

New reaction kinetic data on enantioselective hydrogenation of activated ketones over Pt-cinchona catalysts

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Introduction

Heterogeneous catalytic enantioselective hydrogenation of activated ketones over Pt-cinchona catalysts has widely been investigated. In this reactions not only high enantioselectivities, but pronounced rate acceleration (RA) has been observed [1,2]. Recently it was concluded, "rate enhancement in the presence of an alkaloid modifier is attributed to the inhibition of the pyruvate ester polymerization at the Pt surface" [3]. With respect to the enantio-differentiation (ED) step, the involvement of the alkaloid strongly adsorbed by its condensed π system in a parallel way to the Pt surface is suggested. It was also shown that the strength of adsorption plays a critical role in the control of ED. The aim of this contribution is to demonstrate that (i) the RA is an intrinsic behavior of these hydrogenation reactions, and (ii) the strength of adsorption of the alkaloid plays fewer roles in the ED step than it was thought in earlier studies.

Materials and Methods

Ethyl pyruvate purified (EtPy)₁ and contaminated with a dimer (EtPy)₂ (dimer content 20 %) were used as substrates and cinchonidine (CD) was applied as a chiral modifier. Catalysts used are 5 wt % Pt/ Al_2O_3 (E 4759 H/Pt=0.27) and 2.7 w% Pt/ SiO_2 (H/Pt=0.67, CO/Pt=0.85). The hydrogenation was performed in toluene using both injection and premixing techniques and applying kinetic treatments described elsewhere [4].

Results and Discussion

Results given in Figures 1 show that the introduction of CD during racemic hydrogenation induces instantaneous rate increase when (EtPy)₁ and (EtPy)₂ is used. The contamination has no effect on the RA, but slightly decreases the initial rates. It has also minor effect on the ee values. Figure 2 and Table 1 shows the effect of added quinoline (QN) on the ee values and the ratio of $k_{\text{enan}}/k_{\text{racem}}$. The results indicate that the influence of QN is very pronounced.

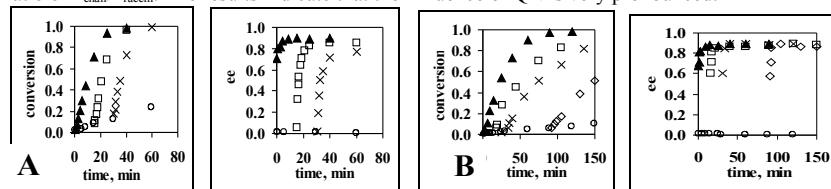


Figure 1. Kinetic curves of EtPy hydrogenation; **A** - (EtPy)₁, **B** - (EtPy)₂. [EtPy]₀ = 1.0 M, [CD] = 5×10^{-5} M, T = 20 °C, P_{H₂} = 50 bar; Pt/ Al_2O_3 , CD injection in min; \blacktriangle - 0; \square - 15; \times - 30; \diamond - 90 min; \circ - no CD.

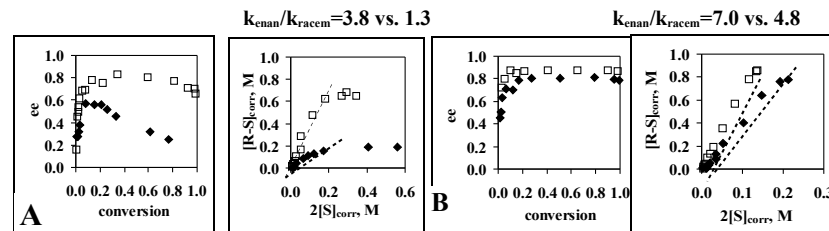


Figure 2. ee vs. conversion and [R-S] vs. 2[S] dependencies obtained in the absence and presence of quinoline (QN). [EtPy]₁ = 1 M, QN premixed followed by injection of CD.

A: [CD]₀ = 0.6×10^{-5} M; **B:** [CD]₀ = 1.2×10^{-5} M; \blacklozenge - no QN; \square - 6×10^{-5} M QN.

Results show also that contrary to expected decrease of ee and rates adding QN or acridine has no negative effect on the enantioselective hydrogenation of EtPy, consequently QN replaces CD from the Pt surface

Table 1. Effect of N-bases on the reaction rate and enantioselectivity in the hydrogenation of EtPy

N°	Catalyst	[CD], 10 ⁻⁵ M	additive	[additive], 10 ⁻⁵ M	k ₁ , min ⁻¹	k ₂ , min ⁻¹	ee _{max}	ee _{end}
1	Pt/ Al_2O_3	0.6	QN	no	0.027	0.015	0.573	0.235
2	Pt/ Al_2O_3	0.6	QN	6.0	0.040	0.069	0.832	0.699
3	Pt/ Al_2O_3	0.9	QN	no	0.032	0.058	0.719	0.575
4	Pt/ Al_2O_3	0.9	QN	6.0	0.045	0.090	0.867	0.813
5	Pt/ Al_2O_3	1.2	QN	no	0.034	0.073	0.830	0.798
6	Pt/ Al_2O_3	1.2	QN	6.0	0.056	0.118	0.874	0.860
7	Pt/ SiO_2	1.2	no	no	0.031	0.053	0.666	0.343
8	Pt/ SiO_2	1.2	acridine	10.0	0.045	0.047	0.690	0.434

[EtPy]₁ = 1 M, mode of introduction: QN premixed followed by injection of CD, conv. > 98%.

Significance

Results show that earlier and new views related to the RA and the ED, respectively, has to be revised. RA is the intrinsic feature of this reaction. The strength of adsorption of CD plays fewer roles in ED. New idea is needed to explain both RA and ED phenomenon.

References

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