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Kinetic coupling in and between catalytic cycles

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Quasi-equilibrium between catalytic reactive intermediates and reactant or product molecules is a common assumption. As process conditions vary, this assumption may cease to be valid because of kinetic coupling between steps in the catalytic cycle. In the case of coupled catalytic cycles, kinetic coupling manifests itself by substantial changes in selectivity. An elegant example of catalytic coupling in and between catalytic cycles is the change in enantioselection with H_2 pressure for the asymmetric hydrogenation of a prochiral alkene, as discovered in the Halpern laboratory.

Keywords: kinetic coupling; equilibrated steps; one-way steps; asymmetric hydrogenation

1. Introduction

In a catalytic cycle, quasi-equilibrium between reactant or product molecules and reactive (Bodenstein) intermediates bound to the catalyst is frequently assumed for the pertinent elementary steps (or steps for short) in the cycle. This assumption is typical of Michaelis–Menten, Langmuir–Hinshelwood, and Hougen–Watson kinetics in enzymatic, homogeneous, and heterogeneous catalysis. Yet, there exist numerous known exceptions to the assumption of quasi-equilibrium. Even though lack of quasi-equilibrium in one or several steps may not manifest itself in the analytical form of the rate equation, it may affect the turnover rate of the catalytic cycle by kinetic coupling between elementary steps in the cycle. Kinetic coupling may also alter in a subtle way the selectivity of a catalytic process when two or more catalytic cycles are coupled together. As an example of the effect

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of catalytic coupling in and between coupled cycles, the change in enantioselection with H_2 pressure will be discussed for the homogeneous hydrogenation of a prochiral alkene with a chiral catalyst, in the light of exhaustive kinetic work published by the Halpern group.

2. A two-step catalytic reaction: quasi-equilibrium and kinetic coupling

A catalytic cycle is normally made up of many elementary steps, or steps for short. Each step (subscript i) proceeds in a *two-way* manner when its rates v_i and v_{-i} in the forward and reverse direction are of the same order of magnitude, or in a *one-way* manner when $v_i >> v_{-i}$. Sometimes, a two-way step is *quasi-equilibrated* when its net rate $v_i = v_i - v_{-i}$ is much smaller than both v_i and v_{-i}. To avoid complications that are treated elsewhere [1], we consider a simple two-step cycle,

$$* + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A* \tag{1}$$

$$A * + B \xrightarrow{k_2} * + P\,, \tag{2}$$

corresponding to the one-way overall reaction

$$A + B \rightarrow P \tag{3}$$

proceeding at a rate v. The asterisk denotes the free catalytic entity. The total concentration of the catalyst is

$$[L] = [*] + [A*]\,. \tag{4}$$

If $[L] << [A]$, $[B]$, and $[P]$, the *quasi-steady-state approximation* applies, as the catalyst is used in small, so-called catalytic amounts. Thus, at the steady state

$$v = v_1 = v_1 - v_{-1} = v_2 \tag{5}$$

with

$$v_1 = k_1[*][A]\,, \tag{6}$$

$$v_{-1} = k_{-1}[A*]\,, \tag{7}$$

$$v_2 = k_2[A*][B]\,. \tag{8}$$

We want to show what happens kinetically when the pressure of B, say dihydrogen, is either very low (LP) or very high (HP) for the catalytic hydrogenation of A, say an alkene.

First, let us handle the case of LP. Whatever the values of k_{-1} and k_2 may be, a low pressure of B exists for which

$$v_{-1} >> v_2 \tag{9}$$

or

$$k_{-1} >> k_2[\mathrm{B}]\,. \tag{10}$$

Since $v_1 >> v_{-1}$ and $v = v_2$, we have at LP:

$$v_1 \text{ and } v_{-1} >> v = v_2\,. \tag{11}$$

This inequality tells us that the first step is in quasi-equilibrium since its rates forward and reverse are much larger than the net rate and, hence, that the second step is *rate determining* in the sense of Horiuti [1]. The rate is given by

$$v = [\mathrm{L}]\frac{k_2K_1[\mathrm{A}][\mathrm{B}]}{1 + K_1[\mathrm{A}]} \tag{12}$$

with the equilibrium constant $K_1 = k_1/k_{-1}$. Thus the rate determining step is the only step to appear with a rate constant in the expression for the rate. If now the pressure of B is increased progressively, the active intermediate A$*$ will be pumped away more and more by the second step and its steady-state concentration will fall. At the HP limit, in opposition to (9) and (10), new inequalities will hold:

$$v_2 >> v_{-1} \tag{13}$$

or

$$k_2[\mathrm{B}] >> k_{-1} \tag{14}$$

and eq. (11) will be replaced by

$$v = v_1 = v_2\,. \tag{15}$$

Also, since [A$*$] becomes very small, the concentration of free catalytic species, [$*$], becomes practically equal to the total concentration of catalyst, [L], according to eq. (4), so that

$$v = [\mathrm{L}]k_1[\mathrm{A}]\,. \tag{16}$$

Thus, in contrast to the LP case, what happens at HP is that the first step is now the only one that appears through its rate constant in the expression for the overall rate, so that the first step becomes rate determining in the extended sense of the word [2]. At HP, both steps are one-way, while at LP the first step is in quasi-equilibrium and the second step is one-way.

In summary, at LP the two steps are not coupled kinetically and the first step is in quasi-equilibrium. As pressure increases, *kinetic coupling* between the steps becomes important, and the assumption of quasi-equilibrium becomes inadequate, and ultimately both steps are one-way. As a result of kinetic coupling, the rate determining step shifts from the second to the first step, as pressure rises. Kinetic coupling is important in catalytic cycles as it helps in driving forward steps that would otherwise be limited by unfavorable equilibria [3]. The purpose of this Letter is to illustrate the importance of kinetic coupling in shifting selectivity with pressure when two catalytic cycles of the type just considered become coupled in two parallel reactions.

3. Kinetic coupling in coupled catalytic cycles: effect on selectivity

Let us now treat the case of two catalytic cycles similar to the one just considered but coupled through $*$, i.e. the catalytic species. Both cycles are identical except for the values of their rate constants labeled S and R for the left or right cycles respectively (fig. 1). Correspondingly the active intermediates, labeled $A*^S$ and $A*^R$, $*$ are assumed to be the most abundant ones so that

$$[*] + [A*^S] + [A*^R] = [L]\,. \tag{17}$$

The products are now called S and R; they may be treated as final products, although they may not be such, but additional following steps consume the most abundant reactive intermediates. $A*^S$ and $A*^R$ are not kinetically significant, and need not be specified. At the end of the left or right cycle, the catalyst $*$ is regenerated.

As before, at the steady state:

$$v_1^S - v_{-1}^S = v_2^S\,, \quad v_1^R - v_{-1}^R = v_2^R\,. \tag{18}$$

Dividing eqs. (18) side by side, rearranging and expressing the rates in terms of rate constants and concentrations, yields the ratio of concentrations of reactive intermediates

$$\frac{[A*^S]}{[A*^R]} = \frac{k_1^S}{k_1^R}\,\frac{k_{-1}^R + k_2^R[B]}{k_{-1}^S + k_2^S[B]}\,, \tag{19}$$

from which the selectivity, i.e., the ratio of overall rates that is also the ratio of concentrations of products at constant [B] is obtained:

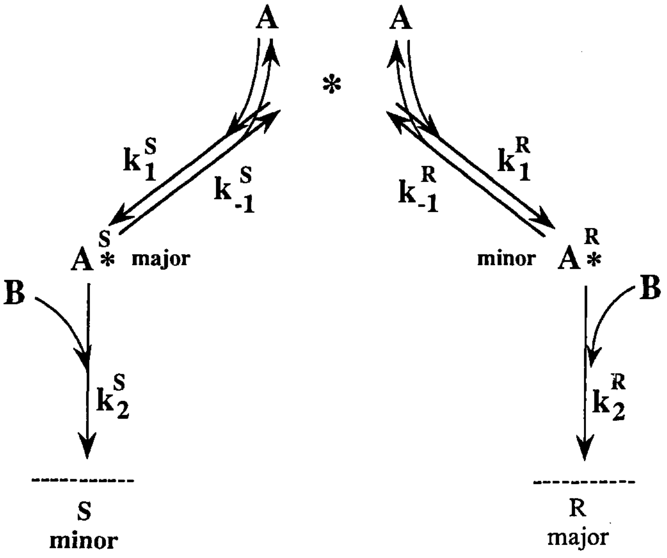

Fig. 1. Scheme of the coupled catalysis cycles.

$$\frac{[\mathrm{R}]}{[\mathrm{S}]}=\frac{v^{\mathrm{R}}}{v^{\mathrm{S}}}=\frac{k_2^{\mathrm{R}}}{k_2^{\mathrm{S}}}\,\frac{k_1^{\mathrm{R}}}{k_1^{\mathrm{S}}}\,\frac{k_{-1}^{\mathrm{S}}+k_2^{\mathrm{S}}[\mathrm{B}]}{k_{-1}^{\mathrm{R}}+k_2^{\mathrm{R}}[\mathrm{B}]}\,. \tag{20}$$

The reason for writing (19) as $[\mathrm{A}{*}^{\mathrm{S}}]/[\mathrm{A}{*}^{\mathrm{R}}]$ on the one hand and (20) as [R]/[S] on the other hand will become apparent later as it turns out that $\mathrm{A}{*}^{\mathrm{S}}$ is the major intermediate but R is the major product. Eqs. (19) and (20) will now be simplified for the two limited cases of low pressure (LP) and high pressure (HP) of B.

At sufficiently low pressure of B

$$k_{-1}^{\mathrm{S}} \gg k_2^{\mathrm{S}}[\mathrm{B}] \quad \text{and} \quad k_{-1}^{\mathrm{R}} \gg k_2^{\mathrm{R}}[\mathrm{B}]\,, \tag{21}$$

so that for both cycles, we have a case of *pre-equilibrium* followed by a rate determining step. The ratio of concentrations of most abundant reactive intermediates and the selectivity simplify to

$$\frac{[\mathrm{A}{*}^{\mathrm{S}}]}{[\mathrm{A}{*}^{\mathrm{R}}]}=\frac{[K_*^{\mathrm{S}}]}{[K_*^{\mathrm{R}}]}\,, \tag{19L}$$

$$\frac{[\mathrm{R}]}{[\mathrm{S}]}=\frac{k_2^{\mathrm{R}}\,K_1^{\mathrm{R}}}{k_2^{\mathrm{S}}\,K_1^{\mathrm{S}}}\,. \tag{20L}$$

On the other hand, at sufficiently high pressures of B,

$$k_{-1}^{\mathrm{S}} \ll k_2^{\mathrm{S}}[\mathrm{B}]; \quad k_{-1}^{\mathrm{R}} \ll k_2^{\mathrm{R}}[\mathrm{B}]\,, \tag{22}$$

we have a case of kinetic coupling, with

$$\frac{[\mathrm{A}{*}^{\mathrm{S}}]}{[\mathrm{A}{*}^{\mathrm{R}}]}=\frac{k_1^{\mathrm{S}}}{k_1^{\mathrm{R}}}\,\frac{k_2^{\mathrm{R}}}{k_2^{\mathrm{S}}}\,, \tag{19H}$$

$$\frac{[\mathrm{R}]}{[\mathrm{S}]}=\frac{k_1^{\mathrm{R}}}{k_1^{\mathrm{S}}}\,. \tag{20H}$$

In particular, it must be noted that the selectivity does not depend on pressure at low or high pressure. But between low and high pressure, selectivity depends on pressure according to eq. (20), through a ratio of sums of terms that are the ones involved in the inequalities (21) and (22) that, in turn, determine low and high pressure behavior respectively.

4. Application to asymmetric catalytic hydrogenation

The effect of pressure of dihydrogen on the enantiomeric selectivity for hydrogenation of an alkene with a soluble organometallic chiral catalyst has been studied exhaustively in Halpern's laboratory, together with a quantitative determination of all the rate constants shown in fig. 1 and table 1, and the identification of the active intermediates [4–7]. These studies are not only unique in catalytic kinetics, but they rapidly became a textbook example [8] because of their unexpected striking implications. The data of Halpern et al. also offer the only *quantitative* example of kinetic coupling in the literature of homogeneous, heterogeneous, and enzymatic catalysis.

The first surprising implication of this work was that the enantiomer R was the major one, i.e., more abundant, because of the higher rate constant for the oxidative addition of H_2 to the active intermediate $A*^{R}$. Yet it was the other active intermediate $A*^{S}$ that was major, i.e., more abundant. Indeed, as seen in table 1, the equilibrium constant K_1^S for the binding of the alkene to the catalyst is more than 10 times higher than the value of K_1^R. Thus, the conventional wisdom based on the lock and key analogy fails in this uniquely documented situation: the large enantiomeric selectivity is ordained not by thermodynamics, but in spite of thermodynamics, by kinetics, as the rate constant for reaction of $A*^{R}$ with H_2 is almost 60 times larger than that of addition of H_2 to $A*^{S}$.

The second surprising implication was the discovery that this kinetically controlled selectivity, [R]/[S], decreased with increasing pressure of H_2. The reason, again, is a kinetic one. As pressure rises, the steady-state concentration of $A*^{R}$ decreases faster than the steady state concentration of $A*^{S}$ because $k_2^R > k_2^S$: i.e., the kinetic coupling on the R branch is stronger than that on the S branch. This can be seen more simply by using eqs. (19L) and (19H) as well as (20L) and (20H) with the assumption that all rate constants of fig. 1 are equal, in the units of table 1, except that the "pumping away" rate constant for the R branch k_R is taken to be 100 times larger than that for the S branch. Then at the low pressure thermodynamic limit, the steady state concentrations of $A*^{R}$ and $A*^{L}$ are identical and equal to their equilibrium values, and the selectivity, [R]/[S], is equal to 100 in favor of R. By contrast, at the high pressure or kinetic coupling limit, the selectivity is down to unity, as the steady-state concentration of $A*^{R}$ has fallen to one hundredth of the corresponding value of $A*^{S}$. The effect of kinetic coupling appears very clearly in this simple illustration.

Finally, let us note that in the work of the Halpern group, as seen from table 2, all experimental data were obtained in between the thermodynamic (LP) and kinetic coupling (HP) limits, so that neither limiting assumption was strictly valid.

Table 1
Parameters for the asymmetric hydrogenation of methyl-(Z)-α-acetamidocinnamate catalyzed by {1,2-bis((phenyl-*o*-anisoyl)phosphino)ethane} rhodium(I). Values at 298 K [a]

See fig. 1	S branch	R branch
k_1 (ℓ mmol^{-1} s^{-1})	5.3	11
k_{-1} (s^{-1})	0.15	3.2
K_1 (ℓ mmol^{-1})	35	3.3
k_2 (ℓ mmol^{-1} s^{-1})	1.1×10^{-3}	0.64

[a] From Landis and Halpern, ref. [7].

Table 2
Enantiomeric selectivity: [R] / [S], at 298 K from Landis and Halpern, ref. [7], table V

p_{H_2} (atm)	[R] / [S]
LP limit eq. (20L) [a]	54
0.35	49
1.1	24
9.07	6.6
HP limit eq. (20H) [a]	2

[a] From parameters of table 1.

5. Conclusion

In the light of the original findings of Halpern and co-workers, it appears that kinetic coupling between steps in coupled catalytic cycles may affect profoundly product selectivity. Kinetic coupling can be modified by changing process variables such as concentration and temperature. The concept of kinetic coupling applies to all catalytic cycles. Its importance for selectivity may ultimately be revealed in heterogeneous catalysis thanks to the growing application of the microkinetic methodology of Dumesic et al. [9]. That methodology permits a numerical calculation of rates and selectivity from known, calculated, estimated, or guessed values of rate constants of elementary steps. This calculation does not rely on any a priori assumption of quasi-equilibria, kinetic coupling, rate determining step, or most abundant reactive intermediates. Rather, these simplifying features [1] appear as a result of the microkinetic methodology.

References

[1] M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton University Press, Princeton, 1984) p. 80 (in French: Masson, Paris, 1982).
[2] M. Boudart and K. Tamaru, Catal. Lett. 9 (1991) 15.
[3] M. Boudart, J. Phys. Chem. 87 (1983) 2786.
[4] J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, J. Am. Chem. Soc. 99 (1977) 8055.
[5] J. Halpern, Science 217 (1982) 401.
[6] J. Halpern, Pure Appl. Chem. 55 (1983) 99.
[7] C.R. Landis and J. Halpern, J. Am. Chem. Soc. 109 (1987) 1746, 6217.
[8] J.P. Collman, L.S. Hegedus, J.R. Norton, and R. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd Ed. (University Science Books, Mill Valley, 1987) pp. 538–541.
[9] J.A. Dumesic, D.F. Rudd, L.M. Aparicio, J.E. Rekoske and A.A. Treviño, *The Microkinetics of Heterogeneous Catalysis* (American Chemical Society, Washington, 1993).