Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 255 (2008) 296–303
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Enantioselective hydrogenation of ketopantolactone using Pt–β-ICN chiral catalyst: Correlation between the solution-state concentration of a nucleophilic β-isocinchonine–ketopantolactone complex and enantioselectivity

Tamás A. Martinek [a], Tibor Varga [b], Katalin Balázsik [c], György Szöllősi [c], Ferenc Fülöp [a], Mihály Bartók [b,c,*]

[a] *Institute of Pharmaceutical Chemistry, University of Szeged, Eötvös u 6, H-6720 Szeged, Hungary*
[b] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary*
[c] *Research Group of Stereochemistry of the Hungarian Academy of Sciences, Dóm tér 8, H-6720 Szeged, Hungary*

Received 18 December 2007; revised 20 February 2008; accepted 20 February 2008

Abstract

Experimental evidence (measured by NMR) is given for the correlation between the solution-state concentration of the nucleophilic 1:1 modifier–substrate complex and the ee on enantioselective hydrogenation of ketopantolactone using Pt–β-isocinchonine chiral catalyst. The relationship displays a saturation-type curve, which may indicate an underlying adsorption process involving the catalytically relevant nucleophilic complex.

Keywords: Pt–cinchona catalyst; Enantioselective hydrogenation; Intermediate complex; Ketopantolactone; NMR; Origin of enantioselection, Organocatalysis

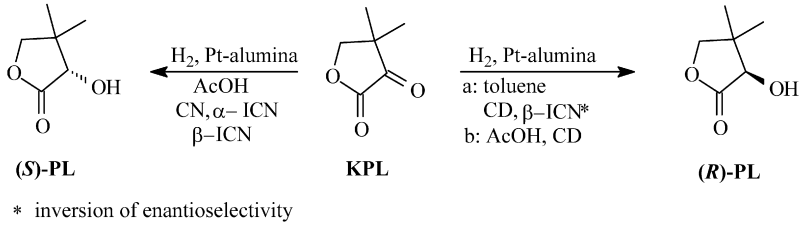
1. Introduction

An important method in various selective catalytic organic reactions (e.g. [1–6]) is the enantioselective hydrogenation of C=O and C=C bonds containing compounds on Ni catalysts modified by tartaric acids [7–11] and Pt and Pd catalysts modified by cinchona alkaloids (Orito reaction [12]). Industrial applications of the Orito reaction in which enantioselectivity exceeds 90% [13–17] have been realized [18]. Scheme 1 shows the Orito reaction in the case of ketopantolactone (KPL) in acetic acid (AcOH) and toluene (T). In addition to parent cinchona alkaloids (CD, CN, Q, QD), β-isocinchonine (β-ICN) also was used as chiral modifier (Fig. 1). The results of the study of cyclic ethers [3,19–21] have led to the application of β-ICN as chiral modifier in the Orito reaction, to the discovery of the unexpected inversion of enantioselection, and to a proposed interpretation of this phenomenon [22–24]. The inversion observed in aprotic solvent has been explained by the formation of a so-called "nucleophilic complex" [24]; the existence of such complex in solution has been demonstrated by NMR measurements and theoretical calculations [25].

The main objectives of recent studies on the enantioselective hydrogenation of activated ketones have been to expand its field of utilization and to interpret chiral induction. The results described in this study represent the continuation of our previous work [25]. To avoid repetition, we simply refer to the Introduction of Ref. [25], in which the significance of this research, its status, and future research objectives were discussed in detail (see also recent reviews [26–30]). Recent studies have aimed to elucidate the relationships between enantiomeric excess (ee) and conversion and between the rates of enantioselective and racemic hydrogenation in this context, which have been violently disputed [31–38]. Addressing the structure of the intermediate responsible for chiral induction has greatly contributed

* Corresponding author.
E-mail address: bartok@chem.u-szeged.hu (M. Bartók).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2008.02.020



Scheme 1.

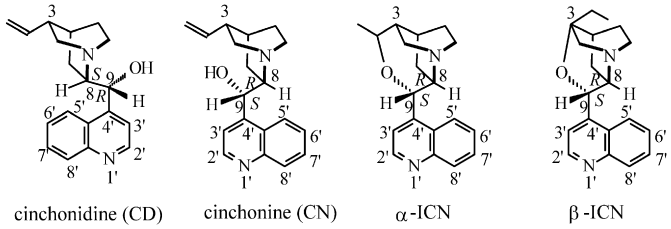
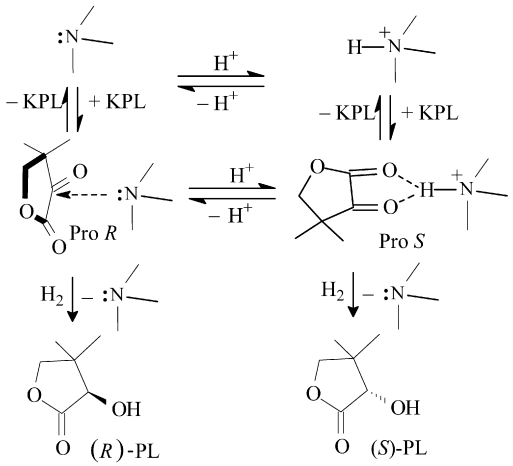


Fig. 1. The structure of chiral modifiers.



Scheme 2.

to clarifying the mechanism of enantioselective hydrogenation and the origin of chiral induction [25,39–41].

It is generally accepted [26–30] that the intermediate complex (IC) responsible for enantioselection is the 1:1 N–H–O complex of the cinchona alkaloid as the chiral modifier and the substrate (Scheme 2). New experimental results also indicate H bonding between the protonated quinuclidine moiety of the modifier in open conformation and the substrate [42,43]. The interpretation of these findings has led to a single-mechanism approach in which the protonated cinchona–substrate complex plays pivotal role. It has been proposed that in aprotic solvents, the quinuclidine nitrogen can be protonated by the H_2 adsorbed on the Pt surface [44]. According to a two-point H-bonding model, the C5′–H of CD also interacts with methyl pyruvate [40,41]. Considering the present understanding of the possible structures of the IC and the fact that enantioselection is highly sensitive not only to the steric structure of modifier and substrate, but also to the reaction conditions, the approach of the competing mechanisms appears to be reasonable, involving both the protonated (electrophilic) and unprotonated (nucleophilic) complexes (Scheme 2).

The composition of the solvent mixture applied in the Orito reaction using β-ICN chiral modifier (Fig. 1) strongly affects enantioselectivity; for example, on increasing the ratio of AcOH in the T:AcOH mixture, the sense of enantioselection is inverted for ethyl pyruvate (EP) [22,23,45,46], for bulky esters of phenylglyoxylic acid [47], and for KPL [24]. Our previous observations indicated that the nucleophilic cinchona–KPL complex can tolerate a certain amount of AcOH, but the concentration of the complex has not been established as a function of the AcOH level [25]. In the present work, we set out to determine the relationship between concentration of the nucleophilic β-ICN–KPL complex as detected by NMR and the enantioselectivity measured in hydrogenation experiments, both of which are controlled by the AcOH content of the solvent.

2. Experimental

2.1. Materials

C_6D_6 (99.5 at% D) purchased from Acros was distilled from $LiAlH_4$ under an argon atmosphere before use, to eliminate traces of water. KPL (Aldrich) was subjected to azeotropic distillation with toluene to remove water. Before use, the crystals were dried over KOH in vacuum at 323 K for 24 h. β-ICN preparation has been described elsewhere [48]. β-ICN was dried over KOH in vacuum at 363 K for 24 h.

Engelhard E4759 5% Pt/Al_2O_3 was pretreated in a fixed-bed reactor by flushing with 30 mL min^{-1} of He at 300–673 K for 30 min and 30 mL min^{-1} of H_2 at 673 K for 100 min. After cooling to room temperature in H_2, the catalyst was flushed with He for 30 min and then stored under air until use [23,24,49]. Ultrasound treatment also improved the catalyst performance [50–52].

2.2. NMR experiments

Between 71 and 200 mM of KPL and 2 and 10 mM of β-ICN were added to C_6D_6 and transferred to a 5-mm NMR tube. After the equilibrium concentrations of the β-ICN–KPL complexes were reached (which took less than 15 min), a prespecified amount of CD_3COOD was added to reach the target composition in the final volume of 500 μL. NMR measurements were performed on a Bruker *Avance* DRX 400 MHz spectrometer with a multinuclear probe with a z-gradient coil at 303.1 K. The processing was carried out using the exponential window function, single-zero filling, and automatic baseline correction.

For NOESY, mixing times of 400 and 600 ms were used, and 64 scans were obtained. The TOCSY measurements were per-

formed through homonuclear Hartman-Hahn transfer with the MLEV17 sequence, with a mixing time of 80 ms; 32 scans were performed. For all 2D spectra, 2 k time domain points and 512 increments were applied. The processing was performed using a cosine-bell window function, single-zero filling, and automatic baseline correction.

2.3. ESI-measurements

The ESI-MSD and ESI-MSD ion trap (AGILENT 1100 LC-MSD TRAP SL ion-trap MS) was operated under a positive ion and auto MS-MS mode, as described previously [53].

2.4. Molecular modeling

Molecular modeling was done on an SGI Altix 3000. Force field calculations (MMFF94) [54] and input generation were conducted using the Chemical Computing Group's Molecular Operating Environment. In *ab initio* quantum chemical calculations, the molecular structure, stereochemistry, and geometry were defined exclusively in terms of their *z*-matrix internal coordinate system. The optimizations and the NMR shielding tensor calculations were done using the Gaussian03 program [55]. The optimizations were performed in a cascade manner: force field—HF/3-21G–B3LYP/6-31G*. The BSSE-corrected energies were calculated by using the keyword "counterpoise" in the route card. All of the other parameters were set as defaults in Gaussian03.

2.5. Hydrogenation

The hydrogenation procedure and analysis were performed as described previously [24], with 12.5 mg of E4759, 2 mL of toluene or a toluene–AcOH mixture, [modifier] = 0.01–1 mM, 295–298 K, 1 bar H_2, 0.5 mmol KPL, 800–900 rpm.

3. Results and discussion

3.1. Previous results on the interaction between tertiary amines and ketones

In terms of the interaction between tertiary amines and ketones, little data are available in the literature. Before our investigations, only intramolecular interactions had been demonstrated by spectroscopic [56–59] and crystallographic methods [60,61]. To the best of our knowledge, Ref. [25] can be considered the first to verify the intramolecular interaction between a tertiary nitrogen and a carbonyl group. Our recent contribution pointed out that the nucleophilic β-ICN–KPL complex formed readily in deuterobenzene without protonation on the quinuclidine nitrogen (Pro *R* in Scheme 2). Ab initio modeling based on the experimental data predicted that the substrate–modifier adducts are stabilized at three points by (i) attraction between the partially positive C=O C atom and the negatively charged quinuclidine *N* atom; (ii) weak C=O...HC H-bonding to the H5' region of the quinoline moiety in various patterns, depending on the specific complex geometry; and (iii) C=O...HC H-bonding to H9 or H8 [25]. This type of interaction may play an important role in organocatalysis. Previous work has led to some suggestions as to the role of a nucleophylic complex in the Orito reaction, which was later supported by theoretical calculations [22,62–65].

Table 1
^{1}H chemical shifts of the cinchona modifier observed in benzene-d_6 for pure β-ICN and β-ICN–KPL mixture

Proton	δ (TMS) (ppm)	
	β-ICN	β-ICN + KPL
H2′	9.04	8.97
H3′	7.80	7.47
H5′	8.01	8.39
H6′	7.26	7.90
H7′	7.43	7.51
H8′	8.50	8.46
H6ax	2.76	2.71
H6eq	2.76	2.91
H5ax	1.28	0.87
H5eq	1.09	0.98
H4	1.54	1.57
H2ax	2.34	2.30
H2eq	3.45	3.72
H7eq	0.89	0.62
H7ax	1.67	1.44
H8	3.41	3.70
H9	6.03	6.05

3.2. NMR measurements

The cinchona-activated keton complex formation was observed earlier in aprotic solvent by using NMR [25]. In that work, two examples were studied, the MeOCN–KPL and β-ICN–KPL model systems. These molecules proved to be fortunate choices for detecting the weakly bound complexes by NMR, because the substrate is conformationally very rigid, and thus the loss of the torsional entropy on complex formation is limited. At room temperature, this corresponds to a free energy gain of ca. 1–2 kcal/mol, which can lead to a greater than one magnitude increase in the equilibrium constant. Consequently, the free energy change affords equilibrium concentrations for the complexes, which can be detected on NMR. On the other hand, it is possible that flexible substrates may not afford NMR-detectable concentrations for the modifier–substrate complex in the solution phase, due to the conformational entropy loss, but we cannot rule out the existence of such complexes for the non-rigid partners using NMR. Besides the free-energy balance, the chosen models have further advantages; their compositions prevent undesired chemical reactions during complex formation.

When the rigid components (KPL and β-ICN) were mixed in similar concentrations as used in the Orito reaction, NMR revealed the most important spectral changes according to our earlier results [25]. First, a drift in the chemical shifts of the cinchonas was observed, with the largest downfield differences at around H5′, H6′, H2eq, and H8 (representative data are given in Table 1). Second, along with signals belonging to the pure KPL, new sets of resonances appeared for KPL that attained equilibrium intensity in a finite time frame (see Fig. S1). Among these,

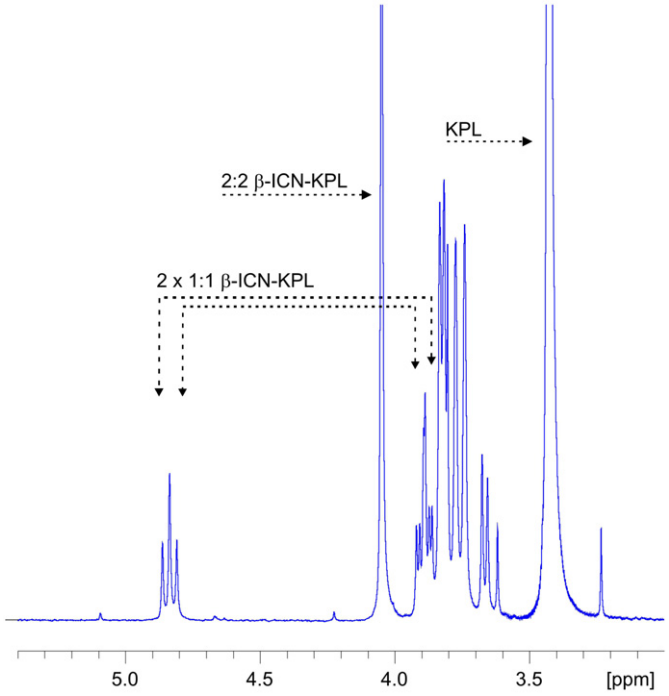


Fig. 2. ^{1}H NMR methylene signals of KPL origin in KPL (200 mM)–β-ICN (2 mM) mixture (in benzene-d_6). Assignments of the resonances are indicated in the spectrum; the upfield methylene peaks (3.88 and 3.86 ppm) are overlapped by the cinchona signals (from the quinuclidine moiety). In the ^{1}H NMR spectrum of the pure KPL in benzene-d_6, only the CH_2 peak at 3.6 ppm was detected.

the methylene resonances exhibited the most interesting pattern (Fig. 2). Two methylenes appeared with scalarly coupled doublets with chemical shift differences of ca. 1 ppm, indicating the newly formed asymmetric environment in the complex. Interestingly, a new methylene singlet downfield from the pure KPL methylene singlet appeared as well, pointing to the magnetically symmetric environment of the species. These peaks were assigned to the complexed forms of KPL. Representative results for the β-ICN–KPL system are shown in Figs. 2 and 3. Third, the diffusion constant measured on the new peaks revealed hydrodynamic radii larger than even those of the pure cinchonas; the same increased hydrodynamic radii were measured for the cinchonas (see Ref. [25] for the diffusion constants). The co-diffusion of KPL with the cinchonas in the complexes was demonstrated. Fourth, even with significant changes in the spectral parameters, no proton resonance of acidic or quaternary nitrogen origin was observed in the spectra (for the carefully dried samples, even the water signal was missing at around 0.4 ppm), supporting the proposal that protonation of the cinchona plays no role in complex formation.

We carried out an additional experiment to investigate the β-ICN origin of the new signals. The β-ICN–KPL mixture affords the integration of the nonovelapping peaks belonging to the complexes. With constant KPL concentration (71 mM), the β-ICN concentrations were set to 2.0, 4.9, and 9.8 mM, and the concentrations of complexes were calculated from the integrated intensities. Our initial hypothesis was that the singlet at around 4.0 ppm belongs to the 2:1 β-ICN:KPL species [25].

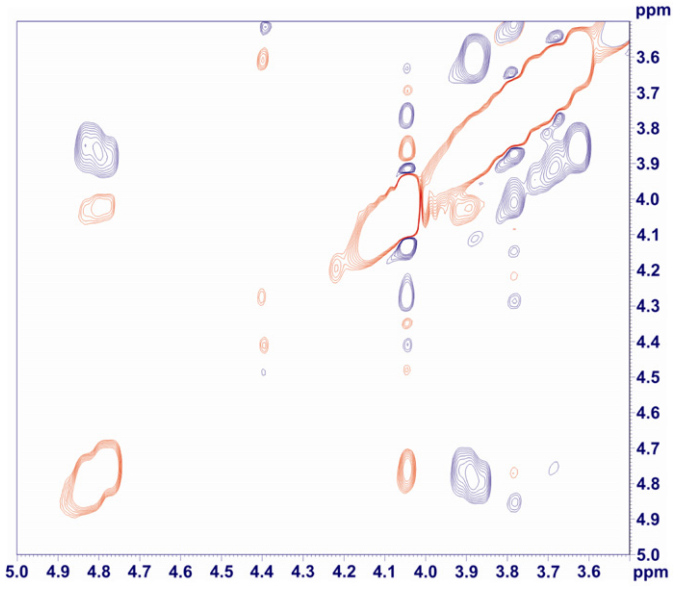


Fig. 3. NOESY cross-peaks (blue) between the magnetically not equivalent CH_2 protons assigned to the two 1:1 β-ICN–KPL complexes (4.78–3.88 ppm and 4.80–3.86 ppm), and the EXSY cross-peaks (red) between former resonances and the singlet (4.05 ppm) assigned to the quasi-symmetric 2:2 β-ICN–KPL complex (see Ref. [25] for the structure models).

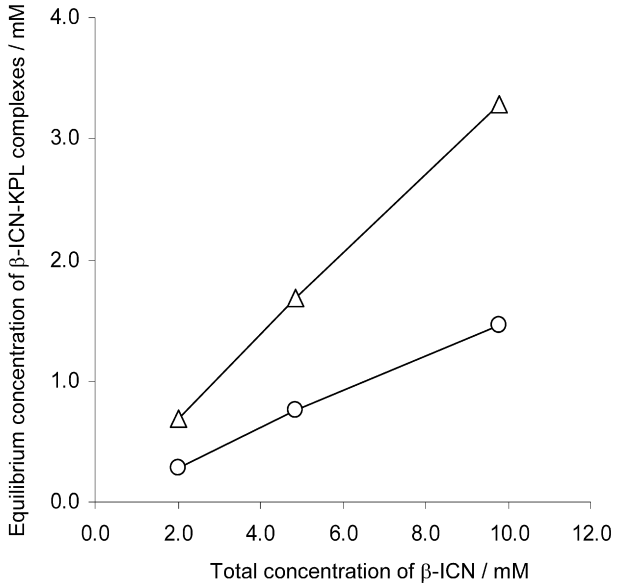


Fig. 4. Equilibrium concentrations of the 1:1 (sum of ProR and ProS, circles) and 2:2 (triangles) β-ICN–KPL complexes determined by NMR vs the total concentration of β-ICN at the constant KPL concentration of 71 mM.

This calculation indicated that the β-ICN:KPL complexes altogether require a 1.5-fold greater total β-ICN concentration than that measured for the sample preparation.

To maintain the material balance, we need to refine our model of the dimeric β-ICN:KPL complex. Assuming that 2:2 β-ICN:KPL species give rise to the singlet at around 4.00 ppm, the mass balance is not violated, and the proposed dimer is still in accordance with the hydrodynamic radii measured [25]. The resulting concentrations are given in Fig. 4. The possible spatial arrangements of such 2:2 β-ICN:KPL adducts were modeled

Table 2
Characteristic distances computed for the stabilizing contacts at the B3LYP/6-31G* level in the most stable 2:2 complex

Contact	Å
N...C=O (ester)	2.92
N...C=O (ketone)	3.10
H5′...O=C (ester)	2.76
H5′...O=C (ketone)	2.50
H6′ (cinchona #2)...O=C (ketone)	2.55

at the DFT level (B3LYP/6-31G(d)). Two possible structures were obtained starting from the ProS and ProR 1:1 complexes (Fig. S2). *Ab initio* calculations revealed that the symmetric 2:2 complexes can be stable, which is facilitated by the formation of two extra C=O...HC hydrogen bonds between the proton H6′ of the cinchonas and the keto group of the distal KPL (Table 2), which are nearly identical to the experimentally (IR, STM) determined values [66–69]. The corresponding N...C=O distance for the 1:1 complexes is ca. 3.1 Å [25,64,65]. Of note, the N...C=O distances are well below the sum of the van der Waals radii (3.72 Å) for C and N, indicating significant $n \rightarrow \pi^*$ orbital overlap, resulting in an extra stabilization in range of 1.4–2.5 kcal/mol for each N...C=O contact. The proposed 2:2 model with the involvement of H6′ in H-bonding provides a much better explanation of the significant downfield shift of H6′ ($\Delta\delta = 0.64$ ppm, Table 1) on complex formation compared with the 2:1 hypothesis.

The concentrations of the complexes increased monotonously with the amount of β-ICN (Fig. 4), as expected due to the great excess of KPL. These findings corroborate our earlier conclusions regarding the origin of the new NMR signals.

We studied the effect of acidification on the stability of the complex on the β-ICN–KPL mixture, because the CH_2 signals of the 1:1 β-ICN–KPL are not overlapped by the resonances of the olefinic protons of the modifier (as is the case for MeOCN) [25]. Within 12 min (the first possible NMR measurement after tuning, locking, and shimming), the ^{1}H NMR spectrum of the CD_3COOD-free sample exhibited the previously assigned nonoverlapping signals (see above) characteristic of the 1:1 cinchona–KPL complexes (ProS and ProR): doublets at 4.78 and 4.80 ppm (Fig. 5, bottom panel). As expected, the singlet of the 2:2 complexes appeared at 4.05 ppm (shown in Fig. 2). Concomitantly, significant changes in the chemical shifts in the aromatic region were observed, indicating the substantial structural differences from the pure, noncomplexed cinchona (Fig. 5, top panel).

The 0.1 v/v% of CD_3COOD, which has an 8.6-fold molar excess relative to the cinchona modifier, did not decrease the concentration of the 1:1 β-ICN–KPL complexes. At 1.0 v/v% of CD_3COOD (86-fold molar excess relative to β-ICN and ca. 1:1 relative to the KPL), the nucleophilic complexes survived, but their NMR signals indicated only half concentrations compared with the initial value. This was accompanied by a noticeable drift in the chemical shifts in the aromatic region. Most importantly, the largest change was an upfield shift for H6′ (triplet at around 7.95 ppm), the proton of which certainly is involved only in the β-ICN–KPL interface, and its upfield shift indicated

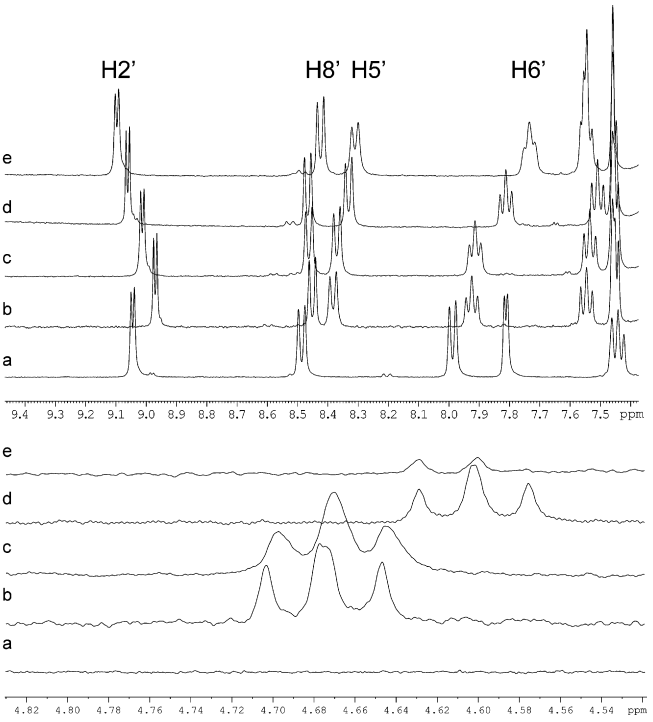


Fig. 5. ^{1}H NMR signals in pure β-ICN (a) and in β-ICN–KPL mixture indicating the presence of the 1:1 β-ICN–KPL complexes, and their sensitivity to the CD_3COOD concentration of 0 (b), 0.1 (c), 1.0 (d) and 10 (e) v/v%. Annotations of the aromatic signals of β-ICN (top panel) refer to spectra (b–e). Indicator methylene protons of 1:1 β-ICN–KPL complexes displayed on the bottom panel.

decomposition of the cinchona–substrate complex. Meanwhile, the rest of the cinchona NMR signals gradually attained such chemical shifts, in agreement with protonation on the quinuclidine nitrogen. The amount of 10 v/v% CD_3COOD still left some residual intensity for the indicator protons; nonetheless, it can be concluded that CD_3COOD can successfully compete with KPL if the KPL: CD_3COOD molar ratio reaches a value of 1:10.

These findings confirm the presence of the nucleophilic complexes in solution, which are in competition with the AcOH. The results provide supporting evidence of the stability of the unprotonated cinchona–KPL complex against acidic attack of the AcOH, which may indicate that the nucleophilic complex also can be stable against the mildly acidic hydrogen adsorbed on the Pt surface.

3.3. Correlation between hydrogenation and NMR results

To reveal any possible correlation between the concentration of the nucleophilic complexes and the enantioselectivity in the Orito reaction, we carried out hydrogenation experiments using the same toluene: AcOH ratios and similar modifier and KPL concentrations as were used in the NMR experiments. The enantioselectivity displayed a significant decrease at 10 v/v% AcOH, whereas a magnitude drop occurred in the solution-phase concentration of the nucleophilic complexes (Fig. 6). These findings strongly suggest that the destruction of nucleophilic complexes leads to strongly altered enantioselectivity.

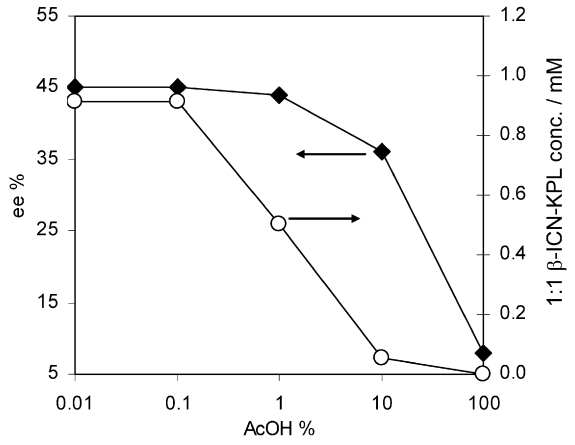


Fig. 6. Comparison of the total concentration of the 1:1 β-ICN–KPL complexes measured by NMR (circles) with the enantioselectivities (diamonds) obtained at identical AcOH (CD_3COOD for the NMR) concentrations (logarithmic scale).

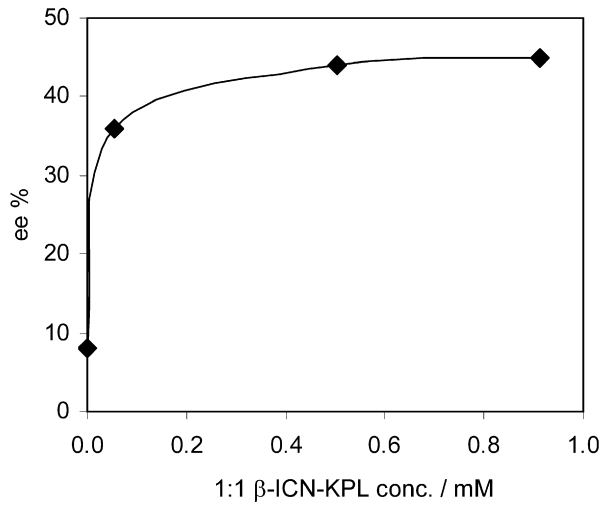


Fig. 7. Saturation-type relationship between the concentration of 1:1 nucleophilic complex and the ee.

Of course, the *ex situ* nature of the parallel NMR and hydrogenation measurements necessitates caution when drawing conclusions regarding the observed quantitative relationship. Nevertheless, the correlation between the enantioselectivity and the solution-phase concentration of the β-ICN–KPL complexes display a saturation-type curve (Fig. 7), possibly indicating an underlying adsorption phenomenon governing the surface coverage by the catalytically relevant species (Langmuir isotherm).

4. Interpretation of the results and conclusions

Because studying the structure of the IC involves reaction mechanism-related research, the following phenomena cannot be disregarded: (i) the presence of a certain structure is verified by NMR and computations; (ii) the concentration of the said structure decreases with increasing AcOH concentration; and (iii) there is a correlation between the concentration of this complex and enantioselectivity (ee%). Based on these experimental results, enantioselection also can be interpreted by nucleophilic interaction, which naturally does not mean that this is

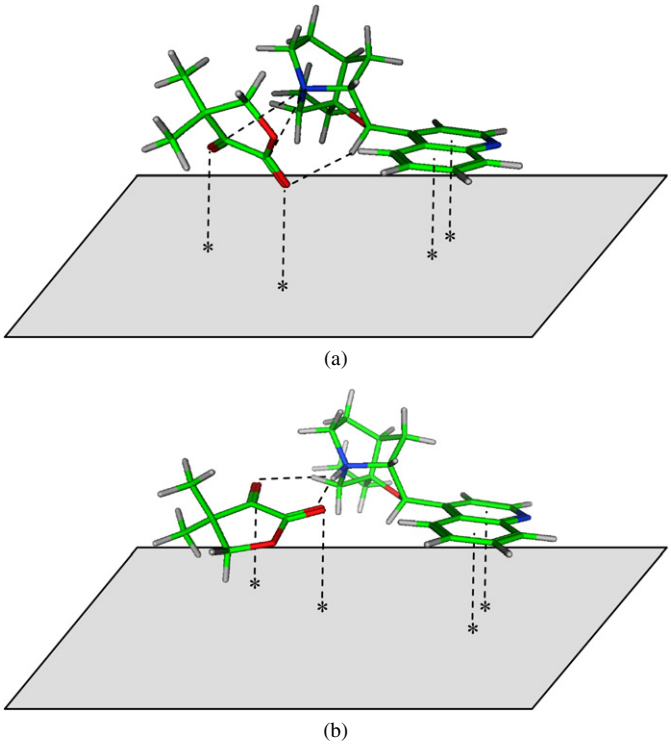


Fig. 8. The proposed structures of the adsorbed KPL–β-ICN 1:1 complexes in nucleophilic- (a) and electrophilic-type (b) interactions.

undoubtedly how enantioselection occurs. It is understood that the results obtained in the KPL + β-ICN system hold only for this pair of compounds and cannot be generalized for the entire Orito reaction. Based on these findings, we disagree with some of the conclusions specified in section 5.3 of Ref. [30]. In the absence of the appropriate instrumental techniques, at present it cannot be determined for certain which of the various ICs, assumed to have been verified in various ways or not even suggested yet, may be responsible for enantioselection in any given case (see, e.g., [26–30]).

As to the absence of Pt and H_2 in our experiments, unfortunately there is no experimental NMR method or any other method available at present that can verify the participation of bonds of noncovalent character in the interaction of two different adsorbed molecules under the conditions of the Orito reactions. Nonetheless, we still claim that the supramolecular complexes with the corresponding $n \rightarrow \pi^*$ orbital overlap exist in solution, and believe that their presence over the Pt surface cannot be ruled out due to their stability, especially against molar excess of acetic acid.

The modeled structures of the nucleophilic (a) and the protonated (b) complexes are presented in Fig. 8. In agreement with the two-point H-bonded model proposed by McBreen et al. [41] based on measurements under ultra-high vacuum, our NMR investigations [25] also support the multipoint interaction—including the Pt surface—for the structure of the IC. In our opinion, the adduct (a) which has been proven to exist in solution, also may adsorb on the Pt surface and may be transformed to structures similar to those formed on the surface by the interaction of KPL and β-ICN.

We never questioned the role of the protonated amine modifier on the Pt surface in enantioselection. We did not doubt the role of the protonated cinchona despite the fact that the spectroscopy data published previously [44,70,71], obtained under the conditions of the Orito reaction in toluene, are not totally convincing in terms of protonation of the N atom of quinuclidine. The authors of those previous reports also seemed to have had the same thought; as one report states, "although this conclusion is tempting, further studies are needed to confirm its validity" [44]. We refer to earlier results obtained in the Pt + H_2 system, namely that at low hydrogen coverage, hydrogen adsorbed on the platinum surface, particularly in the adsorbed complex, is present as a negatively charged species [72–75]. This statement holds in general, and in the presence of CO in particular (cf. hydrogenation of α-ketoesters). On the other hand, more recent spectroscopic investigations under ultra-high vacuum have demonstrated the protonation of pyridine and its derivatives in the Pt + H_2 system [76].

Finally, at the present time, which of the complexes is indeed responsible for chiral induction under the experimental conditions of the Orito reaction cannot be confirmed. Naturally, we cannot exclude the possibility that none of the ICs suggested up to now is responsible for the enantiodifferentiation, with an as-yet unknown effect/phenomenon instead accountable for the chiral induction.

In conclusion, our latest observations on the correlation between the solution-state concentration of a nucleophilic β-ICN–KPL complex and its enantioselectivity provide new evidence on the possible role of the nucleophilic modifier–substrate complex in the enantioselective hydrogenation of KPL on a Pt-alumina–β-ICN catalyst carried out in nonpolar solvent.

Acknowledgments

Financial support was provided by the Hungarian National Science Foundation (OTKA Grants T 048764, D 048512 and K 72065). G.S. thanks the Hungarian Academy of Sciences for the award of a János Bolyai scholarship. The computational resources of HPC.U-Szeged (ALAP4-00092/2005) is ackowledged.

Supporting information

Supporting information for this article may be found on ScienceDirect, in the online version.

Please visit DOI: 10.1016/j.jcat.2008.02.020.

References

[1] G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley, New York, 1997.
[2] R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley, Weinheim, 2001.
[3] M. Bartók, F. Notheisz, Á.G. Zsigmond, J. Catal. 63 (1980) 364.
[4] Á. Molnár, K. Felföldi, M. Bartók, Tetrahedron 37 (1981) 2149.
[5] Á. Molnár, G.V. Smith, M. Bartók, J. Catal. 101 (1986) 67.
[6] Á. Molnár, T. Katona, M. Bartók, K. Varga, J. Mol. Catal. 64 (1991) 41.
[7] Y. Izumi, Angew. Chem. Int. Ed. 10 (1971) 871.
[8] Y. Izumi, Adv. Catal. 32 (1983) 215.
[9] M. Bartók, Gy. Wittmann, Gy. Göndös, G.V. Smith, J. Org. Chem. 52 (1987) 1139.
[10] Gy. Wittmann, G.B. Bartók, M. Bartók, G.V. Smith, J. Mol. Catal. 60 (1990) 1.
[11] T. Osawa, T. Harada, O. Takayasu, Curr. Org. Chem. 10 (2006) 1513.
[12] Y. Orito, S. Imai, S. Niwa, N.G. Hung, J. Synth. Org. Chem. 37 (1979) 173;
Y. Orito, S. Imai, S. Niwa, N.G. Hung, J. Chem. Soc. Jpn. (1979) 1118.
[13] M. Studer, S. Burkhardt, H.-U. Blaser, Chem. Commun. (1999) 1727.
[14] B. Török, K. Felföldi, K. Balázsik, M. Bartók, Chem. Commun. (1999) 1725.
[15] K. Balázsik, K. Szöri, K. Felföldi, B. Török, M. Bartók, Chem. Commun. (2000) 555.
[16] M. von Arx, T. Bürgi, T. Mallat, A. Baiker, Chem. Eur. J. 8 (2002) 1430.
[17] M. Sutyinszki, K. Szöri, K. Felföldi, M. Bartók, Catal. Commun. 3 (2002) 125.
[18] H.U. Blaser, E. Schmidt (Eds.), Asymmetric Catalysis on Industrial Scale, Challenges, Approaches and Solutions, Wiley–VCH, 2004, p. 480.
[19] M. Bartók, Sh.A. Gilde, Acta Phys. Chem. Szeged 9 (1963) 25.
[20] M. Bartók, J. Chem. Soc. Chem. Commun. (1979) 139.
[21] Á. Molnár, I. Bucsi, M. Bartók, G. Resofszki, Gy. Gáti, J. Catal. 129 (1991) 303.
[22] M. Bartók, M. Sutyinszki, K. Felföldi, Gy. Szöllősi, Chem. Commun. (2002) 1130.
[23] M. Bartók, M. Sutyinszki, I. Bucsi, K. Felföldi, Gy. Szöllősi, F. Bartha, T. Bartók, J. Catal. 231 (2005) 33.
[24] M. Bartók, K. Balázsik, I. Bucsi, Gy. Szöllősi, J. Catal. 239 (2006) 74.
[25] T.A. Martinek, T. Varga, F. Fülöp, M. Bartók, J. Catal. 246 (2007) 266.
[26] A. Baiker, Catal. Today 100 (2005) 159.
[27] D.Y. Murzin, P. Maki-Arvela, E. Toukoniitty, T. Salmi, Catal. Rev. Sci. Eng. 47 (2005) 175.
[28] G.J. Hutchings, Annu. Rev. Mat. Res. 35 (2005) 143.
[29] M. Bartók, Curr. Org. Chem. 10 (2006) 1533.
[30] T. Mallat, E. Orglmeister, A. Baiker, Chem. Rev. 107 (2007) 4863.
[31] D.J. Jenkins, A.M.S. Alabdulrahman, G.A. Attard, K.G. Griffin, P. Johnston, P.B. Wells, J. Catal. 234 (2005) 230.
[32] E. Toukoniitty, D.Y. Murzin, J. Catal. 241 (2006) 96.
[33] J.L. Margitfalvi, E. Tálas, E. Tfirst, Top. Catal. 39 (2006) 77.
[34] Z.M. Liu, X.H. Li, P.L. Ying, Z.C. Feng, C. Li, J. Phys. Chem. C 111 (2007) 823.
[35] D.M. Meier, D. Ferri, T. Mallat, A. Baiker, J. Catal. 248 (2007) 68.
[36] E. Toukoniitty, D.Y. Murzin, J. Catal. 251 (2007) 244.
[37] T. Mallat, A. Baiker, J. Catal. 251 (2007) 246.
[38] L. Xing, F. Du, J.J. Liang, Y.S. Chen, Q.L. Zhou, J. Mol. Catal. A Chem. 276 (2007) 191.
[39] S. Diezi, D. Ferri, A. Vargas, T. Mallat, A. Baiker, J. Am. Chem. Soc. 128 (2006) 4048.
[40] S. Lavoie, G. Mahieu, P.H. McBreen, Angew. Chem. Int. Ed. 45 (2006) 7404.
[41] S. Lavoie, M.A. Laliberte, I. Temprano, P.H. McBreen, J. Am. Chem. Soc. 128 (2006) 7588.
[42] N. Bonalumi, A. Vargas, D. Ferri, A. Baiker, J. Phys. Chem. C 111 (2007) 9349.
[43] F. Hoxha, L. Konigsmann, A. Vargas, D. Ferri, T. Mallat, A. Baiker, J. Am. Chem. Soc. 129 (2007) 10582.
[44] A. Vargas, D. Ferri, A. Baiker, J. Catal. 236 (2005) 1.
[45] J.L. Margitfalvi, E. Tálas, Appl. Catal. A 301 (2006) 187.
[46] F. Hoxha, T. Mallat, A. Baiker, J. Catal. 248 (2007) 11.
[47] K. Szőri, K. Balázsik, K. Felföldi, M. Bartók, J. Catal. 241 (2006) 149.
[48] M. Bartók, M. Sutyinszki, K. Felföldi, J. Catal. 220 (2003) 207.
[49] M. Bartók, Gy. Szöllősi, K. Balázsik, T. Bartók, J. Mol. Catal. A Chem. 177 (2002) 299.
[50] Gy. Szöllősi, B. Török, G. Szakonyi, I. Kun, M. Bartók, Appl. Catal. A 172 (1998) 225.
[51] K. Balázsik, B. Török, K. Felföldi, M. Bartók, Ultrason. Sonochem. 5 (1999) 149.

[52] B. Török, K. Balázsik, Gy. Szöllösi, K. Felföldi, M. Bartók, Chirality 11 (1999) 470.
[53] M. Bartók, T. Bartók, Gy. Szöllösi, K. Felföldi, Catal. Lett. 61 (1999) 57; M. Bartók, P.T. Szabó, T. Bartók, Gy. Szöllösi, Rapid Commun. Mass Spectrom. 14 (2000) 509.
[54] T.A. Halgren, J. Comput. Chem. 20 (1999) 720.
[55] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, revision C.02, Gaussian, Inc., Wallingford, CT, 2004, http://www.gaussian.com.
[56] E.H. Mottus, H. Schwarz, L. Marion, Can. J. Chem. 31 (1953) 1144.
[57] F.A.L. Anet, L. Marion, Can. J. Chem. 32 (1954) 452.
[58] N.J. Leonard, M. Öri, J. Brader, H. Boaz, J. Am. Chem. Soc. 77 (1955) 6237, 6239.
[59] L.H. Briggs, R.C. Cambie, B.J. Candy, G.M. O'Donovan, R.H. Russel, R.N. Seelye, J. Chem. Soc. (1965) 2492.
[60] G.I. Birnbaum, J. Am. Chem. Soc. 96 (1974) 6165 and references therein.
[61] F.M. Menger, Tetrahedron 39 (1983) 1013.
[62] R.L. Augustine, S.K. Tanielyan, J. Mol. Catal. A Chem. 112 (1996) 93.
[63] J.L. Margitfalvi, M. Hegedűs, J. Mol. Catal. A Chem. 107 (1996) 281.
[64] G. Vayner, K.N. Houk, Y.-K. Sun, J. Am. Chem. Soc. 126 (2004) 199.
[65] J.W.D. Carneiro, C.D.B. de Oliveira, F.B. Passos, D.A.G. Aranda, P.R.N. de Souza, O.A.C. Antunes, J. Mol. Catal. A Chem. 226 (2005) 221.
[66] V.S. Bryantsev, B.P. Hay, J. Am. Chem. Soc. 127 (2005) 8282.
[67] V. Venkatesan, A. Fujii, T. Ebata, N. Mikami, J. Phys. Chem. A 109 (2005) 915.
[68] J.R. Hahn, W. Ho, J. Phys. Chem. B 109 (2005) 20350.
[69] B. Brutschy, Chem. Rev. 100 (2000) 3891.
[70] D. Ferri, T. Bürgi, J. Am. Chem. Soc. 123 (2001) 12074.
[71] N. Bonalumi, T. Bürgi, A. Baiker, J. Am. Chem. Soc. 125 (2003) 13342.
[72] S. Tsuchiya, Y. Amenomiya, R.J. Cvetanovic, J. Catal. 19 (1970) 245.
[73] A. Palasov, G. Kadinov, D. Shopov, Izv. Otdel. Khim. Nauk 6 (1973) 553.
[74] P.M. Gundry, F.C. Tompkins, Quart. Rev. 14 (1960) 257.
[75] R. Suhrmann, G. Wedler, H. Gentsch, Z. Phys. Chem. Neue Folge 17 (1968) 350.
[76] I.C. Lee, R.I. Masel, Catal. Lett. 83 (2002) 43.