

THE STEP THAT DETERMINES THE RATE OF A SINGLE CATALYTIC CYCLE

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If there exists a unique step that determines the rate of a single catalytic cycle at the quasi-steady state, the identification of that step provides useful information, in theory and practice. An operational definition of such a unique step is proposed and illustrated by means of specific examples.

Keywords: One-way and two-way catalytic cycles, steps that control catalytic cycles, rate of a single catalytic cycle

1. Introduction

The turnover frequency (TOF) of a catalytic cycle is the quantitative expression of the activity of the catalyst. It is reasonable to expect that the TOF is limited by one or perhaps several steps in the cycle. These steps are intuitively regarded as *bottlenecks* and are called by various names. Examples are rate determining step, rate limiting step, rate controlling step, or sometimes just slow step.

If there exists such a step, its determination contributes an interesting and useful detail of the reaction mechanism. For instance, if it is the activation of a reactant, rational modifications of the catalyst may lead to an enhancement of the turnover frequency. Unfortunately, there exists no generally accepted definition of the rate determining step except one that was first introduced by J.

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Horiuti [1]. The purpose of this Letter is to propose a useful generalization of the concept of Horiuti. This generalization is unambiguous as it is based on a clear operational definition containing a simple kinetic criterion. It embraces Horiuti's definition as a particular case.

2. Kinetics of catalytic cycles

Strictly speaking, all chemical reactions and elementary steps can proceed in both directions, forward or from left to right and reverse or from right to left. This is best commented upon by means of the relation of De Donder [2]:

$$\vec{v}_i/\tilde{v}_i = \exp(A_i/RT)$$

that applies to any elementary step, with the affinity A_i of each step, defined as

$$A_i = \left[\frac{\delta(-\Delta G_i)}{\delta \xi} \right]_{T,p}$$

where ξ is the extent of reaction and $-\Delta G_i$ is the Gibbs free energy drop. Thus, a reaction generally proceeds in the forward direction, in a *two-way* manner with $\vec{v}_i > \tilde{v}_i$, until $A_i = 0$, as equilibrium is reached and $\vec{v}_i = \tilde{v}_i$. It is never correct to write $\tilde{v}_i = 0$; that entails $A_i = \infty$. But, when $\vec{v}_i \gg \tilde{v}_i$, the reaction can be said to go *one-way*, in an experimental kinetic sense, as $v_i \cong \vec{v}_i$. Then, we will say, for short, that the reaction goes one-way or is a *one-way* reaction. The approximation $v_i \cong \vec{v}_i$ is defined operationally as follows: the reaction is said to be *one-way* if the rate in the reverse direction is too small to be measured. If one or more steps in a catalytic cycle goes one way, so will the overall reaction: $v \cong \vec{v}$. We will say one-way and two-way in a kinetic sense, instead of irreversible and reversible because the latter words are frequently used in a thermodynamic sense, as in "thermodynamics of irreversible processes".

The universally accepted way to handle the kinetics of chain and catalytic reactions is to assume the validity of the quasi-steady state approximation as introduced by Bodenstein. At the quasi-steady state, the net rate $v = \vec{v} - \tilde{v}$ of a single catalytic cycle is equal to the net rate $v_i = \vec{v}_i - \tilde{v}_i$ of any elementary step (or step for short) in the cycle, divided by the stoichiometric number of the step, σ_i . The latter is defined as the number of times that the step must occur for the cycle to turnover once. The equation for each step must be written the way it is believed to take place at the molecular level.

One important remark can be made already. At the quasi-steady state, it is meaningless to talk about a *slow step* since the net rate of all steps divided by their respective stoichiometric number is equal to the net rate of the overall cycle. To state that a given step is the slow step makes no sense at the quasi-steady state.

At equilibrium, the De Donder equation with all concentrations at the chosen standard state denoted by \ominus becomes

$$\vec{k}_i/\bar{k}_i = \exp(A_i^\ominus/RT) = K_i$$

where A_i^\ominus is the standard affinity, \vec{k}_i and \bar{k}_i are rate constants, and K_i is the equilibrium constant. We shall say that a step or reaction is in quasi-equilibrium at the quasi-steady state when both \vec{v}_i and \bar{v}_i are much larger than $v_i = \vec{v}_i - \bar{v}_i$. The symbol \rightleftharpoons will be used for a step in quasi-equilibrium. A step in quasi-equilibrium is one for which $A_i \cong 0$. For all other steps, either one-way or two-way steps, $A_i \neq 0$. The approximation $A_i \cong 0$ is defined operationally in a kinetic manner as follows: $A_i \cong 0$ if for that step, the rate constants \vec{k}_i and \bar{k}_i appear in the rate equation, if they appear at all, only through the equilibrium constant $K_i = \vec{k}_i/\bar{k}_i$. Such steps are *exergic* according to the terminology denoting reactions for which $\Delta G_i < 0$ or $A_i > 0$ [3]. We shall use the symbol \rightleftharpoons for a two-way step that is not in quasi-equilibrium and the symbol \longrightarrow for a one-way step in the kinetic sense discussed above.

All that precedes has been described elsewhere [2,4]. We are now ready to introduce the classical definition of a two-way rate determining step for which the common symbol is \rightleftharpoons .

3. Horiuti's rate determining step for two-way reactions [1]

In any two-way catalytic cycle at the quasi-steady state, there may exist a unique step called the rate determining step (*rds*). It is the only exergic step in the cycle. All the other steps are in quasi-equilibrium, with essentially zero affinity. It is convenient to write the stoichiometric equation for the overall reaction in such a way that the stoichiometric number of the *rds* is unity. If that is done, the following statement is exact and illustrates the fact that the *rds* truly *determines* the rate: *at the quasi-steady state the forward rate and the reverse rate of the rds are equal respectively to the forward and reverse rate of the overall reaction* [5]. Horiuti's *rds* is the *only* exergic step of the cycle. It is the only one that contributes rate constants to the rate equation for the overall reaction: the rate constant of the forward *rds* and the rate constant of the reverse *rds*. As already mentioned, the quasi-equilibrated steps may appear in the rate equation for the overall reaction only through their equilibrium constants $K_i = \vec{k}_i/\bar{k}_i$ or a product of these.

The best example is the ammonia synthesis on iron, much studied far from and near equilibrium [2,4]. Not too far from equilibrium, the non-equilibrated step is a two-way step. The generally accepted *rds* in the sense of Horiuti is the dissociative adsorption of dinitrogen and its reverse, the associative desorption of adsorbed nitrogen. Ammonia synthesis has been the most important reaction in establishing Horiuti's concept of the *rds* as well as that of the stoichiometric

number of the *rds* [2,4]. Let us now consider what to do when there exists more than one exergic step in the catalytic cycle.

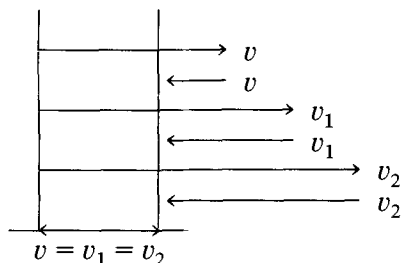
4. A two-catalytic cycle with two exergic steps

Consider a catalytic cycle at the quasi-steady state with two two-way exergic steps with non-zero affinity A_1 and A_2 , $A_1 > A_2$. There may be one or several quasi-equilibrated steps. The affinity A of the overall reaction is $A = A_1 + A_2$. From the corresponding De Donder relations it is easy to show that:

$$\vec{v} < \vec{v}_1 < \vec{v}_2$$

$$\bar{v} < \bar{v}_1 < \bar{v}_2$$

or pictorially with all stoichiometric numbers equal to unity:



Among the two exergic steps, which one is the most important kinetically? Is it step 1 with the larger values of the affinity? Clearly neither step 1 nor step 2 “determines” the rate. Admittedly \vec{v}_1 and \bar{v}_1 have values *closer* to \vec{v} and \bar{v} respectively, but this does not qualify step 1 as an *rds*, unless step 2 would be in quasi-equilibrium as defined above, with $A_2 = 0$. Thus when there is more than one exergic step but all exergic steps are two-way steps, the concept of *rds* is not clear.

5. One-way catalytic cycles with more than one exergic step

To handle the common situation where more than one step is exergic, let us propose the following operational definition. *When there is more than one exergic step in a one-way catalytic cycle, the rate determining step is the only one-way exergic step, whose forward rate constant appears in the rate equation for the overall reaction.*

It must be emphasized that the *rds* as just defined shares with Horiuti’s *rds* the same unique feature: in both cases, the only step whose rate constant appears in the rate equation for the overall reaction is the one to be singled out as rate determining step or main exergic step. In Horiuti’s case, the *rds* is a two-way step and it is the only exergic step. In the broader definition that we propose, the *rds*

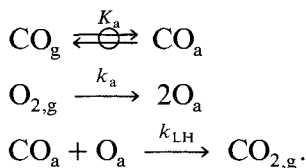
is a one-way step but there may be more than one exergic step. If there is only one exergic step, our definition is identical to that of a two-way rate determining step following Horiuti.

Let us now illustrate the extended definition of a rate determining step by means of several examples.

6. The rate determining step: oxidation of carbon monoxide

The kinetics of this reaction was first studied in a definitive manner by I. Langmuir, who reported his results on platinum at a 1921 Discussion of the Faraday Society [6]. Langmuir's results were confirmed many times, most recently by Ertl and co-workers [7], who extended all earlier studies by systematic investigations on large single crystals, especially palladium. Next to the two-way ammonia synthesis, the one-way oxidation of carbon monoxide is today the best understood catalytic reaction. Thus, it may be the best suited to explore the possibility of extending Horiuti's concept of the *rd*s to a one-way reaction.

With almost equimolar mixtures of CO and O₂, between 400 and 600 K, from 10⁻⁶ to 10² mbar, the important steps in the catalytic sequence seem to be:



Thus, CO is chemisorbed without dissociation, in quasi-equilibrium (equilibrium constant K_a); O₂ is chemisorbed dissociatively in a one-way step (rate constant k_a); and CO_a reacts in one-way with O_a to form CO₂ in a verified Langmuir-Hinshelwood (LH) step (rate constant k_{LH}). Because of the existence of *two* exergic steps, there is no *rd*s in the classical sense of Horiuti. But what about the kinetics?

Two temperature regimes are recognized: between ~ 400 and ~ 500 K with a normal exponential increase of the rate with temperature, and above ~ 500 K (T_{max}) where the rate decreases exponentially with T .

Between ~ 400 and ~ 500 K, over eight orders of magnitude of total pressure [8], the rate equation is that first proposed by Langmuir, or very close to it, with the turnover rate v_t given by the expression:

$$v_t = \frac{k_a [\text{O}_2]}{K_a [\text{CO}]}.$$

This is explained by assuming that the chemisorption of O₂ occurs on a surface saturated with CO_a. The apparent activation energy is $-\Delta H_{a,\text{CO}}$ since the activation energy for chemisorption of O₂ is zero. The only rate constant appearing in the rate equation is k_a , corresponding to the chemisorption of O₂.

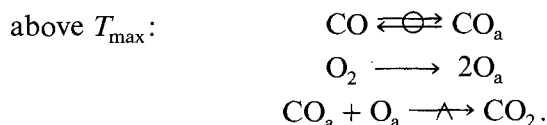
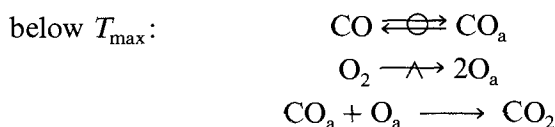
The latter is then the rate determining step according to the operational definition proposed in this Letter. This is so, in spite of the fact that the affinity of reaction is spent in two irreversible steps, a situation not covered by Horiuti's definition.

By contrast, above T_{\max} at low pressure, the rate equation is different [5]:

$$v_t = k_{\text{LH}} K_a [\text{CO}].$$

This is explained by assuming that CO is adsorbed on the free palladium surface that is sparsely covered with CO_a in quasi-equilibrium and that CO_a diffuses to the periphery of islands of O_a where the irreversible LH step occurs. The apparent activation energy is $E_{\text{LH}} + \Delta H_a$, a negative quantity as observed. Now the LH step can be called the rate determining step if we follow the prescription of this Letter.

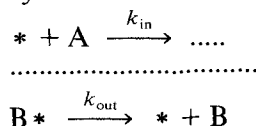
In summary, if the customary symbol \wedge is adopted for the rate determining step as defined in this Letter, we write:



Thus the rate determining step shifts from the first exergic step in the cycle to the second one as the temperature rises. Another possible way to handle the situation would be to state that both exergic steps determine the rate of the catalytic cycle. We believe that this simple prescription carries less useful information than the one we favor. Next and finally, let us consider another frequent kinetic pattern from the viewpoint of the rate determining step.

7. Catalytic cycles with two one-way steps

Consider a one-way reaction $\text{A} \Rightarrow \text{B}$ with two one-way steps: the entry step (in) and the exit step (out). There may exist many intermediate steps, reversible, irreversible, or quasi-equilibrated, but there is no need to consider them explicitly if adsorbed B is the most abundant reactive intermediate, so that $[*] + [\text{B}*] = [\text{L}]$, where $[\text{L}]$ is the total density of sites. To obtain the rate \bar{v} for the overall one-way reaction, the only kinetically significant steps are the first and the last in the cycle:



At the quasi-steady state:

$$\vec{v} = \vec{v}_{\text{in}} = \vec{v}_{\text{out}}$$

so that the turnover rate v_t is:

$$\vec{v}_t = \vec{v}/[L] = k_{\text{in}}[A]/\{1 + (k_{\text{in}}/k_{\text{out}})[A]\}.$$

This rate expression is observed in the one-way decomposition of ammonia at low pressure on several metals [9]. Thus, according to our definition, there is no rate determining step in this general case. But, as the temperature rises from low values, the rate goes from one limiting case [10], namely $(k_{\text{in}}/k_{\text{out}})[A] \gg 1$

$$\vec{v}_t = k_{\text{out}}$$

with desorption of nitrogen being the rate determining step to the other limiting case [11]:

$$v_t = k_{\text{in}}[\text{NH}_3], \text{ namely } (k_{\text{in}}/k_{\text{out}})[A] \ll 1$$

with adsorption of ammonia being the rate determining step.

There are many examples of first order rate equations corresponding to adsorption on a sparsely covered surface being the rate determining step, and of zero order rate equations corresponding to desorption from a saturated surface being the rate determining step. An example of the first kind is the oxidation of propylene to acrolein [12]. An example of the second kind is the decomposition of germane on a germanium film saturated with adsorbed H [14].

In both cases, we cannot use the original definition of Horiuti. We could say that there exists an unknown number of exergic steps, but that does not carry useful information. Indeed, we have no kinetic information on intermediate steps between the entry step and the exit step: some may be in quasi-equilibrium, some may be exergic. Even in the general case treated above, we may say: both the entry step and the exit step are kinetically significant, because they are exergic, but what about the intermediate ones? How many are also exergic? What is the meaning of these exergic steps?

By contrast, our proposed definition of the rate determining step is consistent with common usage, except that common usage usually lacks precision. Thus it is frequently said that the rate determining step in the oxidation of propylene to acrolein is the abstraction of a hydrogen atom from propylene to form an allylic surface intermediate. We say that this conforms to our definition because the measured overall rate is that of the entry step. This is confirmed by the observed kinetic isotope effect in the ratio of $k_{\text{in,H}}$ to $k_{\text{in,D}}$. The latter is equal to what is expected if the transition state of the *rd*s corresponds to the formation of the light or heavy allylic intermediate [12].

8. Conclusion

For a one-way catalytic cycle, the rate determining step, if there is one, is defined as the one-way step whose forward rate constant is the only one to appear in the rate equation for the overall one-way reaction. In the case of a two-way catalytic cycle with a single exergic step, the definition agrees with the original definition of Horiuti: for that case both forward and reverse rate constants are the only ones to appear in the rate equation for the overall two-way reaction.

Acknowledgement

This Letter is dedicated to the memory of J. Horiuti, one of the early key contributors to the formulation of catalytic kinetics. Indeed, this Letter was motivated many years ago by a conversation between Professor Horiuti and one of us (KT). In this conversation, Horiuti expressed the wish to generalize for one-way reactions, the definition of a *rds* that he had rigorously introduced for two-way reactions. While all reactions are two-way in theory, many are one-way in a practical kinetic sense. It is our hope that our attempt at the generalization of the useful concept of a *rds* will be commented upon by the practitioners of kinetics in homogeneous, heterogeneous, and enzymatic catalysis, with the hope that a consensus will be reached ultimately concerning a general operational definition of a rate determining step.

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