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Kinetic aspects of nonlinear phenomena in heterogeneous enantioselective catalysis

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The nonlinear behavior of modifier mixtures has been discussed for heterogeneous enantioselective catalysis. A kinetic model is developed, which is based on molecular mechanism. Numerical calculations as well as comparison with experimental data on ketopantolactone, isophorone and 4-methoxy-6-methyl-2-pyrone hydrogenation demonstrate applicability of the model to explain nonlinear phenomenon. Within the framework of the advanced model, which has several simplifications, an attempt is made to analyze striking nonlinear phenomena in terms of rate constants and adsorption enthalpies. In order to account for this behavior solely based on adsorption enthalpy (i.e., neglecting the possible difference between adsorption entropy) corresponding difference between two modifiers should be 8–17 kJ mol^{-1}. Alternatively, the reaction rates should have two to three orders of magnitude difference over different modifiers in order to observe strong nonlinear phenomena in a system with modifier mixtures.

KEY WORDS: asymmetric hydrogenation; nonlinear phenomenon; kinetics.

1. Introduction

One of the interesting theoretical questions regarding asymmetric catalysis, which is discussed in the literature, is the origin of nonlinear effect (NLE). The interest originated first from kinetic resolution achieved with enantiopure catalysts and then has been extended to the cases where enantioimpure catalysts are used. Kagan [1, 2] discovered the first examples of NLE in homogeneous asymmetric catalysis, where there was no proportionality between the enantiomeric excess (*ee*) of the auxiliary and the *ee* of product and gave some mathematical models to discuss these effects. The NLE originates from the formation of diastereomeric species when the chiral auxiliary is not enantiomerically pure, either inside or outside the catalytic cycle. The observed effects were classified as (+)–NLE and (−)–NLE where "asymmetric amplification" and "asymmetric depletion" respectively occurred. The origin of NLE in homogeneous catalysis was connected to formation of dimeric or higher-order catalyst species.

In heterogeneous catalysis few publications have addressed enantioselective hydrogenation in the presence of a mixture of two chiral catalyst modifiers [3–7] also called as chiral auxiliaries. The experiments with modifier mixtures have been utilized to extract mechanistic information about competitive modifier adsorption, adsorption strength, etc. Typically a mixture of two modifiers, which are diastereomers [3,4], (e.g., cinchonine (CN) and cinchonidine) two completely different chiral modifiers or more recently enantiomers [7] have been used simultaneously in the same hydrogenation experiment. This approach has been named as nonlinear phenomena to separate it from NLE observed in homogeneous catalysis. As the chiral modifiers are mixed in various amounts, in ideal (linear) case the prediction of product *ee* should follow a linear relationship. Experiments with two modifiers, which were chemically similar, resulted in small deviations from the linear correlation; while with certain mixtures [7] deviations from nonlinearity were profound. For instance in a mixture of cinchonidine (CD) and (*S*, *S*) – pantoylnaphthylethylamine in hydrogenation of ketopantolactone (KPL) addition of 0.5% (relative to the other modifier) changes *ee* from ca. 70% in (*S*)-product to 26.5% in (*R*)- product. Similar behavior was reported for mixture of (*R*, *R*) – pantoyl-naphthylethylamine and cinchonine (CN) [8]. Another interesting modifier pair is CD and O-phenylcinchonidine (PhOCD) exhibiting similar striking nonlinear behavior [9]. Less than 0.7% of CD is needed to control the excess product. Examples [3, 5, 7, 9, 10] of non linear phenomena are illustrated in figure 1.

The nonlinearity has been attributed to the different adsorption strength or adsorption modes of the modifiers. However, it is known that the different modifiers induce different *ee* as well as different reaction rates [11, 12], e.g. in 1-phenylpropane-1,2-dione hydrogenation *ee* and rate with CD and CN were 55 (*R*), 27 (*S*) and 18.6 and 7.5 × 10^{-4} mol min^{-1} g$_{cat}$$^{-1}$, respectively [11]. Therefore, the difference in reaction rates results in nonlinearity, *i.e.* the plot of *ee* versus mole fraction of one modifier x(M) is not a straight line. Furthermore,

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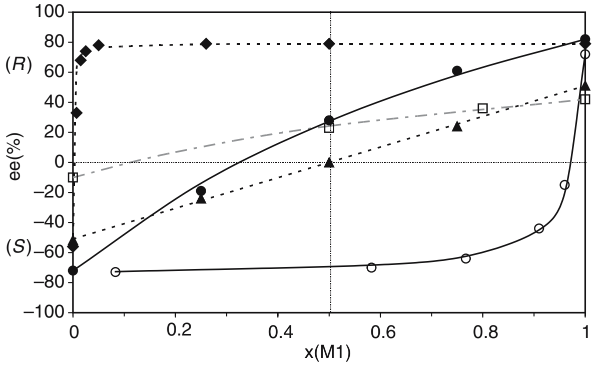


Figure 1. Nonlinear phenomena observed in enantioselective hydrogenations using binary modifier mixture. Symbols: (♦) see in ketopantolactone hydrogenation, 5 wt% Pt/Al_2O_3, toluene, M_1:O-phen oxycinchonidine/M_2:cinchonidine, $n = 0.001$; (□) *ee* in isophorone hydrogenation, Pd black, methanol, M_1:(−)-dihydrovinpocetine/M_2:dihydrocinchonine, $n = 0.52$; (○) *ee* in 4-methoxy-6-methyl-2-pyrone hydrogenation, 5 wt% Pd/TiO_2, 2-propanol, M_1:quinidine/M_2:cinchonidine, $n = 42$; (●) *ee* in 4-methoxy-6-methyl-2-pyrone hydrogenation, 5 wt% Pd/TiO_2, 2-propanol, M_1:cinchonine/ M_2:cinchonidine, $n = 0.55$; (▲) *see* in ketopantolactone hydrogenation, 5 wt% Pt/Al_2O_3, 1,1,1-trifluorotoluene, M_1:(*R,R*)-pantoyl-naphtylethylamine/M_2:(*S, S*)-pantoyl-naphtylethylamine, $n = 1$. Data points adapted from [5, 7, 9, 10]. Lines represent the model predictions (equation 5) for different values of *n*.

the difference in absolute *ee* values with single modifiers results in that an experiment with 50:50% modifier mixture rarely gives 0% *ee*. Therefore, it is expected that when mixtures of two diastereomers or structurally different modifiers are used the nonlinear behavior is more a rule than an exception. In this work we define the nonlinear behavior accordingly: When the plot of *ee* versus mole fraction of one modifier x(M) is not a straight line in experiments with binary modifier mixtures.

In order to address this in a quantitative way kinetic analysis is needed, especially to reveal the possible contribution of different adsorption strengths and reaction rates. In the present contribution we analyze for the first time quantitatively the dependence of *ee* on composition of modifier mixtures.

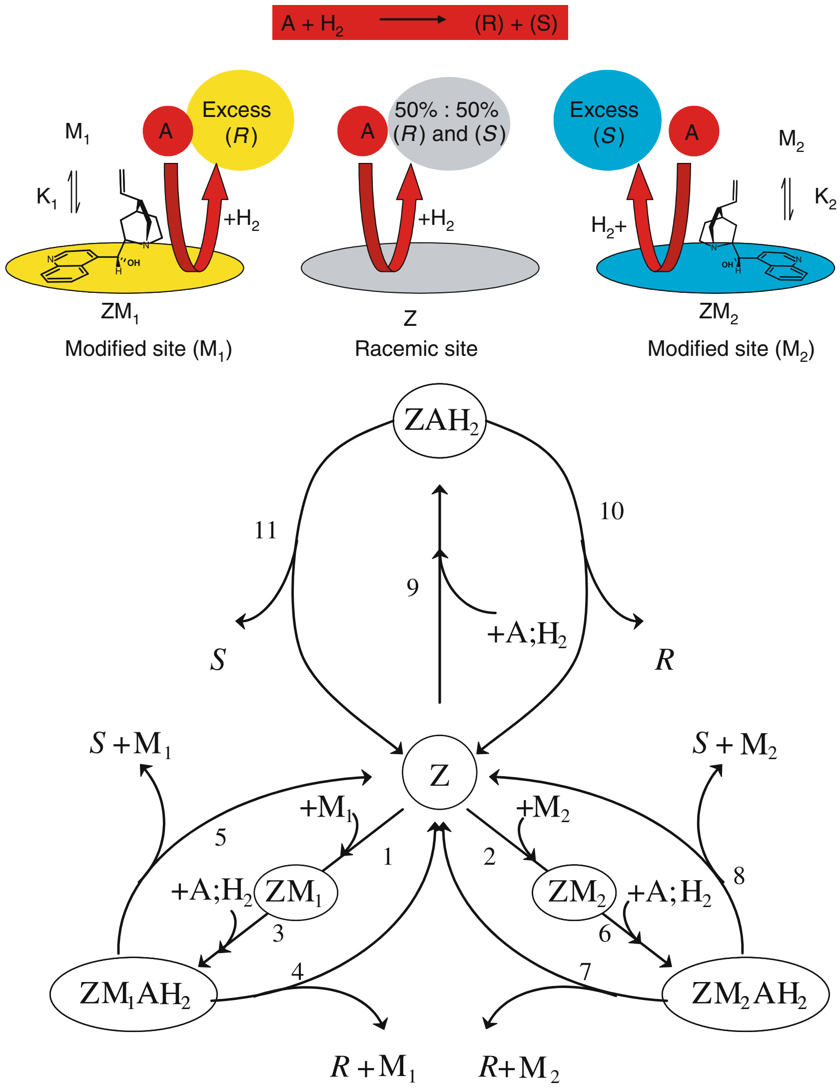
1.1. Model

It is well accepted in the literature that the enantiodifferentiation over cinchona alkaloid modified Pt is due to 1-to-1 modifier reactant interactions on the catalyst surface and e.g., not due to long-range ordered patterns of the chiral modifier on the metal surface. There are several theoretical and experimental observations, which support 1-to-1 interaction model. Recent details from mechanistic models can be found in [13–15]. The accepted 1-to-1 interaction model predicts a linear dependence of *ee* on mole fraction of one modifier. However, this holds only in the case when the two catalyst modifiers result in the same reaction rate. In a special case when the rates are equal and the *ee*s are equal but opposite one gets a linear dependence and 0% *ee* at 50:50% modifier molar ratio. This should be the case when mixtures of enantiomers are used as catalyst modifiers. Otherwise, one could use racemic modifiers mixture and end up with notable *ee*, which is a rather unusual symmetry breaking phenomenon. To the best of our knowledge all reports where two enantiomers have been used as chiral modifiers for heterogeneous catalysts separately they have resulted within experimental error to the same rate and the same *ee* [7, 16, 17]. Therefore, when mixture of two catalyst modifiers which are not enantiomers of each other are utilized noticeable nonlinear phenomena are to be expected due to differences in reaction rates and *ee*.

The following model can be considered for enantioselective hydrogenation (equation 1). The model contains racemic route ($N^{(5)}$ and $N^{(6)}$), which produces a racemic mixture of (*R*)- and (*S*)-product enantiomers (Scheme 1). There are two enantioselective routes where either modifier M_1 ($N^{(1)}$, $N^{(2)}$) or M_2 ($N^{(3)}$, $N^{(4)}$) are involved.

$$\begin{array}{lcccccc}
 & N^{(1)} & N^{(2)} & N^{(3)} & N^{(4)} & N^{(5)} & N^{(6)} \\
1.\ Z + M_1 \Leftrightarrow ZM_1 & 1 & 1 & 0 & 0 & 0 & 0 \\
2.\ Z + M_2 \Leftrightarrow ZM_2 & 0 & 0 & 1 & 1 & 0 & 0 \\
3.\ A + H_2 + ZM_1 \Rightarrow ZM_1AH_2 & 1 & 1 & 0 & 0 & 0 & 0 \\
4.\ ZM_1AH_2 \Rightarrow R + Z + M_1 & 1 & 0 & 0 & 0 & 0 & 0 \\
5.\ ZM_1AH_2 \Rightarrow S + Z + M_1 & 0 & 1 & 0 & 0 & 0 & 0 \\
6.\ A + H_2 + ZM_2 \Rightarrow ZM_2AH_2 & 0 & 0 & 1 & 1 & 0 & 0 \\
7.\ ZM_2AH_2 \Rightarrow R + Z + M_2 & 0 & 0 & 1 & 0 & 0 & 0 \\
8.\ ZM_2AH_2 \Rightarrow S + Z + M_2 & 0 & 0 & 0 & 1 & 0 & 0 \\
9.\ A + H_2 + Z \Rightarrow ZAH_2 & 0 & 0 & 0 & 0 & 1 & 1 \\
10.\ ZAH_2 \Rightarrow R + Z & 0 & 0 & 0 & 0 & 1 & 0 \\
11.\ ZAH_2 \Rightarrow S + Z & 0 & 0 & 0 & 0 & 0 & 1
\end{array} \tag{1}$$

$$N^{(1)}, N^{(3)}, N^{(5)} : A + H_2 = R; N^{(2)}, N^{(4)}, N^{(6)} : A + H_2 = S$$



Scheme 1. The kinetic model containing two types of modified sites (ZM_1 and ZM_2) and racemic sites (Z).

On the right hand side of the equations, stoichiometric numbers for the different routes are reported. In equation 1 A denotes the substrate, M_1 and M_2 two different modifiers, R and S are the (*R*) and (*S*) product enantiomers respectively, Z is the surface site and ZM_1AH_2 and ZM_2AH_2 are intermediate surface complexes. Steps with sign ⇔ are in equilibria. Assuming, that hydrogen does not compete for sites with the bulky organic molecules adsorbed on the surface and that adsorbed hydrogen is in equilibrium with hydrogen dissolved in the liquid phase, it is convenient to express the reaction rate as a function of hydrogen pressure in the gas phase in equilibrium with the liquid phase rather than as a function of hydrogen concentration in the liquid phase [18].

The reaction mechanism can be described by six reaction routes. The number of basic routes, P, is determined by the following equation [18]:

$$P = Q + W - J, \qquad (2)$$

where Q is the number of steps, W is the number of links between intermediates e.g., most often number of balanced equations and J is the number of intermediates. Balanced equations determine the relationships between adsorbed intermediates, for example, equality of the sum of species coverage to unity. It follows from equation (2) that there are 11 steps, 1 balanced equation, 6 intermediates (Z, ZM_1, ZM_2, ZM_1AH_2, ZM_2AH_2, ZAH_2), and therefore 6 basic routes, out of which $N^{(1)}$ and $N^{(3)}$ describe formation of R–products with involvement of modifiers M_1 and M_2 respectively, while $N^{(2)}$ and $N^{(4)}$ correspond to formation of S products with these modifiers. Racemic reactions are taken care of by inclusion of routes $N^{(5)}$ and $N^{(6)}$.

The detailed mechanism could be more complicated that the simplified version of it presented in equation 1. It is important to remember when dealing with bulky organic molecules adsorbed on supported metal catalysts that their catalytic transformations occur over nanometer-sized transition metal clusters dispersed on oxide supports. In catalysis involving complex organic molecules with different functional groups, both the number of sites and the mode of adsorption are important. The changes of adsorption geometry are a common phenomenon and the mode of adsorption can be dependent on the concentration. Kinetic modeling of catalytic asymmetric hydrogenation on supported metal (Pt) catalysts in the presence of a chiral modifier-cinchonidine was performed [19] taking into account that depending on concentration the adsorption mode is changing from parallel to the surface to a tilted one requiring different number of metal sites for adsorption.

For the sake of clarity in considerations of mechanism (equation 1), the number of sites for organic molecule A and both modifiers was supposed to be the same, moreover no changes of adsorption mode with concentration are considered. Despite these simplifications, the mechanism is, however, sufficient for discussing the kinetic aspects of nonlinear phenomena. Note that kinetic treatment presented below can be very easily extended to other reactions, but not only hydrogenations.

2. Results and discussion

2.1. Derivation of kinetic equations

In the derivation of kinetic equations based on the model presented in equation 1. It is assumed that the catalyst surface is uniform or quasi-uniform and organic compounds form an ideal liquid mixture. It should be noted that although surface nonuniformity (e.g., dependence of adsorption and rate constants on coverage) is well documented in adsorption kinetics and adsorption isotherms, temperature programmed desorption, etc., kinetic regularities for multiphase systems seldom require utilization of kinetic models for non-ideal (either apriori or due to lateral interactions) surfaces. It is thus a hope of the authors that the developed model despite a number of simplifications could serve not only as a framework for qualitative analysis, but could be also helpful in actual fitting of experimental data. Detailed derivation of kinetic equation is available by request from the authors.

2.2. Enantioselectivity

For enantiomeric excess, defined as

$$ee = \frac{C_R - C_S}{C_R + C_S}, \tag{3}$$

where C_R and C_S are the concentrations of (*R*)- and (*S*)-enantiomers, respectively. One arrives finally at

$$ee = \frac{(ee_1^{ena} - ee_2^{ena} n)x_1 + ee_2^{ena} n}{(1-n)x_1 + n + f}, \tag{4}$$

$$\text{(for racemic reaction } f = 0\text{)},$$

which gives dependence of overall *ee* as a function of the mole fraction (x_1) of one modifier in a mixture with another one. Values of $ee_1{}^{ena}$ and $ee_2{}^{ena}$ correspond to maximum enantioselectivity with modifier M_1 or M_2 respectively, which could be achieved when the contribution of racemic reaction could be neglected. The parameter n is defined as

$$n = \frac{k_6 K_2}{k_3 K_1}, \tag{5}$$

where k_3 and k_6 are the rate constants in steps 3 and 6 respectively, (see equation 1) and k_1 and k_2 are the adsorption equilibrium constants for modifiers M_1 or M_2, respectively. Definition of the parameter f can be found in the supplementary material.

2.3. Numerical examples

Let us analyze equation 4 for several values of parameters $ee_1{}^{ena}$, $ee_2{}^{ena}$, n and f. First we start with a case when contribution of racemic reaction can be neglected ($f = 0$). The racemic route can be neglected in the case of strong rate acceleration (i.e., parameter $f = 0$) and when the catalyst surface can be considered to be fully modified. Such case was considered in hydrogenation of α-keto esters over cinchonidine modified Pt catalysts, in particular ethyl pyruvate [20]. Up to 6-fold rate acceleration have been reported for KPL hydrogenation over cinchona alkaloid modifier Pt catalysts [21]. One of the most astonishing features of α-keto esters hydrogenation has been the considerable rate acceleration observed in the presence of trace amounts of cinchona alkaloid modifier. The modifier induces high enantioselectivity (*ee* >95%) and up to 100-fold higher reaction rate with respect to racemic hydrogenation in batch reactors. In mechanistic considerations [22, 23] the overall rate acceleration and enantioselectivity have been taken as intrinsic kinetic features which are interrelated. The overall rate acceleration has been explained with one-to-one reactant-CD interactions, which result in higher overall hydrogenation rate and excess formation of one product enantiomer. Such rate acceleration was not reported for a number of other substrates [15], thus it cannot be considered an integral part of asymmetric heterogeneous catalysis.

Numerical examples are provided in figure 2, clearly demonstrating nonlinear behavior. In fact, only when the parameter n is equal to unity the overall *ee* depends linearly on the composition of the modifier mixtures. For a situation when racemic reaction cannot be neglected, (negligible rate acceleration or well below full surface coverage of the modifier) (figure 3) NLE are less pronounced compared to a case of strong rate acceleration.

This parameter n is equal to the ratio of kinetic and adsorption terms for both modifiers (see equation 5). Very strong nonlinear dependence follows from figure 2

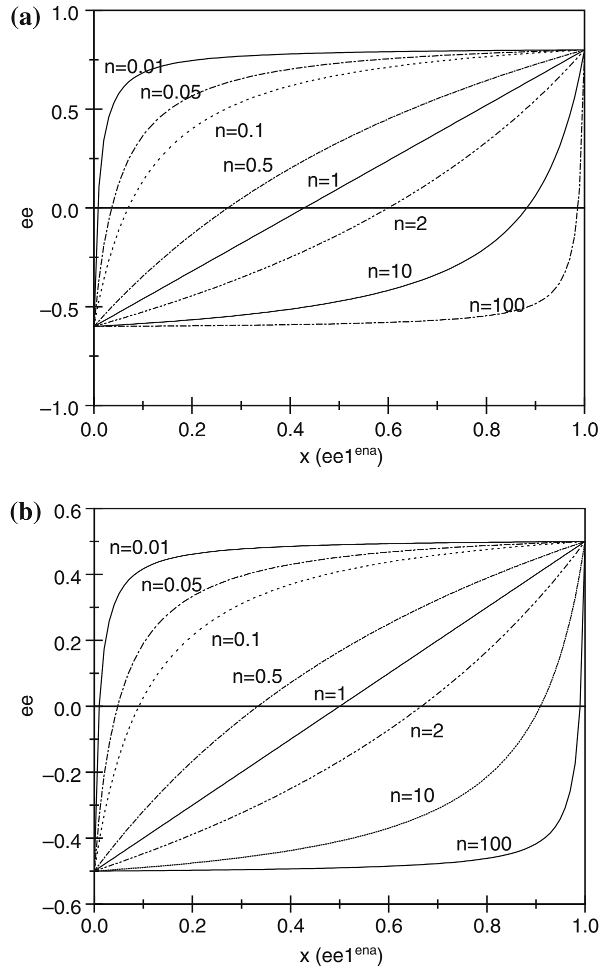


Figure 2. Dependence of overall *ee* in case of rate acceleration ($f = 0$) on parameter n and enantiomeric excess of single modifiers: (a) $ee_1^{ena} = 0.8$, $ee_2^{ena} = -0.6$ and (b) $ee_1^{ena} = 0.5$,$ee_2^{ena} = -0.5$.

in case parameter n is below ca. 0.05 (or alternatively above 100), indicating substantial differences either in kinetic or adsorption terms.

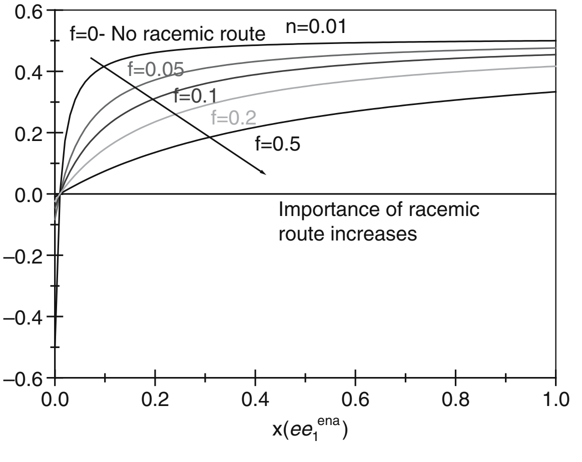


Figure 3. Dependence of overall *ee* on f at $n = 0.01$ and $ee_1^{ena} = 0.5$, $ee_2^{ena} = -0.5$.

Let us analyze the physical meaning of parameter n (Detailed mathematical analysis can be found in supplementary material). Neglecting the racemic reaction ($f \asymp 0$) the rates of transformation in the presence of the only one (the first or the second) modifier at low coverage follows the first order dependence in all components (reactant, modifiers, hydrogen pressure). The ratio of rates with different modifiers (when their concentrations are the same) corresponds to parameter n

$$\left(\frac{r^{(1)}+r^{(2)}}{r^{(3)}+r^{(4)}}\right)_{\theta\to 0}=\frac{k_3K_1C_{M_1}C_AP_{H_2}}{k_6K_2C_{M_2}C_AP_{H_2}}=\frac{k_3K_1C_{M_1}}{k_6K_2C_{M_2}}=\frac{1}{n}\frac{C_{M_1}}{C_{M_2}}, \tag{6}$$

when the surface species AH_2M_1 and AH_2M_2 are the most abundant it follows that the reaction rates obey zero order dependence in all reactants

$$\left(\frac{r^{(1)}+r^{(2)}}{r^{(3)}+r^{(4)}}\right)_{\theta_{AH_2M}\to 1}=\frac{k_4+k_5}{k_7+k_8}. \tag{7}$$

Values of reaction rates in the presence of different modifiers reported in general in the literature [15] correspond to cases of zero reaction order, showing very little dependence on the chemical nature of the modifier. The same observations hold for hydrogenation of ketopantolactone [7], indicating that the while the experimentally observed rates correspond to zero order kinetics (e.g., independent on modifier concentration) being defined by equation 7, enantioselectivity is mainly governed by the difference in rates at low coverage, which takes into account differences in adsorption strengths of the modifiers.

Next we analyze the parameter n in terms of rate constants and adsorption enthalpies ΔH_1. According to equation 5 parameter n corresponds to the ratio of the rate coefficients (k_3 and k_6) and equilibrium constants (k_1 and k_2). In order to separate contribution of adsorption entropy and enthalpy changes in the modifier adsorption process at constant temperature and pressure the following form of the equation 5 can be obtained

$$n=\frac{k_6}{k_3}e^{(\Delta G_2-\Delta G_1)/RT}=\frac{k_6}{k_3}e^{(\Delta H_2-\Delta H_1)/RT}\times e^{(\Delta S_1-\Delta S_2)/R}, \tag{8}$$

where ΔG is the Gibb's free energy change for the modifier adsorption from liquid to catalyst surface. ΔH and ΔS are the corresponding enthalpy and entropy changes for the adsorption. Assuming that the adsorption entropy change terms of both modifiers are equal one gets the following expression

$$n=\frac{k_6}{k_3}e^{(\Delta H_2-\Delta H_1)/RT,} \tag{9}$$

where ΔH_1 and ΔH_2 correspond to the adsorption enthalpies of the first and the second modifier and k_3 and

k_6 are the rate constants in reactions with the first and the second modifier, respectively. To justify the canceling of the adsorption entropy effect one can imagine that as very similar modifiers are used (enantiomers of diastereomers of each other) the entropy change upon adsorption on Pt metal surface is very similar. Entropy decreases notably as modifiers adsorb strongly on Pt from liquid phase. In case structurally very different pair of modifiers is used the adsorption entropy might contribute to some extent to the value of parameter n. In general the modifier, which is more bulky and flexible in the liquid phase upon adsorption to Pt suffers larger degrease of entropy, which disfavors the adsorption on the surface.

Imagine now that the rate coefficients do not differ very much (e.g., $k_6 = k_3$) as is often observed experimentally, then the value of n should be mainly due to the differences in the adsorption enthalpies. Simple calculations of this difference at 300 K, typically used in enantioselective hydrogenation experiments, give for $n = 0.001\text{->}0.05$ values of $\Delta H_2 - \Delta H_1$ from -17 to -7.5 kJ mol^{-1}. Such a difference in adsorption strength requires most probably substantial differences in the chemical structures of these modifiers or differences in the adsorption modes (e.g., parallel versus tilted). It is therefore, not surprising that considerable nonlinear behavior was observed only when the modifiers had different anchoring moieties. A literature survey reveals that experimental or theoretical adsorption enthalpy values for different modifier on Pt are not readily available. Nevertheless, it is interesting to compare the adsorption energy difference reported in [24] for CD and PhOCD anchoring moieties on Pt. It was rationalized that for the most probable adsorption modes of CD and PhOCD on cluster with 38 Pt atoms the adsorption energy difference was 27 kJ mol^{-1}, which would be sufficiently high to induce striking nonlinear phenomena according to our kinetic analysis. The theoretical adsorption energies reported in [24] were calculated at 0 K in vacuum neglecting the zero point vibrations and therefore, the results cannot be fully comparable with the results obtained in presence of solvent at 293 K. Experimental *ee* versus x(CD) data have been reported for CD and PhOCD and based on this data (adapted from [9]) an adsorption enthalpy difference of -16 kJ mol^{-1} in favor of CD was obtained (n = 0.001, 293 K) by utilizing equation 9 (figure 1).

Kinetic contribution in the nonlinear phenomena can be considered assuming that the adsorption enthalpy and entropy terms are unity in equation 8. The differences in the reaction rates with different modifiers should be two to three orders of magnitude to explain the reported nonlinear phenomena solely on differences in reaction rates. Typically the reaction rates with different modifiers are similar and vary less than one order of magnitude. This suggest that the striking nonlinear phenomena observed e.g., in KPL hydrogenation originates from modifier adsorption induced effects rather than differences in reaction rates.

At the same time if k_6/k_3 or $e^{(\Delta S_1 - \Delta S_2)/R}$ are different from unity the requirement for the big differences between the adsorption strength is relaxed, since for $k_6/k_3 \times e^{(\Delta S_1 - \Delta S_2)/R}$ equal to 5 or 10 one gets respectively $\Delta H_2 - \Delta H_1$ equal to -3.5 and -1.7 kJ mol^{-1}.

3. Conclusions

A kinetic model is proposed for heterogeneous enantioselective catalysis in the presence of binary modifier mixtures. Appearance of nonlinear phenomenon, e.g., nonlinear dependence of the enantiomeric excess on the composition of the modifier mixtures, is discussed. Numerical analysis as well as comparison with experimental data revealed conditions when the nonlinear behavior is manifested. For strong deviations from linearity substantial differences in adsorption strengths (7.5–17 kJ mol^{-1}) of modifiers are required, which could be achieved when the anchoring moieties of the modifiers are chemically different.

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