Supplementary Information

Kinetic Analysis of the Asymmetric Hydrogenation of (*E*)-2,3-diphenylpropenoic acid over Cinchonidine Derivative-Modified Pd/C: Quinoline Ring Modification

Makoto Nakatsuji, Morifumi Fujita, Yasuaki Okamoto,* Takashi Sugimura*

Graduate School of Material Science, University of Hyogo, Kohto, Kamigori, Hyogo 678-1297, Japan

*E-mail: sugimura@sci.u-hyogo.ac.jp (TS), yokamoto@sci.u-hyogo.ac.jp (YO)

Derivations of Kinetic Equations

Kinetic equations in the text are presented in our previous study.[1] The surface coverage of the modifier, for example, is shown by Eq. (S1), neglecting the term of adsorbed products because of the initial stage of the reaction concerned.

$$\theta_M = K_M C_M/(1+K_M C_M+K_S C_S+K_A C_A+K_H^{1/2} P_H^{1/2}) \quad (S1)$$

where θ, K, C, and P represent the surface coverage, equilibrium adsorption constant, concentration, and pressure, respectively. The subscripts, M, S, A, and H show the modifier, substrate, benzylamine, and hydrogen, respectively. Assuming the formation of the modifier-substrate 1:1 interaction complex, the surface coverage of the interaction complex (θ_{MS}) can be simply expressed by Eq. (S2) instead of $\theta_M\theta_S$ used in other research groups. This is a novel kinetic model in the present study, leading to much simplified formulation.

$$\theta_{MS} = \theta_M [K_{MS} C_S/(1+K_{MS} C_S)]$$

$$= [K_M C_M/(1+K_M C_M+K_S C_S+K_A C_A+K_H^{1/2} P_H^{1/2})]\times[K_{MS} C_S/(1+K_{MS} C_S)] \quad \text{(S2)}$$

where K_{MS} shows the equilibrium adsorption constant of the substrate on the preadsorbed modifier to form a modifier-substrate complex through hydrogen bonding. Thus, the initial reaction rates at the modified sites (r_m) and unmodified sites (r_u) can be described as follows, assuming that in the presence of BA the rate determining steps are the addition of a dissociatively adsorbed surface hydrogen atom to the modifier-substrate complex and adsorbed substrate for the enantioselective and racemic hydrogenations, respectively.

$$r_m = k_m \theta_{MS} \theta_H$$

$$= [k_m K_M C_M (K_H P_H)^{1/2}/(1+K_M C_M+K_S C_S+K_A C_A+K_H^{1/2} P_H^{1/2})^2] \times [K_{MS} C_S/(1+K_{MS} C_S)] \quad \text{(S3)}$$

$$r_u = k_u \theta_S \theta_H$$

$$= k_u K_S C_S (K_H P_H)^{1/2}/(1+K_M C_M+K_S C_S+K_A C_A+K_H^{1/2} P_H^{1/2})^2 \quad \text{(S4)}$$

where k_m and k_u are the rate constants for the selective and nonselective hydrogenations, respectively. Thus, observed enantioselectivity, as represented by ee, can be described by Eq. (S6)

$$r_m/(r_m + r_u) = [k_m K_M C_M K_{MS}/(1+K_{MS} C_S)] /[k_m K_M C_M K_{MS}/(1 + K_{MS} C_S) + k_u K_S]$$

$$= 1/(1+\beta/C_M) \quad \text{(S5)}$$

where $\beta = (k_u/k_m)\,(K_S/K_M)\,(1 + K_{MS} C_S)/\,K_{MS}$

$$ee = i^e\, r_m/(r_m + r_u)$$

$$= i^e/(1+\beta/C_M) \quad \text{(S6)}$$

where the intrinsic enantioselectivity, i^e, is defined by the enantiomeric excess (ee) of the hydrogenation at the modified sites; $i^e = |[S]_m - [R]_m|/([S]_m + [R]_m)$. $[S]_m$ and $[R]_m$ represent the amounts of the *S*- and *R*-enantiomers, respectively.

The reaction rate r_m at the modified sites shows a maximum r_m* at a certain

concentration of the modifier, C_M*. From $dr_m/dC_M = 0$, we can obtain the concentration of the modifier C_M* for r_m*.

$$C_M^* = \alpha/K_M \quad \text{(S7)}$$

where $\alpha = 1 + K_S C_S + K_A C_A + K_H^{1/2} P_H^{1/2}$

Equation (S7) predicts that C_M* is inversely proportional to the adsorption constant of the modifier.

Reference

[1] B. Kim, M. Nakatsuji, T. Mameda, T. Kubota, M. Fujita, T. Sugimura, Y. Okamoto, *Bull. Chem. Soc. Jpn*., 2020, **93**, 163-175.

Kinetic Analysis of CD-Ph, CD-6'OH, QN, and QN-Me

We applied Eq. (3) or Eq. (S6) to the analysis of the observed enantioselectivity in Figs 2 and 3 for the asymmetric hydrogenation of PCA over CD derivative-modified Pd/C to estimate the intrinsic enantioselectivity i^e and the kinetic parameter β in a logarithm scale. Figure S1 illustrates log ee/(i^e – ee) against log C_M for the modifier after choosing appropriate value of i^e.

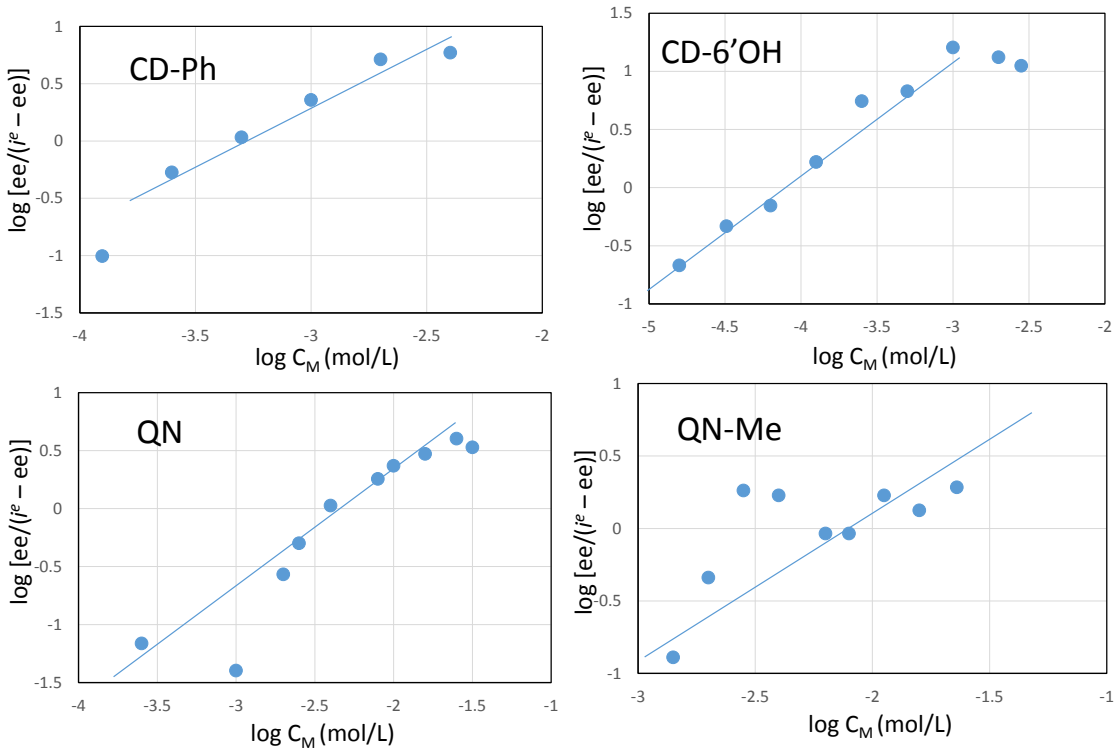
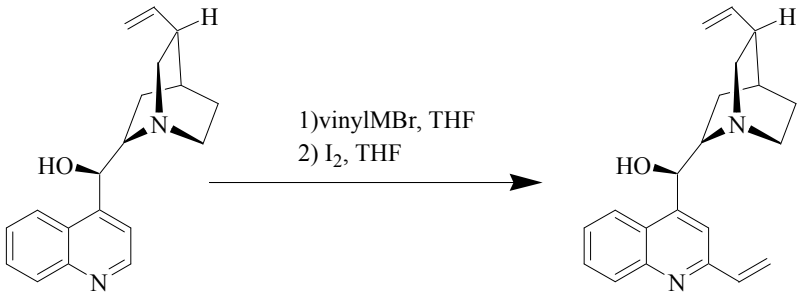


Figure S1. Correlation between log [ee/(i^e – ee)] and log C_M for CD-Ph, CD-vinyl, QN, and QN-Me. The linear line in the plot is a hypothetical line with a slope of unity according to Eq. (3) or Eq. (S6). The values of i^e and log β thus obtained are listed in Table 2.

Synthesis and Chemical Data of CD-vinyl

CD-vinyl



CD-vinyl

Colorless solid: mp. 236.8-237.2 ℃, ^{1}H NMR ($CDCl_3$, 600MHz) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.75 (s, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 17.9, 10.3 Hz, 1H), 6.26 (d, *J* = 17.9 Hz, 1H), 5.70 (m, 1H), 5.59–5.61 (m, 2H), 4.94–4.86 (m, 2H), 3.47 (m, 1H), 3.11–3.04 (m, 2H), 2.67–2.61 (m, 2H), 2.23 (br, 1H), 1.81–1.67 (m, 4H), 1.51–1.41 (m, 2H), HRMS (ESI) m/z ($M+H^+$) calcd for $C_{21}H_{25}N_2O$ 321.20 found 321.20.