

# Kinetic Models of Multi-Route Reactions in Homogeneous Catalysis with Metal Complexes (A Review)

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**Abstract**—The state-of-the-art in the theory of routes for multi-route reactions in the homogeneous catalysis with metal complexes is reviewed. Key problems and the possible approaches to their solution based on the Horiuti–Temkin theory of steady-state reactions, which are useful in constructing the kinetic algebraic models of multi-route processes, are discussed. A classification of the mechanisms of real processes involved in the homogeneous catalysis with metal complexes is presented. The chain mechanisms of catalytic processes, conjugated and associated reactions, and critical phenomena in the dynamics of homogeneous reactions are considered.

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## INTRODUCTION

The statement that correct kinetic investigations and the construction of an experimentally and theoretically justified adequate physical kinetic model of a chemical process provide the basis for adequate modeling and calculations of a chemical reactor is now commonly accepted and treated as obvious. However, the construction of kinetic models for multi-route homogeneous (as well as heterogeneous) catalytic reactions still remains, for many reasons, a difficult task. In what follows, by the physical structural kinetic model of a catalytic process we will imply a system of kinetic algebraic or differential equations formulated on the basis of a mechanistic scheme of reaction steps that is physicochemically justified and adequately describes the process in a broad range of reactant concentrations and temperatures.

Experimental investigations of the kinetics of homogeneous [1] and heterogeneous [2] multi-route catalytic reactions, employing notions of the theory or routes, revealed a problem of identifying the reaction mechanism on the basis of available kinetic and physicochemical data. In the last quarter of the 20th century, it became clear that the traditional strategy of constructing kinetic models and studying reaction mechanisms by proceeding “from the kinetics to mechanisms” was no longer applicable [3, 4]. It was understood that the notion of “reaction mechanism” had a dual character [5] and that the knowledge of a topological structure of the mechanism was of importance. It has been established that special roles in the procedure of discrimination of the hypothetical mechanistic schemes are played by the (i) dependence of the reaction selectivity on the concentrations of reactants and other participants of the process and (ii) analysis of the “conjugation nodes” in the reaction

network. It was also found useful to create artificial branching points (artificial conjugation nodes) in reaction networks, that is, introduce artificial multi-route character [3, 5]. The development of the theory of multi-route reactions elucidated the general essence of the kinetic and thermodynamic conjugation in all complex reactions [1, 6] and provided deeper insight into the mechanisms of functioning of real catalytic processes [1].

The present review will consider the above issues and discuss the key problems and methods based on the Horiuti–Temkin theory of steady-state reactions, which are useful in studying mechanisms of complex reactions and constructing kinetic models of multi-route processes.

## 1. THEORY OF ROUTES. RELATIONSHIP BETWEEN THE REACTION RATES OVER ROUTES AND THE CHEMICAL AFFINITY OF THE OVERALL EQUATIONS OF ROUTES

The problem of a relationship between the reaction mechanism and the stoichiometry of the overall reaction equation was originally posed by Horiuti [7–10] and then developed by M.I. Temkin [11, 12] in the framework of the theory of steady-state reaction kinetics. The theory of routes introduced the concept of the reaction rate over a route (i.e., for the overall equation of the route), thus showing that a complex reaction as well as a simple reaction can be characterized by a rate invariant (i.e., rate of the overall reaction) that is independent of the nature of reactant N for which the rate is measured:

$$\bar{R}_N = B_p^T \bar{R}_p. \quad (1)$$

The rate  $R_N$  for reactant N is invariant with respect to the choice of a basis set of routes and, accordingly, overall equations:

$$\bar{R}_N = B_N^T \bar{W}, \quad (2)$$

$$\bar{B}_p^T = \bar{B}_p^T \bar{G}, \quad (3)$$

where  $\bar{R}_N$  is the vector of reaction rates with respect to participants of overall equations,  $\bar{B}_p^T$  is the transposed stoichiometric matrix of the overall equations of routes,  $\bar{R}_p$  is the vector of rates over routes,  $\bar{W}$  is the vector of step rates  $W_j$ ,  $\bar{B}_N^T$  is the transposed stoichiometric submatrix of the mechanism for reaction participant N, and  $\bar{G}$  is the matrix of stoichiometric numbers of steps.

A basis set of routes and the overall equations of routes can readily be found for arbitrary linear and nonlinear mechanisms. The theory of routes showed that there is no single correct choice of the set of overall equations. The main point is the reaction mechanism. By comparing Eqs. (1) and (2) and taking into account Eq. (3), one can obtain the following relationship between the rates of steps and overall reaction rates for the  $p$ th route:

$$\bar{W} = \bar{G} \bar{R}_p \quad \text{or} \quad W_j = \sum v_j^{(p)} R_p, \quad (4)$$

where  $W_j$  is the rate of the  $j$ th step,  $v_j^{(p)}$  is the stoichiometric number of the  $j$ th step in the  $p$ th route and  $R_p$  is the reaction rate over the  $p$ th route.

The state-of-the-art in the theory of steady-state reactions and the theory of routes, which was developed by Yablonsky and Lazman in their works of on the kinetic polynomials (see review [13] and monograph [14]) and by Gorskii et al. [15] has been recently presented in monograph [1]. Here we will only briefly consider some important aspects and conclusions of the theory of routes, which are related to solution of the problem of establishing a relationship between the reaction rate over a certain route and the chemical affinity of the overall equation over this route—that is, the equilibrium constant of the overall equation. This problem has been considered for single-route reactions by Horiuti (in 1939–1953) [9] Boreskov (1945) [16, 17], and Weller (1950–1954) [18, 19] and recently called the “Horiuti–Boreskov problem” [13].

Although the choice of routes and the corresponding overall equations is an arbitrary procedure, considerable experience has been gained in considering reaction rates over separate routes. This includes simple derivation of the kinetic equations over routes based on Eq. (4) or by the method of graphs for linear mechanisms, analysis of the ratio of these rates at the conjugation nodes in reaction networks (see Section 5), and analysis of the ratio of rates over the route of a reversible single-route reaction ( $R^+/R^-$ ), as related to the chemical affinity [1]. This experience leads to the conclusion that, in choosing the basis set of routes, it is

desired to take into account the thermodynamically allowed directions of the overall equations of reaction routes, their correspondence to the directions of steps, and particularly to the directions of kinetically irreversible steps. In other words, the overall equation of a route, which follows from the reaction mechanism, as well as the rate over this route must possess a clear chemical and thermodynamic sense.

The concept of the reaction rate  $R$  over route as a difference of the rates of the overall reaction in the forward and reverse directions,

$$R = R^+ - R^- \quad (5)$$

is valid for a single-route kinetically reversible reaction that proceeds according to a linear mechanism. Since a single-route reaction with a nonlinear mechanism may be accompanied by critical phenomena (multiplicity of steady states, etc.), the use of formula (5) is only possible provided that the process approaches the equilibrium along a thermodynamic branch, on which the ratio of the reaction rates is determined by the chemical affinity  $A$  of the overall reaction ( $A = -\Delta\mu$ , where  $\Delta\mu$  is the chemical potential). In this case, the rate of the reverse reaction will approach that of the forward reaction up to  $R = 0$ . It should be noted that the same conclusions follow from an analysis of the validity of Eq. (5) performed by Parmon [20] using the concept of “thermodynamic head,” which is a function of the chemical potentials of reactants and products.

Nonlinear mechanisms do not allow (with seldom exceptions) analytical expressions to be obtained for the rates  $R^+$  and  $R^-$  as functions of the concentrations of reactants and products. However, the  $R^+/R^-$  ratio on the thermodynamic branch can be strictly expressed via the chemical affinity using the following simple thermodynamic relations,

$$A_j = RT \ln \frac{W_j^+}{W_j^-}, \quad (6a)$$

$$A = \sum v_j A_j, \quad (6b)$$

$$A = RT \ln \frac{R^+}{R^-} \quad (6c)$$

(where  $A$  and  $A_j$  is the chemical affinity of the overall reaction and the  $j$ th step, respectively), which yield the following expression:

$$\frac{R^+}{R^-} = \prod_j \left( \frac{W_j^+}{W_j^-} \right)^{v_j}. \quad (7)$$

This formula can be used to determine  $R^+$  from the experimentally measured  $R$  values. Note that Eq. (6c) is naturally also valid for linear mechanisms.

#### (a) Single-route reaction with a linear mechanism.

In this case, the overall equation of a route and its equilibrium constant  $K_{eq}$  are determined from the reaction mechanism ( $K_{eq} = \prod_j K_j$ ) or from the experimental kinetic equation of a reversible steady-

state (or quasi-steady-state) reaction under the condition of equilibrium  $R = 0$  and the assumption that the mechanism is the same both near and far from the equilibrium (which follows from the principles of microscopic reversibility and detailed balance).

For example, if the investigation of a reversible reaction described by a simple stoichiometric equation  $A = B$  ( $K_{eq1}$ ) leads to the following kinetic equation,

$$R = k^+[A]^2 - k^-[B]^2, \quad (8)$$

then the condition  $R = 0$  yields the expression  $K_{eq2} = [B]^2/[A]^2$ . This formula corresponds to the overall equation  $2A = 2B$  that leads to the relation

$$\frac{R^+}{R^-} = \prod_j \left( \frac{W_j^+}{W_j^-} \right) = \frac{K_{eq2}}{[B]^2/[A]^2},$$

which should be used for the determination of  $R^+$  from  $R$  or  $R^-$ .

**(b) Nonlinear single-route reaction mechanism with a limiting step.** For a kinetically reversible reaction with this mechanism, Eq. (7) yields the following relation:

$$\frac{W_1^+}{W_1^-} = \left( \frac{R^+}{R^-} \right)^{\frac{1}{v_1}} = \left[ K_{eq} \frac{f^+(c)}{f^-(c)} \right]^{\frac{1}{v_1}}, \quad (9)$$

where  $f^+(c)$  and  $f^-(c)$  are the functions of reactant concentration  $c$  on the left- and right-hand sides of the overall equation, respectively;  $W_1^+$  and  $W_1^-$  are the rates of the limiting step;  $v_1$  is the stoichiometric number of the limiting step;  $\frac{1}{v_1} = m$  is the multiplicity coefficient of the limiting step according to Boreskov; and  $K_{eq}$  is the equilibrium constant of the overall equation with minimum possible integer stoichiometric coefficients.

The overall equation of the route in this case follows from experimental data and is determined by the nature of the limiting step [1]. For example, the reaction scheme



with two sets of stoichiometric numbers,  $v^{(I)} = (1, 0.5)$  and  $v^{(II)} = (1, 2)$ , yield the following overall equations for two different routes of the single-route reaction:  $A = 0.5P$  (for  $v^{(I)}$ ) and  $2A = P$  (for  $v^{(II)}$ ).

If, according to experimental data,  $R^+ \propto [A]$  far from equilibrium, then the limiting step is 1 and, hence,

$$W_1^+ - W_1^- = k_1^+[A] - k_1^-K_2^{-0.5}[P]^{0.5}.$$

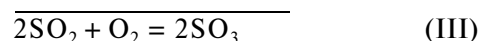
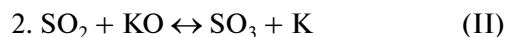
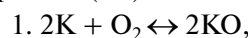
Using the condition of equilibrium, we obtain the following expression for the equilibrium constant of the overall equation of the first route  $K_{eq}^{(I)} = K_1K_2^{0.5}$ . In this case,  $R^+/R^- = (W_1^+/W_1^-)^{v_1^{(I)}}$  for  $v_1^{(I)} = 1$ . Alternatively, if the experimental results correspond to  $R^+ \propto [A]^2$ , then the limiting step is 2 and, hence,

$$W_2^+ - W_2^- = k_2K_1^2[A]^2 - k_2[P].$$

In this case, the equilibrium constant of the overall equation of the first route is  $K_{eq}^{(II)} = K_1^2K_2$  and, hence,  $R^+/R^- = (W_2^+/W_2^-)^{v_2^{(II)}}$  for  $v_2^{(II)} = 1$ .

It is interesting to note the following circumstance. If the value of  $K_{eq}$  for the overall equation that follows from an assumption about the limiting step (or from experimental data), even without minimum possible integer stoichiometric coefficients, is used in Eq. (9), the stoichiometric number will always be  $v_1 = 1$ . In other words, should a certain limiting step be chosen, the overall equation will always correspond to a route in which this step has  $v_1 = 1$ . If the overall equation is selected a priori (which is a common practice), then  $v_1$  can differ from unity. Once the overall equation of a route is known, it is possible to use Eq. (9) for determining  $W_1^+$  from the total reaction rate  $W_1 = W_1^+ - W_1^-$  or determine  $R^+$  from relation (5).

Let us analyze another example that is taken from [13] and consider determination of the stoichiometric number for the limiting step of a catalytic reaction of  $SO_2$  oxidation, which was performed by Boreskov et al. [ $R = R^+ - R^-$ ] using measurements (in particular by the isotope method) of the steady-state rates of the forward and reverse reactions. Route  $v^{(I)} = (1, 2)$  selected for the adopted mechanism (II) corresponds to overall equation (III):



(where K denotes a catalyst).

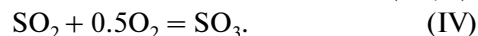
Assuming the existence of a limiting step, Eq. (9) can be rewritten in the following form:

$$\left( \frac{W_1^+}{W_1^-} \right) = \left( \frac{R^+}{R^-} \right)^{\frac{1}{v_1}} = \left( K_{eq} \frac{[SO_2]^2[O_2]}{[SO_3]^2} \right)^{\frac{1}{v_1}}, \quad (10)$$

where  $\frac{1}{v_1} = m$  and  $K_{eq}$  is the equilibrium constant of the overall equation (III). The experimental ratio  $W_1^+/W_1^-$  of the forward and reverse reaction rates is equal to the right-hand side of Eq. (10) with  $m = 0.5$  (or  $v_1 = 2$ ). From this it was concluded that the limiting step is 2. Indeed, the ratio of the forward and reverse reaction rates for this step is

$$W_2^+/W_2^- = \frac{k_2^+K_1^{0.5}P_{O_2}^{0.5}P_{SO_2}}{k_2^-P_{SO_3}}.$$

so that, for  $m = 0.5$ , we obtain  $K_1^{0.5}K_2 = K_{eq}^{0.5} = K'_{eq}$ , where  $K'_{eq}$  is the equilibrium constant of the following overall equation for the second route with  $v^{(II)} = (0.5, 1)$ :



Using this equation with the minimum integer stoichiometric coefficients jointly with Eq. (10), we obtain  $m = 1$  and  $v_1 = 1$ .

Thus, a stoichiometric number of the limiting step as determined from Eq. (9) depends on the choice of the overall equation and the corresponding  $K_{eq}$  and, hence, is not an independent characteristic of the reaction mechanism.

At present, it is evident that there is no need in experimentally determining the stoichiometric number of the limiting step [2, 19] via Eq. (9), although the comparison of obtained  $v_1$  values with the selected overall equation (i.e., route) allows a limiting step to be identified. A kinetic experiment (see above) provides an answer to the question of whether this step exists and what is its nature. An answer to this question is also provided by the discrimination between hypotheses with different limiting steps.

**(c) Single-route reversible reaction with nonlinear mechanism.** In the general case, if the mechanism is known and the route is preset, Eq. (7) for the thermodynamic branch can be alternatively written in terms of step weights  $\omega_j$  as follows:

$$\frac{R^+}{R^-} = \frac{\prod (\omega_j^+)^{v_j^{(p)}}}{\prod (\omega_j^-)^{v_j^{(p)}}} = \frac{f^+(k^+, c)}{f^-(k^-, c)}, \quad (11)$$

where  $f^+(k^+, c)$  and  $f^-(k^-, c)$  are the reaction rates in the form of the law of mass action for the selected overall equation in the forward and reverse direction, respectively. By expressing the rate  $R$  of a kinetically reversible reaction via the rate of product formation—e.g., of  $\text{SO}_3$  according to reaction (III) above—it is possible to determine  $R^+$  from  $R$  using Eq. (11), that is, via the equilibrium constant of the overall equation and the “reaction product”  $\prod c_i^{\beta_i}$ . The choice of another overall equation leads to a different equation of type (11). Evidently, this procedure is not very useful, since analytical expressions for  $R^+$  and  $R$  can be obtained, as was pointed out above, only in seldom cases. Thus, the Horiuti–Boreskov problem for nonlinear mechanisms can be solved, but this solution is senseless.

Attempts at finding an analytical expression for  $R^+ = f(R)$  in the general case by introducing the average stoichiometric step number  $\bar{v}$  [11] via the relation

$$A = \bar{v} \sum A_j, \quad (12)$$

also cannot provide a simple solution of the Horiuti–Boreskov problem in the case of nonlinear mechanisms. The introduction of  $\bar{v}$  is also deprived of physical sense since the product

$$\prod_j \left( \frac{W_j^+}{W_j^-} \right) = \frac{r^+}{r^-}$$

in the equation

$$\frac{R^+}{R^-} = \left[ \prod_j \frac{W_j^+}{W_j^-} \right]^{\bar{v}} \quad (13)$$

can only be measured in the case of linear mechanisms [11, 12]. For a nonlinear mechanism, this value cannot be identified with the ratio of experimentally measured reaction rates. In addition,  $\bar{v}$  is a variable quantity that depends on the reactant concentrations and reaction conditions.

The discrimination of hypotheses concerning any mechanisms can be performed by studying the kinetics of consumption and formation of reactants through an analysis of the systems of differential and/or algebraic equations that describe the reaction mechanisms.

**(d) Invariant of algebraic system (4) for nonlinear mechanisms.** For a given route (overall equation), it was suggested to use an invariant  $f(R, c) = 0$  in the form of a “kinetic polynomial” [13, 14]:

$$B_n R^n + B_{n-1} R^{n-1} + \dots + B_1 R + B_0 = 0, \quad (14)$$

which is the most general form of the equation for the rate of a complex reaction. An algorithm for determining coefficients  $B$  for the known mechanism has been described in [13, 14]. The kinetic polynomial is a thermodynamically consistent function. In particular, coefficient  $B_0$  for a reversible reaction is determined by an equation of the rate over a route written in the form of the law of mass action:

$$B_0 = f^+(k^+, c) - f^-(k^-, c). \quad (15)$$

Under the condition of equilibrium ( $R = 0$ ), we have  $B_0 = 0$  and Eq. (15) can be used to determine the equilibrium constant of the overall equation. Since the roots of polynomial (14) correspond to various steady states, this equation can be used to describe the multiplicity of steady states (poly-steady-state character) [14]. By analogy with the case of linear mechanisms, expression (15) is called a cyclic characteristic,  $C_c = C_c^+ - C_c^-$  [13, 14], although nonlinear mechanisms have no cycles with respect to intermediates because of the presence of steps with  $v_j^{(p)} \neq 1$  (but exhibit contours on bipartite graphs, which do not represent routes).

Based on the kinetic polynomial and hypergeometric functions (Gauss functions), the following “four-term” kinetic equation has been obtained:

$$R = \frac{C_c^+ - C_c^-}{W(k, c)} T(k, c). \quad (16)$$

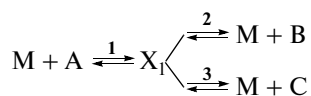
This equation is interesting in that it describes in a fractional-rational form (similar to that of the kinetic equations of steady- or quasi-steady single-route processes with linear mechanisms) the reaction rate for an overall equation of the route of a reversible reaction with a nonlinear mechanism as the difference of rates  $R^+$  and  $R^-$  (i.e., as Eq. (5)) and is consistent with Eq. (11), thus making it possible to find the equilibrium constant in the overall equation of the route. At the same time, Eq. (16) exhibits a phenomenological

character, since polynomials  $W(k, c)$  and  $T(k, c)$  (reflecting the influence of nonlinearity on the process) possess no clear kinetic sense. It was suggested [13, 14] that phenomenological Eq. (16) can provide a kinetic model that is as useful as polynomial (14) for the description of experimental data in the absence of a mechanistic scheme of a reaction under consideration.

**(e) Multi-route reaction.** In this case, the chemical affinity for the overall equation of a  $p$ th route is not described by Eqs. (6b), (6c) and, hence,

$$A_p \neq RT \ln \frac{R_p^+}{R_p^-}, \quad (17)$$

since the rate over the  $p$ th route for a multi-route reaction includes the weights of steps of all other routes. For example, for a reversible steady-state two-route catalytic reaction according to the mechanism



$$(W_1 = W_2 + W_3 = R_B + R_C = R_1 + R_2)$$

the ratio of rates over the second route,  $R_2^+/R_2^-$  includes the weights of steps of the first route:

$$\frac{R_2^+}{R_2^-} = \frac{\omega_3(\omega_1 + \omega_2)}{\omega_{-3}(\omega_{-1} + \omega_2)}.$$

Therefore, the total chemical affinity for the second route,  $A_2^{(2)} = A_1 + A_3$  is not related to the ratio of rates ( $R_2^+/R_2^-$ ) over the second route. In contrast to the case of a single-route reaction (see Eq. (6)), the fractions of the affinity ( $A_1$ ) of the first step are distributed between the two routes. This is clearly illustrated by an analysis of the process near equilibrium (linear region) for  $A_j \ll RT$ , where the expansion into Taylor's series gives the following expressions:

$$1 - \exp\left(-\frac{A_j}{RT}\right) \approx \frac{A_j}{RT} \quad \text{and} \quad W_j = W_j^+ \frac{A_j}{RT}.$$

In the case of the two-route scheme under consideration, this yields the following relation [1]:

$$A_1 = \frac{W_2^+}{W_1^+} A_2 + \frac{W_3^+}{W_1^+} A_3.$$

The features of this scheme also explain, why the rate of a cyclic conversion of intermediates over an "empty" route (i.e., that with "zero" overall equation,  $0 = 0$ ) is nonzero despite the fact that the equilibrium constant for this cyclic route is  $K_0 = \prod K_j = 1$ . Originally, the possibility of using limitations on the ratio of reaction rate constants, which follows from this thermodynamic condition, for estimating rate constants in a kinetic model was probably pointed out by Avetisov et al. [21, 22].

## 2. MULTI-ROUTE MECHANISMS IN CATALYSIS WITH METAL COMPLEXES

Multi-route mechanisms of reactions are a characteristic feature of the catalysis with metal complexes. The main factors that account for the appearance of these mechanisms are as follows:

(i) The presence of several species of active complexes in solution, which catalyze the same or different reactions ("trivial" multi-route character).

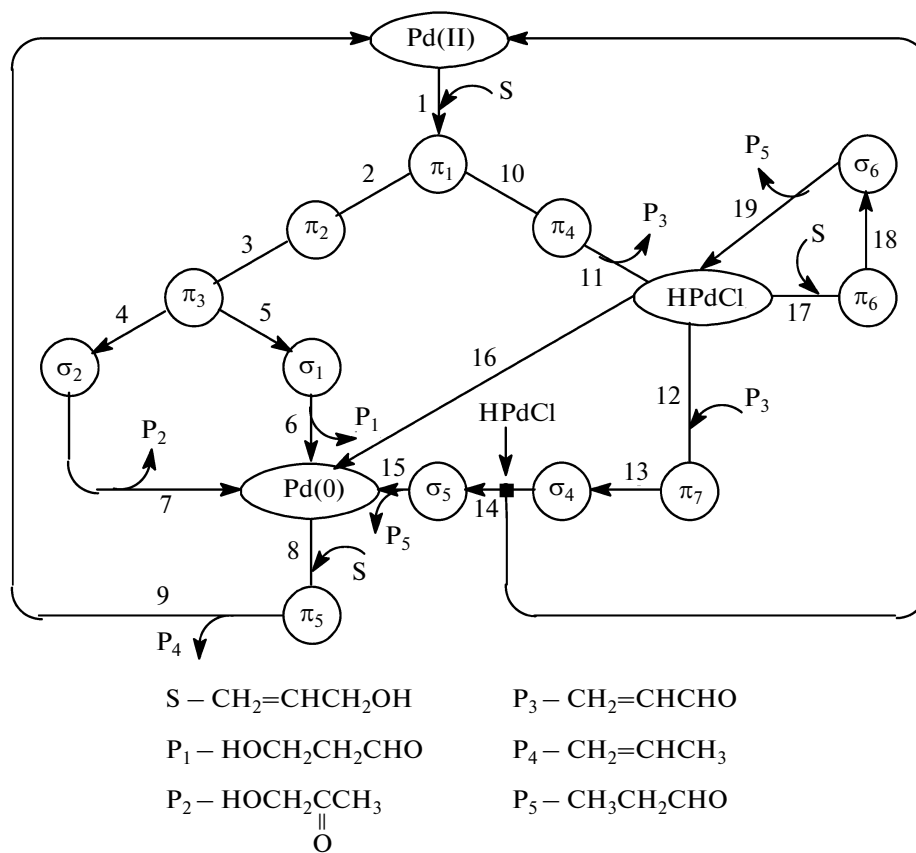
(ii) The variety of pathways for the formation and conversion of intermediate organometallic compounds of transition and post-transition metals, which leads to the construction of large reaction networks (see Schemes 1 and 2), from which a single route can sometimes be "cut" or stabilized by selecting ligands, solvents, and process conditions. For example, a remarkable investigation of Drent et al. [25] from Shell Co. was devoted to a highly active chemo- and regioselective catalytic system for the synthesis of methyl methacrylate by hydromethoxycarbonylation of methylacetylene. The mechanism of this reaction is still a subject for active discussion (see review [26]).

(iii) The variety of mechanisms of the same reaction depending on the nature of a metal, its oxidation state, ligands, and solvent. A good example is the existence of three mechanisms for the hydroalkoxycarbonylation of alkynes in solutions of Pd(II), Pd(0), and Pd(I) complexes [26].

The role of the last two factors can be demonstrated by example of a five-route mechanism of the conjugate process of acetylene carbonylation in solutions of Pd(I) complex (Scheme 3) with the formation of acrylate (A), maleate (M); succinate (S), propionate (P), and ethylene (E) [1, 27, 28]. As can be seen from Scheme 3, acrylate is formed via two routes according to the "alcoholate" and "hydride" mechanisms, and it is the existence of these two routes that allowed an adequate kinetic model to be obtained, which describes all branches of the mechanistic scheme (i.e., the structure of conjugation nodes).

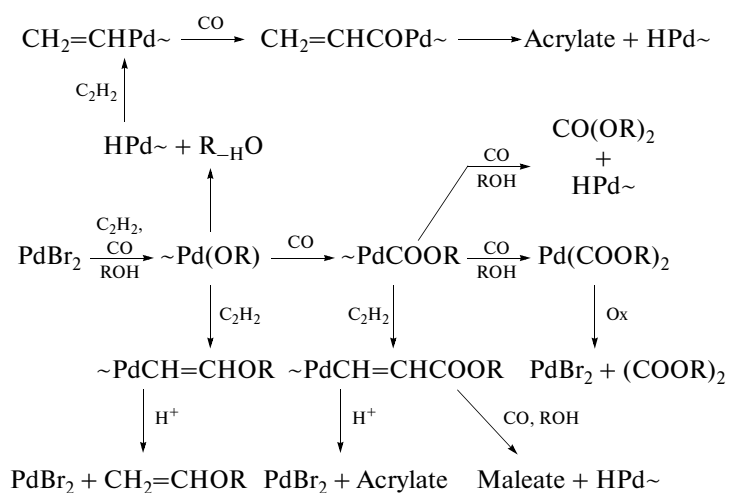
A multi-route character is also inherent in all other types of catalysis. For example, in homogeneous acid catalysis, the acidity (e.g.,  $h_0$ ) in aqueous and non-aqueous media is determined by calculating the concentration of protonated  $C_{BH^+}$  indicator species as the difference  $C_{BH^+} = C_{B_0} - C_B$ . However, several  $BH^+$  species (and, respectively,  $SH^+$ , where S is substrate), which possess different catalytic activities [1], coexist in solution. In particular, three types of HCl compounds with solvent are formed in the DMF-HCl system—namely,  $(DMF)_2HCl$  (K1),  $(DMF)HCl$  (K2), and  $(DMFH)^+HCl_2^-$  (K3)—which exhibit different substrate-protonating ability [29]. Figure 1 shows how the concentrations of complexes K2 and K3 vary in comparison to the acidity function  $H_0$  depending on the HCl solution concentration in water and DMF.

Conversions of allyl alcohol (S) in  $\text{PdCl}_4^{2-}$  solution [23, 24]



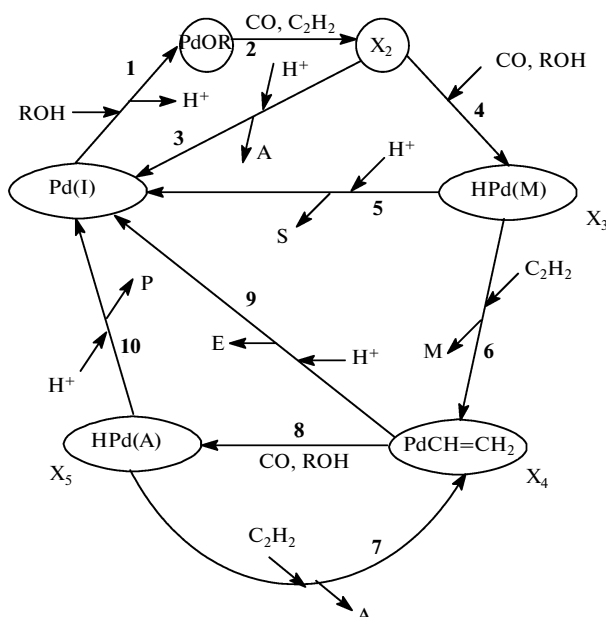
Scheme 1.

Conversions of CO and  $\text{C}_2\text{H}_2$  in alcohol solutions of Pd bromide complexes in the presence or absence of an oxidant [1]



Scheme 2.

Kinetic graph for the mechanism of acetylene carbonylation:  
(A) acrylate; (M) maleate; (S) succinate; (E) ethylene; (P) propionate



Scheme 3.

Enzymatic processes in most cases also represent conjugate multi-route reactions. For example, a reaction with very simple stoichiometry that proceeds *in vivo* (ornithine cycle),



includes nine enzymes and nine enzyme-catalyzed conjugated reactions involving four ATP molecules [30].

In heterogeneous catalysis, the diversity of pathways for the conversion of surface intermediates also accounts for the appearance of large reaction networks even in simple reactions with single-valued stoichiometry (see, e.g., [2]) and the more so in complex multi-step processes such as the Fischer–Tropsch synthesis [31, 32]. The existence of large reaction networks has been theoretically justified even in the combined synthesis of methanol and CO<sub>2</sub> from CO and H<sub>2</sub> [33].

In order to describe the topological structure of complicated mechanisms and reaction networks, it is expedient to use the kinetic graphs of M.I. Temkin for linear, and the bipartite graphs—for nonlinear mechanisms.

### 3. KINETIC AND BIPARTITE GRAPHS AS GEOMETRIC IMAGE OF THE STRUCTURE OF REACTION MECHANISMS

The first researcher who paid attention to the possibility of using graphs for the investigation of complex reaction mechanisms was Balandin [34, 35]. Follow-

ing these investigations and the works by Christiansen [36] and King and Altman [37], M.I. Temkin [38, 39] originally proposed to describe the linear mechanisms of both catalytic and noncatalytic reactions using planar cyclic graphs (so-called Temkin kinetic graphs, KGs) in the space of intermediates (Scheme 4). The vertices of these graphs correspond to intermediates, while the edges connecting these vertices represent elementary reaction steps. Kinetically reversible steps are depicted by non-oriented edges. For example, a two-route mechanism of the catalytic reaction

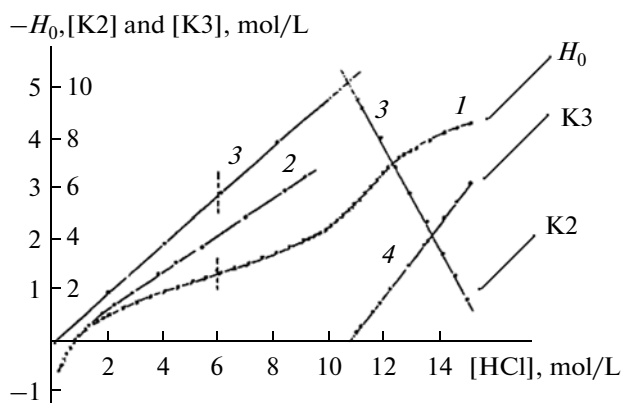
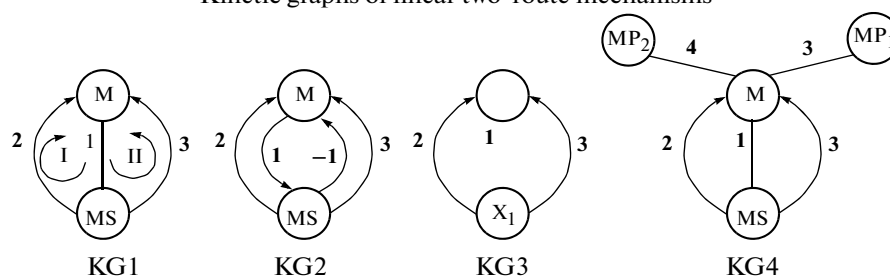


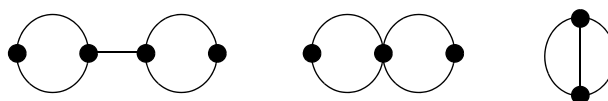
Fig. 1. Plots of the acidity functions of (1) HCl–DMF and (2) HCl–H<sub>2</sub>O systems and the concentrations of (3) K2 and (4) K3 complexes versus initial concentration of HCl in solution [29].

## Kinetic graphs of linear two-route mechanisms

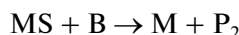
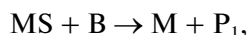
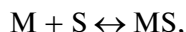


Scheme 4.

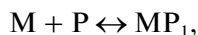
## Topological classes of linear two-route mechanisms



Scheme 5.



is described by the kinetic graphs KG1 or KG2 (Scheme 4). Graph KG4 includes two “pendant” vertices, which correspond to steps



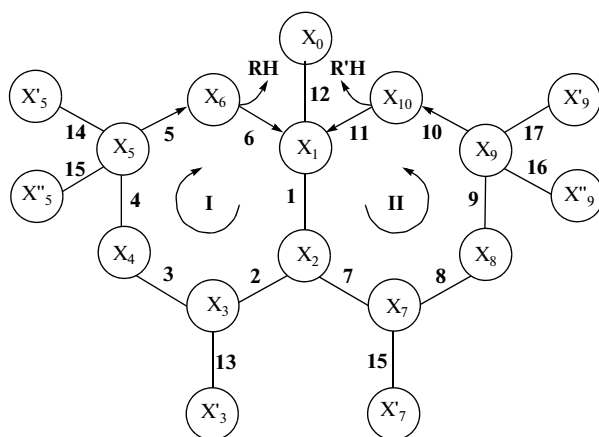
i.e., to the formation of catalyst compounds that do not participate in steps of the catalytic cycles. Finally, graph KG3 with an empty (null) vertex representing a hypothetical intermediate (so-called null-species)

with a unity concentration describes the mechanism of a noncatalytic reaction.

The ideas of M.I. Temkin have been developed by Volkenstein and Goldstein (see, e.g., [40]) and Yablonsky et al. [41] (see also [42, 43]), which led to the creation of a graph-theory apparatus for deriving the kinetic equations of steady-state reactions with linear mechanisms [1, 41, 43, 44]. The author together with Bonchev (see, e.g., [43, 45, 46]) proposed to classify and encode the mechanisms of complex reactions in terms of KGs. For example, two-route reactions with linear mechanisms can be described by three topologically different classes of mechanisms (Scheme 5), while three-route reactions are described by 15 classes of KGs [43].

For the description of nonlinear mechanisms, it was proposed to use bipartite graphs (BGs), which contain vertices of two types, namely, those for the intermediates and steps [42, 43, 47]. Using the kinetic (KG) and bipartite (BG) graphs, it is possible to construct a geometric image of the structure of a mechanism. For example, the classical mechanism of hydroformylation of  $\alpha$ -olefins in solutions of  $HRh(CO)_2L_2$  complexes [48] can be represented by a KG (Scheme 6) of a two-route mechanism with the formation of linear (I) and branched (II) products. In fact, the number of routes is greater, since complexes with one ligand L ( $RhL$ ) and three ligands ( $RhL_3$ ) also contribute to the process [48].

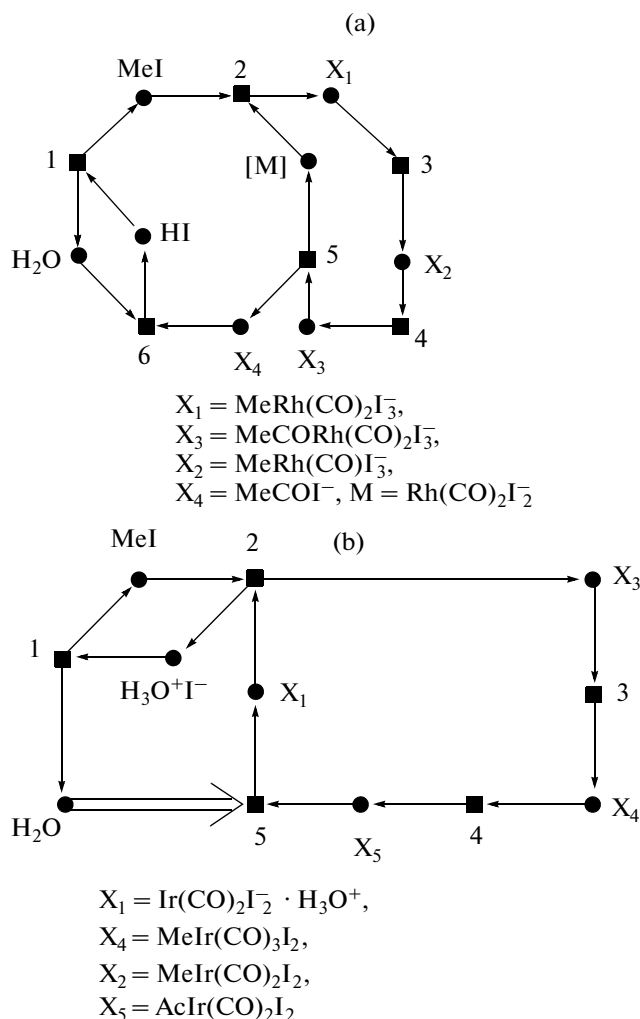
Using BGs of nonlinear mechanisms, it is possible to establish the kinetic functions (KFs) of various catalysts in multicomponent (MCSs) and polyfunctional (PFCS) catalytic systems [43], i.e., to elucidate which reactions (with the corresponding overall equations) are accelerated by one or another catalyst species in a given reaction system. MCSs have drawn considerable

Kinetic graph for two-route mechanism of hydroformylation of  $\alpha$ -olefins

Scheme 6.



Bipartite graphs of subnetworks of intermediates for reaction mechanisms (a) V and (b) IX  
(simplified by assuming all steps to be irreversible)

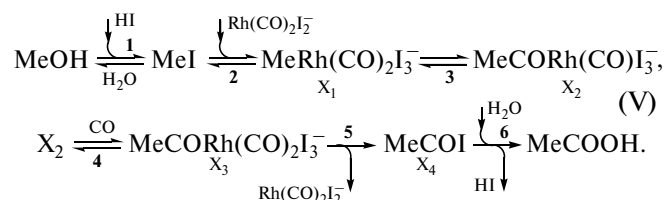


Scheme 7.

interest of researchers beginning with the works of Price [49] and Spitalsky [50]. Systems such as  $\text{PdCl}_2\text{--CuCl}_2$  (used for the oxidation of CO [51] and olefins [52, 53]) have provided a basis for several commercial processes (in particular, Wacker process). Several variants of classification were proposed for MCSs and PFCSS (see, e.g., [43, 54–61]). In recent years, systems with several catalysts have been also actively used in the synthetic organic chemistry (see Section 6), including the so-called “tandem catalysis” [62] and systems combining metal complexes with acid–base [63] or organic [64] catalysts.

Let us consider the KFs of catalysts in MCSs for some processes.

**Carbonylation of methanol to acetic acid.** The mechanism of conversions in the  $\text{Rh}(\text{CO})_2\text{I}_2\text{--HI--MeOH}$  system (Monsanto process) [65] is described by the following sequence of reactions in the framework of a common route:



As can be seen, components Rh(I) and HI in this system perform two KFs. Namely, Rh(I) catalyzes the carbonylation of MeI to MeCOI (steps 2–5) according to the following overall equation:

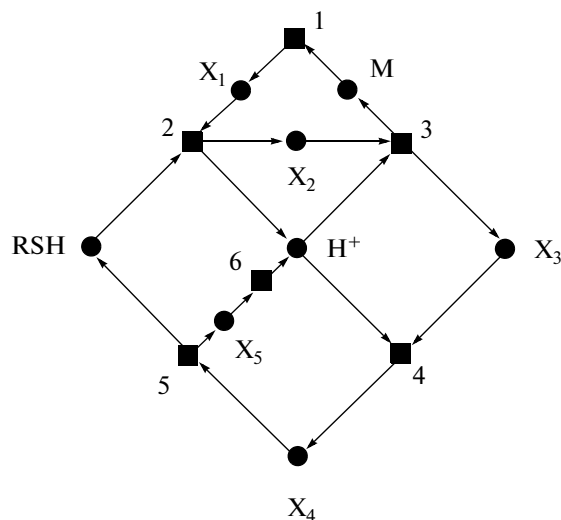


while HI catalyzes the following overall process (steps 1–6):



These KFs are determined by the corresponding contours on a BG (Scheme 7a), i.e., by the cyclic sequences of intermediates. This BG also suggests

Bipartite graph of subnetwork of intermediates for reaction mechanism (XIII)

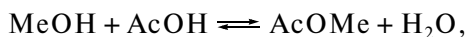


Scheme 8.

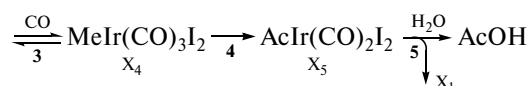
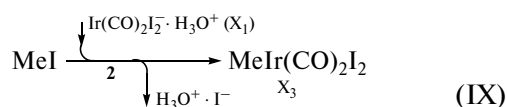
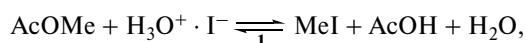
another (non-evident) KF of HI according to the following overall equation:



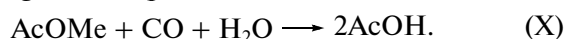
Following [66–68] the mechanism of methanol carbonylation in the  $\text{Ir}(\text{CO})_2\text{I}_2^- \text{HI} \text{MeOH}$  solutions (Cativa–BP Chemicals process) is described by a sequence of reactions at  $[\text{H}_2\text{O}] \leq 0.5 \text{ wt } \%$ . Assuming the low concentrations of water and methanol and taking into account the following equilibrium,



AcOMe (rather than methanol) is considered as the initial reactant in this system. Then, the mechanism of the process is described as follows:



and five steps in this mechanism are combined into the following overall equation:



Considering contours in the corresponding BG (Scheme 7b), it is possible to assign KFs in this system as follows. The KF of  $\text{H}_3\text{O}^+ \cdot \text{I}^-$  is to catalyze the reaction

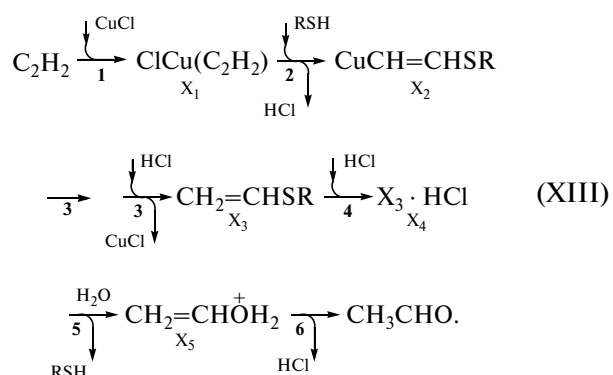


(steps 1 and 2), while the KF of  $\text{Ir}(\text{CO})_2\text{I}_2^- (\text{X}_1)$  is to catalyze the reaction

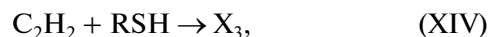


(steps 2–5), and the KF of  $\text{X}_1$  and  $\text{H}_3\text{O}^+ \cdot \text{I}^-$  is to catalyze the overall reaction (X) (steps 1–5). Complex  $\text{X}_2$  ( $\text{MeIr}(\text{CO})_2\text{I}_3^-$ ) accounts for  $\sim 95\% [\text{Ir}]_0$ ; this complex can be represented by a pendant vertex in the BG.

**Hydration of alkynes.** Investigations of the hydration of methylacetylene in solutions of the three-component catalytic system  $\text{Cu}(\text{I})\text{RSHHCl}$  showed that acetone and propionaldehyde are formed in a 1 : 2.3 ratio, that is, the hydration of alkyne proceeds via both Markovnikov and anti-Markovnikov addition of water molecule [69–71]. Let us consider the mechanism of operation of this three-component catalytic system by example of a simpler reaction of acetylene hydration. The sequence of steps in this MCS is as follows:



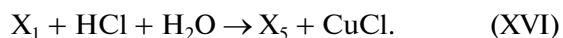
A bipartite graph of the subnetwork of intermediates for this mechanism (Scheme 8) contains seven contours that characterize the KFs of active species. The most obvious of these from the chemical point of view are as follows. The KF of  $\text{CuCl}$  is to catalyze the formation of  $\text{X}_3$  (steps 1–3 with participants  $\text{CuCl}$ ,  $\text{X}_1$  and  $\text{X}_2$ ):



the KF of  $\text{HCl}$  is to catalyze the hydrolysis of  $\text{X}_3$  (steps 4–6):



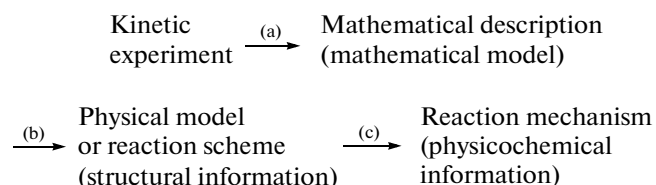
and the KF of  $\text{RSH}$  is to catalyze the conversion of  $\text{X}_1$  into  $\text{X}_5$  (steps 2–5):



The same steps comprise an unbalanced contour involving the vertex with  $\text{HCl}$  (which is both reactant and intermediate). Another unbalanced contour includes steps 3–6. Mechanism (XIII) for the hydration of acetylene and methylacetylene was established as a result of investigations of the kinetics of hydration and hydrolysis of alkenylthioesters using approaches described in [1, 70, 71]. Consideration of more complicated multi-route reactions requires different approaches.

#### 4. RATIONAL STRATEGY FOR DESIGNING KINETIC MODELS AND STUDYING COMPLEX REACTION MECHANISMS

With the implementation of graphs to describe the reaction mechanisms in the space of intermediates, it became clear that the notion of “reaction mechanism” has a dual character and includes two equally important components (elements) and two types of information, namely, physicochemical and structural (topological) [5]. In the case of multi-route reactions, it is impossible to determine the structure of a mechanism (i.e., the mode of linking intermediates) based entirely on the kinetic data and ignoring the physicochemical information [1, 3, 4]. The traditional pathway of elucidating the structure of a mechanism, mechanistic scheme, or physical sense of a mathematical model turned out to be inapplicable to multi-route reactions. The conventional, “traditional” procedure of investigation of a reaction mechanism includes the following stages:



It is assumed that a physical model (mechanistic scheme) allows the structure of a mechanism to be established. On this basis, a notion of the reaction mechanism is formulated, which includes (together with step rate constants) data on the compositions and structures of intermediates and the nature of transition states on each step. The main drawbacks of this strategy are as follows:

- (i) the absence of general algorithms for stages (a)–(c);
- (ii) the assumption that a linear mechanism is realized that should be studied under steady-state or quasi-steady-state conditions, thus admitting the possibility of describing kinetic dependences in terms of fractional-rational equations;
- (iii) the need in accomplishing numerous iterations.

An algorithm for stage (b) has a clear sense only in the case of single-route reactions with linear mechanisms. In implementing this iterative strategy, the physical (non-kinetic) methods of hypothesis dis-

crimination (stage (c)) are usually employed after carrying out complicated and expensive kinetic experiments. Although, some hypotheses can naturally be formulated in selecting a mathematical model (stage (a)), this is more frequently done upon accomplishing the stage of kinetic experiments.

The idea of a strategy of constructing arbitrary models based on the generation of hypotheses, which is referred to below as the “rational” strategy, was probably originally formulated by an American geologist Chamberlin [72] in his article entitled “The Method of Multiple Working Hypotheses” published in *Science* in 1890 (and reproduced by the same journal in 1965). This approach has been actively implemented in the catalytic chemistry since the last quarter of the 20th century, when sufficiently large body of information on intermediates and steps of catalytic reactions has been gained [1, 3, 4, 27, 30]. However, it should be noted that some investigations in heterogeneous catalysis already in 1940s employed discrimination between large sets of relatively simple hypotheses. For example, in 1946 Tchernitz et al. [73] studied the kinetics of hydrogenation of a mixture of isooctenes on a Ni/kieselguhr catalyst and considered 17 kinetic models, while Lumpkin et al. [74] analyzed the same data [73] by discriminating between 74 kinetic models.

The degree of complexity of reaction mechanisms and kinetic models is determined primarily by the topological structure of a mechanism and the way of conjugating routes in a multi-route process [3, 5, 43]. It is this complexity that predetermines the practical impossibility of passing from an empirical kinetic equation providing an adequate mathematical description of the kinetic experiment to a reaction mechanism (stage (c)). For example, the investigation of a conjugate multi-route reaction of acetylene carbonylation in Pd(I) complex solutions in *n*-butanol [26–28] with the formation of five products (see Scheme 3) showed that the measured reaction rate  $r_A = f[H^+]$  of butylacrylate formation was well described by the following empirical formula:

$$r_A = \frac{k'_{10}[H^+]^2}{1 + k'_1[H^+] + k'_2[H^+]^2}. \quad (18)$$

However, the simplest scheme of a five-route mechanism (see KG in Scheme 3), where  $H^+$  is involved in five steps leads to the following expression:

$$r_A = \frac{k_{10} + k_{11}[H^+] + k_{12}[H^+]^2 + k_{13}[H^+]^3 + k_{14}[H^+]^4}{k_1 + k_2[H^+] + k_3[H^+]^2 + k_4[H^+]^3 + k_5[H^+]^4 + k_6[H^+]^5}. \quad (19)$$

Evidently, there is no (and, probably, cannot be) a transition from Eq. (18) to (19) and Scheme 3.

Considering the rational strategy of constructing kinetic models for (primarily) multi-route reactions, a

new paradigm in the investigation of chemical kinetics should consist in the following sequence of stages [1, 3, 4]:

- (i) generation of hypotheses;
- (ii) analysis of hypotheses (derivation of kinetic equations under various assumptions and determination of critical factors for each hypothesis);
- (iii) hypotheses discrimination planning;
- (iv) experimental verification (all kinds of experiment);
- (v) selection of retained working hypotheses.

Evidently, the value of obtained information and constructed kinetic models will be determined by the number and quality (level of justification) of the initial hypotheses. A negative result returns the study to the first step and there appears a probability of gaining new knowledge.

In the framework of the rational strategy, the reaction mechanism occupies an equal (rather than secondary) position with respect to the physical model (structure of reaction mechanism). There are well-known formalized procedures (computer routines) for generating hypotheses (see, e.g., [75–78]). Methods for reduction of the complexity of hypotheses have been proposed and approaches to the analysis of large reaction networks have been developed [33, 79–81].

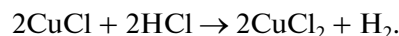
Naturally, a hybrid (iterative) strategy of studying reaction mechanisms (kinetics → hypothesis → kinetics → hypotheses...) with recourse to physicochemical methods is possible as well. In the field of homogeneous catalysis, the best kinetic models in the 20th century were in most cases obtained exactly in this way, although these results primarily refer to not very complicated, mostly single-route mechanisms. In the case of multi-route reactions, a useful tool for discriminating hypotheses and elucidating the structure of mechanisms is offered by the analysis of so-called “conjugation nodes” in reaction networks. For example, in a KG presented in Scheme 3, some intermediates that are linked to other via three or more steps represent such conjugation nodes.

## 5. CONJUGATION NODES IN REACTION NETWORKS AND ARTIFICIAL MULTI-ROUTE CHARACTER OF REACTIONS

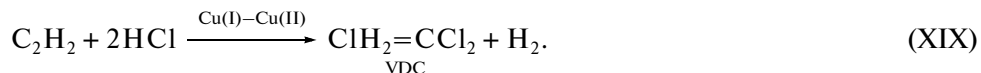
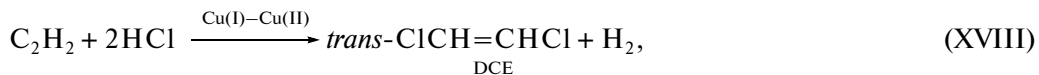
The presence of conjugation nodes in generated hypotheses about mechanisms of a multi-route reaction allows these hypotheses to be discriminated with respect to the rates of product formation, product concentrations, or selectivities without using complete kinetic equations for the reaction network under consideration [3, 5]. In the case of single-route processes, a useful procedure is the creation of an artificial multi-route character in order to obtain information about steps following the last irreversible one (frequently, a limiting step). In order to create these conjugation nodes, it is possible to introduce isotope-labeled substrates, use reactants capable of specifically acting upon certain intermediates (i.e., inhibitors in enzyme catalysis), or employ mixtures of reactants with close natures (method of competitive reactions). Let us consider some examples of using this approach.

### 1. Oxidative chlorination of acetylene [1, 82, 83].

The kinetics of acetylene hydrochlorination to vinyl chloride (VC) was studied in the  $\text{NH}_4\text{Cl}$  (12  $\tilde{m}$ )– $\text{CuCl}$  (3–9  $\tilde{m}$ )– $\text{HCl}$  (0.1–0.5 M– $\text{CuCl}_2$  ( $5 \times 10^{-3}$ – $1.7 \times 10^{-1}$  M) system at 80°C, under the conditions of *trans*-1,2-dichloroethylene (*trans*-DCE) and vinylidene chloride (VDC) formation ( $\tilde{m}$  denotes solution molality, mole/kg  $\text{H}_2\text{O}$ ). The process was carried out in a flow gradient-free reactor under the steady-state conditions with respect to  $[\text{CuCl}_2]$ , whereby  $\text{CuCl}$  is electrochemically oxidized to  $\text{CuCl}_2$  via the following reaction:



The overall reactions were described by the following equations:

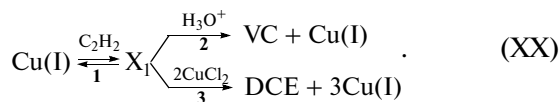


The constancy of  $[\text{H}_3\text{O}^+]$  and the activity ( $a_{\text{Cu}^+}$ ) in each series of experiments with variable  $[\text{CuCl}_2]_\Sigma$  was checked using a pH-meter and a potentiometer, respectively. Under the indicated conditions, we have  $a_{\text{Cu}^{2+}} \propto [\text{CuCl}_2]_\Sigma$  and  $a_{\text{Cu}^{2+}} \propto [\text{Cu}^{2+}]$ . The activities of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions were determined from in situ measurements of the potentials of platinum and copper electrodes. The observed effect of the concentration of

$\text{CuCl}_2$  on the rate of VC formation ( $r_{\text{VC}}$ ) suggested that all three products (VC, DCE, and VDC) are interrelated via conjugation nodes. An analysis of the dependence of the ratio  $r_{\text{DCE}}/r_{\text{VC}}$  on  $\text{CuCl}_2$  ( $a_{\text{Cu}^{2+}}$ ,  $[\text{Cu}^{2+}]$ ) and  $[\text{H}_3\text{O}^+]$  yielded the following equation:

$$\frac{r_{\text{DCE}}}{r_{\text{VC}}} = \bar{k}_1 \frac{[\text{CuCl}_2]_\Sigma^2}{[\text{H}_3\text{O}^+]} \quad (20)$$

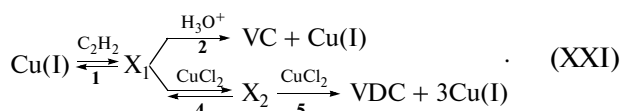
which was indicative of a very simple structure of the conjugation node for the steps of formation of these products:



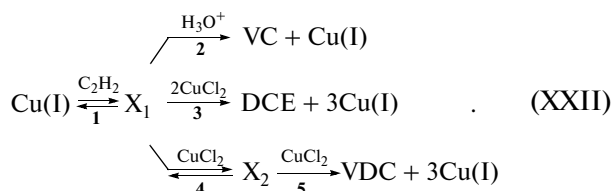
The dependence of the ratio  $r_{\text{VDC}}/r_{\text{VC}}$  on  $[\text{CuCl}_2]_{\Sigma}$  obeyed a more complicated relation,

$$\frac{r_{\text{VDC}}}{r_{\text{VC}}} = \bar{k}_2 \frac{[\text{CuCl}_2]_{\Sigma}^2}{[\text{H}_3\text{O}^+](\bar{k}_3 + [\text{CuCl}_2]_{\Sigma})}, \quad (21)$$

which showed evidence that the intermediates converted into VC and VDC are connected via at least one slow (non-quasi-equilibrium) step 4:



Combining the conjugation nodes (XX) and (XXI) yields the following structure of a mechanism



All the three overall reactions are of the first order with respect to  $P_{\text{C}_2\text{H}_2}$ . In order to verify the proposed conjugation node structure and find the kinetic equations for each product (route), it is possible to use Eq. (22), which follows from scheme (XXII) for  $a_{\text{Cu}^+} = \text{const}$  and  $W_1 = r_{\Sigma} = r_{\text{VC}} + r_{\text{DCE}} + r_{\text{VDC}}$ . Therefore, the entire body of data obtained for various  $[\text{CuCl}]$  and  $a_{\text{Cu}^+} = \text{const}$  for each CuCl concentration is described by the following equation:

$$\frac{r_{\text{VC}}}{P_{\text{C}_2\text{H}_2}[\text{H}_3\text{O}^+]} = \bar{k}_6 - \bar{k}_7 \frac{r_{\Sigma}}{P_{\text{C}_2\text{H}_2}}. \quad (22)$$

Solving the system of three equations (20)–(22) with three unknowns rates ( $r_{\text{VC}}$ ,  $r_{\text{DCE}}$ ,  $r_{\text{VDC}}$ ) leads to the corresponding kinetic equations. For example, an expression for  $r_{\text{VC}}$  is as follows:

$$r_{\text{VC}} = \frac{P_{\text{C}_2\text{H}_2}[\text{H}_3\text{O}^+](\bar{k}_3 + [\text{CuCl}_2]_{\Sigma})}{\frac{\bar{k}_3}{\bar{k}_6} + \frac{\bar{k}_7\bar{k}_3}{\bar{k}_6}[\text{H}_3\text{O}^+] + \frac{[\text{CuCl}_2]_{\Sigma}}{\bar{k}_6}(1 + \bar{k}_7[\text{H}_3\text{O}^+]) + \frac{\bar{k}_7}{\bar{k}_6}[\text{CuCl}_2]_{\Sigma}^2(\bar{k}_2 + \bar{k}_1\bar{k}_3) + \frac{\bar{k}_1\bar{k}_7}{\bar{k}_6}[\text{CuCl}_2]_{\Sigma}^3}. \quad (23)$$

By the same approach, for  $P_{\text{C}_2\text{H}_2} = \text{const}$  and  $[\text{H}_3\text{O}^+] = \text{const}$ , we have

$$r_{\text{VC}} = \frac{\alpha + [\text{CuCl}_2]_{\Sigma}}{D}, \quad (24)$$

$$r_{\text{DCE}} = \frac{\phi[\text{CuCl}_2]_{\Sigma}^2(\alpha + [\text{CuCl}_2]_{\Sigma})}{D}, \quad (25)$$

$$r_{\text{VDC}} = \frac{\chi[\text{CuCl}_2]_{\Sigma}^2}{D}, \quad (26)$$

where

$$D = \varepsilon + \delta[\text{CuCl}_2]_{\Sigma} + \gamma[\text{CuCl}_2]_{\Sigma}^2 + \beta[\text{CuCl}_2]_{\Sigma}^3. \quad (27)$$

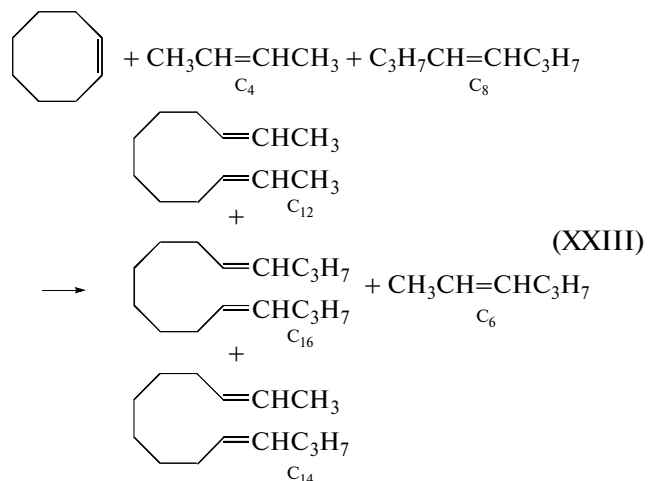
Obviously, it would be difficult to describe how the rate of product formation (VC and VDC) passes through a maximum with respect to  $[\text{CuCl}_2]_{\Sigma}$  (according to the experimental data) and to find equations of the type (24)–(27) from the known dependence of  $r_{\text{P}_i} = \phi([\text{CuCl}_2]_{\Sigma})$ . Additional information on the mechanism of a conjugate process and the influence of activities  $a_{\text{Cu}^+}$  and  $a_{\text{Cl}^-}$  was obtained [83] from an analysis of the constants of a dimensionless “criterion” equation

$$\frac{r_{\text{DCE}}}{r_{\text{VDC}}} = k_1 + k_2[\text{H}_3\text{O}^+]^{1/2} \left( \frac{r_{\text{DCE}}}{r_{\text{VC}}} \right)^{1/2}, \quad (28)$$

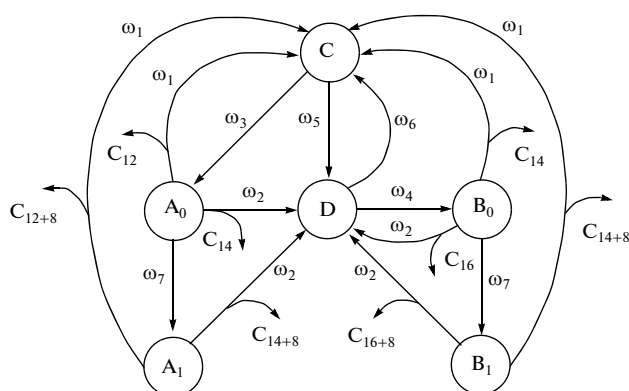
which follows from Eqs. (20) and (21).

**2. Double cross-metathesis.** Investigation of the kinetics of ring opening metathesis with two acyclic olefins allowed the proposed carbene mechanism of met-

athesis [84, 85] to be kinetically confirmed for the first time. The reaction



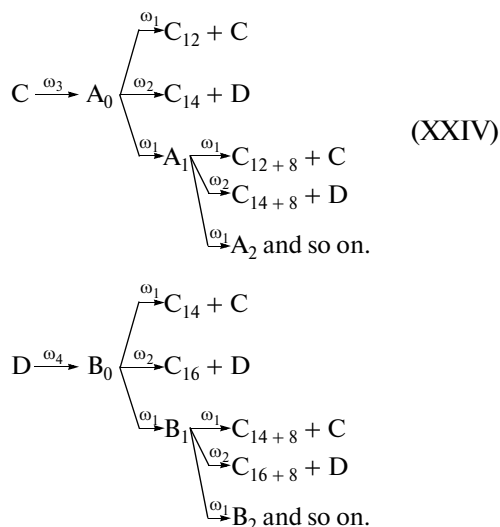
Kinetic graph of double cross metathesis according to reaction mechanism (XXIV)  
with the formation of  $C_{m+8n}$  ( $m = 12, 14, 16; n = 0.1$ ) [1]



Scheme 9.

was studied in a chlorobenzene solution of  $\text{Mo}(\text{PPh}_3)_2\text{Cl}_2(\text{NO})_2$  and  $\text{MeAlCl}_2$  at  $0^\circ\text{C}$  and  $25^\circ\text{C}$  by measuring the temporal variation of the concentrations of all reactants and products in a closed reactor. The values of  $[\text{C}_{14}]/[\text{C}_{12}]$  and  $[\text{C}_{14}]/[\text{C}_{16}]$  were extrapolated to  $t \rightarrow 0$  [i.e., to the conditions of negligibly small  $\rightarrow 0$  degree of cyclooctene (Cy) conversion]. Since the indicated relative selectivities were significantly different from zero, it was concluded that product  $\text{C}_{14}$  (that appeared in parallel to  $\text{C}_{12}$  and  $\text{C}_{16}$ ) could not be formed via consecutive reactions (such as, e.g.,  $\text{C}_4 + \text{C}_8 \rightarrow 2\text{C}_6$  or  $\text{Cy} + \text{C}_6 \rightarrow \text{C}_{14}$  within the framework of a “pairwise” (cyclobutane) mechanism, since the initial concentrations of intermediate products  $\text{C}_6$ ,  $\text{C}_{12}$ , and  $\text{C}_{16}$  are very small as compared to the concentrations of reactants.

The obtained results well agree with the following kinetic scheme, in which products  $\text{C}_{12}$ ,  $\text{C}_{14}$ ,  $\text{C}_{16}$ , and  $\text{C}_6$  are formed via competitive reactions of the active carbene complexes of four types (for  $\text{C}_{m+8n}$  with  $m = 12, 14, 16; n = 0, 1$ ) with three olefins including Cy, 2-butene (Bu), and 4-octene (Oc) [84, 85]:



C:  $\text{CH}_3\text{CH}=\text{M}$ ,  $\text{A}_n$ :  $\text{CH}_3\text{CH}=[\text{CH}(\text{CH}_2)_6\text{CH}]_{n+1}=\text{M}$ ,  
D:  $\text{C}_3\text{H}_7\text{CH}=\text{M}$ ,  $\text{B}_n$ :  $\text{C}_3\text{H}_7\text{CH}=[\text{CH}(\text{CH}_2)_6\text{CH}]_{n+1}=\text{M}$ .

The weights of steps in reaction scheme (XXIV) can be described by the following formulas:

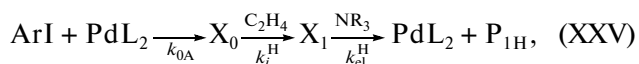
$$\begin{aligned}
 \omega_1 &= k_1[\text{Bu}], \quad \omega_2 = k_2[\text{Oc}], \quad \omega_3 = k_3[\text{Cy}], \\
 \omega_4 &= k_4[\text{Cy}], \quad \omega_7 = k_7[\text{Cy}].
 \end{aligned}$$

Scheme 9 shows a KG for the proposed reaction mechanism. The presence of four conjugation nodes on carbenoids  $\text{A}_0$ ,  $\text{A}_1$ ,  $\text{B}_0$ , and  $\text{B}_1$  allows expressions to be obtained for the relations between  $\text{C}_{14}$ ,  $\text{C}_{12}$ , and  $\text{C}_{16}$  and all their homologs ( $\text{C}_{14+8n}$ ,  $\text{C}_{12+8n}$ , and  $\text{C}_{16+8n}$ ), for example:

$$\begin{aligned}
 \alpha_1 &= \frac{[\text{C}_{14}]}{[\text{C}_{12}]_{t \rightarrow 0}} = \frac{\omega_2[\text{A}_0] + \omega_1[\text{B}_0]}{\omega_1[\text{A}_0]} = \frac{\omega_2}{\omega_1} + \frac{[\text{B}_0]}{[\text{A}_0]} = 2 \frac{\omega_2}{\omega_1}, \\
 \alpha_2 &= \frac{[\text{C}_{14}]}{[\text{C}_{16}]_{t \rightarrow 0}} = \frac{\omega_2[\text{A}_0] + \omega_1[\text{B}_0]}{\omega_2[\text{B}_0]} = \frac{\omega_1}{\omega_2} + \frac{[\text{A}_0]}{[\text{B}_0]} = 2 \frac{\omega_1}{\omega_2}.
 \end{aligned}$$

As can be seen, under the adopted assumptions  $\alpha_1\alpha_2 = 4$ . The average experimental value of the  $\alpha_1\alpha_2$  product obtained by extrapolating  $\alpha_1$ ,  $\alpha_2$ , or  $\alpha_1\alpha_2$  to  $t \rightarrow 0$  amounted to  $4.05 \pm 0.05$  and, in agreement with the theory, was independent of the time. These results confirmed the proposed carbene mechanism of metathesis.

**3. Studying mechanism of the Heck (Heck–Mizoroki) reaction using a mixture of isotopomers.** In order to obtain information concerning slow reaction steps and the structure of material balance with respect to a catalyst, the kinetics of the Heck reaction was studied for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{D}_4$ , and a styrene- $h_8$ /styrene- $d_8$  (1 : 1) mixture (for the creation of a conjugation node) [86, 87]. For the reaction of ethylene according to the scheme



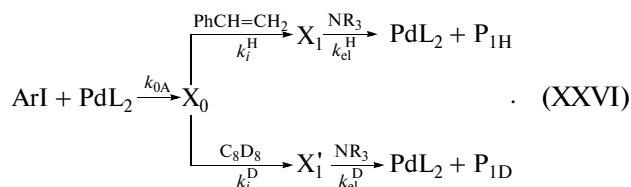
with quasi-steady-state condition for  $\text{X}_0$  and  $\text{X}_1$ , the kinetic equation is as follows:

$$r_{\text{P}_{\text{IH}}} = \frac{k_{0\text{A}}[\text{ArI}][\text{Pd}]_{\Sigma}}{1 + \frac{k_{0\text{A}}[\text{ArI}]}{k_i^{\text{H}}[\text{C}_2\text{H}_4]} + \frac{k_{0\text{A}}[\text{ArI}]}{k_{\text{el}}^{\text{H}}[\text{C}_2\text{H}_4]}} \quad (29)$$

Accordingly,  $r_{\text{P}_{\text{IH}}} = k_{0\text{A}}[\text{ArI}][\text{Pd}]_{\Sigma}$  for  $[\text{Pd}]_{\Sigma} \approx [\text{PdL}_2]$ ,  
 $r_{\text{P}_{\text{IH}}} = k_i^{\text{H}}[\text{C}_2\text{H}_4][\text{Pd}]_{\Sigma}$  for  $[\text{Pd}]_{\Sigma} \approx [\text{X}_0]$  and  
 $r_{\text{P}_{\text{IH}}} = k_{\text{el}}^{\text{H}}[\text{Pd}]_{\Sigma}$  for  $[\text{Pd}]_{\Sigma} \approx [\text{X}_1]$ .

The large kinetic isotope effect (KIE) of  $r_{\text{P}_{\text{IH}}}/r_{\text{P}_{\text{ID}}} = 3.2$  observed on the passage from  $\text{C}_2\text{H}_4$  to deuterioethylene is indicative of a significant contribution of the  $\beta$ -elimination step to the reaction rate, that is, of the proximity of  $[\text{Pd}]_{\Sigma}$  and  $[\text{X}_1]$ . Therefore, the slow stage in the process under consideration must be the last step, for which  $k_i^{\text{H}}[\text{C}_2\text{H}_4][\text{X}_0] \gg k_{\text{el}}^{\text{H}}[\text{X}_1]$  and  $k_i^{\text{D}}[\text{C}_2\text{D}_4][\text{X}'_0] \gg k_{\text{el}}^{\text{D}}[\text{X}'_1]$ .

These assumptions were confirmed in the experiments with an equimolar mixture of styrene and styrene- $d_8$ . Under the conditions of high regioselectivity, the mechanistic scheme is as follows:



It was experimentally established that the product formation rates  $r_{\text{P}_{\text{IH}}}$  and  $r_{\text{P}_{\text{ID}}}$  are approximately the same, while the total rate  $r_{\Sigma}$  is about half that for  $r_{\text{P}_{\text{IH}}}$  observed in the absence of deuterostyrene. The equality of  $r_{\text{P}_{\text{IH}}}$  and  $r_{\text{P}_{\text{ID}}}$  values under quasi-steady-state conditions is evidence for the equality of  $k_{\text{el}}^{\text{H}}[\text{X}_1] = k_{\text{el}}^{\text{D}}[\text{X}'_1]$ , in which the distribution of  $[\text{Pd}]_{\Sigma}$  (between  $\text{X}_1$  and  $\text{X}'_1$ ) is determined by the KIE magnitude:

$$\text{KIE} = \frac{k_{\text{el}}^{\text{H}}}{k_{\text{el}}^{\text{D}}} = \frac{[\text{X}'_1]}{[\text{X}_1]} \quad (30)$$

For the equal concentrations of  $[\text{C}_8\text{H}_8] = [\text{C}_8\text{D}_8]$ , the  $r_{\Sigma}$  value can be described as

$$r_{\Sigma} = r_{\text{P}_{\text{IH}}} + r_{\text{P}_{\text{ID}}} = \frac{[\text{Pd}]_{\Sigma} k_{\text{el}}^{\text{H}} k_{\text{el}}^{\text{D}} (L + 1)}{L k_{\text{el}}^{\text{D}} + k_{\text{el}}^{\text{H}}}, \quad (31)$$

where  $L = k_i^{\text{H}}/k_i^{\text{D}}$ .

For the reaction with nondeuterated olefin at  $[\text{Pd}]_{\Sigma} \approx [\text{X}_1]$ , the rate is

$$r'_{\text{P}_{\text{IH}}} = k_{\text{el}}^{\text{H}}[\text{Pd}]_{\Sigma}. \quad (32)$$

Then, for the same rate of olefin insertion ( $k_i^{\text{H}} = k_i^{\text{D}}$ ,  $L = 1$ ), we obtain

$$\frac{r'_{\text{P}_{\text{IH}}}}{r_{\Sigma}} = \frac{k_{\text{el}}^{\text{D}} + k_{\text{el}}^{\text{H}}}{2k_{\text{el}}^{\text{D}}} = \frac{1}{2} \left( \frac{k_{\text{el}}^{\text{H}}}{k_{\text{el}}^{\text{D}}} + 1 \right). \quad (33)$$

For  $r'_{\text{P}_{\text{IH}}}/r_{\Sigma} \approx 2$  (experiment), we obtain  $\text{KIE} = k_{\text{el}}^{\text{H}}/k_{\text{el}}^{\text{D}} = 3$ , which is close to the value of 3.2 known for the reactions with  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ . Thus, the method of competitive reactions according to the adopted mechanistic scheme with the indicated ratios of step rates yields the ratio  $r_{\text{P}_{\text{IH}}}$  and  $r_{\text{P}_{\text{ID}}}$  for the last step with a KIE value close to 3. In this case, only a comparison of the sum of product formation rates in a competitive reaction to the rate of conversion of one isotopomer can be used for determining the KIE or other relative rate constants.

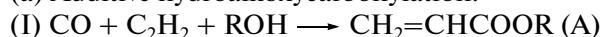
The mechanism of the conjugated carbonylation of acetylene (Scheme 3) was also identified by means of the analysis of conjugation nodes [3, 27]. The use of competitive reactions significantly promoted elucidation of the nature of active catalytic centers in the Heck–Mizoroki and Suzuki–Miyaura reactions (see Section 7).

In addition to the above examples of the successful application of the rational strategy with the analysis of the hypothetical conjugation nodes (1)–(3), this approach was also used to study mechanisms of the reactions of alkylbenzene oxidation by  $\text{Mn(VII)}$  compounds [88, 89], oxidation of hydrocarbons and perfluorocarbons [90], acetylene hydroacetoxylation [91], acetylene carbonylation with the formation of succinic and maleic anhydrides [93], oxidative dimerization of alkynes [94, 95], and some other processes [1].

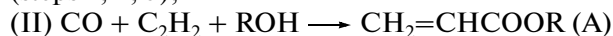
## 6. CONJUGATED AND ASSOCIATED PROCESSES

The mechanism of acetylene carbonylation (Scheme 3) features the following conjugated routes and corresponding processes.

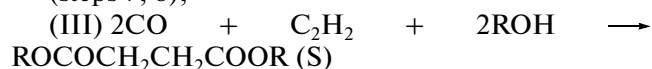
(a) Additive hydroalkoxycarbonylation:



(steps 1, 2, 3);

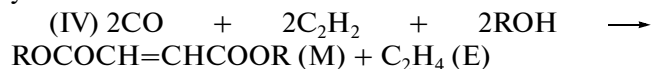


(steps 7, 8);



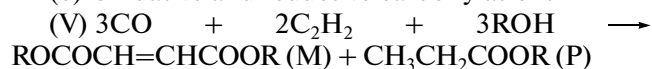
(steps 1, 2, 4, 5);

(b) Oxidative carbonylation: and reduction of acetylene:



(steps 1, 2, 4, 6, 9);

(c) Oxidative and reductive carbonylation:



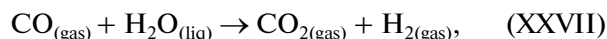
(steps 1, 2, 4, 5, 8, 10).

The kinetic conjugation of steps and routes is the most general feature of complex single- and multi-route reactions. Conjugated reactions were separated into a special group of processes (Ostwald, Shilov)

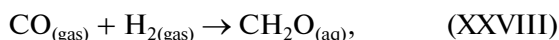
more than a century ago (see, e.g., [96]), long before the appearance of the theory of chain reactions (Bodenstein, Semenov, Hinselwood) and the theory of multi-route processes. This specificity was related to the discovery of an interesting phenomenon, whereby the rate of one reaction depended on the rate of another process and even the onset of the former reaction was possible on the simultaneous occurrence of the latter process. The type of conjugation in a complex reaction, which was discovered by Shilov and called "chemical induction," occupies a special place among the known mechanisms of kinetic conjugation and still attracts special attention. This mechanism is based on the kinetic conjugation of sequential steps via a common intermediate, which was established due to the investigations of de Donde [97, 98], Prigogine [99], Boudart [100], and other researchers, which elucidated the phenomena of kinetic and thermodynamic conjugation [1, 101].<sup>1</sup>

### 6.1. Multi- and Single-Route Reactions: Classical Case

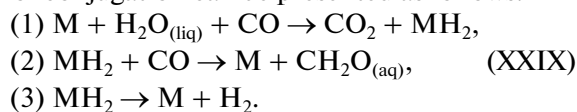
Conjugate reactions of the classical type appear when an intermediate of one thermodynamically allowed reaction (base reaction) makes another thermodynamically forbidden process exoergonic or makes a kinetically hindered process allowed due to the appearance of a new route with the corresponding new overall equation. For example, in the case of combination of a base reaction



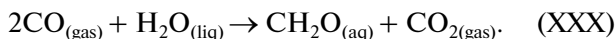
and endoergonic reaction of CO reduction



in solutions of Mo(IV) dimer clusters [102], the mechanism of conjugation can be presented as follows:

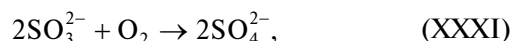


As a result of the summation of sequential steps (1) and (2), there appears a new reaction with the overall equation

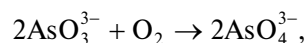


The contribution of the route described by equation (XXVII) is not large and the product of this step ( $\text{H}_2$ ) does not enter into the overall equation of the new process. Hydrogen may be even not at all evolved, and then the reaction will be single-route. The main point is the kinetic conjugation of sequential steps (1) and (2) in mechanism (XXIX) and the new stoichiometry of the overall equation. Indeed, mechanism

(XXIX) exhibits the kinetic conjugation of routes corresponding to the overall equations (XXVII) and (XXX). The overall equation of the base reaction can enter as a whole into a new equation of the conjugate process. An example is offered by the oxidation of  $\text{SO}_3^{2-}$



conjugated with kinetically hindered oxidation of  $\text{AsO}_4^{3-}$



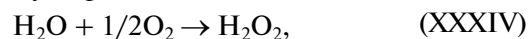
which results in a new process (of overall equation) [103]



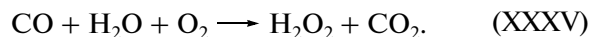
Using the exoergonic reaction



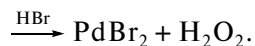
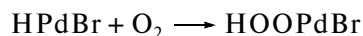
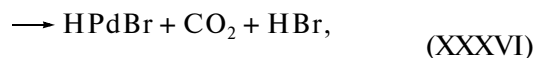
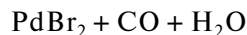
as the base, it is possible to carry out otherwise endoergonic reactions. For example, it is possible to oxidize water to dehydroperoxide



but this takes place in the framework of a new reaction (new overall equation) that is conjugated with the base reaction [6, 101, 104–106]:

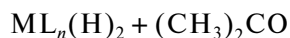
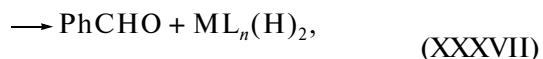


By this reaction it is possible to obtain a 7% hydrogen peroxide solution in a two-phase system using Pd(II) complexes with phenanthroline ligands [105]. One possible mechanism of this process is as follows [101]:

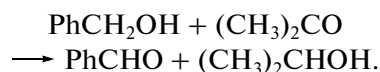


The partial decomposition of  $\text{H}_2\text{O}_2$  leads to the appearance of a second route with the overall equation of base reaction (XXXIII).

The phenomenon of chemical induction is also manifested in the single-route reaction of transferred hydrogenation-dehydrogenation (without  $\text{H}_2$  evolution) [107], which proceeds due to the kinetic conjugation of two steps:



In this case, the thermodynamically constrained reaction of dehydrogenation is replaced by the following reaction with a new overall equation of the single-route process:

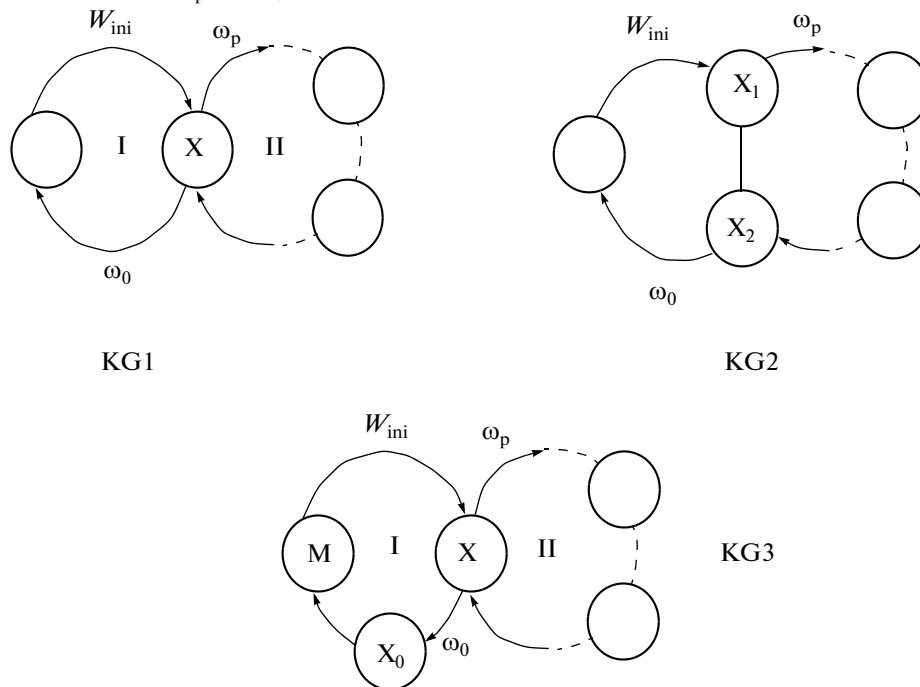


<sup>1</sup> The more common term "conjugate reactions" was introduced by N.A. Shilov instead of the term "coupled reactions" (gekoppelte Vorgänge) that was previously used by W. Ostwald.



## Kinetic graphs for non-branched chain processes

( $W_{\text{ini}}$  is the rate of initiation step;  $\omega_p$  and  $\omega_t$  are the weights of the chain propagation and termination steps, respectively)



Scheme 10.

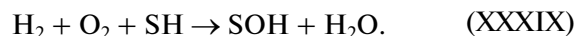
## 6.2. Multi-Route Reactions: Chain Processes

In chain processes, the presence of routes involving the steps of chain nucleation and termination makes possible the implementation of kinetically hindered thermodynamically allowed routes involving the steps of chain propagation (Scheme 10). In these processes, as well as in the classical variant of conjugated reactions [101], the reactants are consumed for the creation of an active center, but without changing the stoichiometry of overall equations of the steps of kinetic chain growth (transfer). If the appearance of a new overall equation is considered as the essence of the phenomenon called by the historically important term of “chemical induction,” this phenomenon should only imply the classical variant of conjugate single- and multi-route reactions. When the main criterion is considered to be the consumption of additional reactants (additional amount of reactants or new reactants that are not involved in the step of chain growth) for the creation of new active intermediates, then the concept of chemical induction can be also extended to include chain processes. Chain mechanisms are generally characteristic of the catalysis with metal complexes. A chain mechanism in the catalysis with metal complexes was kinetically confirmed for the first time by Moiseev et al. [108, 109] in investigations of the positional isomerization of butenes. During the oxidation of a sum of butenes by Pd(II) chloride to methyl

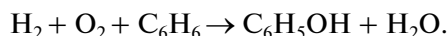
ethyl ketone and  $\text{Pd}_{\text{solid}}$ , an intermediate  $\text{Pd}_2\text{Cl}_4^{2-}$  complex was generated that catalyzed the isomerization of 1-butene to 2-butene (KG1 in Scheme 10).

The formation of an active hydride intermediate via Eq. (XXXVI) was successfully used to carry out the chain process of olefin hydrocarboxylation (hydrohydroxycarbonylation) under mild conditions (30°C, 1 bar) in the “ligand-free”  $\text{PdBr}_2\text{—CuBr}_2\text{—H}_2\text{O—THF}$  system [6, 101], where the route of CO and  $\text{H}_2\text{O}$  oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}_2$  according to Eq. (XXXV) was conjugated with the routes of cyclohexene hydrohydroxycarbonylation and THF oxidation by hydrogen peroxide (see KG in Scheme 11).

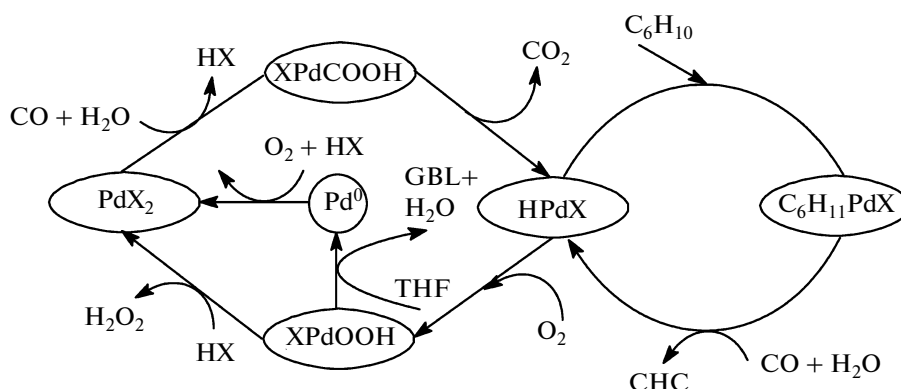
The generation of intermediate hydride complexes of transition metals also probably takes place during the chain oxidation of organic substances conjugated with the oxidation of hydrogen [110–112], e.g., via the following two-route process:



For example, the use of two catalysts,  $\text{Pt/SiO}_2$  for the synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  and heteropolyacids for the hydroxylation of  $\text{ArH}$  by dihydroperoxide or  $\text{PtOOH}$  intermediate, makes possible the following process [112]:



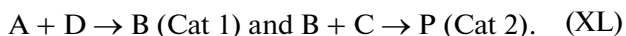
Kinetic graph for conjugated routes of CO oxidation and cyclohexene hydrohydroxycarbonylation in the  $\text{PdBr}_2\text{--CuBr}_2\text{--THF}$  system (CHC = cyclohexanecarboxylic acid; THF = tetrahydrofuran; GBL = g-butyrolactone)



Scheme 11.

### 6.3. Associated Processes

In recent years, the organic synthesis widely employs the principle of combining several reactions described by different overall equations in the same reaction system (one-pot reactions). These processes are also referred to as domino, cascade, tandem, or multicomponent reactions [62, 113–117]. For example, it is possible to combine reactions that proceed in the presence of a system of two catalysts (Cat1 and Cat2):



Although these associated processes can also be classified into conjugated reactions, since product B is involved in the kinetic conjugation between the two catalytic reactions, there is some difference: in contrast to most conjugated reactions, the associated processes (XL) can also proceed independently of each other. At the same time, the domino, cascade, and tandem catalytic reactions can also involve unstable reactive inter-

mediates like those encountered in conjugated processes. An analysis of the conjugated reactions showing the signs of chain processes provides deeper insight into the principles of functioning of “real” catalysts.

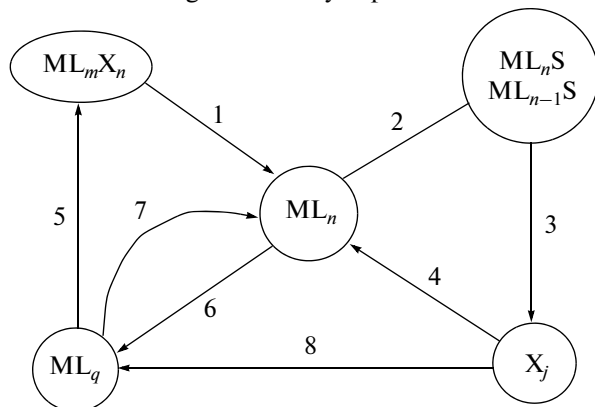
## 7. MECHANISMS OF FUNCTIONING OF “REAL” METAL COMPLEX CATALYSTS

It is well known that, in most cases, a “real” catalytic process differs from its ideal counterpart by the presence of the blocks of steps featuring the formation and loss of active centers, that is, by a finite length of the kinetic chain that is approximately characterized by the catalyst turn-over number (TON). Scheme 12 shows a KG containing all blocks of steps characteristic of a real catalytic process (in a linear variant of the mechanism). This KG includes a block of steps related to the formation of the active center  $\text{ML}_p$  (1), a block of steps comprising a simple “ideal” catalytic cycle (2–3–4), steps responsible for the loss of active centers (6, 8), and the steps of their regeneration (5, 7). The latter steps are not frequently encountered in practice. In the presence of step 7 the sequence of steps 2–3–8–7 also becomes a catalytic cycle, while the presence of all steps corresponds to a multi-route process with an ideal catalyst.

The KG presented in Scheme 12 can serve a basis for the classification of the mechanisms of functioning of catalysts (for simple variants with one and two routes) [1]. It is natural to distinguish between the following five classes of mechanisms (Scheme 13):

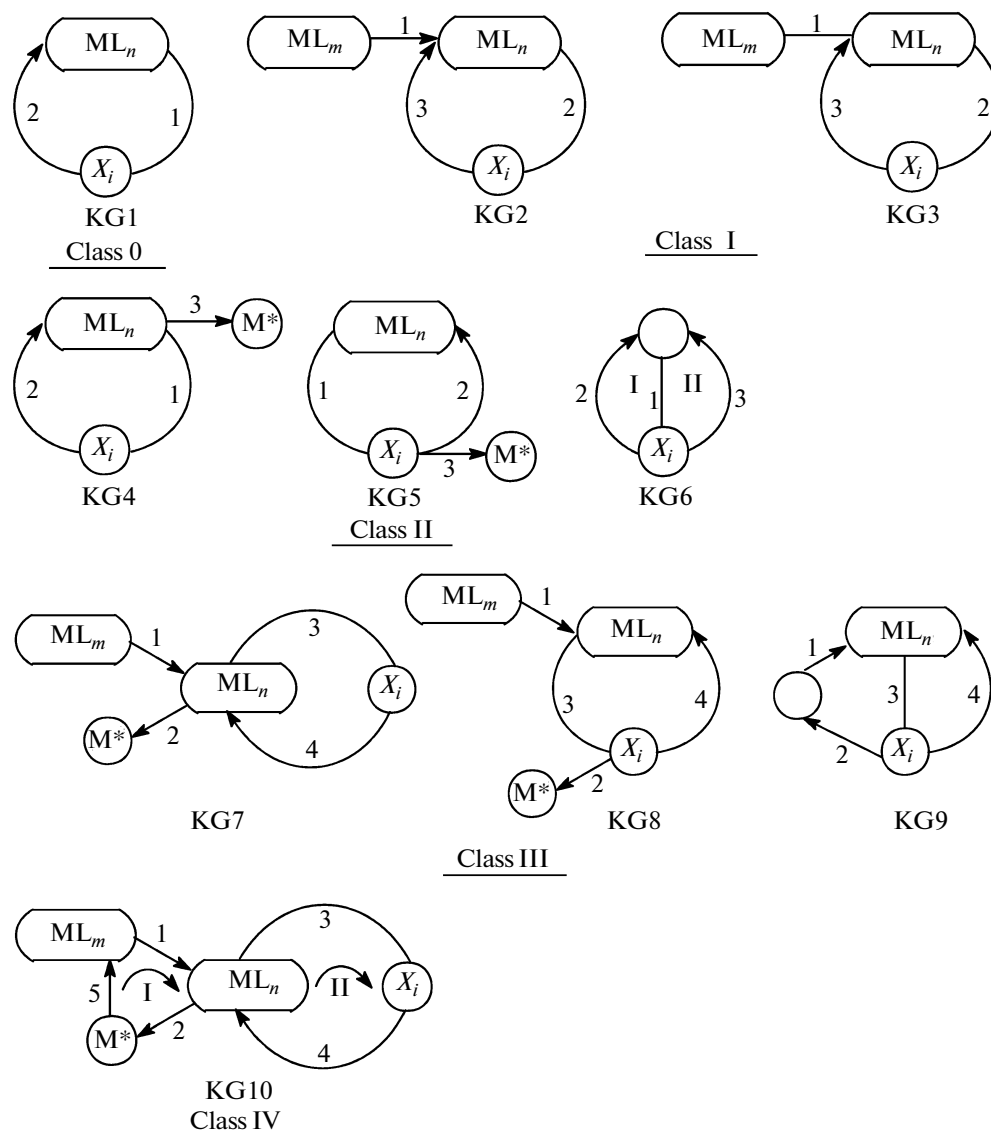
- (i) class 0 represents the ideal catalytic cycle (KG1);
- (ii) class I includes a step of active center formation (KG2 and KG3);
- (iii) class II includes the steps of the decomposition of active centers (KG4) and intermediates (KG5); the latter can be represented by a Temkin’s KG with a null-vertex (KG6);
- (iv) class III simultaneously includes the steps of formation and loss of active centers (KG7) or inter-

Kinetic graph corresponding to the main stages of a catalytic process



Scheme 12.

Kinetic graphs and classes of mechanisms of real catalytic processes [1]



Scheme 13.

mediates (KG8, see also KG9); both variants refer to the typical mechanisms of chain processes (see Scheme 10).

(v) class IV represents the ideal catalytic process (naturally over a finite interval of time) with all characteristic features of a non-branched chain process (KG10).

Now let us consider several examples of the mechanisms of real catalytic processes.

#### 7.1. Isomerization of 1-Butene in $\text{NiL}_4\text{--H}_2\text{SO}_4\text{--MeOH}$ System

The mechanism of this process (Scheme 14) includes the steps of catalyst formation (1–2), steps of

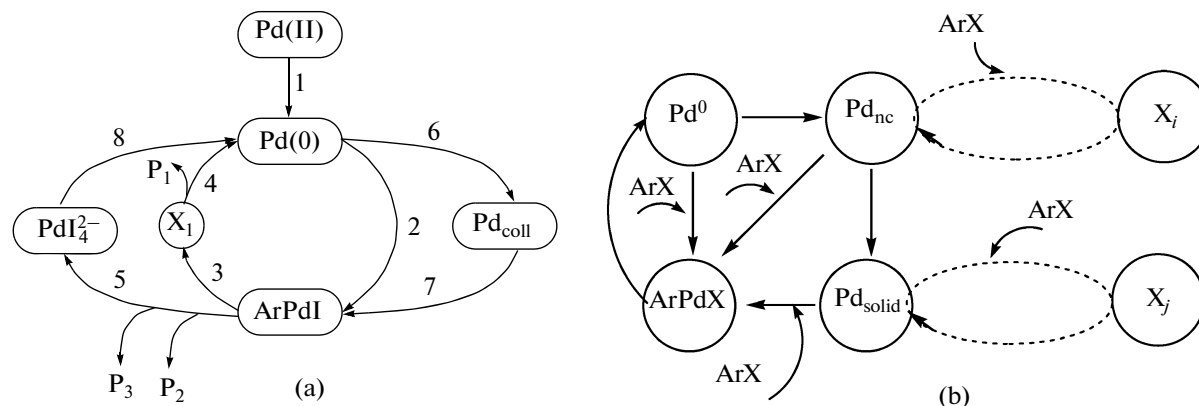
the loss of catalyst and intermediate species (7–10), and steps of the catalytic cycle (3–6). This important reaction scheme combines the variants represented by KG7 and KG8 (class III) in Scheme 13. Alternative notions about the nature of active Ni-containing centers in the reactions of isomerization, dimerization, and oligomerization of olefins have also been developed [118–120], including those with the possible participation of Ni(I) complexes [120].

#### 7.2. Cross Metathesis of Olefins in Solutions of Grubbs [121–126] and Hoveida [127, 129] Catalysts

Simplified Scheme 15 [1] includes the steps of nucleation of an active center (K1), the steps of cata-



- (a) Scheme of real catalytic process of olefin arylation according to Heck:  $P_1$  is the product of olefin arylation;  $P_2$  and  $P_3$  are the products of reactions of formation of  $\text{Ar}-\text{Ar}$  and  $\text{ArH}$ , respectively;  
 (b) generalized mechanistic scheme of coupling reactions on active centers of various types

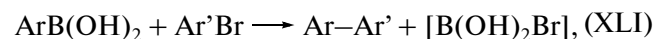


Scheme 16.

and regeneration of the active center (8) of intermediate (7), represents an example of the catalytic process of class IV, which homogeneously proceeds according to a chain scheme. In the presence of colloidal particles—nanoclusters ( $\text{Pd}_{\text{nc}}$ ) and  $\text{Pd}_{\text{solid}}$  (palladium black,  $\text{Pd}/\text{support}$ )—aryl iodide oxidizes  $\text{Pd(0)}$  to  $\text{ArPdI}$  and returns it back to the process (Scheme 16a). Strictly speaking, a route involving the steps of formation and conversion of colloidal particles ( $\text{Pd}_{\text{coll}}$ ) and nanoclusters ( $\text{Pd}_{\text{nc}}$ ) (steps 3, 4, 6, 7) represents a mixed homogeneous-heterogeneous (more exactly, homogeneous-microheterogeneous) process, the contribution of which in the case of  $\text{ArI}$  is not large.

It is commonly accepted [130–135] that, in the case of “ligand-free” phosphine-containing and metallocycle precursors, the Heck reaction proceeds as a homogeneous process (Scheme 16a), including the routes involving  $\text{Pd}_{\text{nc}}$  and  $\text{Pd}_{\text{solid}}$  particles. A variant of the mechanism with a new additional catalytic cycle, stipulating the formation and conversion of  $\text{Pd}_{\text{coll}}$  into intermediates of the “classical” cycle involving “molecular”  $\text{Pd(0)}$  complexes and “molecular” intermediates, was apparently proposed for the first time in [129, 136] and then developed in [131, 137] and other investigations.

In contrast to the Heck process, the Suzuki–Miyaura coupling reaction [138]



is catalyzed by both the microheterogeneous  $\text{Pd}$  clusters and heterogeneous  $\text{Pd}$ -containing catalysts [139–141]. A significant (and sometimes the main) contribution to the process rate is from the catalytic cycles (routes) that proceed immediately on the surface of microheterogeneous and heterogeneous particles (dashed contours in Scheme 16b) Using a combina-

tion of the Operando XANES/EXAFS and X-ray photoelectron spectroscopy (XPS) techniques and kinetic methods, the first experimental evidence was obtained that the Suzuki–Miyaura coupling proceeds heterogeneously on  $\sim 2\text{-nm}$ -sized  $\text{Pd}$  nanoclusters stabilized by poly(vinyl pyrrolidone), without the stage of intermediate passage to a solution [140, 141].

An important role in answering the question concerning homogeneity or “heterogeneity” of the processes considered above was played by the investigations of competitive Heck reaction [142–144] and Suzuki–Miyaura coupling [139] in respect of selectivity, which employed the creation of artificial conjugation nodes at various stages of the process involving the expected active species. The problem of the nature of active centers is not always simple to solve even in the case of homogeneous reactions not involving microheterogeneous species.

## 8. THE KEY ROLE OF HYPOTHESES ABOUT THE NATURE OF ACTIVE CENTERS IN HOMOGENEOUS CATALYTIC PROCESSES

An important role of information concerning the structure of the complexity functions of a catalyst ( $M$ ) and substrate ( $S$ ),  $F_M = [M]_{\Sigma}/[M]$  and  $F_S = [S]_{\Sigma}/[S]$ , for the construction of kinetic models has been recently analyzed in monograph [1]. Approaches to investigation of the kinetic of various reactions in aqueous solutions of polynuclear copper(I) halide complexes involving a large number (more than 20) of  $\text{CuCl}_n^{(n-m)-}$ – $\text{CuCl}_n^{(n-m)-}$  complex anions have been reviewed in [70]. In Section 7, we have already considered system, in which active molecular complexes are formed in the course of reactions—and not only from

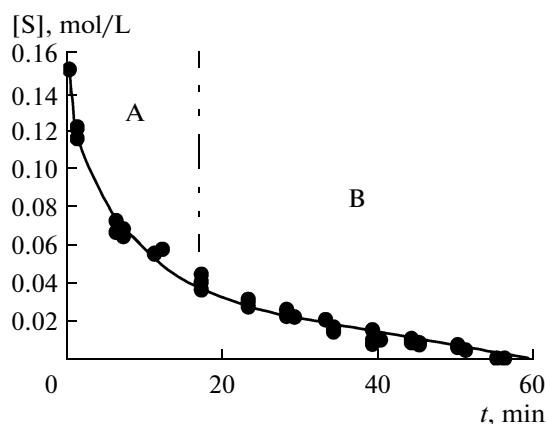


Fig. 2. Plot of the cyclohexene concentration  $[S]$  versus reaction time  $t$  in oxidation reaction (XLII) with  $[Pd]_0 = 0.004$  M,  $[BQ]_0 = 0.2$  M, and  $[HClO_4] = 0.2$  M [145].

precursors, but also from generated palladium nano-clusters (colloids) and even from  $Pd_{solid}$  particles. The importance of gaining information about the pathways of formation of the active centers in the course of a catalytic process is convincingly demonstrated by the experience in constructing kinetic models of the reaction of cyclohexene oxidation by *para*-quinones in solutions of initial cationic Pd(II) complexes that play the role of precursors of the active catalytic centers [145].

Since the discovery of the reaction of oxidation of olefins to aldehydes and ketones in aqueous solutions of Pd(II) and Cu(II) chloride complexes [52, 53], chloride systems have been extensively studied in aqueous organic solvents [146–148] with various oxidants and cocatalysts, including  $H_2O_2$  and *para*-quinones [149],  $R_2O_2$  [150], heteropolyacids [151, 152], etc. (see reviews [153–155]). It was established that aerobic oxidation in chloride systems is possible without oxidants and cocatalysts, for example, in the  $PdCl_2$ –dimethylacetamide (DMA)– $H_2O$  system at 80°C and an oxygen pressure of 6 bar [156]. The complex of  $PdCl_2(DMA)_2$  in ethanol catalyzes the oxidation of cyclopentene by oxygen, which is conjugated via  $LPdOOH$  with the reaction of ethanol oxidation to acetaldehyde [155, 157]. Apparently, the most interesting results were obtained in systems free of chloride ions, in acid aqueous media [158–165], and in aqueous organic solutions of Pd(II) complexes [166–170] with various oxidants (*para*-quinones, heteropolyacids). The complex of  $Pd(OAc)_2$  catalyzes the oxidation of olefins to ketones by hydrogen peroxide in acetic acid [171, 172], while  $Pd(OAc)_2Py_2$  catalyzes the oxidation of ethanol by oxygen under the conditions of conjugation with the oxidation of an olefin [173]. The introduction of *para*-benzoquinone or hydroquinone into the  $Pd(OAc)_2-H_2O_2$  system significantly accelerates the process of olefin oxidation [174, 175]. The oxidation with oxygen at an  $O_2$  pressure of 5 bar and a

temperature of 80°C also proceeds in the  $Pd(OAc)_2-Cu(OAc)_2$ –methanol system [176]. In the  $Pd(OAc)_2$ –heteropolyacid (HPA)–hydroquinone– $CH_3COOH$  system, cyclohexene is quantitatively oxidized by oxygen at 60°C to 3-acetoxy-1-cyclohexene, while in the  $Pd(OAc)_2$ –HPA–hydroquinone–ethanol–water system with additives of strong acid  $CH_3SO_3H$  under the same conditions the oxidation proceeds to cyclohexanone with a 82% yield [153].

Considerable interest has been devoted to processes in non-chloride systems with strong acids in aqueous organic media, which is explained by the high selectivity of oxidation of higher olefins and cycloolefins under these conditions by *para*-quinones (without positional isomerization), mild reaction conditions, and unusual kinetic behavior of  $Pd^{2+}$  cationic complexes formed in strongly acidic media [153, 166–168]. In these systems, the reaction rate increases with increasing  $[H^+]$  and also depends on the concentration and nature of quinone (Q) [167, 168, 170]. This behavior is significantly different from that observed in classical chloride catalytic Wacker oxidation systems ( $PdCl_2-CuCl_2$  and  $PdCl_2-Q$ ), in which the reaction rate either decreases with increasing  $[H^+]$  [52, 53] or is independent of  $[H^+]$ , e.g., in the case of cyclohexene oxidation by benzoquinone [177, 178].

In order to obtain information about the possible nature of active centers in these systems and the probable mechanistic schemes, we have recently studied the laws of oxidation of cyclohexene (S) by *para*-quinones (Q) via reaction



in the  $Pd(OAc)_2-HClO_4-CH_3CN-H_2O$  (molar fraction of water, 0.28) system at 20–23°C [145]. In addition to cyclohexanone, the products included small amounts of cyclohex-1-en-3-ol and cyclohex-1-en-3-one. The experimental data revealed the following principal differences of this system from the classical system with benzoquinone, in which the reaction proceeds on a single active center ( $PdCl_4^{2-}$ ):

- (i) the kinetic curves of  $[S]$  vs.  $t$  exhibit two regions—fast (A) and almost linear slow (B) (Fig. 2);
- (ii) the reaction rate in region B is almost constant (formal zero-order process with respect to  $[S]$ ) and independent of  $[Pd]_0$  (Fig. 3).
- (iii) the initial reaction rate increases with  $[HClO_4]$  (at a fixed ionic strength) and passes through a small maximum; a curve with maximum is also observed with increasing  $[Q]_0$ , while the dependence on  $[Pd]_0$  has an S-like shape;
- (iv) no hydroxocomplexes of palladium are detected by UV spectroscopy in the  $CH_3CN-H_2O$  system in the interval of  $HClO_4$  concentrations within 0.2–0.5 M (at a molar fraction of water, 0.28);
- (v) transmission electron microscopy data show the absence of Pd clusters with dimensions above 1 nm;

(vi) the nature of quinine Q influences the course of reaction.

Based on these data, we have analyzed various hypotheses concerning the nature of active centers:

I. Active centers of a single type,  $\text{Pd}^{2+}$  or  $\text{Pd}(\text{CH}_3\text{CN})_x(\text{H}_2\text{O})_{4-x}^{2+}$ , are present in solution. Four hypothetical kinetic models characteristic of single-route reactions with allowance for the dependence on benzoquinone concentration (or with neglect of this effect in excess of benzoquinone) were checked and it was found that not one of these models could describe the kinetic curves and other features of the process:

$$-d[\text{S}]/dt = k[\text{S}]^n,$$

$$-d[\text{S}]/dt = k[\text{S}]^n/(1 + k_1[\text{S}]^m) \text{ (excess Q),}$$

$$-d[\text{S}]/dt = k[\text{S}]^n[\text{Q}]^m = k[\text{S}]^n(a + [\text{S}])^m \text{ ([Q] = } a + [\text{S}]),$$

$$-d[\text{S}]/dt = k[\text{S}]^n(a + [\text{S}])/(1 + k_1[\text{S}]^m).$$

II. Active centers are formed as a result of the reduction of initial  $\text{Pd}^{2+}$  species by the substrate ( $[\text{Q}]_0 \approx \text{const}$ ).

III. Catalytic cycles proceed on the initial  $\text{Pd}^{2+}$  complex species and on  $\text{Pd}_2^{2+}$  and/or  $\text{Pd}(0)$  complexes formed from  $\text{Pd}^{2+}$  ( $[\text{Q}]_0 \approx \text{const}$ ).

IV. The reaction is catalyzed by pairs of centers ( $\text{Pd}_2^{2+}\text{Q}$  and  $\text{Pd}^0\text{Q}$ ;  $\text{Pd}^{2+}$  and  $\text{Pd}_2^{2+}\text{Q}$ ; or  $\text{Pd}_2^{2+}\text{Q}$  and  $\text{Pd}^0\text{Q}$ ) with the participation of Q in variable concentration.

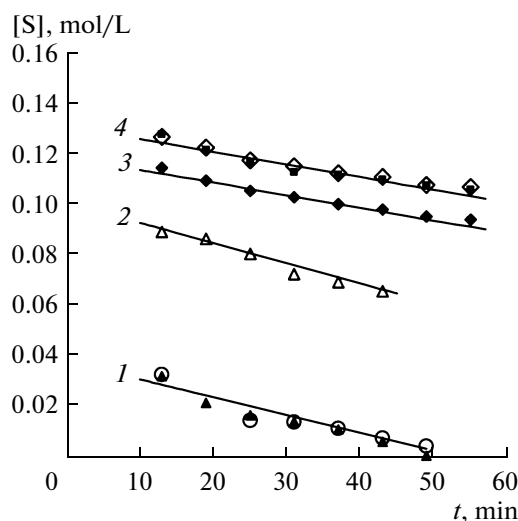
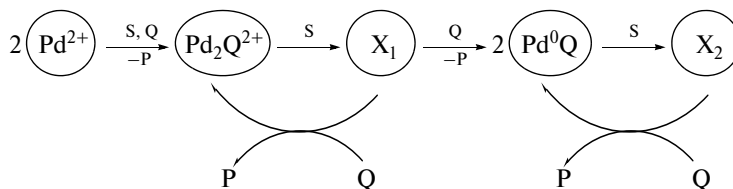


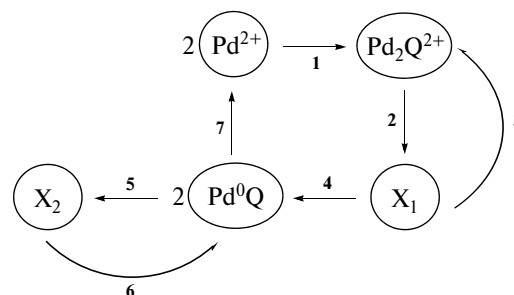
Fig. 3. Fragments of kinetic curves in region B, obtained for various initial concentrations of palladium ( $[\text{Pd}]_0$ , M): (1) 0.004; (2) 0.002; (3) 0.0015; (4) 0.001 ( $[\text{BQ}]_0 = 0.5$  M,  $[\text{HClO}_4] = 0.2$  M) [145].

V. Same pairs of catalytic centers are involved, but additionally the stage of reduced palladium species formation from  $\text{Pd}^{2+}$  was taken into consideration, e.g., via mechanism 1.5.M3:



It was found that only the last kinetic model satisfactorily described the process kinetics, but this hypothesis implied that all palladium species must eventually convert into one type ( $\text{Pd}^0\text{Q}$  complex), which is the main active center in the system at the slow stage (region B of the kinetic curve). From this assumption, it follows that adding substrate at the end of experiment to the initial level must lead to realization of a slow stage of the oxidation process. However, in practice the addition of cyclohexene always led to reproduction of the initial shape of the kinetic curve, which indicated that (in the framework of the adopted model) both  $\text{Pd}^0\text{Q}$  and  $\text{Pd}_2^{2+}\text{Q}$  complexes are converted into the initial state (Fig. 4). Accordingly, the 1.5.M3 scheme was supplemented with the steps of  $\text{Pd}^0$  oxidation by quinone to  $\text{Pd}^{2+}$  (step 7) and by  $\text{Pd}(\text{II})$  to  $\text{Pd}_2^{2+}\text{Q}$  (step 8:  $\text{Pd}^{2+} + \text{Pd}^0\text{Q} \leftrightarrow \text{Pd}_2^{2+}\text{Q}$ ). The resulting modified kinetic model (4.1.5.M3) allowed kinetic

features of the process to be described, including the behavior in region B (see curve in Fig. 2).



An analysis of the kinetic model for a non-steady-state process showed that, at the initial stage,  $\text{Pd}^{2+}$  species are rapidly converted into  $\text{Pd}_2^{2+}\text{Q}$  complexes (which account for the main contribution to oxidation in region A) and then into  $\text{Pd}^0\text{Q}$  species (which are active together with  $\text{Pd}_2^{2+}\text{Q}$  in region B). As the reductant (substrate) is consumed, the main role is played by the

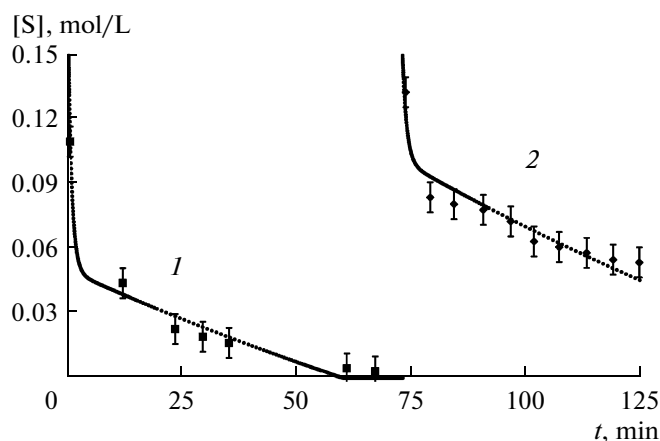


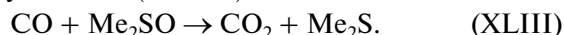
Fig. 4. Comparison of the kinetic curves measured (1) before and (2) after adding substrate at the initial concentration ( $[Pd]_0 = 0.004$  M,  $[HClO_4] = 0.2$  M) [145].

reaction of  $Pd^0Q$  oxidation by quinone (step 7) with the participation of  $H^+$  and the regeneration of active  $Pd^{2+}$  and  $Pd_2^{2+}Q$  species. Published data suggest that the system under consideration may also contain other complex species, including  $Pd(CH_3CN)_4^{2+}$ ,  $Pd_2(CH_3CN)_6^{2+}$  [179],  $Pd_2SO_4(Q)$  [180],  $LPdQ$  ( $L = 1.5$ -cyclooctadiene) [181], and  $PddQ$  complexes with  $Q$  and triphenylphosphin [182]. Detailed mechanistic schemes of cyclohexene conversions in this system are presented in [145].

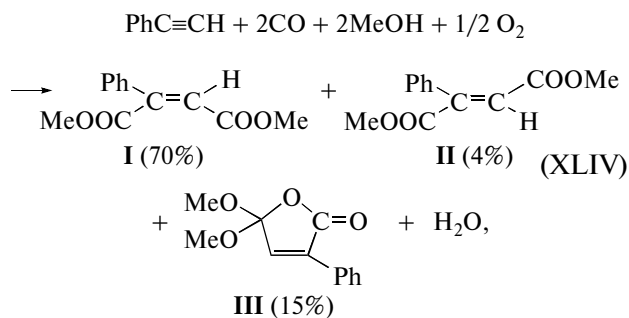
## 9. CHAIN SCHEMES OF MECHANISMS WITH AUTOCATALYSIS AND CRITICAL PHENOMENA IN CATALYSIS WITH METAL COMPLEXES

The presence of steps involving the formation and loss of active centers, autocatalytic and other nonlinear steps in the mechanisms of catalytic reactions, and nonlinear dependences on the substrate concentration in the material balance for catalyst is a necessary condition for the appearance of critical dynamic phenomena in homogeneous catalysis [1]. Apparently, the first homogeneous catalytic oscillatory process in the catalysis with metal complexes was the Belousov—Zhabotinskii (BZ) reaction discovered in 1951, which represents the reaction of citric acid oxidation by bromate anions catalyzed with  $Ce(IV)$  complexes [1, 183]. Later, it was established that the oxidation of organic substrates by bromate anions (and other oxidants) in oscillatory regimes can also be catalyzed by  $Fe(III)$ ,  $Mn(II)$ ,  $Ag(I)$ ,  $Cr(III)$ ,  $Cu(II)$ ,  $Ni(II)$ ,  $Co(II)$ ,  $Os(II)$ , and  $Ru(II)$  complexes (see [1]). For example, the oscillatory character of benzaldehyde oxidation in 90% acetic acid, catalyzed by the  $Co(OAc)_2-Br^-$  system, has been studied in detail by Roelofs et al. [184]. At preset, the thermodynamic,

chemical, and mathematical conditions necessary for the excitation of oscillations and the manifestation of other critical phenomena are established [1]. In the reaction of classical catalysis with metal complexes, where complicated molecules are synthesized from relatively simple substrates, an oscillatory behavior was originally observed for the oxidative carbonylation of acetylene to diesters of  $\alpha, \beta$ -unsaturated acids in the  $PdBr_2-KBr-HBr-DMSO-n$ -butanol system in a gas-flow gradientless reactor [185], where oscillations were manifested in the rates of  $CO$  and  $C_2H_2$  absorption and the platinum electrode potential ( $E_{Pt}$ ). It should be noted that the oxidation of  $CO$  to  $CO_2$  and the oxidation of  $CO$  and acetylene to diesters of maleic and fumaric acids in this system was performed by dimethylsulfoxide (DMSO):

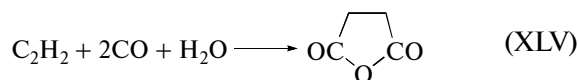


The reactions of oxidative carbonylation of phenylacetylene (and other alkynes) to diesters and other products according to the scheme



which proceed in the  $PdI_2-KI-MeOH-H_2O$  (0.05–1.0 M) system at  $40^\circ C$  in closed gradientless reactors were also found to exhibit oscillations (Fig. 5) in the rates of gas ( $CO + O_2$ ) absorption, pH, and the electrode potential ( $E_{Pt}$ ) [186–188]. The initial pH level was controlled by  $NaOAc$  additions. The oscillatory regime of these reactions was also studied by Novakovic et al. [189–192], but under partly modified conditions (400-mL gas-flow reactor, air instead of oxygen, and different method of gas–liquid system mixing). These experiments revealed the formation (in addition to diesters) of phenylmaleic anhydride, 3-phenyl-5H-furan-2-one, and 2-phenylacrylate at an amount dependent on the reaction conditions [190] and the oscillatory evolution of heat synchronous with pH oscillations [189].

The introduction of oxygen into  $CO$  and  $C_2H_2$  gas mixture under the conditions of acetylene carbonylation to succinic anhydride (SA) via reaction



in the  $PdBr_2-LiBr-CH_3CN-H_2O$  or  $PdBr_2-LiBr-KCl-CH_3CN-H_2O$  systems at  $40^\circ C$  leads to a decrease in the steady-state rate ( $r_{SA}$ ) of SA formation and an increase in the rate ( $r_{MA}$ ) of maleic anhydride



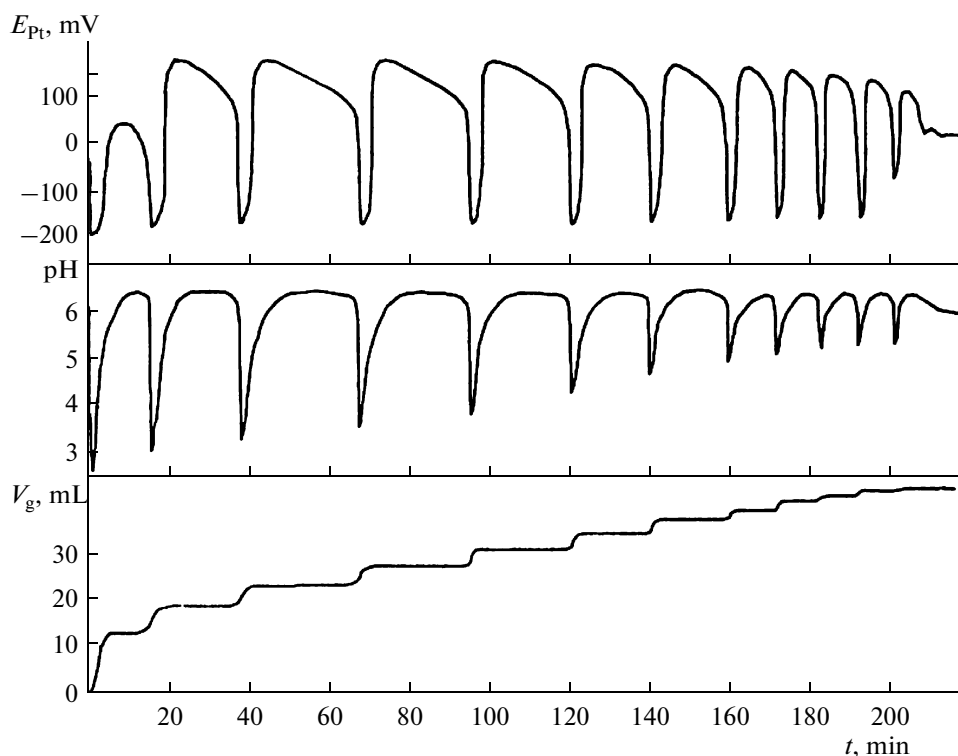


Fig. 5. Oscillations of  $E_{Pt}$ , pH, and  $CO + O_2$  gas absorption rate in the  $PdI_2$ –KI–NaOAc–phenylacetylene system with component concentrations 0.01, 0.4, 0.0024, and 0.1 M, respectively [1].

(MA) formation. At a certain partial pressure of oxygen at the reactor input, both  $r_{SA}$  and  $r_{MA}$  sharply change and the system switches to a new steady state in which these rates are independent of  $P_{O_2}$  (Fig. 6) [193]. The same change in the selectivity was observed with increasing reaction time at an oxygen concentration growing from 37% (initial) to 65% (in the output gas flow), which was related to the absorption of two molecules of CO and acetylene in the course of attaining steady state in the open system [194].

At the early stage of investigations of the kinetics and mechanisms of oscillatory reactions, because of the lack of information concerning the steps of these processes (e.g., BZ reactions), it seemed to be inexpedient to formulate and discriminate hypotheses about the reaction mechanism [195]. A different approach, close to the traditional strategy of constructing kinetic models, appeared to be more reasonable. According to this, experiments were first described by a simple idealized empirical model (set of differential equations) and then variables (intermediates) and steps were added so as to ensure that only terms corresponding to the law of mass action would be retained in the right-hand parts of equations. This approach was called the “inverse method of steady-state concentrations” [195]. Korzukhin [196] has proved a theorem, according to which any empirical system of equations can be reduced to this form. However, later it became clear [197] that this approach is ineffective and provides lit-

tle knowledge about the real mechanism of reaction, since there are many ways to transform the experimental kinetic model to a chemically (and kinetically) plausible form. For this reason, the main approach to studying oscillatory reactions is presently also based on the formulation of hypotheses as a stage of the rational strategy, supported by the experimental investigation of probable steps or blocks of steps.

In constructing kinetic models of the irreversible reaction (XLIV) occurring far from equilibrium in both open and closed systems, it was established that

(i) the role of an active center for diester formation is played by  $Pd(I)$  complexes (e.g.,  $Pd_2I_4^{2-}$ ), same as those in the conjugate reaction of acetylene carbonylation [26–28]; the addition of a synthesized  $Pd(I)$  iodide complex to the system removes the induction period [187];

(ii) at the initial stage,  $PdI_2$  is reduced by carbon oxide with the formation of  $CO_2$  and HI (and decrease in pH);

(iii) HI and  $I_2$  retard the reaction of phenylacetylene carbonylation;

(iv) known mechanisms of SA and MA synthesis [129] (see also reviews [199–201]) suggest that the formation of an intermediate  $HPdI$  hydride complex is possible;

(v) formation of  $H_2O_2$  was observed in  $Pd(II)$  bromide solutions;

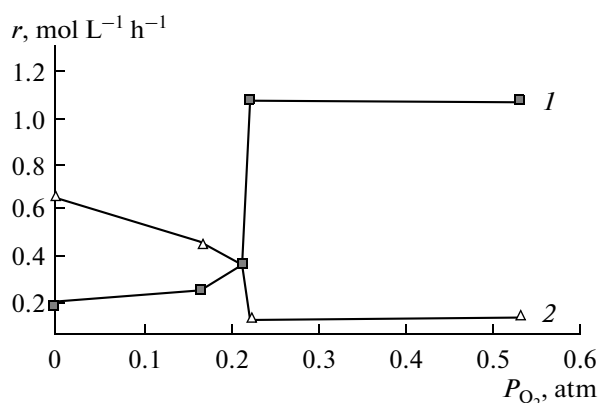
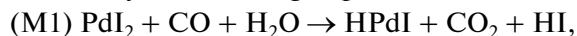


Fig. 6. Plots of the rates of (1) maleic and (2) succinic anhydride formation versus partial pressure of oxygen in the  $\text{PdBr}_2\text{--LiBr--KCl--CH}_3\text{CN}$  system [193].

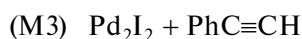
(vi) oxidation of Pd hydride complexes by oxygen with the formation of  $\text{H}_2\text{O}_2$  [202, 203].

One of the simplest kinetic models of the process under consideration, which is based on the above observations and data on the oxidative carbonylation reactions [200, 201], includes the steps of formation of an active center ( $\text{Pd}_2\text{I}_2$ ), a block of steps related to the carbonylation of phenylacetylene (PA), and the steps of autocatalyst ( $\text{HPdI}$ ) decomposition and the conversions of intermediates.

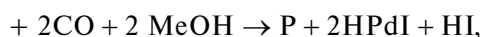
The formation of active centers (chain nucleation) is described by the following steps:



Block M3 includes the limiting stage of  $\text{Pd}_2\text{I}_2$  interaction with phenylacetylene and enters into the system of chain propagation steps:

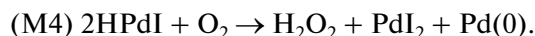
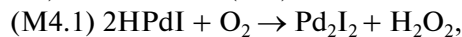


The sum of steps (M2) and (M3) represents the autocatalytic stage (quadratic autocatalysis):

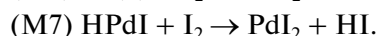
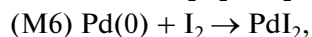
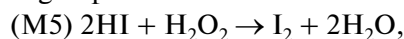


where P is the product of the carbonylation reaction.

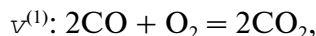
A combination of the step of active center regeneration (M4.1) and the step of  $\text{Pd}_2\text{I}_2$  disproportionation (M4.2) creates block (M4):



The conversion of intermediates and the regeneration of the initial precursor  $\text{PdI}_2$  is described by the following steps:



Thus, the proposed mechanism includes seven steps, five linearly independent intermediates, and two routes with vectors of stoichiometric numbers  $\mathbf{v}^{(1)} = (2001110)$  and  $\mathbf{v}^{(2)} = (0221110)$ , which correspond to the following overall equations:



It is interesting to note that a quite plausible step of transition between intermediates (M7) proved to be unbalanced ("defect" of mechanism [43]) with  $\mathbf{v}_7^{(1)} = 0$  and  $\mathbf{v}_7^{(2)} = 0$ . The lower limit of numerical values of the rate constants  $k_1$  and  $k_3$  was evaluated from the rate of  $\text{CO}_2$  evolution and the rate of  $\text{CO} + \text{O}_2$  absorption. The ratios of rate constants of the fast steps (autocatalysis) and the steps of autocatalyst decomposition, (M4) and (M7), were estimated using an analogy of these steps to the Oregonator scheme [204]. Analysis of the proposed kinetic model revealed auto-oscillations related to HI (pH) and  $\log[\text{PdI}_2]^2/[\text{Pd}_2\text{I}_2]$  ( $E_{\text{Pt}}$ ) with the period and shape close to those observed in experiments [1, 187, 188].

Thus, the presence of characteristic elements of a chain mechanism, nonlinear steps, and autocatalysis in the process under consideration, which is a typical reaction of the catalysis with metal complexes, leads to the appearance of critical phenomena in the dynamics of a catalytic process. The aforementioned changes in the process selectivity as a result of the bistability manifestations [193, 194] and the development of auto-oscillations [190, 191] can be of considerable practical value. It was also demonstrated that the experimentally observed multiplicity of steady states offers a powerful discriminating factor for an analysis of the generated set of hypothetical reaction mechanisms [205, 206].

## CONCLUSION

An analysis of key problems in the theory of mechanisms of catalytic reactions and approaches to the investigation of multi-route processes using the kinetic method leads to a conclusion that certain achievements have been reached in the use of effective strategies for studying mechanisms and constructing kinetic models, in understanding the essence of the kinetic and thermodynamic conjugation and the use of these principles for the creation of new catalytic processes, and in establishing the mechanisms of functioning of real catalytic systems and the nature of critical phenomena in the catalysis with metal complexes. However, there are still many unsolved problems, which hinder effective use of the kinetic method.

The existing approach to constructing kinetic models for the catalysis with metal complexes still does not devote proper attention to the steps of formation and loss of active reaction centers. Elucidating the nature of active species and the mechanisms of their

formation from precursors in solution is still among the most difficult tasks. These issues have become even more topical since there appeared evidence for the catalysis by colloidal metals, nanoclusters, giant clusters, and other nanodimensional particles, which can either behave as inactive species and reservoirs of active ones (sleeping catalysts) or serve as microheterogeneous catalysts and/or participants of homogeneous-heterogeneous catalytic reaction cycles.

While all the restrictions and difficulties encountered in solving the inverse problem of chemical kinetics in the case of linear mechanisms for both steady- and non-steady-state kinetic models are quite clear, questions concerning the choice of initial approximations for the rate constants, the identifiability of parameters, and the evaluation of constants from the results of measurements of the concentrations and reaction rates for the processes with nonlinear mechanisms and complicated dynamic behavior (oscillatory reactions) are not as clear. Solving the inverse kinetic problem in this case is still very difficult, and no effective algorithm is available for this purpose so far.

For elucidating the topological structure of linear or artificially linearized multi-route mechanisms and discriminating between generated hypotheses, it is possible to use an analysis of the conjugation nodes (or relative selectivities). For nonlinear multi-route mechanisms, establishing a structure of the mechanism based on simple kinetic dependences is very difficult if possible at all. In this case, the procedure of generating and discriminating hypotheses provides the only effective approach.

Another complicated task is the investigation of reaction kinetics in solutions of polynuclear complexes, especially in cases where the processes of association and clusterization accompany a given catalytic reaction, involve reactants, and are kinetically irreversible. A solution of this task can be provided by measuring in situ the concentrations of complexes under steady-state or quasi-steady-state conditions using spectroscopic and/or electrochemical methods or by determining in situ the concentrations of metal ions and ligands as was demonstrated for  $\text{Cu}_m\text{Cl}_n^{(n-m)-}$  complexes [70]. In this context, it is necessary to mention an evident deficit of data on the thermodynamic characteristics of polynuclear metal complexes in solution.

An analysis of the dynamic behavior of various kinetic models of homogeneous catalytic reactions and the necessary chemical conditions (related to the mechanism) for the appearance of critical phenomena such as self-oscillations showed that processes with the mechanisms including steps that are nonlinear with respect to intermediates, nonlinear material balances with respect to the catalyst, substrates, and products, and the steps of formation and loss of active centers (chain mechanisms) can be considered as systems admitting the manifestation of nonlinear dynamic

phenomena. There are many potential systems for investigations of the phenomena of nonlinear dynamics in the catalysis with metal complexes [1].

It should be emphasized that, despite the aforementioned problems, difficulties, and unanswered questions, a kinetic investigation correctly carried out within the framework of the rational strategy of kinetic model construction, with understanding of all possibilities and limitations of the kinetic method, is the necessary stage in studying a mechanism of any reaction. The author must ascertain regretfully that the number of publications devoted to the mechanisms of chemical reactions in general and the reaction kinetics in particular has dramatically decreased for the last 10–15 years. A shift of research interests from the basic problems of chemical science toward the search for new ligands, catalysts, materials, “smart” molecules, and molecular devices is quite natural and explainable, but this is hoped to be only a temporal stage in the “oscillating” development of chemistry.

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