Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 254 (2008) 339–348
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Hydrogenation of 1-phenyl-1,2-propanedione over Pt catalysts modified by cinchona alkaloid *O*-ethers and the kinetic resolution of the 1-hydroxyketones generated

Igor Busygin [a], Johan Wärnå [b], Esa Toukoniitty [b], Dmitry Yu. Murzin [b,*], Reko Leino [a,*]

[a] *Laboratory of Organic Chemistry, Åbo Akademi University, 20500 Åbo, Finland*
[b] *Laboratory of Industrial Chemistry, Åbo Akademi University, 20500 Åbo, Finland*

Received 18 December 2007; revised 10 January 2008; accepted 12 January 2008

Available online 28 January 2008

Abstract

Nine cinchona alkaloid *O*-ethers together with cinchonidine and cinchonine were studied as chiral modifiers in the enantioselective hydrogenation of 1-phenyl-1,2-propanedione over Pt/Al_2O_3. The influence of the *O*-substituent on the reaction rate, selectivity and product distribution was investigated. Apparent rate constants for all hydrogenation steps were calculated using a first-order kinetic approach resulting in a good agreement between the experimentally recorded and predicted concentrations. The experimentally observed structure–selectivity effects indicate that the mechanisms of enantiodifferentiation over the catalyst modified by parent cinchona alkaloids and their ether derivatives differ from each other. Moreover, the modifier structure–selectivity dependence and the solvent effect were different for enantio- and diastereoselection in the 1-phenyl-1,2-propanedione and 1-hydroxyketone hydrogenations. Correlation between the modifier substituent bulkiness and diastereoselectivity of the 1-hydroxyketone hydrogenation was observed. Data on the inversion of enantioselectivity of 1-phenyl-1,2-propanedione hydrogenation, diastereoselectivity and the sense of kinetic resolution of the 1-hydroxyketones were presented. Due to the complexity of the reaction network, several competing mechanistic pathways may be present in a single reaction system.
© 2008 Elsevier Inc. All rights reserved.

Keywords: Cinchona alkaloids; Heterogeneous catalysis; Hydrogenation kinetics; 1-Phenyl-1,2-propanedione; Inversion of enantioselectivity; Inversion of diastereoselectivity

1. Introduction

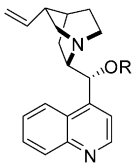
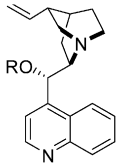
Chiral induction over heterogeneous metal catalysts is one of the most rapidly progressing methods for generating asymmetric centers in organic molecules [1,2]. Enantioface discriminating hydrogenation of a prochiral C=X functionality produces one enantiomer of the molecule in excess over the other. Cinchona alkaloids are efficient chiral surface modifiers for enantioselective hydrogenation of various activated ketones over heterogeneous catalysts. A micromolar quantity of the chiral modifier in the reaction milieu allows producing one product enantiomer in high enantiomeric excess (*ee*). Since the first report on the enantioselective hydrogenation of methyl pyruvate over a heterogeneous catalyst by Orito and co-workers in 1978 [3], applications of the Pt/cinchona alkaloid system have been successfully extended to a number of substrates. Several recent reviews are available on this subject [4–10].

Three functional parts of the cinchona alkaloids can be distinguished, namely, the bicyclic quinuclidine part, the aromatic quinoline ring, and the stereogenic region which couples the two rigid moieties together by two carbon–carbon bonds (Table 1). It is well documented that cinchonidine (CD) and cinchonine (CN) induce an excess of opposite product chirality in hydrogenations. Recently, *O*-ether derivatives of cinchona alkaloids have attracted considerable attention as modifiers for enantioselective hydrogenations of activated ketones [11–17]. This interest originates from the capacity of changing the sense of product chirality by derivatization of the hydroxyl group in

* Corresponding authors. Faxes: +358 2 2154479, +358 2 2154866.
E-mail addresses: dmitry.murzin@abo.fi (D.Yu. Murzin), reko.leino@abo.fi (R. Leino).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2008.01.012

Table 1
Structures of the modifiers

R	
CD	–H
MeOCD	$–CH_3$
PhOCD	$–C_6H_5$
TMSOCD	$–Si(CH_3)_3$
TBDMSOCD	$–Si(CH_3)_2t$-Bu
ADMSOCD	$–Si(CH_3)_2A$[a]
DPMSOCD	$–Si(C_6H_5)_2CH_3$

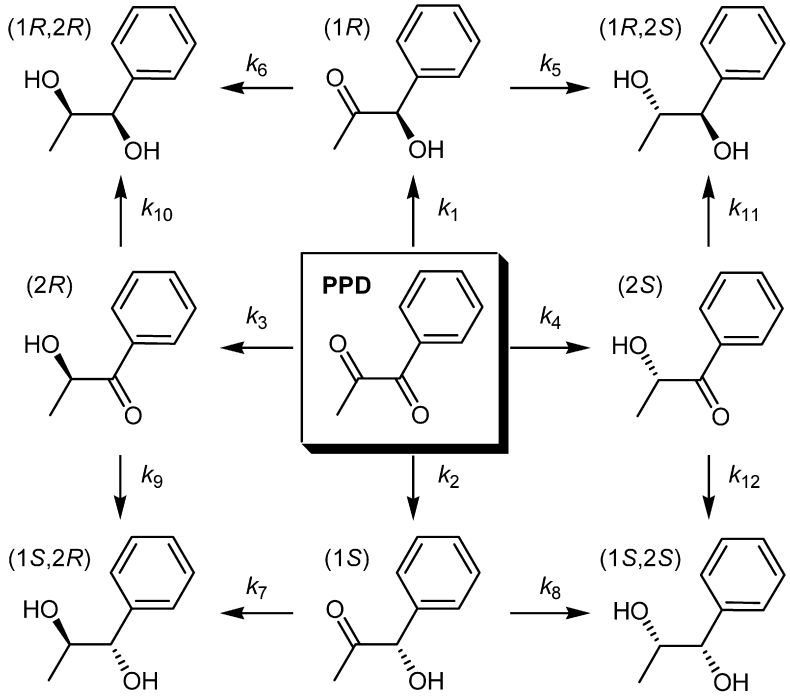
R	
CN	
MeOCN	
PhOCN	
TMSOCN	
–	
–	
–	

[a] A = $–CH_2C(H)=CH_2$.

the alkaloid while retaining the same the absolute configurations of the alkaloid asymmetric centers. Isocinchonas, which are cyclic *O*-ether derivatives of cinchona alkaloids, have been studied actively as well [18–20]. Studies on the structure–selectivity relationships provide valuable information for understanding the experimentally feasible reaction mechanisms and potentially broaden the application area of heterogeneous catalysts in enantioselective hydrogenation [21–23].

Study of the reaction kinetics is one of the approaches for elucidating the reaction mechanisms and interpreting the role of the chiral modifier in enantiodifferentiation. Several reports on studies of kinetics of ethyl pyruvate hydrogenation [24–26] are available. Kinetic analysis of the complex reaction systems consisting of parallel and consecutive steps is represented in the literature only by a few examples. When considering the kinetics of butane-2,3-dione [27,28] and cyclohexane-1,2-dione hydrogenation [29], at least six rate constants should be accounted for. The hydrogenation of unsymmetrical diketones, such as 1-phenyl-1,2-propanedione (PPD), is even more complex and consist of nine steps (Scheme 1). In our laboratories, kinetics of the enantioselective hydrogenation of PPD (Scheme 1), have been studied for some years [14,15,30–32]. Some characteristic features have been revealed: (1) The presence of two inequivalent keto groups in the molecule raises the issue of regioselectivity; Hydrogenation of the carbonyl adjacent to the phenyl ring is always preferred over hydrogenation of the aliphatic one [33]; (2) Under the currently optimal conditions, the main product, (*R*)-1-hydroxy-1-phenyl-2-propanone (depicted as (1*R*) in Scheme 1), can be obtained in 65% *ee* using cinchonidine as the chiral catalyst modifier; (3) When *O*-methyl or *O*-silyl ethers of cinchona alkaloids are used as chiral modifiers, a loss or inversion of enantioselectivity results [14,15,34]. This observation is indicative of a significant difference in the enantioselection mechanisms operating in the diketone and the classical keto ester hydrogenations, as in the latter case, the *O*-methyl derivatives of CD and CN induce, in toluene [13], enantioselectivities similar to those obtained with the parent alkaloids, and in acetic acid even higher selectivities than the parent modifiers [22].

Baiker and co-workers [35] reported the phenomenon of enantioselectivity inversion in the hydrogenation of 4,4,4-trifluoroacetoacetate which is related to the hydrate formation from the ketone in THF. This opened a new approach to research on the nature of modifier–substrate–metal surface interactions in the Orito reaction [4–10]. Since then several investigation have been published reporting inversion of enantioselectivity due to changes in the modifier structure, change



Scheme 1. 1-Phenyl-1,2-propanedione hydrogenation reaction scheme.

Download English Version:

https://daneshyari.com/en/article/62478

Download Persian Version:

https://daneshyari.com/article/62478

Daneshyari.com