



Requiem for the Rate-Determining Step in Complex Heterogeneous Catalytic Reactions?

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Article

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Abstract: The concept of the rate determining step, i.e., the step having the strongest influence on the reaction rate or even being the only one present in the rate equation, is often used in heterogeneous catalytic reactions. The utilization of this concept mainly stems from a need to reduce complexity in deriving explicit rate equations or searching for a better catalyst based on the theoretical insight. When the aim is to derive a rate equation with eventual kinetic modelling for single-route mechanisms with linear sequences, the analytical rate expressions can be obtained based on the theory of complex reactions. For such mechanisms, a single rate limiting step might not be present at all and the common practice of introducing such steps is due mainly to the convenience of using simpler expressions. For mechanisms with a combination of linear and nonlinear steps or those just comprising non-linear steps, the reaction rates are influenced by several steps depending on reaction conditions, thus a reduction in complexity to a single rate limiting step can lead to misinterpretations. More widespread utilization of a microkinetic approach when the reaction rate constants can be computed with reasonable accuracy based on the theoretical insight, and availability of software for kinetic modelling, when a system of differential equations for reactants and products will be solved together with differential equations for catalytic species and the algebraic conservation equation for the latter, will eventually make the concept of the rate limiting step obsolete.

Keywords: rate determining step; linear steps; nonlinear steps

1. Introduction

The kinetics of heterogeneous catalytic reactions has been the focus of numerous studies because of its theoretical and practical importance [1–10]. Kinetic analysis was applied for decades to assist reactor design and scaling up of various reactions relevant for oil refining and synthesis of basis and specialty chemicals. More recently, because of a widespread application of so-called flow chemistry to streamline pharmaceutical research and products, kinetic analysis also started to be more widely utilized in the field of fine chemicals [11–13]. It was argued [11] that the framework of a mechanistically based rate equation combined with in situ experimental data is useful for the interpretation of complex reaction networks. Increasing complexity of the catalytic reactions, either relevant for oil refining or pharmaceutical synthesis, poses some restrictions regarding incorporation of such complex mechanisms into tractable rate equations.

Thus, another trend is to simplify complex reaction networks and assume that there is a limiting step, the rate of which is a good approximation of the reaction rate of the whole network [14,15]. This approach of a rate-determining step (RDS) became very popular in chemical reaction engineering, allowing the derivation of kinetic equations for reaction mechanisms of differing complexity. Such an assumption of a rate-determining step makes the rate expressions more tractable, facilitating the kinetic modelling of mainly steady-state kinetics even at the expense of losing important mechanistic information. Moreover, in several instances, without a substantial reduction in complexity, kinetic modelling can be computationally very demanding, especially when coupled with transport phenomena [16].

On the other hand, the concept of RDS was suggested to give fruitful ideas for modifying the reaction conditions or design the catalyst. Subsequently, there have been many theoretical papers addressing how to determine the step which is the rate determining [17,18]. The most popular is probably the degree of rate control proposed by Campbell, based on the general principles of differential sensitivity analysis to determine sensitivity of the output to one input parameter [19–25]. It was argued [16] that an approach analogous to electrical networks is even better suited for the identification of the key steps determining the reaction rate allowing the derivation of accurate rate expressions even for mechanisms with nonlinear steps. Such nonlinear steps are present not only in heterogeneous catalytic reactions, such as, for example, a water gas shift reaction [16], decomposition of ammonia [26,27] or methanol [28], but also in organometallic catalysis. In the latter case, the reaction order in catalysts deviates from unity [5]. The formation of dimeric catalytic species, on the contrary, results in the reaction order being below one, which is rather rare [29–31].

Contrary to the case of linear (Christiansen) sequences of a single-route reaction [5,32,33] for single-route mechanisms with nonlinear steps, a general expression for the reaction rate in steady-state and quasi-steady-state conditions cannot be derived [34]. When such derivation is possible, the rate expressions become rather complicated to handle [5,35–37].

To overcome difficulties in deriving explicit rate expressions, a semi-empirical kinetic polynomial was proposed [38] as a substitute of analytical rate equations.

However, in catalysis by solids or organometallic complexes, quite often either there are nonlinear steps involved or the rate equations for even single-route mechanisms and obviously multi route reactions do not have rate limiting steps [34].

It was recognized a long time ago that for multi-route (or composite) reactions, the concept of the rate-controlling steps is not required [34,39], while in other cases it should be considered with care, as misinterpretation is easily possible.

In the current work, several cases of complex single- and multi-route heterogeneous catalytic reactions will be presented, highlighting an apparent danger of falling into a trap of using the rate determining step, which leads to confusion rather than clarification of reaction mechanisms.

2. Three Step Sequence

Let us consider first a three-step linear sequence (Figure 1)



Figure 1. Potential energy diagram using Gibbs energy and Gibbs activation energy for the reaction S->P. T_1 – T_3 represent transition states, and I_1 – I_2 intermediates, I_0 is the free form of catalyst. Adapted from [40].

The general equation for this three-step sequence in the case of all reversible steps can be written in a form of frequencies of steps [6]

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3} - \omega_{-1}\omega_{-2}\omega_{-3}}{\omega_{+2}\omega_{+3}\omega_{+2} + \omega_{-3}\omega_{-2} + \omega_{+3}\omega_{+1} + \omega_{-1}\omega_{+3} + \omega_{-1}\omega_{-3} + \omega_{+1}\omega_{+2} + \omega_{-2}\omega_{+1} + \omega_{-2}\omega_{-1}}C_{cat}$$
(1)

where *r* is the reaction rate, ω_{+1} is the frequency of step 1, etc., and C_{cat} is the catalyst concentration. The frequencies of steps are obtained by dividing the rate expressions of a particular step by the concentration of catalytic species in that expression. For example, in the case of the reaction mechanism presented in Figure 2, the general form of the Equation (1) gives [6]



Figure 2. Three-step direct ethylene hydrogenation mechanisms.

Thus, the frequency of the first step in the forward direction is $k_{+1}C_{H_2}$, while for the reverse step it would be just k_{-1} . When all steps are irreversible, Equation (2) can be easily simplified, giving

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3}}{\omega_{+2}\omega_{+3}+\omega_{+3}\omega_{+1}+\omega_{+1}\omega_{+2}}C_{cat} = \frac{k_{+1}C_{H_2}k_{+2}C_{C_2H_4}k_{+3}C_{cat}}{k_{+2}k_{+3}+k_{+3}k_{+1}C_{H_2}k_{+1}C_{H_2}k_{+2}C_{C_2H_4}} = \frac{k_{+1}C_{H_2}C_{C_2H_4}C_{cat}}{1+\frac{k_{+1}}{k_{+2}}C_{H_2}+\frac{k_{+1}}{k_{+2}}C_{H_2}C_{C_2H_4}}$$
(3)

It follows from Equation (3) that depending on the values of partial pressures of, for example, hydrogen, the reaction order can change from unity at low pressures, to zero at high hydrogen pressures. The relative contribution of the last term in the denominator of Equation (3) $k_{+1}C_{H_2}C_{C_2H_4}/k_{+3}$ in comparison with two other terms defines the reaction order towards ethylene.

This example illustrates an apparent danger of defining the rate and even more turnover frequency through just one rate limiting step without taking into account kinetic regularities. To highlight the need to consider all steps in a linear catalytic sequence even further, let us consider the apparent activation energy for the three-step mechanism (Equation (3)). In what follows, the term "apparent" corresponds to the observed activation energy of a complex multistep reaction in the kinetic regime, which should not be confused with the case when the observed kinetics is influenced by the transport phenomena.

A more simple case of the two-step sequence was addressed in the literature [41] using the definition of the apparent activation energy

$$E_{\rm a,app} = -R \frac{\partial \ln r}{\partial (1/T)} \tag{4}$$

and giving

$$E_{a,app} = \frac{\omega_{+2}}{\omega_{+1} + \omega_{+2}} E_{a,1} + \frac{\omega_{+1}}{\omega_{+1} + \omega_{+2}} E_{a,2}$$
(5)

As follows from Equation (5), the apparent activation energy depends not only on the step with the highest activation energy, but also on the contribution of the other step with a lower activation energy. For the three-step sequence using Equations (3) and (4), one gets

$$E_{a,app} = RT^{2} \frac{\partial}{\partial T} (\ln k_{+1} + \ln C_{H_{2}} + \ln k_{+2} + \ln C_{C_{2}H_{4}} + \ln k_{+3} + \ln C_{cat} - \ln(k_{+2}k_{+3} + k_{+3}k_{+1} C_{H_{2}} + k_{+1}C_{H_{2}}k_{+2}C_{C_{2}H_{4}}))$$
(6)

Some terms in Equation (6) can be easily differentiated

$$\frac{\partial}{\partial T}(\ln k^{0}_{+1} \exp(-E_{+1}/RT) = \frac{\partial}{\partial T}(\ln k^{0}_{+1} - E_{+1}/RT) = \frac{E_{+1}}{RT^{2}}$$
(7)

Taking Equation (7) into account and also using a standard approach for the differentiation of a complex function

$$\frac{\partial \ln U}{\partial T} = \frac{\partial \ln U}{\partial U} \frac{\partial U}{\partial T} = \frac{1}{T} \frac{\partial U}{\partial T}$$
(8)

one gets the final expression for the activation energy of a three step sequence

$$E_{a,app} = \frac{\omega_{+2}\omega_{+3}E_{a,1} + \omega_{+1}\omega_{+3}E_{a,2} + \omega_{+1}\omega_{+2}E_{a,3}}{\omega_{+2}\omega_{+3} + \omega_{+3}\omega_{+1} + \omega_{+1}\omega_{+2}}$$
(9)

It can be shown that in only exceptional cases the apparent activation energy of the overall reaction is determined by the activation energy of only one rate-limiting step in a steady-state sequence.

3. Four Step Sequence

As an example of such a sequence, the liquid-phase hydrogenation of aromatic compounds will be considered. The reaction kinetics was extensively investigated previously in [42–46]. The following generic scheme for hydrogenation of an aromatic compound A to the product B was proposed

$$1.*A + H_{2} \Leftrightarrow *AH_{2}$$

$$2.*AH_{2} + H_{2} \Leftrightarrow *AH_{4}$$

$$3.*AH_{4} \Rightarrow *Y$$

$$3'.*Y + H_{2} \Leftrightarrow *B \text{ (fast)}$$

$$\frac{4.*B + A \Xi *A + B}{A + 3H_{2} = B}$$
(10)

where Y is cyclohexene or its derivative, AH_2 and AH_4 are intermediate complexes, step 3' is fast because hydrogenation of cycloalkenes is much faster than aromatic compounds and step 4 is at quasi-equilibrium.

A general equation for the four step sequence is [6]

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3}\omega_{+4} - \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}}{D}C_{cat}$$
(11)

where

$$D = \omega_{+2}\omega_{+3}\omega_{+4} + \omega_{-1}\omega_{+3}\omega_{+4} + \omega_{-1}\omega_{-2}\omega_{+4} + \omega_{-1}\omega_{-2}\omega_{-3} + \omega_{+1}\omega_{+2}\omega_{+3} + \omega_{-4}\omega_{-1}\omega_{+3} + \omega_{-4}\omega_{-1}\omega_{-2} + \omega_{+4}\omega_{+1}\omega_{+2} + \omega_{-3}\omega_{+1}\omega_{+2} + \omega_{-3}\omega_{-4}\omega_{+2} + \omega_{-3}\omega_{-4}\omega_{-1} + \omega_{+3}\omega_{+4}\omega_{+1} + \omega_{-2}\omega_{+4}\omega_{+1} + \omega_{-2}\omega_{-3}\omega_{+1} + \omega_{-2}\omega_{-3}\omega_{-4}$$
(12)

Because of irreversibility of step (3), Equations (11) and (12) can be simplified

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3}\omega_{+4}}{D}C_{cat} \tag{13}$$

$$D = \omega_{+2}\omega_{+3}\omega_{+4} + \omega_{-1}\omega_{+3}\omega_{+4} + \omega_{-1}\omega_{-2}\omega_{+4} + \omega_{+1}\omega_{+2}\omega_{+3} + \omega_{-4}\omega_{+2}\omega_{+3} + \omega_{-4}\omega_{-1}\omega_{+3} + \omega_{-4}\omega_{-1}\omega_{-2} + \omega_{+4}\omega_{+1}\omega_{+2} + \omega_{+3}\omega_{+4}\omega_{+1} + \omega_{-2}\omega_{+4}\omega_{+1}$$
(14)

Step 4 is at quasi-equilibrium, and therefore the rates are fast in both directions. Further simplifications of Equation (13) are thus possible by dividing the numerator and the denominator by ω_{+4} , neglecting subsequently the terms $\omega_{+1}\omega_{+2}\omega_{+3}/\omega_{+4}$ and $\omega_{-3}\omega_{+1}\omega_{+2}/\omega_{+4}$. Then the following holds

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3}}{(\omega_{+2}\omega_{+3} + \omega_{-1}\omega_{+3} + \omega_{-1}\omega_{-2})(1 + \frac{\omega_{-4}}{\omega_{+4}}) + \omega_{+1}\omega_{+2} + \omega_{+3}\omega_{+1} + \omega_{-2}\omega_{+1}}C_{cat}$$
(15)

Replacing frequencies in Equation (15) with the explicit expressions, one gets

$$r = \frac{k_{+1}C_{H_2}k_{+2}C_{H_2}k_{+3}}{(k_{+2}C_{H_2}k_{+3} + k_{-1}k_{+3} + k_{-1}k_{-2})(1 + \frac{C_B}{K_4C_A}) + k_{+1}C_{H_2}k_{+2}C_{H_2} + k_{+3}k_{+1}C_{H_2} + k_{-2}k_{+1}C_{H_2}}C_{cat}$$
(16)

where $K_4 = k_{+4}/k_{-4}$. For a binary mixture of the reactant and substrate, it is possible to use mole fractions instead of concentrations. Moreover, quite often partial pressures of hydrogen are applied instead of concentrations, resulting in another form of the rate equation

$$r = \frac{k_{\prime+1}P_{H_2}k_{\prime+2}P_{H_2}k_{+3}}{(k_{\prime+2}P_{H_2}k_{+3} + k_{-1}k_{+3} + k_{-1}k_{-2})(1 + \frac{1 - N_A}{K_4N_A}) + k_{\prime+1}P_{H_2}k_{\prime+2}P_{H_2} + k_{+3}k_{\prime+1}P_{H_2} + k_{-2}k_{\prime+1}P_{H_2}}C_{cat}$$
(17)

where N_A is the mole fraction of the reactant. Equation (16) contains the modified rate constants $k_{\prime+1}$; $k_{\prime+2}$ as instead of hydrogen concentration in the liquid phase, the pressure of hydrogen is used.

Equation (17) presented in a slightly different form

$$r = \frac{\frac{k_{+1}k_{+2}k_{+3}}{k_{+3}k_{+1}k_{-2}k_{+1}+k_{+2}k_{+3}}P_{H_2}N_AC_{out}}{\frac{k_{-1}k_{+3}+k_{-1}k_{-2}}{k_{+3}k_{+1}+k_{-2}k_{+1}+k_{+2}k_{+3}+k_{+1}+k_{-2}(1-N_A)}}{\frac{k_{+2}k_{+3}k_{+1}+k_{-2}k_{+3}+k_{+2}+k_{+3}+k_{+2}+k_{+3}+$$

was derived in [43] using a more tedious procedure, namely applying directly the steady-state conditions

$$\mathbf{r}_{+1} - \mathbf{r}_{-1} = \mathbf{r}_{+2} - \mathbf{r}_{-2} = \mathbf{r}_{+3} \tag{19}$$

as well as the quasi-equilibrium for step 4 and finally the balance equation (i.e., the sum of all coverages is equal to unity).

All steps in Equation (10) are needed to explain the observed kinetic regularities, because it was demonstrated that at low hydrogen partial pressures, the reaction order in hydrogen can exceed unity, which is possible when $k_{-1} \neq 0$, while at high pressures the reaction kinetics obeys frequently observed zero orders in the substrate and hydrogen. In the latter case, the overall rate is determined by the isomerization of the adsorbed AH₄ species. The surface of the catalyst is completely covered with this complex and the reaction rate ceases to depend on either hydrogen pressure or the concentration of the substrate.

Apparently, the concept of a single rate-determining step is not able to account for a rich kinetic behavior, observed experimentally in hydrogenation of aromatics.

4. Oxidative Dehydrogenation of Ethanol: A Multi-Route Mechanism with Nonlinear Steps

The mechanism and kinetics of oxidative dehydrogenation of ethanol over gold catalysts was recently reported [47]. DFT calculations indicated that the activation of molecular oxygen is facilitated in the presence of ethanol acting as a hydrogen donor. As a result of hydrogen abstraction from the

donor leading to the formation of an OOH intermediate, the dioxygen undergoes dissociation on the catalyst surface. The scheme of the reaction mechanism is given below

N ^(1a)	$N^{(1b)}$	N ^(1c)	
1	1	1	
2	2	2	
2	1	2	
2	1	1	
2	2	2	(20)
2	2	2	
1	0	0	
0	1	0	
0	0	1	
	N ^(1a) 1 2 2 2 2 1 0 0 0	$\begin{array}{ccc} N^{(1a)} & N^{(1b)} \\ 1 & 1 \\ 2 & 2 \\ 2 & 1 \\ 2 & 1 \\ 2 & 2 \\ 2 & 2 \\ 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

In (20), on the right hand side of the equations for the steps (i.e., 1 to 7c), the stoichiometric numbers (i.e., 0, 1, 2) along alternative routes $N^{(1a)} - N^{(1c)}$ are given [32]. These numbers can be equal to zero, if a particular step is not involved in the reaction mechanism. In Equation (20), EtOH stands for ethanol, while AcH represents acetaldehyde and * denotes a surface site.

According to the DFT calculations [47] illustrated in Figure 3, the largest activation barrier corresponds to step 3 in Equation (20), and thus superficially it can be considered in the conventional approaches as the rate limiting step. However, the activation energy of the same step in the reverse direction is very low and step 3 can even be viewed to be close to the quasi-equilibrium.



Figure 3. The minimum energy path for ethanol (EtOH) dehydrogenation. The black and orange bars correspond to minima and transition states, respectively. * denotes adsorbed species, while (g) refers to gas phase species. Square brackets enclose a transition state structure where ' - -' marks the bond being broken. Reproduced with permission from [47].

From the considerations above on the apparent activation energy of the three-step sequence with linear steps, it is clear that the apparent activation energy and the reaction rate depend on the contribution of all steps in the mechanism, which could be treated using the steady-state approximation. This approach is possible because of the specific features of the reaction mechanism comprising only nonlinear steps and thus allowing derivation of an analytic rate expression. Such derivation was done in [47] based on the DFT computed reaction energies assuming quasi-equilibria for steps 1 and 2, irreversibility for steps 4 and 5 and reversibility for steps 3 and 6.

From the viewpoint of the global reaction kinetics, not only steps 3–6 are important but also the final step in the mechanism, step 7, reflecting the fate of atomically adsorbed oxygen. Therefore, three options are possibly influencing the stoichiometric numbers of other steps. Step 7a in the route

 $N^{(1a)}$ corresponds to recombination of atomic oxygen, while such recombination in step 7c (route $N^{(1c)}$) involves a reaction with a peroxy species OOH. In the route $N^{(1b)}$, atomically adsorbed oxygen assists in the abstraction of hydrogen from the substrate.

Derivation of the rate expression (per mole of oxygen) for the route $N^{(1b)}$ was described in [47], giving

$$r^{N^{(1b)}} = \frac{\frac{\frac{k_{+3}k_{+4}K_{1}K_{2}C_{02}c_{EIOH}}{k_{+4}k_{-3}\frac{k_{+75}}{k_{+5}}c_{EIOH}}}{(1+K_{2}C_{EIOH}+K_{1}C_{02}+\frac{2k_{+75}K_{2}C_{EIOH}}{k_{+5}}+\frac{k_{+3}k_{+4}K_{1}C_{02}}{k_{+75}(c_{EIOH})} + \sqrt{\frac{2}{k_{+6}}\left(\frac{k_{+3}k_{+4}K_{1}K_{2}C_{02}C_{EIOH}}{k_{+5}k_{+5}c_{EIOH}}+\frac{k_{-6}k_{+3}k_{+4}K_{1}C_{02}C_{2}C_{EIOH}}{k_{+75}(k_{+4}+k_{-3}\frac{k_{+75}}{k_{+5}}c_{EIOH})}\right)} + \sqrt{\frac{2}{k_{+6}}\left(\frac{k_{+3}k_{+4}K_{1}K_{2}C_{02}C_{EIOH}}{k_{+5}k_{+5}c_{EIOH}}+\frac{k_{-6}k_{+3}k_{+4}K_{1}C_{02}C_{2}C_{EIOH}}{k_{+75}(k_{+4}+k_{-3}\frac{k_{+75}}{k_{+5}}c_{EIOH})}\right)}}\right)}$$
(21)

Just for illustration purposes, let us consider a case when step 3 is at quasi-equilibrium and step 6 is irreversible. Equation (21) is then transformed to

$$r^{N^{(1b)}} = \frac{K_{3}k_{+4}k_{+5}K_{1}K_{2}C_{O_{2}}C_{EtOH}/k_{7b}}{(1+K_{2}C_{EtOH}+K_{1}C_{O_{2}}+\frac{2k_{+7b}K_{2}C_{EtOH}}{k_{+5}}+\frac{K_{3}k_{+4}k_{+5}K_{1}C_{O_{2}}}{k_{2}+7b^{C}EtOH}} + \sqrt{\frac{2}{k_{+6}}(\frac{k_{+4}k_{+5}K_{1}K_{2}K_{3}C_{O_{2}}}{k_{+7b}})} + \frac{K_{3}K_{1}K_{2}k_{+5}C_{O_{2}}C_{EtOH}}{k_{+7b}})^{2}}$$
(22)

For two other options also considering the quasi-equilibria of the step 3, the rates are for the routes $N^{\left(1b\right)}$

$$r^{N^{(1c)}} = \frac{k_{+4}k_{+5}/2k_{+7c}\sqrt{\frac{2k_{+7c}K_3}{k_{+5}}}K_1K_2C_{O_2}C_{EtOH}}{(1+K_2C_{EtOH}+K_1C_{O_2}+\frac{k_{+4}}{k_{+7c}}+(1+k_{+5}/2k_{+7c})\sqrt{\frac{2k_{+7c}K_3}{k_{+5}}}K_1K_2C_{O_2}C_{EtOH}+\sqrt{\frac{k_{+4}k_{+5}}{k_{+6}k_{+7c}}}(\frac{2k_{+7c}K_3}{k_{+5}}K_1K_2C_{O_2}C_{EtOH})^{0.25}}^2$$
(23)

and N^(1a), respectively

$$r^{N^{(1c)}} = \frac{k^{2} + 5/k_{+7a} \left(\frac{2k_{+7a}k_{+4}}{k^{2} + 5} K_{1}K_{2}K_{3}C_{O_{2}}C_{EtOH}\right)^{2/3}}{\left(1 + K_{2}C_{EtOH} + K_{1}C_{O_{2}} + \left(\frac{2k_{+7a}k_{+4}}{k^{2} + 5} K_{1}K_{2}K_{3}C_{O_{2}}C_{EtOH}\right)^{1/3} \left(1 + \frac{k_{+5}}{2k_{+7a}} + \sqrt{\frac{k_{+4}}{k_{+6}}} \left(\frac{k^{2} + 5}{2k_{+7a}k_{+4}}\right)^{1/6} + \left(\frac{k^{2} + 5}{2k_{+7a}k_{+4}}\right)^{1/3} \left(K_{1}K_{2}K_{3}C_{O_{2}}C_{EtOH}\right)^{2/3}}\right)^{2}$$
(24)

illustrating that the rate expression and even the kinetic regularities which follow from the corresponding rate expressions are very sensitive to the chemistry of step 7 and the rate constant of this step. The mechanism $N^{(1a)}$ is less probable compared to other alternatives considering a high activation barrier anticipated for this step [47], while other options in principle are possible. For kinetic modelling in [47], a feasible channel of atomically adsorbed oxygen consumption with a low activation energy barrier was considered to be step 7b (Equation (20)).

5. Conclusions and Outlook

Apparently, the concept of the rate limiting will continue to be utilized in the future. This concept is useful as a part of the education of future specialists in chemical reaction engineering and catalyst development. For simple single-route reaction mechanisms, the application of the rate-determining step along with the quasi-equilibria of other steps results in easily derived rate equations. For more complex cases with several linear steps, the general approach based on the theory of complex reactions of Horiuti–Temkin allows the derivation of the corresponding rate equations. Apparent difficulties in doing this, as illustrated above for the four-step sequence, often result in a reductionistic approach assuming a rate-determining step either based on chemical intuition or a more rigorous theoretical analysis based on quantum chemical calculations.

There are cases when the rate equation for linear sequences with a small number of steps was not derived and a system of differential equations was solved even if the rate equation for the steady -state system can be readily derived. This was done, for example in [48], when a solver of differential equations was used for a four step sequence of the Fujiwara–Moritani reaction (Figure 4), unfortunately not reporting how the balance equation for catalytic species was taken into account,



Figure 4. Reaction mechanism for the Fujiwara–Moritani reaction [48]. Published by The Royal Society of Chemistry.

For a particular case of the mechanism in Figure 4, the rate equation can be easily derived as this mechanism is a special case of Equations (11) and (12) with irreversible steps 2 and 3 simply resulting in

$$r = \frac{\omega_{+1}\omega_{+2}\omega_{+3}\omega_{+4}C_{cat}}{\omega_{2}\omega_{3}\omega_{4} + \omega_{-1}\omega_{3}\omega_{4} + \omega_{1}\omega_{2}\omega_{3} + \omega_{-4}\omega_{2}\omega_{3} + \omega_{-4}\omega_{-1}\omega_{3} + \omega_{4}\omega_{1}\omega_{2} + \omega_{3}\omega_{4}\omega_{1}}$$
(25)

Or, after introducing the explicit expressions for the frequencies of steps

$$r = \frac{k_{+1}k_{+2}k_{+3}k_{+4}C_{acrylate}C_{BQ}C_{cat}}{k_{+2}k_{+3}k_{+4}C_{acrylate}C_{BQ}+k_{-1}k_{+3}k_{+4}C_{acrylate}C_{BQ}+k_{+1}k_{+2}k_{+3}C_{acrylate}C_{BQ}+k_{+1}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+3}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+3}k_{+2}k_{+2}k_{+3}C_{acrylate}k_{+2}k_{+3}k_{+2}k_{+2}k_{+3}k_{+2}k_{+2}k_{+3}k_{+3}k_{+2}k_{+3}k_{+3}k_{+2}k_{+3}k_{+3}k_{+2}k_{+3}k_{+$$

In a more general case, when the reaction mechanisms comprise linear and nonlinear steps without any rate-limiting ones, derivation of an explicit rate equation can be too tedious. Instead, a comparison between the experimental and calculations should be done in an implicit form using a system of differential equations considering also an algebraic balance equation for the catalytic species. Availability of computer programs with a customer written subroutine comprising a set of elementary reactions will pave the way for eventual marginalization of the concept of the rate-determining step in the kinetic modelling of complex heterogeneous catalytic reactions.

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