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QUANTUM STATISTICAL AND DYNAMICAL CHARACTER OF THE ELEMENTARY STEP OF CATALYTIC PROCESSES

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Mechanisms of the elementary step of catalytic processes are discussed from the viewpoint of the quantum mechanical theory of the elementary act of chemical reactions in solutions. Expressions are reported for the rate constant in multistep reactions and in reactions going via short-lived complexes. It is shown that the quantum statistical or quantum dynamical character of the reaction is governed by the relation between the lifetime of intermediate states and the vibrational relaxation time in these states.

Catalytic processes are diverse, and very important in the kinetics of liquid-phase reactions. They include reactions in the bulk of the solution (homogeneous catalysis), reactions at the surface of solids (heterogeneous catalysis), and, in particular, electrocatalysis. Important among the catalytic processes are enzymatic reactions which are very important in biochemical processes. For a detailed description of catalytic processes one must know the mechanism of catalyst action, the influence of catalyst properties on the catalytic activity,

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etc. A catalytic reaction is complicated, in the general case, and consists of a series of chemical changes. But despite all variety displayed by the catalytic processes, each of them is based on individual, elementary steps. The microscopic theory of the kinetics of the elementary act of chemical reactions in condensed media has been developed to a significant extent [1]. On this basis we can draw certain conclusions as to how the rate of a given reaction depends on the properties of the species involved in it (including the catalyst).

It is the aim of the present work to analyze expressions for the rate of catalytic reactions, to find the basic factors influencing this rate, and to discuss the question whether the elementary step of a catalytic process is stochastic (statistical) or deterministic (dynamical); this is important, in particular, for enzymatic reactions [2].

GENERAL REACTION SCHEMES

In the absence of catalyst, one can write the rate of a simple chemical reaction

$$A+B\rightarrow D+E \tag{1}$$

in the form

$$v=\vec{k}AB, \tag{2}$$

where the rate constant $\vec{k}$, according to [1], is given by

$$\vec{k}=\delta V\frac{kT}{h}\varkappa\exp(-U_{A/B}/kT)e^{-\sigma}\cdot\exp\{-[E_a(\Delta J, U_{A/B}, U_{D/E})-TS_a]/kT\}, \tag{3}$$

where $\delta(V)$ is the volume of the reaction zone, $\varkappa$ is the transmission coefficient, $U_{A/B}$ ($U_{D/E}$) is the free energy of interaction of the reactants (products) in the reaction zone, σ is the tunneling factor which describes the probability of rearrangement of the quantum vibrational degrees of freedom of the reacting particles during the reaction, E_a and S_a are the energy and entropy of activation of the elementary act of the chemical change in the reaction zone, and ΔJ is the difference between the minimum energies of the final and initial state.*

In the presence of a catalyst C, there is a substantial change in the mechanism of reaction (1). On principle there are two basic possibilities: a multistep reaction involving intermediates:

$$A+B+C\rightleftarrows P_1\rightleftarrows P_2\rightleftarrows\ldots\rightarrow D+E+C, \tag{4}$$

and the formation of a short-lived complex with the catalyst:

$$A+B+C\rightarrow[ABC]_{tr}\rightarrow D+E+C. \tag{5}$$

A special case are processes following the type of enzymatic reactions. Below we shall discuss each of these cases individually.

MULTISTEP REACTIONS

The rate of multistep reaction (4) where one of the steps (j) is slow and all steps preceding it are in equilibrium can be written in the form [3]

$$v_{(j)}=\vec{k}_j\Pi_j, \tag{6}$$

where Π_j is the concentration product of the particles involved in the j-th step, and $\vec{k}_j$ is the rate constant of the j-th step. Taking into account that all preceding steps are in equilibrium we have for Π_j

$$\Pi_j=K_jABC, \tag{7}$$

where K_j is the equilibrium constant of the reaction

$$A+B+C\rightleftarrows P_j, \tag{8}$$

$$K_j=\exp(-\Delta F_j/kT), \tag{9}$$

where ΔF_j is the free energy of reaction (8).

* For a clearer exposition of the factors influencing the kinetics of the elementary act of the reaction it is assumed in (3) that all vibrational degrees of freedom of the reactants and of the solvent can be separated into classical and quantum degrees [1].

After writing for $\vec{k}_j$ an expression which is analogous to (3) we obtain for the effective rate constant $\vec{k}_{(j)}$ of reaction (4) ($V_{(j)}$ $\vec{k}_{(j)}$ABC) the expression

$$\vec{k}_{(j)}=\vec{k}_jK_j=\Pi(\delta V)\frac{kT}{h}\varkappa_j e^{-U_j/kT}e^{-\sigma_j}\cdot\exp\left[-\frac{E_a(\Delta J_j, U_j, U_{j+1})-TS^a}{kT}\right]e^{-\frac{\Delta F_j}{kT}}. \quad (10)$$

Suffix j indicates that all quantities in Eq. (10) refer to the j-th step.

Leaving aside theunimportant factor $\Pi(\delta V)$, one can state that the rate constant of the catalytic reaction is determined by a number of factors associated with different properties of the reacting particles: 1) The electronic factor is introduced chiefly by the transmission coefficient $\varkappa_j$; 2) the factor $\exp(-Uj/kT)$ which determines the probability that the reactants will approach to a distance where the reaction effectively is taking place we shall conditionally designate as the electrostatic factor; 3) the structural factor $\exp(-\sigma j)$ characterizes the probability that the configuration of the particles changes along the quantum degrees of freedom by tunneling beneath the barrier; 4) the structure–energy factor $\exp[-E_a(\Delta J_j, U_j, U_{j+1})/kT]$ determines the probability that the system overcomes the potential barrier along the classical degrees of freedom;* 5) the energy factor $\exp(-\Delta F_j/kT)$ defines the concentration of particles involved in the j-th step and existing in equilibrium with the original reactants. Taking into account the remark made in the footnote this factor is wholely determined by the energy characteristics of the reactants, catalyst, and species involved in the j-th step, and does not require any knowledge of the detailed structural features.

It must be noted that these factors in the general case will not be independent, and several factors may change at the same time as one goes from one catalyst to another. Since in this situation they also can change in opposite directions, one must take all of them into account, in general, when estimating any changes in catalytic activity.

FORMATION OF SHORT-LIVED COMPLEXES

When short-lived complexes with the catalyst are formed, the process will occur in a single step, and the reaction rate is determined by the expression

$$v_c=\vec{k}_c\text{ABC}, \quad (11)$$

where

$$\vec{k}_c=\Pi\delta V\frac{kT}{h}\varkappa_c e^{-U_{ABC}/kT}e^{-\sigma_c}\cdot\exp\left[-\frac{E_a(\Delta J)-TS_a}{kT}\right]. \quad (12)$$

As an example of reactions involving the formation of short-lived complexes not held together by chemical forces one can cite the catalysis of the electroreduction of anions afforded by cations [4]. In this case the catalyst chiefly influences the electrostatic factor $\exp(-U_{ABC}/kT)$, by facilitating the approach of the reactants. In the case of strongly polarizable ions it can also influence the electronic factor.

It is also possible that the electronic orbitals of the catalyst are involved in the reaction. This is the case with the so-called bridged electron-transfer reactions [5]. In this case the electron transfer from ion A to ion B occurs via an intermediate state on the catalyst. But this transition occurs in a single step, in contrast to the multistep processes, since the intermediate state is virtual (short-lived).

The bridged reactions also include certain intramolecular electron-transfer reactions [6] as well as electron-transfer reactions between different molecules involving virtual intermediate states of one of the reactants [7]. The theory of bridged reactions has been developed in a number of papers (cf., e.g., [8, 9]). The microscopic mechanism of this type of reaction has much in common fundamentally with enzymatic reactions [2]. Both types can be regarded as reactions taking place in a single reaction complex. For both types it is of

* For the sake of simplicity we disregard entropy effects, even though in a number of cases they may turn out to be very important.

interest to find out about the nature of the elementary step, viz., whether this is quantum statistical or dynamical. We therefore discuss these reactions separately below.

QUANTUM STATISTICAL AND DYNAMICAL MECHANISM OF THE ELEMENTARY ACT. ENZYMATIC AND BRIDGED REACTIONS

In reactions involving complex molecules (especially in enzymatic reactions), the system in going from the reactants to the products can pass through a number of configurations corresponding to stable states of the molecule (chemical complex) with respect to small vibrations. These transformations lead to a change in the structure of the complex while leaving its chemical composition unaffected. As an example for such transformations one can cite the conformational transitions in enzymes. The question arises of how to describe these transformations. It will be simplest to single out two limiting cases.

1. If the system exists near said intermediate configurations over a period of time which is significantly longer than the vibrational relaxation time, then the transition can be referred to the first type, i.e., multistep reactions, and one can formally regard the intermediate configurations as intermediates (even though they possibly have the same chemical composition). The kinetics of such transitions is formally the same as the kinetics of multistep reactions discussed above, and the expression for the rate constant is described by a relation of the type of Eq. (10).

It is a particular feature of the intermediate state being discussed that as a result of the vibrational relaxation processes it completely "forgets" in which way it had been produced. For a transition to occur from this state to some other state a particular fluctuation must arise so that in this sense such a transition is quantum statistical (stochastic) in character. The energy set free as the result of each such transition is dissipated into the surrounding medium, i.e., is evolved as heat. Similarly, the energy required for the generation of fluctuations is drawn from the surrounding medium.

2. The second limiting case arises when the system spends a time near the intermediate configurations which is much shorter than the vibrational relaxation time. In this case the kinetics of the process is completely different in character. The process occurs essentially in a single step, since the transition from the initial to the final state in this case is a continuous, dynamical transition. Since there is no relaxation taking place in the intermediate states, the motion of the system turns out to be quantum dynamical (deterministic), and determined by the starting conditions and the shape of the potential energy surfaces [10]. In complex reactions (in particular, in enzymatic reactions), these intermediate transformations can lead to the breaking of some and the formation of other chemical bonds, which in the final analysis gives rise to new chemical compounds. It is essential that during these transformations there is no dissipation of energy into the surrounding medium. In such transitions, therefore, the energy which is set free as a result of each intermediate transformation is absorbed (in part or completely) during subsequent transformations, i.e., the energy of one set of chemical bonds is stored by the system in the form of energy of other chemical bonds.

In addition to the above limiting cases one also can have intermediate cases with partial relaxation of energy in intermediate states.

It is clear from what has been said that the problem the dynamical or statistical behavior of a system (and in particular of an enzymatic system) is associated with the lifetime, τ_c, of the intermediate states, and the vibrational relaxation time, τ_r. For $\tau_c \gg \tau_r$ the behavior of the system is quantum statistical. For $\tau_c \ll \tau_r$ the behavior of the system (enzyme) is quantum dynamical.

This difference in the character of the reaction has effects on the kinetic parameters of the process. Since the paper is short, we shall limit ourselves to a single example. In the presence of a single intermediate state, the expression for the rate constant of a completely nonadiabatic reaction will contain: 1) in the case of a quantum dynamical (bridged) reaction, the product of the two transmission coefficients corresponding to the transition from the initial to the intermediate state, and to the transition from the intermediate to the final state; 2) in the case of a quantum statistical (multistep) reaction, only one transmission coefficient, viz., that corresponding to the slow step.

CONCLUSIONS

It follows from the above discussion that the catalytic activity is influenced by a large number of interrelated factors which must be taken into account when comparing different catalysts. Depending on the character of the process one can divide the catalytic reactions into multistep processes (with relaxation in intermediate

states) and direct processes (without relaxation). In principle one also can have combined reactions. The dynamical or quantum statistical character of the transition is determined by the relationship between the lifetime of the intermediate state and the vibrational relaxation time in this state. The expressions reported for the reaction rate constants can be used when analyzing specific catalytic reactions in terms of different models.

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ROLE OF THERMAL CONCENTRATION FLUCTUATIONS IN BIMOLECULAR REACTION KINETICS

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Certain special features of chemical reactions are discussed which arise when diffusion and thermal fluctuations spontaneously upsetting the uniform distribution of the reactants are taken into account. The natural nonuniformity of the concentrations can influence the course of the chemical reaction. A simple analysis shows that for bimolecular reactions the concentration of the reactants ought to decrease with time following a $t^{-3/4}$ law rather than the t^{-1} law which is correct when fluctuations are not taken into account. The change in the asymptotic relation is due to the fact that in the late stages the change in concentration is determined by diffusion rather than by the reaction rate. Possibilities are discussed for the experimental detection of the asymptotic concentration law and for applying the ideas presented here to electrolytes.

Academician Aleksandr Naumovich Frumkin devoted his life to physical chemistry, and primarily to electrochemistry as that branch of physical chemistry where the investigation of elementary processes flows together with that of the macroscopic phenomena of diffusion and motion of matter.

With his exceptional talent, capacity for work, and impeccable honesty as a scientist, Aleksandr Naumovich was able to achieve outstanding results and universal recognition.

Unforgettable for me are Aleksandr Naumovich's wise suggestions, which sometimes extended to problems very far from his immediate scientific interests. Deep sympathy was aroused by the difficulties which

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