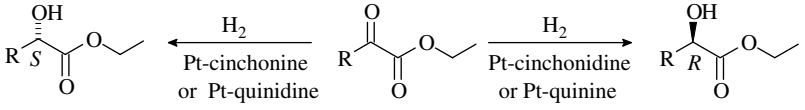


Figure 1. The structure of parent cinchona alkaloids (CD = cinchonidine, CN = cinchonine, Q = quinine, QD = quinidine).

CD has also gained industrial importance in enantioselective heterogeneous catalytical hydrogenations, namely in the hydrogenation of α-ketocarboxylic acid esters on Pt–alumina catalysts modified by cinchona alkaloids (Orito reaction) [8,9], which enables, after optimization, the preparation of α-hydroxycarboxylic acid esters in an outstandingly high enantiomeric excess (ee) [10,11] (optical purity 96–98%) (Scheme 1). This procedure has been applied to the hydrogenation of activated ketones of various types (see in the most recent review, Ref. 12).

In view of the well-known advantages of heterogeneous catalytical enantioselective reactions as well as the high enantioselectivity of the Orito reaction, a better



R = Me (ethylpyruvate = EtPy), R = Ph (ethylbenzoylformate= EtBFt)

Scheme 1. The structure of parent cinchona alkaloids (CD = cinchonidine, CN = cinchonine, Q = quinine, QD = quinidine).

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understanding of the reaction mechanism has been and still is the objective of a great many research projects [12–14], because knowledge of as many details as possible of the highly enantioselective reaction would promote the versatile utilization of the reaction and the development of further new procedures realizing high ee.

The most widely studied model compound is ethyl pyruvate (EtPy). Although numerous details have been elucidated, many questions concerning EtPy hydrogenation still await answers. The subject of the present work is our research aimed at answering one of these questions, namely why, in the reaction shown in Scheme 1, (*S*)-EtLt is formed in lower ee (in the presence of CN) than is (*R*)-EtLt (in the presence of CD), under identical experimental conditions. In other words, why is the ee achievable with CD slightly higher than that obtained with CN?

At the time of the discovery of the reaction, Orito and his coworkers already recognized that, in the case of both methyl pyruvate and ethyl benzoylformate (Scheme 1), not only did the presence of CD and CN result in the formation of compounds with opposite configuration in the course of hydrogenation [9], but ee was also higher with CD than with CN. Later this phenomenon was also observed in other reactions with other catalysts, however, reviews summarizing this field of research have not attempted to give an explanation [13–16]. The latest review closes the discussion of this problem with the following conclusion: "...cinchonine derivatives give the (*S*)-enantiomer, albeit with lower ees" [12]. In their Systematic Structure-Selectivity Study Exner *et al*. [16] paid special attention to the phenomenon in their experiments carried out in the two best solvents (AcOH, toluene), but did not address its interpretation.

2. Experimental

2.1. Materials

Cinchonidine (CD), cinchonine (CN), AcOH and toluene were purchased from Fluka. EtPy (Aldrich) was distilled before use to 99.5% purity.

Based on the data in the literature [12–14], from several catalysts the one most often used is Engelhard 4759 (E4759). E4759 was pretreated before use in a fixed bed reactor by flushing with 30 mL min^{-1} helium at 293–693 K for 30 min and 30 mL min^{-1} hydrogen at 693 K for 100 min. After cooling to room temperature in hydrogen, the catalyst was flushed with helium for 30 min and was stored under air before use.

2.2. Hydrogenation

Hydrogenation was performed in an atmospheric batch glass reactor with volume of 10 mL [17]. The agitator speed was 1200 rpm to avoid the diffusion range. The catalytic system including catalyst and 5 mL solvent was purged three times with hydrogen and after re-reduction (30 min), the calculated amount of modifier (CD or CN) and after 1 min 0.1 mL of EtPy was introduced and stirred in the presence of hydrogen for the required reaction time. Standard conditions are: 25 mg E4759, 5 mL solvent, hydrogen pressure: 1 bar, 297–298 K, 1200 rpm, 0.1 mL EtPy. The quantification of conversion and ee are based on GC data [17]. The measurements were reproduced several times (an effect was accepted as significant only after several convincing reproductions).

2.3. ESI-MS and ESI-MS-MS measurements

There have been described in an earlier publication [17]. ESI-MS examinations were performed by using a HP 1090 ser. II liquid chromatograph-HP 5989B MS Engine mass spectrometer. Prior to ESI-MS, the sample withdrawn from the deuterated mixture was diluted with a 10-fold amount of MeOH containing 2% AcOH.

2.4. H–D exchange measurements of alkaloids

These measurements were carried out in an atmospheric batch reactor under the experimental conditions described for hydrogenation, using ethanol as a solvent but in the absence of reactant. The assembled system was first deaerated and then re-reduced for 2–5 h. After flushing with deuterium the mixture was stirred in deuterium atmosphere for 15–65 h. Both the re-reduced and the deuterated mixtures were subjected to MS analysis (table 1).

2.5. Measurements using mixtures of modifiers

Hydrogenation was carried out like in Section 2.2, with the exception that hydrogenation was continued after the addition of a second modifier to the hydrogenation mixture containing a first modifier. The procedure was the following: hydrogenation was performed at a modifier concentration of 0.05 mmol L^{-1} until 10–20% conversion was achieved; at this point, stirring was stopped and after 1 min a sample was taken. The second modifier was next added and hydrogenation and sampling were continued. Ee was measured as described in Ref. 12.

3. Results and discussions

In these investigations we selected one of the most commonly used catalysts (E4759), EtPy as model compound, CN and CD modifiers and toluene and acetic acid as solvents, because these two solvents have allowed the highest ees [12–14]. In the following discussion we will use the designations DHCD and DHCN instead of CD and CN, respectively, keeping in mind that it is the former ones that actually participate in enantioselection, since the vinyl group is rapidly

Table 1
Degree of H–D exchange of DHCD and DHCN on Pt–alumina catalyst by measurement of data of ESI-MS

Modifier	Hydrogenation		Deuteration		m/z values (relative peak intensity of $M+H]^+$, %)							
	K	Hour	K	Hour	297	298	299	300	301	302	303	304
1. CD	293	2			100	18	13	–	18	3		
2. CD	293	5			100	16	16	4	22	7		
3. CN	293	5			100	16	21	4	29	8		
4. DHCD	293	5	293	15	28	17	14	16	100	72	25	9
5. DHCN	293	5	293	15	58	25	42	25	100	47	15	1
6. DHCD	293	5	333	16	40	15	28	4	64	100	36	7[a]
7. DHCN	293	5	333	65	–	–	–	–	55	100	45	10[b]

Conditions: 50 mg E4759, 50 mg modifier, 50 mL EtOH, 1 bar H_2 and D_2), m/z 305–311: [a]31%, [b]113%.

saturated under the conditions of catalytic hydrogenation [18].

There is ample information available on the relationship between ee and CD concentration under the widest range of conditions [12–14], since this is one of the most important characteristics of any chiral catalyst system. We retained the mild experimental conditions applied in the case of CD (hydrogen pressure of 1 bar, room temperature). Although the results of the experiments with CD under these conditions have been reported in detail [17,19], they were repeated along with those with CN in order to provide a comparison that stands up to the severest criticism, because it is a widely shared experience that it is very difficult to create and maintain identical experimental conditions for these reactions, raising the necessity of multiple repetitions and lengthy investigations.

3.1. The effect of modifier concentration

In spite of the widely varying experimental conditions used, it is by now a well-known fact that the rate of the enantioselective hydrogenation of EtPy as well as ee depend on the concentration of CD [12]. The original data revealing this relationship for the first time were published by Blaser *et al*. [20] who made the measurements at hydrogen pressures of 20–100 bar in toluene and in AcOH. Later this relationship was also confirmed for hydrogenation on Pt modified with CD under mild experimental conditions (hydrogen pressure 1 bar, temperatures below room temperature) [17,19]. To our best knowledge, such data in the case of CN have not been published. Our results summarized in figure 2 lead to the following main conclusions: (i) similarly to CD, both reaction rate and ee are dependent on CN concentration in both solvents; (ii) the functions describing the dependence of the reaction rate on modifier concentration have a maximum, whereas the dependence of ee exhibits a steep rise with a plateau; (iii) under identical experimental conditions, higher ee values are attainable in AcOH than in toluene; (iv) CD allows higher ee values than does CN in both solvents, in agreement with the data in literature; (v) maximal ee values attained at 298 K and a hydrogen pressure of 1 bar are: $ee_{CD,\,AcOH} \sim 93\%$, $ee_{CD,T} \sim 84\%$, $ee_{CN,AcOH} \sim 88\%$, $ee_{CN,T} \sim 72\%$; (vi) maximal ee in AcOH for both modifiers is close to a modifier/$Pt_{surface}$ ratio of 0.01, whereas in toluene this value is 0.1; (vii) the increasing order of ee values attained at a modifier concentration of 0.001 mmol L^{-1} is characteristic of Pt-solvent-modifier systems: CN/T < CD/T < CN/AcOH < CD/AcOH.

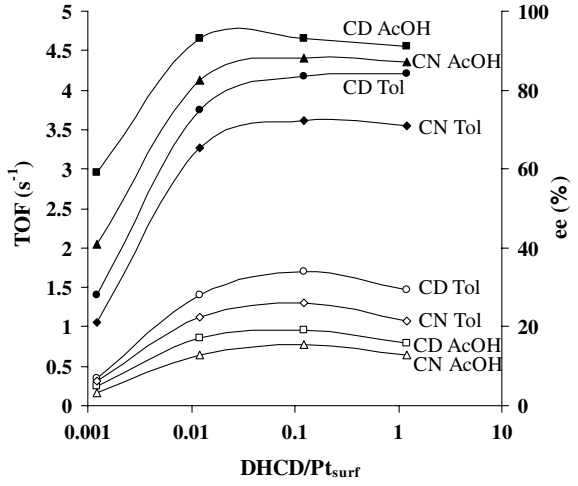

Figure 2. Initial rate and enantioselectivity as functions of modifier/$Pt_{surface}$ (defined in Ref. 17) for hydrogenation of EtPy in toluene and AcOH (standard conditions, TOF = open symbols, ee = closed symbols).

To sum up what has been said, it can be established that a significant characteristic difference was observed between the effects of the two pseudoenantiomers (CD, CN) in the Orito reaction and, in order to interpret this difference, we chose to perform H–D exchange experiments and studies with modifier mixtures.

3.2. H–D exchange of modifiers

Both H–D exchange and deuterium addition have been used for studies on the mechanism of hydrogenation over Pt catalyst modified with CD [21,22]. These

studies give information on the adsorption of DHCD and its geometry on the surface. According to these studies, DHCD adsorption takes place through multicenter π-bonds between the quinoline ring and the Pt surface, since D–H exchanges were observed at the C2′, C3′, C5′, C6′, C7′, C8′ and C9 carbon atoms but no exchange happened on the quinuclidine ring (figure 3). The adsorption of DHCN was not studied. According to electrochemical investigations, however, there is no difference between DHCD and DHCN: both are adsorbed via the quinoline ring [23].

We studied H–D exchange in DHCD and DHCN on catalyst E4759, under the conditions specified by Bond and Wells [22]. The results are presented in table 1, for the interpretation of which the data shown in figure 3 were also utilized [22]. According to Ref. 22, exchange occurred most rapidly at positions 2′ and 8′ and was the slowest at 5′. The most important conclusions are the following: (i) in the course of hydrogenation (entries 1–3) no significant difference was noted between CD and CN; (ii) exchange is faster in CD than in CN (entries 4,5); within an identical time span and under identical conditions, DHCD/DHCN = 28/58 at m/z = 297, i.e. more H atoms were exchanged for D in DHCD than in DHCN; (iii) the main reaction is the exchange of 4H to 4D (this, however, may also include some D_2 addition; the addition/exchange ratio is probably identical for the two molecules); (iv) since, based on Ref. 22, exchange is the fastest at C2′ and C8′, this observation may be used for the establishment of the difference between the adsorptions of DHCN and DHCD, in case if there is a characteristic difference between the H–D exchanges of DHCN and DHCD; (v) according to our data, there is a significant difference between the H–D exchanges of DHCD and DHCN; the exchange ratios for 2 D, 5 D and 7 D (see m/z = 299, 302, 304) are as follows: in the case of 2 D (C2′ and C8′): CD/CN = 14/42; in the case of 5 D (C2′, C8′, C3′, C6′, C9): CD/CN = 72/47; in the case of 7 D (C2′, C8′, C3′, C6′, C5′, C7′, C9): CD/CN = 9/2; (vi) at 333 K, there is significant extent of addition besides exchange.

These experimental results are in agreement with the assumption that the adsorption of DHCD is parallel, whereas the adsorption of DHCN is somewhat different and, probably due to the ethyl group of DHCN close to the surface, it is tilted in some measure. In the case of tilted adsorption (i.e. in the case of DHCN), the H atoms attached to carbon atoms C8′ and C2′ are more readily exchanged, due to their vicinity to the surface. The tilted character of DHCN adsorption is also supported by the lower rate of the C9-H → C9-D exchange in the case of DHCN, since in tilted adsorption the H atom on C9 is far away from the surface.

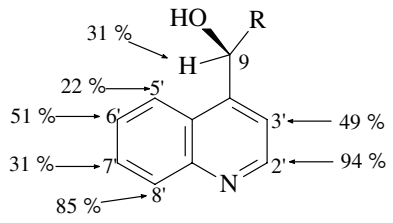

Figure 3. Pattern of exchange (%) of H for D in DHCD determined by ^{1}H NMR [22] (R = ethyl quinuclidine; time = 500 h, temp. = 293 K, EuroPt-1).

The difference in the character of adsorption of the two molecules is also reflected at by their hydrogenation product ratios [24,25]: in the course of hydrogenation in 1 N H_2SO_4, 98% of the hydrogenation takes place on the pyridine skeleton of CD, whereas in the case of CN 63% goes to the benzene ring and 37% to the pyridine ring [25].

3.3. Results of modifier mixtures

According to "nonlinear effect", it was obtained important results in the studies on mixtures of chiral modifiers in the Orito reaction [24,26]. One of the most important conclusions of these studies is the estimation of the relative adsorption strength of the modifiers, information utilizable for the elucidation of the reaction mechanism. We also found it practicable to use this approach for studying the significantly divergent behaviours of CD and CN in the enantioselective hydrogenation of EtPy in toluene and in AcOH.

Some of the results, allowing conclusions to be drawn concerning the adsorption of the parent cinchona alkaloids on Pt–alumina catalyst are presented in figures 4 and 5. It seems highly probable that CD has the highest adsorption strength and that of CN is higher than those of QD in both solvents. The most probable order of adsorption strengths is CD > Q ~ CN > QD, because CD replaces CN on the Pt surface more readily than vice versa, CN is replaced by Q more readily than vice versa and Q affects the adsorption of QD more than does QD that of Q. Adsorption strength of CN and Q depends somewhat on solvent, which may be due to the different solvation of the two alkaloids. This is because Q in AcOH has a higher effect on the adsorption of CN than in toluene.

In agreement with studies employing a variety of instrumental methodologies, it appears that in the concentration range allowing high ee to be attained (0.01–0.1 mmol L^{-1}) the quinoline skeleton of CD is approximately parallel to the Pt surface [24,27–29], whereas the plane of the quinoline skeletons of CN and QD is tilted relative to the Pt surface. Q may take an intermediate position, i.e. its quinoline ring system may be slightly out of parallel.

4. Interpretation of the results and conclusion

The experiments presented in this manuscript had three tightly correlated objectives: (i) by studying the

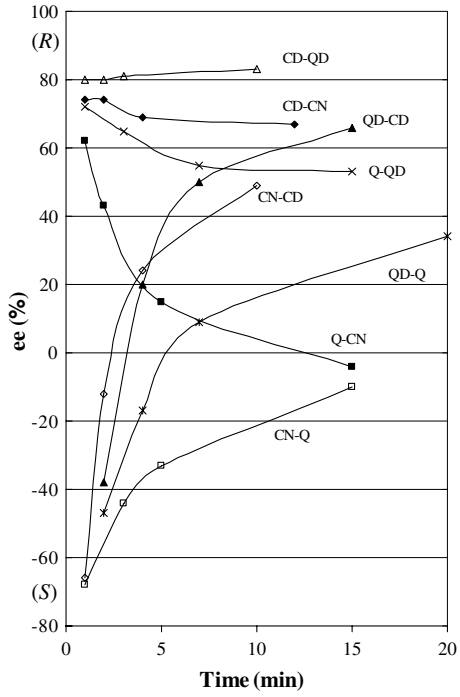

Figure 4. Enantioselective hydrogenation of EtPy in toluene: effect of modifier mixtures (standard conditions, 273 K, [modifiers] = 0.05 mmol L^{-1}, the 2nd modifier was added at 10–20% conversions of EtPy).

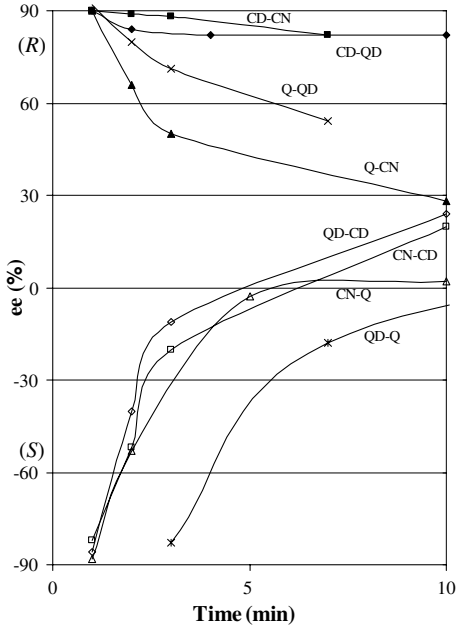

Figure 5. Enantioselective hydrogenation of EtPy in AcOH: effect of modifier mixtures (standard conditions, 273 K, [modifiers] = 0.05 mmol L^{-1}, the 2nd modifier was added at 10–20% conversions of EtPy).

effect of the concentration of CD and CN on the rate of EtPy hydrogenation and on ee under identical experimental conditions, to confirm the earlier observation that out of the two pseudoenantiomers (CD, CN), CN allows lower ee values to be realized than does CD; (ii) if the phenomenon is confirmed, to perform experiments aimed at its interpretation; (iii) to determine the effect of this phenomenon to the reaction mechanism, i.e. whether the adsorption model, widely accepted for the interpretation of the effect of the chiral modifier CD can also be applied to CN.

Regarding these problems, the results of our earlier studies [30] led to the following conclusion. The starting point of the interpretation of the experimental results must be the fact that all factors stereochemically hindering the formation of the 1:1 surface complex of cinchona alkaloid and reactant do not favour high optical yields either. The most important factors to be considered in this respect are: rotation along the C8–C9 axis of cinchona alkaloids, planar adsorption of the quinoline skeleton via multicenter π-bond, possibility of surface adsorption of the ethyl group of the quinuclidine skeleton. In the case of CN, rotation around the C8–C9 axis is hindered due to the proximity to the surface of the ethyl group attached to the quinuclidine skeleton.

The experiments described in this manuscript support the conclusion above with some additional explanation, because – in addition to the already well-known, most important chemical property of the modifiers CD and CN (induction of enantiomeric products of opposite configuration) – we have identified other, so far insufficiently considered characteristic differences in their chemical behaviour. Namely, we observed differences between the two chiral modifiers in the H–D exchange results (table 1), in the results of the experiments using modifier mixtures (figures 4 and 5) and in the effect of modifier concentration on ee (figure 2). It is now quite obvious that the conformation of the chiral molecule is one of the factors determining chiral induction and, based on our present-day knowledge, the conformation of the chiral molecule is responsible for the formation of the intermediate complex making possible high ee.

The first studies on the conformation of cinchona alkaloids [31–33] identified the most probable conformation of CN as the so-called open-3 (in other works, anti-open) conformation, outlined in figure 1, which was later corroborated [34,35]. The studies cited do not report differences between CD and CN that could be evoked for the interpretation of the significant differences described in our manuscript. Conformational changes in these alkaloids are possible by rotation along the C4′–C9 and C8–C9 bonds in liquid phase, but in the case of adsorption on solid surfaces the C4′–C9 rotation is hindered. In the case of CN, however, the formation of the favourable intermediate complex is also affected to some extent by the ethyl group close to the surface by inhibiting movement along the C8–C9 axis.

The results of our H–D exchange studies comparing CD and CN as well as the measurements in modifier mixtures allowed to conclude that the adsorption of CD on platinum is parallel with the theoretical surface, the

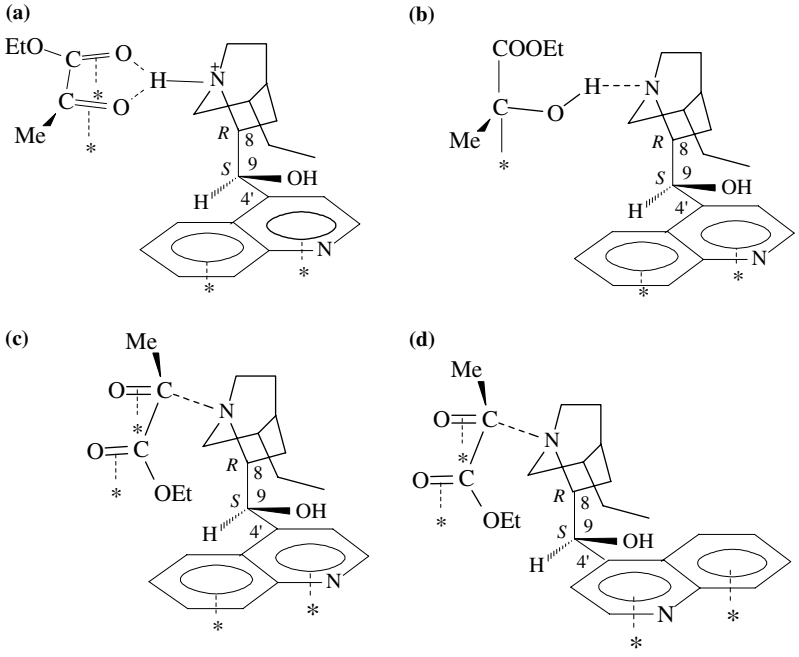

Figure 6. The proposed structures of the adsorbed adduct complexes between DHCN and EtPy: in AcOH = A and in toluene = B, C, D.

molecule being anchored by the multicenter π-bond of the quinoline skeleton, whereas the adsorption of CN is somewhat different, most probably tilted in some measure due to the ethyl group close to the surface, similarly to QD [24,28]. The same is suggested by the different effects of increasing concentrations of the two modifiers on ee: it is well-known that the geometry of CD adsorption changes with increasing surface coverage. At lower CD concentrations, parallel adsorption via the quinoline ring was observed, whereas at higher concentrations the tilted species was also observed [27,29,36].

Based on our experimental data, on the verified structure and conformation [31, 35] of CN (figure 1) as well as on the widely accepted adsorption model [12–14], the proposed structure of the intermediate responsible for the enantioselectivity is outlined in figure 6. In AcOH the intermediate is generated via the interaction of the protonated DHCN, acting as an electrophilic agent, with the nucleophilic oxygen atom of the keto-group of EtPy (figure 6a). In toluene, an intermediate of similar structure was assumed [14], with semihydrogenated EtPy as participant (figure 6b).

According to another suggestion [37] the hydrogenation of EtPy to (*S*)-EtLt on the Pt–alumina–CN–toluene catalyst system can be interpreted on the formation of the surface intermediate C or D (figure 6). In these cases the DHCN binds the EtPy as a nucleophile. The mechanism based on the N → C=O interaction was previous supported [38–40] and later verified by quantum chemical calculations [41] and by hydrogenation of trifluoromethyl ketones [42]. To interpret the enantioselective hydrogenation of EtPy the role of the metal-organic type surface complexes may not be excluded either. The formation of this complex was earlier proposed just for the interpretation of hydrogenation in toluene [19] and was supported by experimental data in the literature.

Acknowledgments

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