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Kinetic models for catalytic selection processes as applied to asymmetric hydrogenation

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Abstract

Kinetic terms for product formation in selection processes are evaluated for the example of asymmetric hydrogenation. The investigated models are characterized by preceding intermolecular equilibria to 2–4 stereoisomeric substrate complexes as well as direct intramolecular interconversion between corresponding diastereomeric intermediates. In the case of isobaric conditions the gross-hydrogen consumption can be described in each case by an equation analogous to simple Michaelis–Menten-type kinetics. The interpretation of the resulting constants is briefly demonstrated for a few practical examples. The temperature dependence of the enantiomeric ratio for the resulting products, as for example for a selection process, is also considered for the investigated models.

Keywords: Asymmetric hydrogenation; Rhodium; Temperature dependence; Isoinversion principle

1. Introduction

Molecular recognition is one of the most fascinating phenomena of life and is therefore a challenge for academic research. The transfer of chirality is the focus of studies on selection processes [1]. Catalytic asymmetric reactions are particularly attractive because the chiral information of the active catalyst is multiply transferred to the product.

Asymmetric hydrogenation using Rh-(I)-chelates of the formula $[Rh(P\,\hat{}\,P^*)(solv)_2]A$ ($P\,\hat{}\,P^*$ = chiral bisphosphane, solv = solvent like MeOH, A = anion like BF_4^-) is one of the best understood catalytic processes and is useful for the synthesis of almost enantiomeric pure aminoacids (enantiomeric excess $\gg 90\%$). Extensive kinetic and complex chemical investigations of five-membered ring chelates by Halpern and coworkers [2] demonstrated that the asymmetric hydrogenation proceeds according to Scheme 1.

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[1] Selectivity as used in this context is the ratio of the rate of formation of a favoured product and the sum of the formation rates of all products [1].

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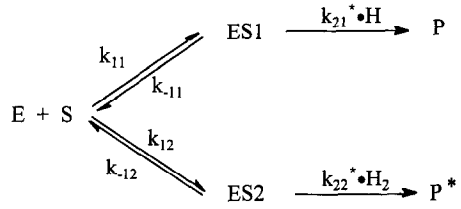
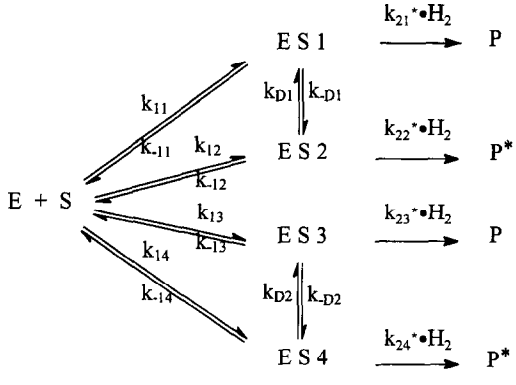


Scheme 1. Asymmetric hydrogenation according to Halpern and coworkers. (E = solvent complex of the type $[Rh(P\,\widehat{}\,P^{*})(solv)_2]^{+}$, S = prochiral olefin, ES_i = substrate complex, P, P* = enantiomeric products, k_i = rate constants: $k_{2i}^{*}\cdot H_2 = k_{2i}$)

Two diastereomeric substrate complexes with the prochiral olefin are formed in a preceding reversible step. In the case of the chiral ligands CHIRAPHOS [2,3-bis(diphenylphosphino)butane] and DIPAMP [1,2-bis-(*o*-methoxyphenyl-phenyl-phosphino)ethane], respectively, this can be proved by ^{31}P-NMR spectra. In a series of elementary steps these substrate complexes react with hydrogen to form the enantiomeric products. The irreversible oxidative addition of hydrogen to the diastereomeric substrate complexes was found to be the rate determining process under normal conditions. A peculiarity in the catalytic cycle is that the thermodynamic less stable *minor* complex reacts considerably faster than the thermodynamic more stable *major* complex, thereby forming the enantiomeric excessive product. Landis and Halpern demonstrated in Ref. [2](b) that the under-represented *minor* complex reacts 580 times faster than the excess diastereomeric *major* complex in the hydrogenation of methyl (*Z*)-2-acetamido-cinnamate by $[Rh(DIPAMP)(MeOH)_2]^{+}$ at 25°C.

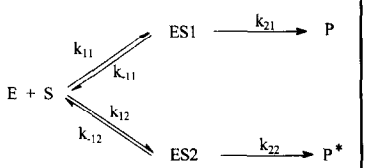
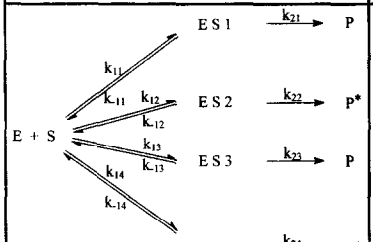
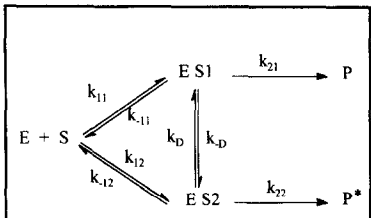
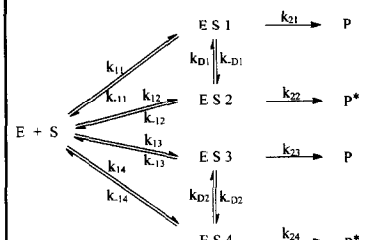
The situation becomes more complicated, if C_1-symmetrical ligands are used as for instance sugar derivatives like bis(phosphinites) [3](a–e) or bis(phosphanes) [3](f) which have been successfully applied for a long time. In principle, with such ligands four stereoisomeric substrate complexes can coexist at the same time. Moreover, it was demonstrated that intramolecular exchange processes take place between the diastereomeric substrate complexes [4]. Also for other selection processes such as asymmetric hydrocyanation for example, such intramolecular interconversions between intermediates have been described [5]. A consideration of these facts leads to a mechanism of asymmetric hydrogenation as outlined in Scheme 2 (see also Ref. [4](e,f)).

In principle the disturbance of established intermolecular equilibria should also be considered. There is some evidence for this in similar proceeding hydrogenation of comparably slow hydrogenable diolefins like (*Z,Z*)-cycloocta-1,5-dien (COD) or norborna-2,5-diene (NBD) with analogous Rh-chelates [6].



Scheme 2. Reaction sequence of the asymmetric hydrogenation with C_1-symmetric ligands, considering intramolecular exchange processes between the diastereomeric substrate complexes. (k_{Di} = rate constants for intramolecular interconversion between diastereomeric substrate complexes: $k_{2i}^{*}\cdot H_2 = k_{2i}$; other symbols according to Scheme 1)

Table 1
$k_{obs.}$-, $1/K_M$-values and *enantiomeric ratio* for different models (steady-state conditions and established preequilibria, respectively, in the case of the enantiomeric ratio)

model [a]	$k_{obs.}$ (the values for $1/K_M$ correspond to the denominators of the terms) as well as enantiomeric ratios
	$k_{obs.} = \dfrac{\left(k_{21}\bullet\dfrac{k_{11}}{k_{-11}+k_{21}}+k_{22}\bullet\dfrac{k_{12}}{k_{-12}+k_{22}}\right)}{\left(\dfrac{k_{11}}{k_{-11}+k_{21}}+\dfrac{k_{12}}{k_{-12}+k_{22}}\right)}$ [b] $\dfrac{P}{P^*}=\dfrac{k_{21}\bullet k_{11}\bullet k_{-12}}{k_{22}\bullet k_{12}\bullet k_{-11}}$ [c]
	$k_{obs.} = \dfrac{\left(k_{21}\bullet\dfrac{k_{11}}{k_{-11}+k_{21}}+k_{22}\bullet\dfrac{k_{12}}{k_{-12}+k_{22}}+k_{23}\bullet\dfrac{k_{13}}{k_{-13}+k_{23}}+k_{24}\bullet\dfrac{k_{14}}{k_{-14}+k_{24}}\right)}{\left(\dfrac{k_{11}}{k_{-11}+k_{21}}+\dfrac{k_{12}}{k_{-12}+k_{22}}+\dfrac{k_{13}}{k_{-13}+k_{23}}+\dfrac{k_{14}}{k_{-14}+k_{24}}\right)}$ $\dfrac{P}{P^*}=\dfrac{k_{21}\bullet\dfrac{k_{11}}{k_{-11}}+k_{23}\bullet\dfrac{k_{13}}{k_{-13}}}{k_{22}\bullet\dfrac{k_{12}}{k_{-12}}+k_{24}\bullet\dfrac{k_{14}}{k_{-14}}}$
	$k_{obs.} = \dfrac{\left(\dfrac{k_{21}\bullet[k_{11}\bullet(k_{-12}+k_{22}+k_D)+k_D\bullet k_{12}]+k_{22}\bullet[k_{12}\bullet(k_{-11}+k_{21}+k_{-D})+k_{-D}\bullet k_{11}]}{[(k_{-11}+k_{21}+k_{-D})\bullet(k_{-12}+k_{22}+k_D)-(k_D\bullet k_{-D})]}\right)}{\left(\dfrac{[k_{11}\bullet(k_{-12}+k_{22}+k_D)+k_D\bullet k_{12}]+[k_{12}\bullet(k_{-11}+k_{21}+k_{-D})+k_{-D}\bullet k_{11}]}{[(k_{-11}+k_{21}+k_{-D})\bullet(k_{-12}+k_{22}+k_D)-(k_D\bullet k_{-D})]}\right)}$ $\dfrac{P}{P^*}=\dfrac{k_{21}\bullet[k_{11}\bullet(k_{-12}+k_D)+k_D\bullet k_{12}]}{k_{22}\bullet[k_{12}\bullet(k_{-11}+k_{-D})+k_{-D}\bullet k_{11}]}$
	$k_{obs.} = \dfrac{\left(k_{21}\bullet\dfrac{U}{A}+k_{22}\bullet\dfrac{V}{A}+k_{23}\bullet\dfrac{X}{B}+k_{24}\bullet\dfrac{Y}{B}\right)}{\dfrac{U+V}{A}+\dfrac{X+Y}{B}}$ [d] $\dfrac{P}{P^*}=\dfrac{\left(k_{21}\bullet\dfrac{[k_{11}\bullet(k_{-12}+k_{D1})+(k_{D1}\bullet k_{12})]}{[(k_{-11}+k_{-D1})\bullet(k_{-12}+k_{D1})-(k_{D1}\bullet k_{-D1})]}+k_{23}\bullet\dfrac{[k_{13}\bullet(k_{-14}+k_{D2})+(k_{D2}\bullet k_{14})]}{[(k_{-13}+k_{-D2})\bullet(k_{-14}+k_{D2})-(k_{D2}\bullet k_{-D2})]}\right)}{\left(k_{22}\bullet\dfrac{[k_{12}\bullet(k_{-11}+k_{-D1})+(k_{-D1}\bullet k_{11})]}{[(k_{-11}+k_{-D1})\bullet(k_{-12}+k_{D1})-(k_{D1}\bullet k_{-D1})]}+k_{24}\bullet\dfrac{[k_{14}\bullet(k_{-13}+k_{-D2})+(k_{-D2}\bullet k_{13})]}{[(k_{-13}+k_{-D2})\bullet(k_{-14}+k_{D2})-(k_{D2}\bullet k_{-D2})]}\right)}$

[a] Values for k_{2i} see Scheme 1.
[b] Corresponds to Eq. (15) in [2](b).
[c] Corresponds to Eq. (19) in [2](b).
[d] The terms for A, B, U, V, X, and Y are the same as used in Eqs. (6)–(11).

Besides the simplest model case (Scheme 1) reported in the literature and the reaction sequence shown in Scheme 2, there is the case of the application of C_2-symmetric ligands with intramolecular exchange processes [4](d). Moreover, one could think about the application of C_1-symmetric ligands without any intramolecular interconversion between diastereomeric substrate complexes (see Table 1). In all of the four models the preceding intermolecular equilibria can be disturbed or not.

The subject of this paper is to evaluate kinetic terms for product formation using the mechanisms discussed above and outlined in Table 1 with a special consideration for the interpretation of the experimentally simply accessible isobaric hydrogen consumption as a variable, which is proportional to the product formation. Also the expected influence of the temperature on the enantiomeric ratio [7] is investigated with respect to the actual model.

2. Results and discussion

Starting from Scheme 2, Eq. (1a) and Eq. (1b) were derived for the temporal alteration of the respective product concentrations, which are in each case the result of two independent processes.

$$\frac{dP}{dt} = k_{21} \cdot ES1 + k_{23} \cdot ES3 \tag{1a}$$

$$\frac{dP^*}{dt} = k_{22} \cdot ES2 + k_{24} \cdot ES4 \tag{1b}$$

Applying the balance $E_0 = E + ES1 + ES2 + ES3 + ES4$, which is valid for any time, and assuming the condition of stationarity for the stereoisomeric substrate complexes, for the temporal alteration of them finally the following can be concluded:

$$ES1 \cdot (k_{21} + k_{-11} + k_{-D1}) = k_{11} \cdot E \cdot S + k_{D1} \cdot ES2 \tag{2}$$

$$ES2 \cdot (k_{22} + k_{-12} + k_{D1}) = k_{12} \cdot E \cdot S + k_{-D1} \cdot ES1 \tag{3}$$

$$ES3 \cdot (k_{23} + k_{-13} + k_{-D2}) = k_{13} \cdot E \cdot S + k_{D2} \cdot ES4 \tag{4}$$

$$ES4 \cdot (k_{24} + k_{-14} + k_{D2}) = k_{14} \cdot E \cdot S + k_{-D2} \cdot ES3 \tag{5}$$

Because of the intramolecular interconversion of the diastereomeric substrate complexes the usual rearrangement becomes impossible, which expresses the substrate complex concentration as a function exclusively of E and S. However, the linear equation system (2)–(5) can be transformed as a whole, using the abbreviations:

$$A = [(k_{21} + k_{-11} + k_{-D1}) \cdot (k_{22} + k_{-12} + k_{D1}) - (k_{D1} \cdot k_{-D1})] \tag{6}$$

$$B = [(k_{23} + k_{-13} + k_{-D2}) \cdot (k_{24} + k_{-14} + k_{D2}) - (k_{D2} \cdot k_{-D2})] \tag{7}$$

$$U = [k_{11} \cdot (k_{22} + k_{-12} + k_{D1}) + (k_{D1} \cdot k_{12})] \tag{8}$$

$$V = [k_{12} \cdot (k_{21} + k_{-11} + k_{-D1}) + (k_{-D1} \cdot k_{11})] \tag{9}$$

$$X = [k_{13} \cdot (k_{24} + k_{-14} + k_{D1}) + (k_{D2} \cdot k_{14})] \tag{10}$$

$$Y = [k_{14} \cdot (k_{23} + k_{-13} + k_{-D2}) + (k_{-D2} \cdot k_{13})] \tag{11}$$

after rearrangement:

$$\mathrm{ES1} = \frac{U}{A} \cdot E \cdot S = K_{\mathrm{ES1}} \cdot E \cdot S \tag{12}$$

$$\mathrm{ES2} = \frac{V}{A} \cdot E \cdot S = K_{\mathrm{ES2}} \cdot E \cdot S \tag{13}$$

$$\mathrm{ES3} = \frac{X}{B} \cdot E \cdot S = K_{\mathrm{ES3}} \cdot E \cdot S \tag{14}$$

$$\mathrm{ES4} = \frac{Y}{B} \cdot E \cdot S = K_{\mathrm{ES4}} \cdot E \cdot S. \tag{15}$$

Introduction of these relations into the balance for the added precatalyst and factorizing E results in an equation, which connects in a usual way the wanted concentration of the free solvent complex (E) and the known initial concentration of the catalyst (E_0).

$$E = \frac{E_0}{1 + S(K_{\mathrm{ES1}} + K_{\mathrm{ES2}} + K_{\mathrm{ES3}} + K_{\mathrm{ES4}})} \tag{16}$$

The consideration of Eqs. (12)–(16) in the product formation rate Eq. (1a), Eq. (1b) leads to:

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{(k_{21} \cdot K_{\mathrm{ES1}} + k_{23} \cdot K_{\mathrm{ES3}}) \cdot E_0 \cdot S}{1 + S \cdot (K_{\mathrm{ES1}} + K_{\mathrm{ES2}} + K_{\mathrm{ES3}} + K_{\mathrm{ES4}})} \tag{17}$$

and

$$\frac{\mathrm{d}P^*}{\mathrm{d}t} = \frac{(k_{22} \cdot K_{\mathrm{ES2}} + k_{24} \cdot K_{\mathrm{ES4}}) \cdot E_0 \cdot S}{1 + S \cdot (K_{\mathrm{ES1}} + K_{\mathrm{ES2}} + K_{\mathrm{ES3}} + K_{\mathrm{ES4}})}. \tag{18}$$

The stoichiometry of the hydrogenation results in a simple equation for the rate of hydrogen consumption under isobaric conditions which can be simply observed as a magnitude proportional to product concentration Eq. (19).

$$-\frac{\mathrm{dH}_2}{\mathrm{d}t} = \frac{\dfrac{(k_{21} \cdot K_{\mathrm{ES1}} + k_{22} K_{\mathrm{ES2}} + k_{23} K_{\mathrm{ES3}} + k_{24} K_{\mathrm{ES4}})}{(K_{\mathrm{ES1}} + K_{\mathrm{ES2}} + K_{\mathrm{ES3}} + K_{\mathrm{ES4}})} \cdot E_0 \cdot S}{\dfrac{1}{(K_{\mathrm{ES1}} + K_{\mathrm{ES2}} + K_{\mathrm{ES3}} + K_{\mathrm{ES4}})} + S} \tag{19}$$

The structure of this relation is analogous to that of the simple Michaelis–Menten-equation [8] (Eq. (20)).

$$-\frac{\mathrm{dH}_2}{\mathrm{d}t} = \frac{k_{\mathrm{obs.}} \cdot E_0 \cdot S}{K_{\mathrm{m}} + S} \tag{20}$$

Also for all the other models discussed before, the respective equations were derived. The relation similar to Eq. (19) for Scheme 1 was already described in [2](b). It turns out that all the reaction sequences mentioned here can be reduced to Eq. (20). Only the physical contents of the macroscopically observed parameters $k_{\mathrm{obs.}}$ and K_{M} differ according to the model chosen. Table 1 summarizes the results, which are obtained assuming stationarity for the respective concentration of the catalyst–substrate complex.

Of course, an exhaustive kinetic description of the catalytic systems is not possible based only on the hydrogen consumption. Nevertheless, the macroscopic obtained constants $k_{obs.}$ and K_M permit conclusions about the catalysis. The value of $1/K_M$ corresponds in all models to the ratio of the concentration sum of all catalyst substrate complexes and the concentration product of E and S. Therefore it is a quantity for the amount of catalyst substrate complex under stationary conditions. This is even true, if the intermolecular equilibria are disturbed. In cases of undisturbed intermolecular equilibria $1/K_M$ corresponds to the sum of all stability constants. The $k_{obs.}$ values are characterized to be the ratio of the maximally obtainable rate and the applied catalyst concentration [$k_{obs.} = (V_{max.}/E_0)$]. In any case they are formed by the sum of all rate constants of the oxidative addition of hydrogen, each multiplied with the molar fraction of the catalyst–substrate complex.

Normally, isobaric conditions are applied, and the rate constants k_{2i} contains the constant hydrogen concentration corresponding to the hydrogen solubility [2]. As can be seen from Table 1, the constant hydrogen concentration can only be separated from $k_{obs.}$ in the case of an established intermolecular preequilibrium, i.e., a linear dependence of the experimental rate constants $k_{obs.}$ on the hydrogen is not necessarily observed, despite the partial reaction order of 1 for hydrogen.

The above discussed interpretation of $k_{obs.}$ and $1/K_M$ is the basis for an orientating estimation of different catalyst systems by use of the overall hydrogen consumption.

Now, this is demonstrated for practical examples. It is known from the literature [10] that five-ring chelates of Rh(I) have in general lower activities in hydrogenations than the corresponding seven-ring chelates. On the other hand, a ring extension from 5 to 7 is accompanied by a decrease of the overall stability constant for the substrate complexes which corresponds to a decrease of the stationary concentrations of catalyst–substrate complexes [10,11]. This conclusion is supported by results of our group for a variety of seven-membered ring chelates. Fig. 1 shows a typical example for the result of a calculation according to Eq. (20), which was taken from Ref. [12] [3].

The reciprocal of the Michaelis constant yields 3.3×10^1 l/mol for the example mentioned. For the system with the five-membered ring chelate DIPAMP a three magnitudes larger value of 3.7×10^4 l/mol was published [2](b) for the overall stability constant (as the upper limit for the reciprocal Michaelis constant). In some cases it is only useful to consider hydrogenations with seven-membered ring chelates to be of first order [4](f) [13], i.e. in the initial range of Eq. (20). So, the reciprocals of the Michaelis constants becomes still smaller [8]. The consequence of these findings from the evaluation of overall hydrogen consumption is that the concentrations of catalyst–substrate complexes are very small in these cases. This might be the reason for the difficulty to isolate single crystals of substrate complexes for seven-membered ring chelates which we unsuccessfully tried to get for X-ray structure analysis. Respective investigations in five-membered ring chelates, which contributed substantially to the elucidation of mechanistic processes (*major / minor* conception), are obviously more favourable with the considerably more stable catalyst–substrate complexes. Perhaps, only such seven-membered ring chelates might offer a useful chance to solve the problem of getting single crystals for substrate complexes, which possesses considerably higher stabilities of these complexes. Macroscopically this becomes evident through an almost constant rate of hydrogenation over the whole conversion range of the substrate, as detected for special hydroxy-phosphines [14].

[2] About the concentration of molecular hydrogen in the liquid phase at hydrogenations under isobaric conditions c.f. [9].

[3] The rate of the hydrogen consumption at time t is estimated by numerical differentiation of the temporal hydrogen consumption. The concentration of the free substrate is evaluated by using the balance $S_0 = S + P$. Initial values for the nonlinear regression are taken from a linearization (Hanes plot).

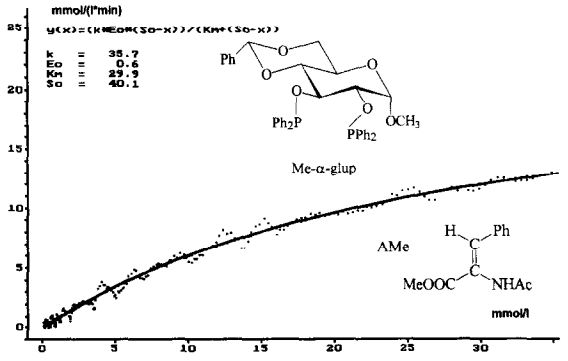


Fig. 1. Comparison of experimental data and those evaluated according to Eq. (20) for the asymmetric hydrogenation of 1.0 mmol methyl (Z)-2-(N)-acetamido-cinnamate (AMe) with [Rh(COD)(Me-α-glup)]BF_4 (0.01 mmol) as precatalyst in 15.0 ml MeOH at 25°C and 1.0 atm total pressure.

Another consequence of the low concentration of the catalyst substrate complex is that all investigation methods giving mixed signals, i.e. UV/Vis spectroscopy or circulardichroism, offer very little information (i.e. about the conformation) about the catalyst–substrate complexes, which are the ones of real interest. To illustrate these fact, Fig. 2 shows the UV/Vis spectrum [4] for the solvent complex $[Rh(Ph\text{-}\beta\text{-glup-OH})(MeOH)_2]^+$ as well as five cyclic recorded spectra after addition of a hundred-fold excess of dimethyl itaconate ($ItMe_2$) under hydrogenation conditions.

The solvent complex and the spectra under hydrogenation conditions do not differ though the substrate complex absorbs in the shown spectra range and the asymmetric hydrogenation proceeds (GC analysis after 30 min hydrogenation: 45% conversion, 67.4% ee (*R*), which is in good accordance with reported results [13]). Obviously the concentration of the solvent complex dominates clearly.

The characterization of the wanted substrate complexes even with the ^{31}P-NMR spectroscopy is possible only at lower temperatures in case of small concentration of catalyst–substrate complexes [4](d), since due to Brown et al. [11](b), [15], the stabilities increase considerably with decreasing temperatures. Unfortunately, the results of such investigations can be extrapolated only with limited validity to usual hydrogenation conditions at room temperature. Thus, for example, the change of rate determining step with decreasing temperature is well known for asymmetric hydrogenations.

However, it should be pointed out here that also the use of the overall hydrogen consumption permits valid interpretations only in the range of the assumed boundary conditions, i.e., the substrate concentration bound to the active catalyst is not considered, which is a useful approximation in large excesses of substrate and high Michealis constants. In case of high substrate conversions and very small Michaelis constants, these can only approximately be determined.

It has been known for a long time that the temperature change does not have an unequivocal influence on the selection processes [7,16].

If there is no reaction product in the system at the beginning at $t = 0$, it becomes possible to evaluate the ratio of the enantiomers for the different models from equations similar to Eq. (17) and Eq. (18), respectively. Table 1 contains the equations for the enantiomer ratio for the basis models mentioned before. The existence of undisturbed preceding equilibria is in each case considered as a boundary.

[4] A description of the UV/Vis experiments using an optical fibre light guide connected to a submersible optrode (Hellma) is given in [6].

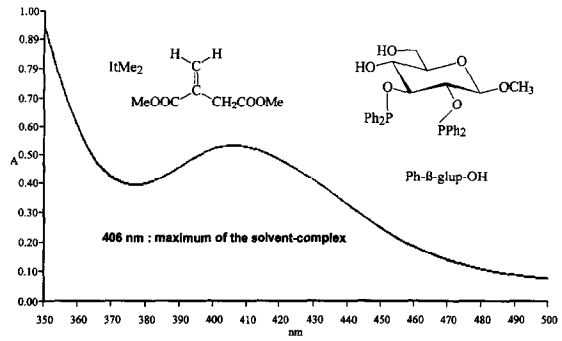


Fig. 2. Spectrum of 0.02 mmol [Rh(Ph-β-glup-OH)$(MeOH)_2$]BF_4 in 35.0 ml of MeOH under argon atmosphere and five spectra (cyclic, every 6 min) after addition of an almost 100-fold excess of dimethyl itaconate ($ItMe_2$) and exchange of argon against hydrogen.

The consideration of temperature dependence in the theoretical sense of the activated complex due to Eyring results [17] is a nonlinear temperature dependence of the enantiomer ratio, if C_1-symmetric ligands are used, and the respective enantiomeric products are formed in two independent ways. Moreover Table 1 shows that the existence of intramolecular exchange processes which are dominant with respect to the intermolecular equilibria on some catalyst systems [4](d–f) is sufficient to cause a nonlinearity in the temperature dependence. Only for the simplest model case, which was already derived in Ref. [2](b), can a linear temperature behaviour be expected, if the preceding equilibria are undisturbed.

If the equilibration is not relevant for the description of the concentration of catalyst–substrate complexes, a nonlinear temperature behaviour is found in any case.

As a summary it can be pointed out that different models based on experimental findings lead to equations similar to the simple Michaelis–Menten equation. Only the content is different from the macroscopic constants which can simply be determined by experimental measurements of the hydrogen consumption. It is common to all the models that the $1/K_M$ value corresponds to the ratio of the sum of all catalyst–substrate complex concentrations and the product of $E \cdot S$. In each case, the $k_{obs.}$ value is to be considered as the sum of all products from the individual rate constants for the oxidative addition of hydrogen and the molar fraction of the corresponding catalyst substrate complex. An orienting description or characterization of different catalytic systems is possible on this basis. Moreover, it could be demonstrated that the temperature dependence of the enantiomer ratio is nonlinear, except in case of the simplest model.

Acknowledgements

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References

[1] H.J. Bittrich, D. Haberland and G. Just, Leitfaden der Chemischen Kinetik, VEB Deutscher Verlag der Wissenschaften, Berlin (1973).
[2] (a) A.S.C. Chan, J.J. Pluth and J. Halpern, J. Am. Chem. Soc. 102 (1980) 5952. (b) C.R. Landis and J. Halpern, J. Am. Chem. Soc. 109 (1987) 1746. (c) B. McCulloch, J. Halpern, M.R. Thompson and C.R. Landis, Organometallics 9 (1990) 1392.

[3] (a) W.R. Cullen and Y. Sugi, Tetrahedron Lett. (1978) 1635. (b) R. Selke, React. Kinet. Catal. Lett. 10 (1979) 135. (c) R. Jackson and D.J. Thompson, J. Organomet. Chem. 159 (1978) C29. (d) R. Selke, J. Organomet. Chem. 370 (1989) 249. (e) T.V. RajanBabu, T.A. Ayers and A.L. Casalnuovo, J. Am. Chem. Soc. 116 (1994) 4101. (f) S.R. Gilbertson and C.W.T. Chang, J. Org. Chem. 60 (1995) 6226.
[4] (a) J.M. Brown, P.A. Chaloner and G.A. Morris, J. Chem. Soc., Chem. Commun. (1983) 664. (b) J.M. Brown, P.A. Chaloner and G.A. Morris, J. Chem. Soc., Perkin Trans. II (1987) 1583. (c) H. Bircher, B.R. Bender and W. v. Philipsborn, Magn. Reson. Chem. 31 (1993) 293. (d) R. Kadyrow, T. Freier, D. Heller, M. Michalik and R. Selke, J. Chem. Soc., Chem. Commun. (1995) 1745. (e) J.A. Ramsden, T.D.W. Claridge and J.M. Brown, J. Chem. Soc., Chem. Commun. (1995) 2469. (f) D. Heller, R. Kadyrov, M. Michalik, T. Freier, U. Schmidt and H.W. Krause, Tetrahedron: Asymmetry, in press.
[5] A.L. Casalnuovo, T.V. RajanBabu, T.A. Ayers and T.H. Warren, J. Am. Chem. Soc. 116 (1994) 9869.
[6] D. Heller, S. Borns, W. Baumann and R. Selke, Chem. Ber. 129 (1996) 85.
[7] (a) H. Buschmann, H.D. Scharf, N. Hoffmann, M.W. Plath and J. Runsink, J. Am. Chem. Soc. 111 (1989) 5367. (b) H. Buschmann, H.D. Scharf, N. Hoffmann and P. Esser, Angew. Chem. Int. Ed. Engl. 30 (1991) 477. (c) K.J. Hale and J.H. Ridd, J. Chem. Soc., Chem. Commun. (1995) 357. (d) K.J. Hale and J.H. Ridd, J. Chem. Soc., Perkin II (1995) 1601. (e) D. Heller, H. Buschmann and H.D. Scharf, Angew. Chem. 108 (1996) 1964
[8] A. Cornish-Bowden, Principles of Enzyme Kinetics (Butterworth, London, 1976).
[9] Y. Sun, R.N. Landau, J. Wang, C. LeBlond and D.G. Blackmond, J. Am. Chem. Soc. 118 (1996) 1348.
[10] C.R. Landis and J. Halpern, J. Organometal. Chem. 250 (1983) 485.
[11] (a) A.S.C. Chan, J.J. Pluth and J. Halpern, Inorg. Chimica Acta 37 (1979) L 477. (b) J.M. Brown and P.A. Chaloner, J. Chem. Soc., Perkin Trans. II (1982) 711.
[12] M. Schwarze, Dissertation, Rostock (1995).
[13] D. Heller, K. Kortus and R. Selke, Liebigs Ann. (1995) 575.
[14] (a) A. Börner, A. Kless, R. Kempe, D. Heller, J. Holz and W. Baumann, Chem. Ber. 128 (1995) 767. (b) D. Heller, S. Borns, A. Kless, J. Holz and A. Börner, unpublished results.
[15] J.M. Brown, P.A. Chaloner, R. Glaser and S. Geresh, Tetrahedron 36 (1980) 815.
[16] (a) H. Pracejus, Liebigs Ann. Chem. 634 (1960) 9. (b) H. Pracejus and G. Kohl, Liebigs Ann. Chem. 722 (1969) 1.
[17] S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes (McGraw-Hill, New York, 1941), Chap.4.