The Rate-Determining Step is Dead. Long Live the Rate-Determining State!

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The concept of a rate-determining step (RD-Step) is central to the kinetics community, and it is basic knowledge even for the undergraduate chemical student. In spite of this, too many different definitions of the RD-Step appear in the literature, all of them with drawbacks. This dilemma has been thoroughly studied by several authors in the attempt to "patch" the drawbacks and bring the RD-Step to a correct physical meaning. Herein we review with simple models the most notable definitions and some challengers of the RD-Step concept, to conclude with the deduction that there are no rate-determining steps, only rate-determining states.

1. The Rate-Determining Step Dilemma

Contrary to other areas of human intellectual endeavor, in science there is no place for ambiguity. A definition of a concept must be (ideally) clear, unique and unequivocal; building those definitions is the raison d'être for the existence of the IUPAC body.[1] When a concept definition loses precision, or grows to an unmanageable series of ad hoc conditions, we may be looking at a case of an imperfect model of the scientific reality. Some examples of this are the concepts of Lewis structures, the formal charge, or the full set of "ideal" systems (ideal gases, ideal solution, ideal covalent bond, etc). Sometimes, as in the previous examples, this is only a philosophical matter, as they are useful models. If we need more accuracy, we can add a correction term or apply a more complex model. However, sometimes the ambiguity in a definition can be a symptom of a very pragmatic problem, which may lead to faulty conclusions.

In chemical kinetics a central concept is the rate-determining step (RD-Step), also called rate-controlling or rate-limiting step.[1,2] Herein we show with simple examples that the definitions of this concept are not clear, unique or unequivocal. The RD-Step description mutated from a clear but imprecise (and frankly wrong) wording, to an obscure mathematical terminology. These are symptoms of a pragmatic problem:[3–11] there are no rate-determining steps![3,4,12] This statement has profound consequences in homogeneous[3,4,13,14], heterogeneous and enzymatic[6,7,15,16] catalysis, kinetic isotope effect studies,[2,6,8,17] and the whole body of kinetic and mechanistic chemistry.

2. Rate-Determining Step Faulty Definitions

Several definitions for the RD-Step can be found in the literature. We will cite the ones we consider most famous or prominent, while the reader is invited to review the rest.[5,18–23]

2.1. The Slowest Step of the Reaction[24–28]

The most typical definition of the RD-Step is "the slowest step of the reaction", always regarded as the "bottleneck". In most texts this definition goes side by side with the description of the steady-state approximation (i.e. all steps in a multistep reaction occur at the same rate when having unstable intermediates). This is a paradox. If we consider that the steady-state regime is a very good approximation, then there is no slower or faster step, and consequently there is no RD-Step![2,5,8,9,18,19]

2.2. The Step with the Smallest Rate Constant[29–31]

Sometimes the RD-Step is more strictly defined as "the step with the smallest rate constant (k)" (strangely, this definition was occasionally considered a synonym with the previous one[29,30]). This definition is equivalent to saying "the step with the highest activation energy". It is a measurable designation, thus more unambiguous and physical. However, unambiguous and physical does not mean correct. A simple example can show why.

Let us have a two-step reaction in the steady-state regime, such as the one in Equation (1), with k_1 the smallest rate constant:

$$C_1 \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} C_2 \overset{k_2}{\longrightarrow} C_3 \tag{1}$$

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The rate of reaction for this system is [Eq. (2)]:

$$r = \frac{k_2 \cdot k_1}{k_{-1} + k_2}[C_1] \tag{2}$$

If we consider k_{-1} smaller than k_2, then the rate of the reaction will be [Eq. (3)]:

$$r = k_1[C_1] \tag{3}$$

Here the RD-Step definition being considered is correct. The rate of the reaction depends solely on k_1 (the smallest rate constant) and neither k_2 nor k_{-1} influence the kinetics.

On the other hand, if k_{-1} is bigger than k_2, the rate equation is [Eq. (4)]:

$$r = \frac{k_2 \cdot k_1}{k_{-1}}[C_1] \tag{4}$$

In this case, how can we say that k_1 determines the rate of reaction, when all the other rate constants have the same weight? Furthermore, taking into account that $k_1/k_{-1}=K_{eq1}$, Equation (2) can be written as Equation (5):

$$r = k_2 K_{eq1}[C_1] \tag{5}$$

and k_2 may be regarded as rate-determining, even though k_1 is the smallest rate constant. Clearly the "smallest rate constant" definition is flawed (especially when having reversible steps[9,32,33]).

2.3. The Step with the Highest-Energy Transition State[34–37]

For the examples of the previous section [Eqs. (3) and (5)] the "highest-energy transition state" definition will indeed work. However, this is hardly a universal scenario. In a non-steady state, two-step reaction of the type given by Equation (6):

$$C_1 \xrightarrow{k_1} C_2 \xrightarrow{k_2} C_3 \tag{6}$$

with an energy profile like that in Figure 1, the highest transition state is T_1. However, the first step has smaller activation energy compared to the second step ($T_1-I_1 < T_2-I_2$, or equivalently $k_1 \gg k_2$). C_1 will be swiftly converted to C_2, and then it will
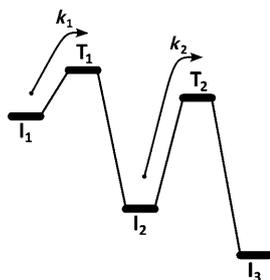

Figure 1. Energy profile of a model non-steady state reaction with two irreversible steps.

slowly "drip" to C_3. In this case the rate of reaction is [Eq. (7)]:

$$r = k_2[C_2] \tag{7}$$

The previous definition of RD-Step ("The step with the smallest rate constant") can work here, but the "highest transition state" definition is erroneous (especially for irreversible steps[2,32]). In Section 4 (catalytic reactions), we show that even for steady-state reactions this definition can be misleading.

2.4. The Step with the Rate Constant that Exerts the Stronger Effect[1,2,6,8]

IUPAC's definition says that "a rate-determining step … is an elementary reaction the rate constant for which exerts a strong effect—stronger than that of any other rate constant—on the overall rate".[1] In other words, a RD-Step is the one whose rate constant is determining. This definition is a tautology (a reiteration of the same idea in different words), but is actually the most accurate definition. In IUPAC's gold book[1] a mathematical description is added: the RD-Step is the one whose control function (CF,[8] also called degree of rate control[20,21,38], and based on the similar concept of the sensitivity function[6]) is the highest [Eq. (8)]:

$$CF_i = \overbrace{\frac{k_i}{r}}^{\text{Normalization factor}} \cdot \underbrace{\frac{\partial_r}{\partial k_i}}_{\substack{\text{Effect of the} \\ \text{rate constant} \\ \text{on the rate} \\ \text{of reaction}}} = \frac{\partial \ln r}{\partial \ln_{k_i}} \tag{8}$$

This differentiation must be computed maintaining all other rate constants (k_j, $j \neq i, -i$) and the equilibrium constant of that step ($K_{eq,i}$) fixed. It is easier to understand these restrictions if we pass from the k-representation (based on rate constants) to the E-representation (based on energies)[3,4,7] according to Equations (9) and (10):

$$K_{eq,i} = e^{-\Delta G_{r,i}/RT} \tag{9}$$

$$k_i = \frac{k_B T}{h}e^{-\Delta G_i^{\ddagger}/RT} \qquad \text{(Transition State Theory)} \tag{10}$$

where $\Delta G_{r,i}$ is the Gibbs reaction energy of step i, and $\Delta G_i^{\ddagger}$ is the Gibbs activation energy of the step, as seen in Figure 2.

If we want to calculate the control function [Eq. (8)] for k_1 in the two-step reaction of Equation (1), we have to calculate the response of the global rate of reaction (r) to an infinitesimal change in k_1, keeping k_2 and K_{eq1} constant (Figure 2). According to Equations (9) and (10), this means we must test r with an infinitesimal change on T_1 (the Gibbs energy of the first transition state). In other words, the control function that is supposed to test a rate-determining *step*, is actually examining a rate-determining *transition state*.

Let us consider the case of Equation (5), where k_2 is the "RD-Step" according to the control factor. In this case, a change in
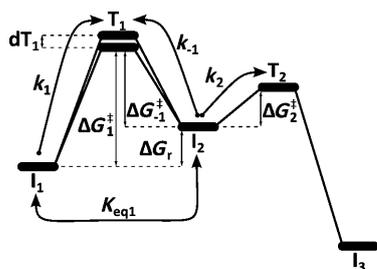
Figure 2. Energy profile of the two steps reaction of Equation (1). I_1, I_2 and I_3 are the Gibbs energies of the C_1, C_2 and C_3 intermediates; T_1 and T_2 the Gibbs energies of the transition states. With Equations (9) and (10) we can convert these energy states into rate and equilibrium constants. The control function of k_1 [Eq. (8)] is measured by calculating the change in the rate of reaction with a change in k_1, maintaining k_2 and K_{eq1} constant. This is equivalent to a change in T_1.

K_{eq1} has the same weight as a change in k_2. A change in K_{eq1} keeping constant k_2 and k_{-1} implies a change in k_1, as appears in Figure 3. So, we can make a change in k_1 that will affect the
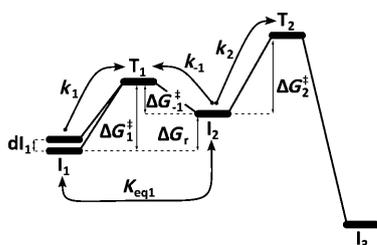

Figure 3. A change in k_1 with fixed k_{-1} and k_2 is equivalent to a change in I_1, the Gibbs energy of the first intermediate.

rate of reaction as much as a change in k_2, in spite of having a null control factor for k_1. How is this possible? [Eq. (11)]:[39]

$$r = \overbrace{k_2}^{\substack{\text{Step 2}\\ \text{is rate−}\\ \text{determining}}} K_{eq}[C_1] = k_2 \cdot \overbrace{\frac{k_1}{k_{-1}}}^{\substack{\text{But step 1}\\ \text{is equally}\\ \text{important}}} [C_1] \qquad (11)$$

The problem resides in the definition of the control factor (hence a problem in the definition of the RD-Step). The constraint of keeping K_{eq1} fixed makes this analysis impossible, but lifting this constraint makes it impossible to define an unequivocal control factor. The reason is that the control factor can only analyze the response to a transition-state change, and in this case we are changing an intermediate (this issue was tackled in different ways by the "degree of turn-over frequency (TOF) control",[3,40] the "thermodynamic rate control for intermediates",[41,42] the "thermodynamic control factor",[43] the "sensitivity",[18,44] and qualitatively by the Curtin–Hammett[45] and Sabatier classical principles[46]).

Let us recapitulate the deficiencies of IUPAC definition of a RD-Step:

1) The control factor, expressed as a function of rate constants, has too many constraints (what we called ad hoc conditions in Section 1). As graphically expressed in Figure 2, the control factor is more a response to a transition state than to a rate constant.

2) The control factor (and consequently this definition of the RD-Step) cannot deal with valid cases that fall outside the constraint of the formula, as in Equation (11) and Figure 3. This needs a new function that measures the response of the rate with a change of intermediate energies.

3. Rate-Determining States: A Physically Correct Concept

In Section 1 we argued that "when a concept definition loses precision, or grows to an unmanageable series of ad hoc conditions, we may be looking at a case of a bad model of the scientific reality". From Section 2 we can conclude that the RD-Step is indeed a bad model of the scientific reality, as expressly highlighted or hinted at by several authors. In that case, what will be a good model for kinetic research? As we saw in Section 2.4, one transition state and one intermediate have the potential to be the factors that shape the kinetics of the cycle. In view of this, the correct concept should be the rate-determining *states* (RD-States), and not the rate-determining *steps*. Can we build an unambiguous, clear, unique and unequivocal definition for the RD-State? By all means.

Definition: Rate-determining states are the transition state and intermediate which exert the strongest effect on the overall rate with a differential change on their Gibbs energies.

Mathematically, the transition state and intermediate with the highest *degree of rate control* (X_{TS} and X_I) are the RD-States [Eq. (12)]:[3,4,40–42]

$$X_{TS,j} = \frac{1}{r} \cdot \frac{\partial r}{\partial \left(\frac{-G_{TS,j}}{RT} \right)}$$
$$X_{I,j} = \frac{1}{r} \cdot \frac{\partial r}{\partial \left(\frac{G_{I,j}}{RT} \right)} \qquad (12)$$

where G_{TS} and G_I are Gibbs energies of the intermediates and transition states, and $1/r$ is a normalization factor. The degree of rate control can be extended to study the sensitivity to concentrations.[12]

What is the reason that makes the RD-State a physically correct concept? The energy states are points in the reaction profile space, while the steps are the processes that bind two consecutive points. In reality, the rate-determining *zone*[7] may cover much more than two consecutive states, thus including several steps (specifically all the steps that are between the RD-States). This can be seen in Figure 3, where I_1 and T_2 are the RD-States, and all the rate constants that are in between (k_1, k_{-1} and k_2) shape the reaction [Eq. (11)].

4. RD-States in Catalysis

4.1. Introduction to Catalytic Cycles

Catalytic reactions are special in that they are cyclic: from the catalyst's perspective the initial and final state can be considered the same state, with the reactants and products as "additions". A steady-state regime is easily achieved for most catalytic 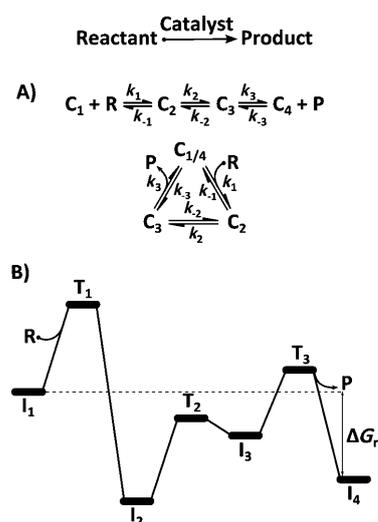cycles. In Figure 4 a model three-step catalytic cycle is depicted, both in the rate-constant (k) representation and the

Figure 4. A three-step model catalytic cycle, in A) the linear and closed k-representations (rate-constant representations) and B) the E-representation (energy representation). The k and E representations are equivalent, and we can translate one to the other with the transition state theory [Eq. (10)]. ΔG_r is the reaction Gibbs energy, independent from the catalyst.

energy (E) representation. Both representations are equivalent, as we can convert each rate constant to an intermediate/transition state energy pair and vice versa, according to the transition state theory given by Equation (10).

In catalysis, the rate of reaction is called the TOF, the number of cycles that occur in a specific time period. The resolution of a three-step catalytic cycle in a steady-state regime is beyond the scope of this text,[46,47] and we write here only the final formula (for simplicity we do not consider the concentration of reactants and products[4,12,47]) [Eq. (13)]:

$$\text{TOF} = \frac{k_1 k_2 k_3 - k_{-1} k_{-2} k_{-3}}{k_2 k_3 + k_3 k_1 + k_1 k_2 + k_{-1} k_3 + k_1 k_{-2} + k_{-3} k_2 + k_{-1} k_{-2} + k_{-2} k_{-3} + k_{-3} k_{-1}} \tag{13}$$

We can simplify the TOF equation by neglecting the lesser terms. First, the product of forward rate constants (first term in the numerator) is always bigger than the backward product (second term) for exergonic reactions. Second, typically only one of the nine terms in the denominator is significant; for a

reaction profile of the type of Figure 4, it will be $k_{-2}k_1$. In this case, the resulting equation is given by Equation (14):

$$\text{TOF} = \frac{k_1 k_2 k_3}{k_1 k_{-2}} = k_3 K_{eq2} \tag{14}$$

Equation (14) shows that the TOF (the rate of reaction) is completely independent of k_1. However, not only is k_1 the smallest forward rate constant, but T_1 is also the highest energy state! Clearly, the rules of "smallest rate constant" and "highest transition state" are not valid to establish the determining kinetic factors. Is there a simple way to find these determining factors? There is, if we work in the E-representation and try to find the RD-States instead of the RD-Step.

4.2. Visual Guide to Find the RD-States in Catalysis[3,4,7]

The net chemical flow in an exothermic reaction in the steady state is always in the forward direction; this fact will be the first clue to find the RD-States in a catalytic cycle. The second clue is that from each intermediate we can consider the effective energy barrier to be crossed as the highest energy transition state that occurs in the forward direction (this can be thought as the Curtin–Hammett principle applied to catalytic cycles[45]). The RD-States are the ones that have the highest effective energy barrier.
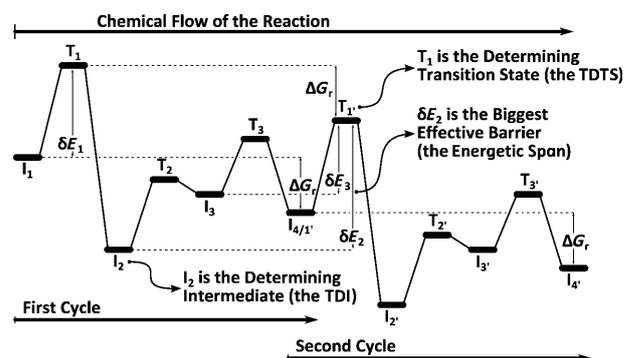

Figure 5. Recipe to find the RD-States in a catalytic cycle: 1) Draw the Gibbs energy profile of two consecutive cycles. 2) From each intermediate, find the highest energy transition state in the forward chemical flow. 3) The determining states are the ones with the biggest span between the intermediate in question and the following highest TS energy. These states are called the TDI (TOF-determining intermediate) and the TDTS (TOF-determining transition state). The energy difference between the TDI and the TDTS is called the energetic span (δE). In this example, I_2 is the TDI, and $T_{1'}$ the TDTS. Note that $T_{1'} = T_1 + \Delta G_r$.

There is one factor that must be taken into account when dealing with these systems. There is no starting or ending point in a catalytic cycle, as the catalyst can theoretically continue to an infinite number of turn-overs. Therefore, when we look for the highest TS following each intermediate, we have to look further than one cycle. In Figure 5 we show the methodology to find the RD-States point by point. Similar methods can be found elsewhere.[6,15,16,32,33,43,48]

4.3. Mathematical Guide to Find the RD-States in Catalysis: the Energetic Span Model

The catalytic profile of Figure 5 corresponds to the following TOF equation [Eq. (15)] [a simplification of Eq. (13)]:

$$\text{TOF} = \frac{k_1 k_2 k_3}{k_{-2} k_{-3}} = k_1 K_{eq2} K_{eq3} \qquad (15)$$

Almost all the rate constants appear in this formulation, thus speaking of an RD-Step is a poor oversimplification (again). From the visual technique of Figure 5, we found that I_2 and T_1 are the RD-States. These two determining species are called the TDI (TOF-determining intermediate, sometimes called the resting state or the MARI[5,11,23,49]) and the TDTS (TOF-determining transition state, also called … RD-Step!).[3] Can we find the TDI and the TDTS from Equation (15)? Yes, if we pass from the *k*-representation to the *E*-representation by applying the transition state theory [Eq. (10)] to all the rate constants [Eq. (16)]:

$$\text{TOF} = \frac{k_1 k_2 k_3}{k_{-2} k_{-3}} = \frac{k_B T}{h} \frac{e^{-T_1+I_1} \cdot e^{-T_2+I_2} \cdot e^{-T_3+I_3}}{e^{-T_2+I_3} \cdot e^{-T_3+I_4}}$$

$$\frac{k_B T}{h} \frac{e^{-T_1+I_1+I_2}}{e^{I_4}} = \frac{k_B T}{h} e^{-T_1+I_2-\Delta G_r} \qquad (16)$$

In the last equality we considered that the starting point of the second cycle is the end of the first one ($I_4 = I_{1'} = I_1 + \Delta G_r$). As with the visual method of Figure 5, writing the rate equation in the *E*-representation naturally gave us I_2 and T_1 as the RD-States. In this case ΔG_r is added as the acting TDTS is in the second cycle (in Figure 5 it is shown as $T_{1'} = T_1 + \Delta G_r$). As a rule, ΔG_r appears in the TOF equation if the TDTS comes before the TDI (when considering only one turn-over). After this example, we can generalize the TOF expression in what is called the Energetic Span Model [Eq. (17)]:[3,4,40]

$$\text{TOF} = \frac{k_B T}{h} e^{-\delta E}$$

$$\delta E = \begin{cases} T_{TDTS} - I_{TDI} & \text{if TDTS appears after TDI} \\ T_{TDTS} - I_{TDI} + \Delta G_r & \text{if TDTS appears before TDI} \end{cases} \qquad (17)$$

δE is the energetic span[50] of the cycle, and serves as the apparent activation energy of the full catalytic cycle.[3,4,40,43,44,48] It depends directly on the RD-States (the TDI and TDTS), and has no need of a cumbersome product of rate constants. Equation (17) is an excellent approximation when the degree of TOF control of the TDI and TDTS is close to one (for the complete TOF formula see references [3,4,12,40]).

5. Conclusions

Herein we saw that the rate-determining step is a hard concept to define, with each one of the definitions having deficiencies. These are symptoms of a faulty concept: either we must choose an RD-Step definition that fits the chemical problem,[2,39] or we are working in an unsuitable framework (Figure 6). The literature is full of discussions and "patches" for
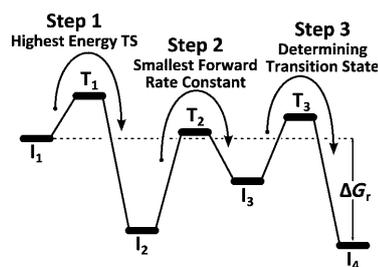
Figure 6. Which step is rate-determining? Step 1, with the highest energy transition state? Step 2, with the smallest forward rate constant (highest activation energy)? Or Step 3, having the determining transition state? There are no rate-determining *steps*, but rate-determining *states*!

these deficiencies, pointing to a new viewpoint: the whole idea of a RD-Step should be relegated to a historical place in chemistry, and should make place for a concept with a stronger physical basis, the rate-determining states.

Keywords: catalysis · kinetics · rate-determining step · reaction mechanisms · transition-state theory

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