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Interpretation of rate optima *vs* reaction parameters in steady state catalytic kinetics: Molecular aspects beyond concentration dependences

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A B S T R A C T

Steady state catalytic reactions often exhibit rate maxima not only as a function of concentration, but also of other reaction parameters such as solvent polarity, Hammett substitution constants or metal cluster size. Analysis of several generic schemes operative in homogeneous and heterogeneous catalysis and comprise linear steps was made showing that kinetic expressions after incorporating dependence of rate constants on abovementioned reaction parameters can be used to model experimental data. Rate minima in steady state reactions depending on substituent constants cannot be easily explained by single route conventional mechanisms even after considering nonlinear steps. Such cases are conventionally explained by a switch in reaction mechanisms. An alternative developed in this study assumes presence of mechanistically similar parallel routes involving at least two different catalytically active species. The advanced model based on two step sequence is capable of explaining concave upward Hammett plots.

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1. Introduction

Kinetic analysis of complex reaction mechanisms is becoming a routine tool nowadays in physical organic chemistry and chemical reaction engineering [1–5]. When the reactions are controlled by some key steps in the reaction sequence, typically the concept of a rate determining steps is applied [6], helping to reduce the complexity of derivation. So-called microkinetic models are used when several steps contribute to the overall kinetics [7].

In deriving the kinetic equations of multistep reactions the concentrations of intermediates are assumed to be steady-state (or stationary). A reaction is at steady-state if the concentration of all species in each element of the reaction space (i.e. volume in the case of a homogeneous reaction or surface in the case of a heterogeneous reaction) does not change in time.

In a steady-state reaction the concentration of an intermediate does not change in time because the sum of the formation rates of this species in elementary reactions is equal to the sum of the rates of its consumption in other elementary reactions. A set of stoichiometric numbers of the stages producing an overall reaction equation is called reaction route [8]. Each route must be essentially different and it is impossible to obtain one route from another through multiplication by a number, even if their respective overall equations can be identical.

Quasi-steady state approximation (QSSA) of Bodenstein [9] is routinely used in derivation of kinetic equations for complex reaction mechanisms. However, recent analysis of QSSA in the case of a two-step sequence [10] has demonstrated the limitations of this approach to describe reaction dynamics. In general QSSA is not necessary and numerical solutions of differential equations for intermediate and terminal species can be made. Such approach is mainly used in studying reaction concentration dynamics (relaxation to steady-state, various nonlinear phenomena, such as oscillations, etc) when under nonstationary conditions the concentrations of intermediates in the catalytic cycles are at a non-steady state [2,11].

In chemical industry, the majority of processes are conducted in stationary conditions. Hence, it is not surprising that the steady-state kinetics is mainly studied, when the concentration of intermediates is time independent.

In order to derive kinetic equations QSSA is thus routinely used for complex reactions networks. Such networks typically consist of linear and nonlinear steps. As an example let us consider a sim-
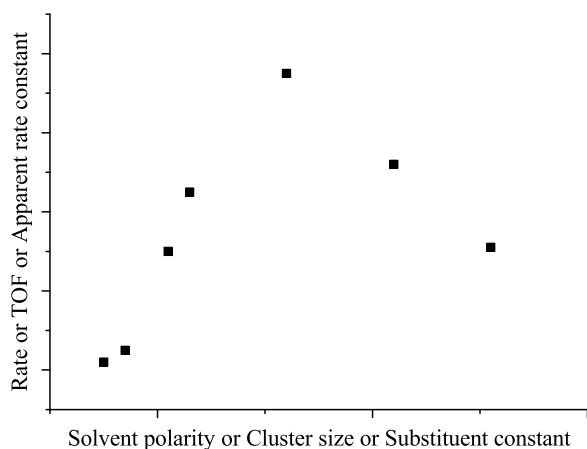
Fig. 1. Dependence of turnover frequency on reaction parameters.

ple mechanism of heterogeneous catalytic hydrogen oxidation with two reaction routes.

	$N^{(1)}$	$N^{(2)}$
1. $O_2 + 2Z \rightarrow 2\,ZO$	1	1
2. $H_2 + 2Z \leftrightarrow 2\,ZH$	0	2
3. $ZO + ZH \rightarrow ZOH + Z$	0	2
4. $ZOH + ZH \rightarrow H_2O + 2Z$	0	2
5. $ZO + H_2 \rightarrow H_2O + Z$	2	0

$N^{(1)}, N^{(2)} : O_2 + H_2 = 2H_2O$　　　　　　　　　　　　　　　　　(1)

In Eq. (1) Z stands for surface sites. In derivation of kinetic expressions adsorption steps 1 and 2 are typically considered to be fast (quasi-equilibria). Steps 3 and 4 in Eq. (1) are nonlinear steps, having concentrations of both intermediates in the kinetic equation of this elementary step, such as for example

$$r_3 = k_3 \theta_H \theta_O \qquad (2)$$

while step 5 is linear with the corresponding linear rate equation

$$r_5 = k_5 P_{H_2} \theta_O \qquad (3)$$

For many catalytic reactions with several non-linear steps derivation of kinetic equations could be challenging. In order to avoid such difficulties Lazman and Yablonsky [12] applied constructive algebraic geometry to nonlinear kinetics expressing the reaction rate of a complex reaction as an implicit function of concentrations and temperature. This concept of kinetic polynomial has found important applications including parameter estimation, analysis of kinetic model identifiability, and, finding all steady states of kinetic models. It can be argued; however [2], that mechanism-free polynomial expressions are in general not reliable, not being able to predict reaction rates, concentration and temperature dependence outside the experimental conditions. Models based on the knowledge of elementary processes provide reliable extrapolation outside of the experimentally studied domain contributing also to better intellectual understanding of the chemical system under consideration.

A so-called Langmuir-Hinshelwood mechanism with a nonlinear step (step 3 in 1) represented by the route $N^{(2)}$ in Eq. (3) gives a rate expression which display a maximum in the reaction rate as a function of reactants concentrations.

Quite often reaction rates or turnover frequencies (TOF) exhibit rate maxima as a function of some other parameters, such as for example solvent polarity, Hammett substituent constant or metal cluster size (Fig. 1).

Influence of the solvent polarity or substituent constants is discussed in detail for elementary reactions and is treated in almost

every textbook on chemical kinetics. Impact of cluster size is also addressed in more specialized monographs [1].

At the same time such treatment for elementary reactions applied directly to elementary reactions, can be also utilized for complex multistep reactions, which comprise different elementary reactions occurring jointly and related to each other by having some of the participating species in common.

In the current work we would like to analyse several generic schemes typical for homogeneous and heterogeneous catalysis incorporating the reaction parameters (solvent or substituent properties, or cluster size) directly into the rate equations.

It would be shown that maxima of the rates as a function of abovementioned reaction parameters can be adequately described by the corresponding rate expressions. Much more challenging is explanation of the rate minima. An attempt was made to explore reaction schemes which contain in one reaction route not only kinetically significant linear, but also nonlinear steps. Such approach in principle can be used for heterogeneous catalytic reactions, as well as homogeneous (enzymatic) catalysis with the only difference that a slight different balance equation should be used for catalytic species.

It is apparently clear that in general the full dynamic analysis of a complex reaction scheme with linear and nonlinear steps is preferred. However, there are important applications of chemical kinetics in physical organic chemistry when analytical solutions for reaction mechanisms comprising linear and nonlinear steps could be of high importance to rationalize observed experimental data for steady state kinetics.

It would be demonstrated that the cases of rate minima exemplified by concave upward Hammett plots cannot be explained by single route conventional mechanisms even after incorporation of nonlinear steps and require inclusion in reaction mechanisms of either parallel routes or several catalytic sites.

2. Two-step sequence with linear steps

2.1. Influence of substrate structure

Influence of the substrate structure in (catalytic) kinetics related to physical organic chemistry is mainly discussed using the approach of Hammett for substrates with substituents in the aromatic ring [13] or by Taft equation valid for aliphatic substrates [14].

Linear free energy relationship was originally applied by Hammett to predict the influence of substituents in the aromatic ring on the reaction rates. It relates the rate constant of a particular reaction k with dissociation constants of substituted benzoic acids K and takes the form

$$lg\left(\frac{k}{k_o}\right) = \rho lg\left(\frac{K}{K_o}\right) = \rho\sigma \qquad (4)$$

where k_0 and K_0 are values corresponding to R = H, ρ is the reaction constant characteristic of a particular reaction of Y, σ is the substituent constant $\sigma = lg(K/Ko)$. For the substituent constant, if $\sigma > 0$, than the functional group R attracts electrons stronger than H, in the opposite case $\sigma < 0$, R attracts electrons weaker than H.

Other models accounting for example for the resonance effect or steric constrains have been proposed. Thus an extended Taft equation for aliphatic systems is

$$lg\left(\frac{k}{k_O}\right) = \rho * \sigma * + \delta E_S + \psi \qquad (5)$$

where σ^* is the polar substituent constant, E_s is the steric substituent constant, δ is the reaction constant, which being independent of the nature of the substituents gives a measure of the relative susceptibility of the reaction series to the steric require-