Application of Graph Theory to Chemical Kinetics. 2. Topological Specificity of Single-Route Reaction Mechanisms

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Graph-theoretical methods for describing complex chemical reactions are reviewed and directed bipartite graphs are found to be the most convenient ones. Subgraphs of reaction intermediates are advocated as a tool for identifying and classifying reaction mechanisms. The notion of reaction intermediate is revisited, and the special class of dualistic intermediates is defined. The topological analysis of the single-route mechanisms resulted in identifying three classes of these mechanisms: catalytic, noncatalytic, and mixed, the latter including among others autocatalytic and autoinhibition reactions. The graph-theoretical basis is thus provided for the mechanistic classification of complex multiroute reactions.

INTRODUCTION

In Part 1 of this series[1] we discussed various aspects of the application of graph theory to chemical kinetics, and some basic notions, definitions, and algorithms for deriving the steady-state rate laws of reactions having linear mechanisms. Graph theoretical approaches were also shown to be very useful in depicting and classifying complex reaction mechanisms[2,3] as well as in analyzing mechanisms (hypotheses) aimed at their discrimination.[3,4]

Graphs of reaction mechanisms have been first used to describe isomerization reactions.[5] These are graphs in which vertexes and edges describe isomers and isomerizations, respectively. A review of these studies is given by Balaban.[6] Dugundji and Ugi introduced their generalized concept of isomerism and used graphs in which vertexes represent ensembles of isomers and edges denote their isomerizations (reactions).[7] These ideas were further developed by Kvasnička and Pospichal.[8]

The description of a mechanism as a set of elementary steps and the subsequent stoichiometric analysis are necessary procedures in such mechanistic and kinetic studies.[1] However, when using such a description, it is not easy to identify specific features of a complex reactions mechanism, such as the sequences of steps in reaction routes,[1] the presence of common intermediates or steps in different routes, the type of link between routes in a mechanism, and the presence of cyclic sequences of steps.

A better understanding of these topological features of a reaction mechanism can be aided by the use of various graphical representations. In references 1−3 we used the method of kinetic graphs, which allows one to depict only linear mechanisms. However, a great variety of chemical reaction mechanisms cannot be reduced to this category, since the kinetic graphs rule out the consideration of nonlinear mechanisms.[1]

In this paper, we review methods for depicting nonlinear mechanisms and show the importance of bipartite graphs in recognizing the topological features of single-route mechanisms as well as in the mechanistic classification of chemical reactions.

THE METHODS FOR DEPICTING NONLINEAR MECHANISMS

Presently, nonlinear mechanisms are very common in homogeneous and heterogeneous catalytic reactions, chain reactions, and some noncatalytic nonchain reactions. Nonlinearity is characterized by the presence of more than one intermediate species on the left-hand or right-hand sides of the chemical equations of the elementary steps in a mechanism.[1] With the assumption that an elementary reaction can either be mono- or bimolecular, the complete set of classes of elementary steps is listed in Table 1.

Table 1. Possible Types of Elementary Steps

type X	"reproduction" steps
1	$X_i \rightarrow X_k$
2	$2X_i \rightarrow 2X_k$
3	$2X_i \rightarrow X_k + X_m$
4	$X_i + X_j \rightarrow 2X_k$
5	$X_i + X_j \rightarrow X_k + X_m$
type Y	**"multiplication" steps**
6	$X_i \rightarrow X_k + X_m$
7	$X_i \rightarrow 2X_k$
8	$\varnothing \rightarrow X_k$
9	$\varnothing \rightarrow 2X_k$
10	$\varnothing \rightarrow X_k + X_m$
type Z	**"elimination" steps**
11	$X_i + X_j \rightarrow X_k$
12	$2X_i \rightarrow X_k$
13	$X_i \rightarrow \varnothing$
14	$2X_i \rightarrow \varnothing$
15	$X_i + X_j \rightarrow \varnothing$

In Table 1, symbols denoting the nonintermediate species are omitted, and the types of elementary steps are classified according to their role of increasing, decreasing, or preserving the number of intermediates; the symbol $\varnothing$. denotes the absence of intermediates on the corresponding side.
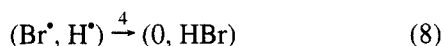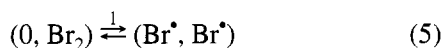

To depict the mechanisms involving nonlinear steps, Willamowski and Rössler[9] used Horn's idea concerning the complexes of species.[10] Following the logic of this idea, each equation of a mechanistic step transforms so that both its sides contain one and only one term that combines species. This term is referred to as a complex. Thus, the species space transforms to the complex space. The example listed below clearly describes this idea.

$$Br_2 \overset{1}{\rightleftharpoons} 2Br^\bullet \tag{1}$$

$$Br^\bullet + H_2 \overset{2}{\rightleftharpoons} H^\bullet + HBr \tag{2}$$

$$H^\bullet + Br_2 \overset{3}{\rightarrow} Br^\bullet + HBr \tag{3}$$

$$Br^\bullet + H^\bullet \overset{4}{\rightarrow} HBr \tag{4}$$

Equations 1−4 represent the nonbranched chain reaction given in ref 11. In terms of Horn's idea, they transform to eqs 5−8

$$(0, Br_2) \overset{1}{\rightleftharpoons} (Br^\bullet, Br^\bullet) \tag{5}$$

$$(Br^\bullet, H_2) \overset{2}{\rightleftharpoons} (H^\bullet, HBr) \tag{6}$$

$$(H^\bullet, Br_2) \overset{3}{\rightarrow} (Br^\bullet, HBr) \tag{7}$$

$$(Br^\bullet, H^\bullet) \overset{4}{\rightarrow} (0, HBr) \tag{8}$$

In eqs 5−8, (X_i, X_j) denotes a complex; X_0 is a conventional "species" that is used to complete each complex with a "second species". Since each complex consists of two species, the complex space can be represented in the form of a Horn graph in which each vertex denotes species and each edge joins two species, constituting a complex (Figure 1).

The reaction mechanism may be depicted by a reaction graph whose vertexes denote complexes and arcs denote elementary reactions (Figure 2). In the general case, the reaction graph is disconnected. The Horn graph and the reaction graph taken together uniquely characterize the reaction mechanism.[9]
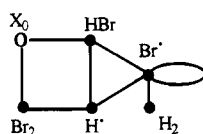

Figure 1. The Horn graph for the nonbranched chain reaction described by eqs 1−4 and 5−8. The graph vertexes denote species (the open circle denotes a X_0-species), whereas the edges (including the loop at $Br^\bullet$) represent complexes of two species.
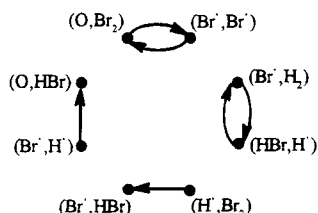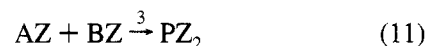

Figure 2. The disconnected reaction graph of the nonbranched chain reaction described by eqs 1−8. The graph vertexes stand for complexes; arcs denote elementary reactions.

Another approach for depicting the nonlinear mechanisms in which each step is irreversible and involves at least three different species was proposed by Sellers.[12] Sellers used triangles and quadrangles to denote the reactions involving three and four species, respectively. The edges of a triangle or quadrangle denote species involved in the reaction. The overall reaction is presented by a geometrical figure which contains faces corresponding to mechanistic steps. Thus, the reaction mechanism is depicted as a map. For example, the well-known Langmuir−Hinshelwood mechanism

$$A + Z \overset{1}{\rightarrow} AZ \tag{9}$$

$$B + Z \overset{2}{\rightarrow} BZ \tag{10}$$

$$AZ + BZ \overset{3}{\rightarrow} PZ_2 \tag{11}$$

$$PZ_2 \overset{4}{\rightarrow} P + 2Z \tag{12}$$
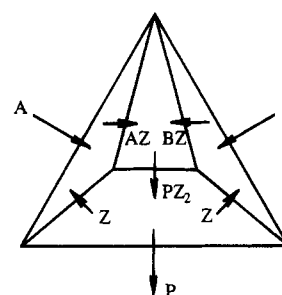
can be depicted as shown in Figure 3.

Figure 3. The dissected triangle depicting the Langmuir−Hinshelwood mechanism for the heterogeneous catalytic reaction as described by eqs 9−12. The edges represent the reaction species. The inner triangles and the quadrangle stand for the elementary reactions whose directions are denoted by arrows.

Balandin[13] proposed to use *bipartite graphs* for the classification of chemical reactions. More recently, these graphs were applied by Vol'pert,[14] Clarke,[15] and Ivanova[16] to study the stability of complex reaction networks. In a bipartite graph, the vertex set is divided into two subsets and the vertexes from the same subset cannot be adjacent. Vertexes from one subset correspond to species, and vertexes from the other subset correspond to elementary reactions. If species w_i is consumed (formed) by the reaction u_j, the related vertexes are joined by an arc a_{ij} (a_{ji}). The order of subscripts denotes the arc orientation. Thus, the reaction mechanism for the reaction of hydrogen with bromine (eqs 1−4) may be depicted by the bipartite graph shown in Figure 4, which is said to be a *reaction network*. For the sake of simplicity, steps 1 and 2 are taken as irreversible; solid circles denote reactions and open circles denote substances; the multiplicity of arcs describes the stoichiometry.

It is impossible to review herein all approaches and to discuss them in detail. However, mention should be made of the method of Sinanoğlu,[17] who used graphs with two types of arcs, and the simplex method of Balandin, which was given in his latest work[13] and was not mentioned elsewhere. The more detailed review of these methods for the description of the linear and nonlinear mechanisms is given in ref 18.

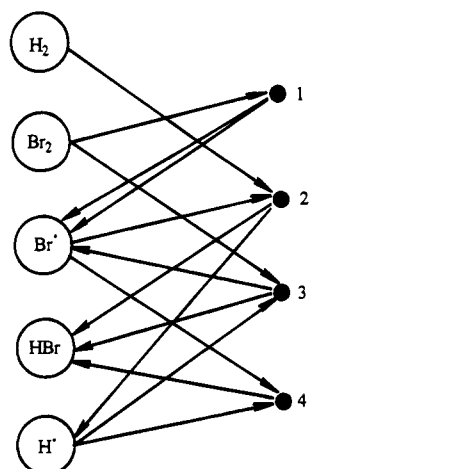Our previous studies of the application of graph theory to reaction mechanisms[18,19] showed that the bipartite-graph

Figure 4. The reaction network (bipartite graph) of the non-branched chain reaction described by eqs 1−4. Open circles correspond to the reaction species; solid circles stand for the elementary reactions numbered as the respective equations. The multiplicity of arcs denote the species stoichiometric coefficients.

method[13−15] is most convenient for describing multiroute reactions. We will discuss multiroute mechanisms in the next paper in this series where also colored bipartite graphs will be used. There we shall also dwell on the computational aspects of the problem. Herein, we use the bipartite-graph method to analyze the specific features of single-route mechanisms.

WHICH SPECIES ARE INTERMEDIATES AND WHICH ARE NOT?

The species that participate in the complex reaction occurring via several consecutive steps are to be divided into two groups: (a) reactants and products (*terminal species*) and (b) *intermediate species*. This assumption is quite common and clear. Earlier we showed that intermediates play a key role in defining the topology of reaction mechanism.[20] Since we decided to formulate the topological features of reaction networks, we thus had to provide an unambiguous definition of the term "intermediate" and answer the question of how to distinguish between terminal and intermediate species.

In principle, several definitions of this term may be gleaned from the literature, but there is no complete agreement between them. Here, we list some typical examples illustrating that these definitions are often partly or completely incorrect:

(i) Suppose that a steady-state reaction occurs in the open continuous well-stirred tank reactor. Then, the terminal species are those whose constant concentrations are maintained by their entering (or being expelled from) the reaction system. The intermediate species are those whose constant concentrations are maintained by their consumption in the system due to some elementary steps that compensate for their origination due to some other steps.[21]

(ii) The terminal species are observed species, and intermediates are species that are not observed.[22]

(iii) An intermediate is a species that is not involved in any of the possible overall equations corresponding to the reaction routes.[23,24]

(iv) Reactants are those that are supplied to the chemical system and undergo further chemical transformations. Products are species produced as a result of the chemical
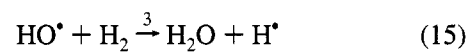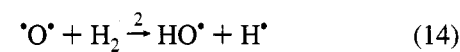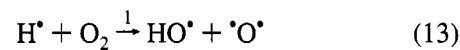
transformation in the system; they do not undergo further transformations. Intermediates are produced by the chemical transformation in the course of the chemical reaction and undergo further transformations.[25]

There are several problems with all these definitions. First, it is absolutely unreasonable to define "intermediate" in terms of the "steady-state" mode or any other kinetic features of the reaction. A reaction may or may not involve intermediates no matter whether it is steady-state or not and no matter which kinetic behavior is observed. Second, the question of which species are observed is answered depending on at what stage the reaction is stopped and how observations are made. Third, the intermediate cannot be defined through the notions of stoichiometry (the overall equation, the stoichiometric number, the reaction route, etc.), because these notions themselves are defined through the term "intermediate". Finally, in defining "intermediate", one should take into account that, among the reactants supplied to the reactor or observed among the products, there may be those that do belong to intermediates. Consider the following example: a catalyst is supplied to the reaction system and undergoes several consecutive transformations so that it takes several intermediate forms and finally returns to its initial state. In this case, the catalyst is among the reactants that are supplied to the reactor and plays the role of an intermediate.

Thus, it is reasonable to define intermediate and terminal species as follows. The *intermediate* is a species produced by any step(s) of the reaction mechanism and consumed by some other step(s). The *terminal species* is that species exclusively produced or exclusively consumed by the steps of the mechanism.

Note that, if a part of elementary steps is reversible, one might treat the reversible steps as irreversible and neglect the reverse elementary reactions. By this, some priority of direct reactions is stated over the reverse ones. There are several mathematical reasons for this assumption.

The essence of the difference of our definition with the definitions (i−iv) is that some authors are not inclined to classify as intermediates all species resulting from any steps and consumed by others, because they implicitly proceed from the possibility of steady-state mode. Indeed, if one takes, for example, a set of steps (Horiuti's example),[26]

$$\underline{H^{\bullet}} + O_2 \xrightarrow{1} \underline{HO^{\bullet}} + \underline{^{\bullet}O^{\bullet}} \tag{13}$$

$$\underline{^{\bullet}O^{\bullet}} + H_2 \xrightarrow{2} \underline{HO^{\bullet}} + \underline{H^{\bullet}} \tag{14}$$

$$\underline{HO^{\bullet}} + H_2 \xrightarrow{3} H_2O + \underline{H^{\bullet}} \tag{15}$$

which determines the branching of the chains in the reaction between hydrogen and oxygen, and then find intermediates (underlined), it will be easy to show that no overall equation exists in which all intermediates vanish. Horiuti concluded that the reaction described by eqs 13−15 cannot be steady-state. To be more specific, eqs 13−15 do not allow for balancing the intermediates. At the same time, if any intermediate will be marked as terminal, it will be possible to find the stoichiometric numbers of steps so that all intermediates except that chosen will vanish. For instance, let us mark H• as a terminal species and choose the stoichiometric numbers 1, 1, and 2 for steps 1, 2, and 3, respectively. Then, we arrive at the following overall

equation:

$$O_2 + 3H_2 \rightarrow 2H_2O + 2\underline{H^{\bullet}} \qquad (16)$$
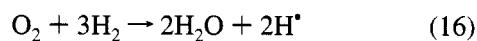
This expedient allows one to discuss the mechanisms that allow for balancing the intermediates and the mechanisms that do not allow for that in the same terms.

The reasons why a reaction may not allow for balancing the intermediates are two:

(i) Part of the intermediate species that is formed cannot be fully consumed. This is the case when we deal with the *autocatalytic* reaction in which a product catalyzes further transformations or when we have a fragment of a *branched chain* process.

(ii) Part of the intermediate species is consumed in stoichiometrically greater amounts than is formed. Such a reaction may be referred to as an *autoinhibition reaction*.
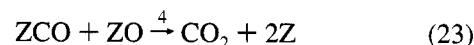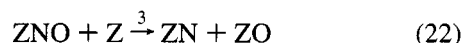
A researcher usually knows from the experiment which intermediates play a two-fold role, that is, which intermediates are also among the terminal species. However, it cannot be determined by the formal methods. Hereinafter, we assume that, in each particular case, we also know which intermediates are of this sort; we term such species *dualistic species*. Thus, all species in the system can be divided into terminal and intermediate species, and the intermediate species can be further subdivided so as to include the subclass of dualistic species.

When revising our accepted manuscript we found that the ambiguity in the choice of intermediates was discussed earlier by Valdes-Peres.[27] His example of unbalanced mechanisms resembles neither autocatalysis nor autoinhibition:

$$A + B \rightarrow X + Y \qquad (17)$$

$$B + X \rightarrow 2Z \qquad (18)$$

$$Y + Z \rightarrow T \qquad (19)$$

At first glance, this mechanisms looks like a noncatalytic single-route mechanism. However, the closer inspection reveals that the balancing is impossible. Valdes-Peres pointed out that the intermediates in this reaction cannot all have zero net formation, unless no reactions occur at all. He also found the statement that a species is either intermediate or terminal species is ambiguous. A linear programming method was proposed to make the choice canonical by choosing the stoichiometry that produces one mol target species at minimum consumption of reactants. For instance, for the above mechanism the overall stoichiometry $2A + 3B \rightarrow 2T + X$ improves as compared to the stoichiometry $A + 2B \rightarrow T + Z$ (Z rather than X thus appears as a terminal species).

The bipartite graphs assist in distinguishing between the terminal and intermediate species. For example, let us discuss the dissociative mechanism of NO reduction by carbon monoxide,[28]

$$Z + NO \xrightarrow{1} ZNO \qquad (20)$$

$$Z + CO \xrightarrow{2} ZCO \qquad (21)$$

$$ZNO + Z \xrightarrow{3} ZN + ZO \qquad (22)$$

$$ZCO + ZO \xrightarrow{4} CO_2 + 2Z \qquad (23)$$

$$2ZN \xrightarrow{5} N_2 + 2Z \qquad (24)$$

which may be presented in terms of the Balandin—Vol'pert—Clarke method[13-15] by the graph shown in Figure 5.

This graph contains vertexes whose indegree [id(w)] or outdegree [od(w)] equals zero: w_{CO_2}, w_{NO}, w_{N_2}, and w_{CO} (terminal vertexes); (outdegree (indegree) of a vertex equals the total number of arcs that come out of (into) this vertex). All these vertexes correspond to terminal (nonintermediate) species. Upon deleting the terminal vertexes and all arcs incident with them, we arrive at the graph, which we refer to as a *subnetwork of intermediates (SI)*. Then, the *SI* for this mechanism is the graph in Figure 6 (note that, according to our definition of "intermediate", reversible steps are depicted as irreversible).
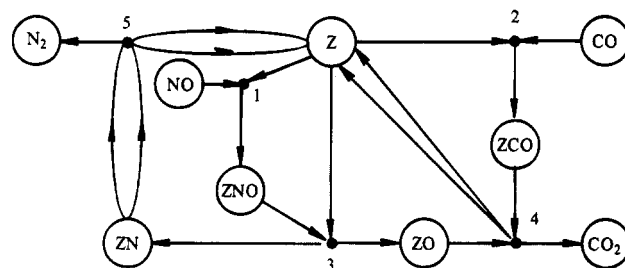

Figure 5. The reaction network (bipartite graph) of the dissociative mechanism for the heterogeneous catalytic reaction of NO reduction by CO described by eqs 20—24.
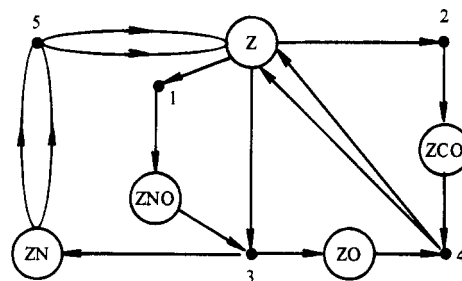

Figure 6. The subnetwork of intermediates (*SI*) of the reaction network shown in Figure 5.

All vertexes in *SI* correspond to intermediate species, but it is impossible to define which of them are dualistic (if any) because this cannot be defined at all using formal methods. We agreed, however, that all dualistic species are known from the experiment. Thus, we are able to delete such species and so arrive at *residual subnetwork of intermediates (RSI)*.

The presence of dualistic intermediates is closely related to the stoichiometric relations in the system. Stoichiometric analysis of the presence of dualistic intermediates can be aided by the use of graph-theoretical methods. However, this analysis reveals only the fact of presence or absence; it fails to define which intermediates are dualistic. Thus, we must discuss this problem in more detail.

In Part 1 of this series[1] we discussed the system of linear homogeneous algebraic equations that characterize the stoichiometric balance of intermediate species participating in

the reaction

$$\sum_j \beta^*{}_{ij}\gamma_j = 0, \quad i = 1, ..., N \tag{25}$$

where $\beta^*{}_{ij}$ is the stoichiometric coefficient of the ith intermediate in a jth step. Solutions to the system of eq 25 are the sets of the stoichiometric numbers of steps γ_j, and each set matches one of the reaction routes up to a constant multiple. System 22 can be rewritten in the matrix form

$$\begin{array}{cccc}
\mathbf{B_X}^T & \times & \Gamma & = & \mathbf{0} \\
(N\times S) & & (S\times 1) & & (N\times 1)
\end{array} \tag{26}$$

where $\mathbf{B_X}^T$ is the transposed stoichiometric matrix for intermediates and Γ is the vector of stoichiometric numbers. The reasonable question arises then as to whether the presence (or absence) of dualistic intermediates affects the solution to system (25) and what kind of solutions (i.e., reaction routes) can generally exist. Here we provide only a rough idea of how to answer this question. This problem will be discussed in more detail elsewhere.

It is a common practice in linear algebra to discuss two types of solutions: (i) rank($\mathbf{B_X}^T$) = S and (ii) rank($\mathbf{B_X}^T$) < S. In the first case, the solution is trivial and unique; that is, there exists only one vector Γ that fully consists of zero entries. In other words, if we delete the terminal vertexes in the reaction network and construct the matrix $\mathbf{B_X}^T$,[16] we will be able to check whether the condition rank($\mathbf{B_X}^T$) = S is met. If this condition is met, there is no overall equation in which all intermediates vanish, and, consequently, there is no reaction mechanism producing this overall equation. This means that it is necessary simply to choose conventionally the intermediates to be qualified as dualistic. Sometimes, there is no need to construct a $\mathbf{B_X}^T$ matrix, because the *SI* directly points to the fact that $\Gamma = \mathbf{0}$. For instance, the *SI* for the reaction sequence described by eqs 13−15 and shown in Figure 7 has no terminal vertexes and contains two steps of the type Y (steps 1 and 2), a step of the type X (step 3), and no steps of the type Z. In the case of the single-route mechanism, this means that the dualistic intermediates must exist in the reaction sequence.
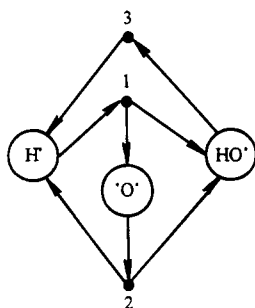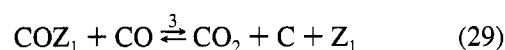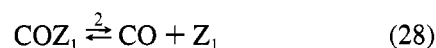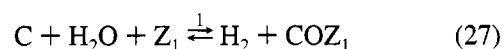

Figure 7. The *SI* for the set of steps determining the chain branching submechanism of the mechanism of reaction between hydrogen and oxygen. Steps 1 and 2 are of the multiplicating type Y and step 3 is of the eliminating type Z.

In the first case, if the *SI* having no terminal u-vertexes contains u-vertexes (steps) of the multiplicating type Y, which are not compensated for by u-vertexes (at least one) of the eliminating type Z (or vice versa), the value of rank($\mathbf{B_X}^T$) will be equal to the number of steps. (In the subnetwork of

intermediates, inequalities od(v) > id(v) and od(v) < id(v) hold for u-vertexes of types Y and Z, respectively.)

In the second case, (rank($\mathbf{B_X}^T$) < S), system 25 has an infinite number of solutions. However, among them are some of special interest. We termed the sets of elementary steps corresponding to the solutions of this special sort *simple submechanisms*.[20] *Each simple submechanism is a subset of steps of the mechanism, which is irreducible in the sense that it cannot be separated into other (smaller) subsets that also correspond to the reaction routes.* A set of simple submechanisms is finite. Each complex submechanism can be separated into two or more simple submechanisms. The number of simple submechanisms in a mechanism is not less than the number of linearly independent routes. For instance, the mechanism of the interaction between water vapor and coal, which was discussed in Part 1,[1]

$$C + H_2O + Z_1 \overset{1}{\rightleftharpoons} H_2 + COZ_1 \tag{27}$$

$$COZ_1 \overset{2}{\rightleftharpoons} CO + Z_1 \tag{28}$$

$$COZ_1 + CO \overset{3}{\rightleftharpoons} CO_2 + C + Z_1 \tag{29}$$

can be depicted by the kinetic graph shown in Figure 8 (Z_1 is an active site on the coal surface). This graph contains two vertexes for intermediates COZ_1 and Z_1 joined by three
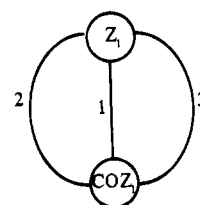

Figure 8. The kinetic graph of the mechanism of catalytic coal conversion by water vapor. Vertexes denote intermediate surface species; edges represent reversible reactions. Z_1 stands for an active site on the coal surface. Only two of the three graph cycles are independent.

edges. It contains three cycles, of which two are independent. Each of the three cycles corresponds to a simple submechanism. When pictured on a plane, this graph forms a map with two faces, each corresponding to a simple submechanism. One of the possible submechanisms has the overall equation

$$C + 2H_2O \rightleftharpoons 2H_2 + CO_2 \tag{30}$$
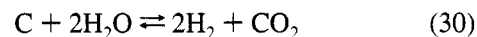
and may be separated into two simple submechanisms: {steps 1 and 2} and {steps 1 and 3}. The procedure for finding the complete set of simple submechanisms for a particular mechanism may be described in the form of an algorithm and carried out with the aid of computer.[20]

If one finds all simple submechanisms of the mechanism, it may appear that some steps of the mechanism will be involved in none of them.[29] There is a simple method for determining these steps in the graphs of linear mechanisms, whether bipartite or ordinary graphs are used: such steps correspond to those u-vertexes of a bipartite graph and those edges in a kinetic graph whose deletion produces a disconnected graph. For instance, the kinetic graph in Figure 9 and the bipartite graph in Figure 10 depict the same mechanism. Deleting edge 2 in Figure 9 and vertex 2 in
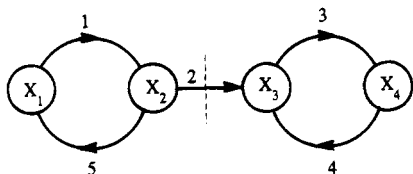
Figure 9. The kinetic graph of a linear five-step mechanism with two routes. Deleting edge 2 produces a disconnected graph.
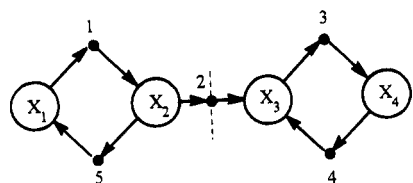

Figure 10. The bipartite graph of the linear five-step mechanism whose kinetic graph is shown in Figure 9. Deleting the u-vertex corresponding to step 2 (the solid circle) produces a disconnected graph.

Figure 10 produces disconnected graphs. If step 2 were reversible, vertexes for intermediates X_2 and X_3 of the kinetic graph would be joined by two arcs having opposite directions (one arc for each direction). Then, deleting one of these arcs would not produce a disconnected graph.

In this section, we discussed several approaches which will make it easier to recognize specific features of the mechanism that are reflected in graphs. In illustrating this, it is convenient to begin with the single-route mechanisms since a multiroute mechanism contains simple submechanisms, which essentially have all the features of single-route ones.
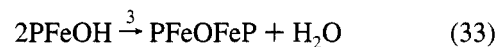
SINGLE-ROUTE MECHANISMS

In our recent review,[19] we discussed a topological classification of complex reaction mechanisms. In this paper, we refine statements and definitions. Two structurally distinct types of single-route reactions are traditionally regarded, the catalytic and noncatalytic. The succeeding discussion will reveal that besides these two types, there is another, which displays some features of both catalytic and noncatalytic reactions.

In *catalytic reactions*, the catalyst is a species that changes its structure and composition and returns to its initial state within a turnover. In the case of "ideal" catalysis, neither of the catalytic species is involved in the overall reaction equation. A catalytic single-route mechanism must contain the species of this type.
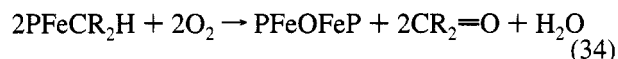
For example, let us discuss the catalytic reduction of nitrogen monoxide by CO via the dissociative mechanism (eqs 20—24). The reaction network of this mechanism is shown in Figure 5, and its subnetwork of intermediates is shown in Figure 6. Among w-vertexes, the graph in Figure 6 contains no vertexes corresponding to the dualistic species. Then, the *RSI* is no different from the *SI* and both contain no terminal u-vertexes; that is, in Christiansen's terms,[30] the sequence of steps (eqs 17—21) is *closed*. All intermediate species return to their initial states within a turnover. Thus, *the SI of a catalytic single-route mechanism contains no terminal u-vertexes corresponding to elementary reactions and no w-vertexes corresponding to dualistic intermediates.*

A *noncatalytic* (stoichiometric) single-route reaction also contains a set of intermediates, but none of them transforms to itself within a turnover. For instance, a reaction between

the alkyliron(III) complex $PFeCR_2H$ (P = porphyrin dianion) and dioxygen occurs via the following mechanism[31]

$$PFeCR_2H + O_2 \xrightarrow{1} PFeOOCR_2H \qquad (31)$$

$$PFeOOCR_2H \xrightarrow{2} PFeOH + CR_2{=}O \qquad (32)$$

$$2PFeOH \xrightarrow{3} PFeOFeP + H_2O \qquad (33)$$

having an overall equation

$$2PFeCR_2H + 2O_2 \rightarrow PFeOFeP + 2CR_2{=}O + H_2O \qquad (34)$$

The reaction mechanism (eqs 31—33) may be depicted by the graph in Figure 11 By deleting the terminal vertexes corresponding to initial and final products, we arrive at *SI* shown in Figure 12. As can be seen from the graph in Figure 12, the *SI* of a noncatalytic reaction contains two terminal u-vertexes, one of which begins the reaction (u_1) and the other of which is responsible for the reaction completion (u_3). The former is characterized by the zero indegree, $id(u) = 0$; the other, by the zero outdegree, $od(u) = 0$. For the ordinary noncatalytic single-route reaction it is known that no dualistic intermediates exist (the case for which a dualistic intermediate exists is discussed below). Since no dualistic intermediate is present in the reaction scheme the *RSI* again is just the same as the *SI*. In Christiansen's terms the sequence of steps (eqs 31—33) is open.
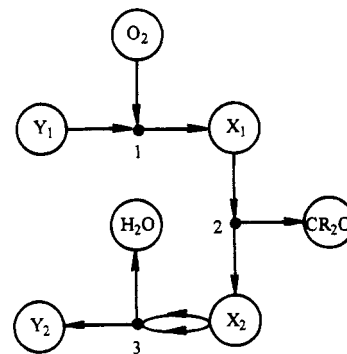

Figure 11. The reaction network (bipartite graph) of the noncatalytic single-route mechanism for the reaction between the alkyliron-(III) complex and molecular oxygen (eqs 31—33): $Y_1 = PFeCR_2H$; $X_1 = PFeOOCR_2H$; $X_2 = PFeOH$; $Y_2 = PFeOFeP$.
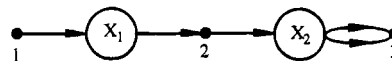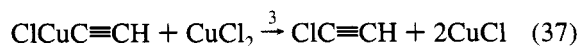

Figure 12. The subnetwork of intermediates (*SI*) of the reaction network shown in Figure 11.

Aside from these two classes, there is also a special class of reactions to which, for instance, well-known autocatalytic reactions belong. An example is the oxidative chlorination reaction occurring via the following three steps:[32]
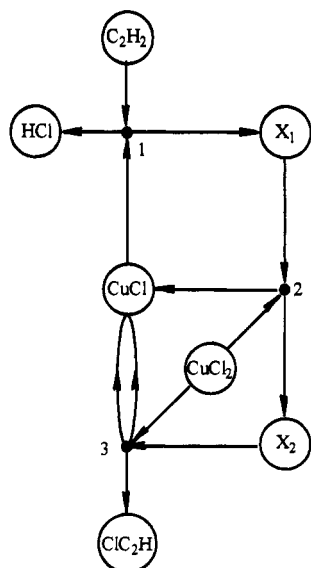
$$C_2H_2 + CuCl \xrightarrow{1} CuC{\equiv}CH + HCl \qquad (35)$$

$$CuC{\equiv}CH + CuCl_2 \xrightarrow{2} ClCuC{\equiv}CH + CuCl \qquad (36)$$

$$ClCuC{\equiv}CH + CuCl_2 \xrightarrow{3} ClC{\equiv}CH + 2CuCl \qquad (37)$$

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Figure 13. The reaction network of the autocatalytic oxidative chlorination reaction (eqs 35−37). $X_1 = CuC\equiv CH$ and $X_2 = ClCuC\equiv CH$.
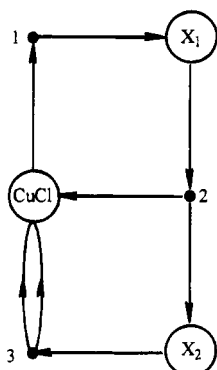

Figure 14. The SI of the reaction network shown in Figure 13. Step 1 is of the reproducting type X; steps 2 and 3 are of the multiplicating type Y.
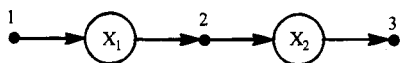

Figure 15. The *RSI* obtained by deleting the vertex corresponding to the dualistic species in the *SIs* shown in Figures 14 and 17.

so that the overall reaction is

$$C_2H_2 + 2CuCl_2 \rightarrow ClC\equiv CH + 2CuCl + HCl \quad (38)$$

The reaction network for this mechanism is depicted by the graph in Figure 13. For the sake of simplicity, reversible steps are treated as unidirectional. After deleting the terminal vertexes, we arrive at the *SI*, which is depicted in Figure 14. Equation 35 shows that CuCl is a product (a terminal species). Consequently, within the frame of this mechanism, CuCl is a dualistic species. In Figure 14, step 1 is of type *X*, steps 2 and 3 are of type *Y*, and no steps are of type *Z*. Then, upon deleting w_{CuCl}, we obtain *RSI* (Figure 15).

As can be seen, *the bipartite SI of this "mixed case" is similar to that of the catalytic reaction in that it contains no terminal u-vertexes, whereas RSI is similar to that of the noncatalytic reaction.*

Another intriguing example of what we call a "mixed case" is the hydrobromination of alkenes in nonpolar solvents occurring via the multicentered transition states (eqs 39−
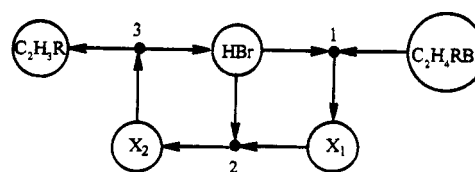

Figure 16. The reaction network of the mechanism for alkene hydrobromination (eqs 39−41). X_1 and X_2 are intermediates.
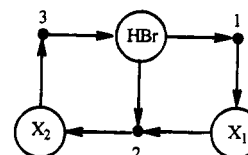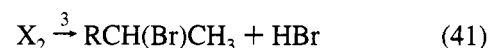

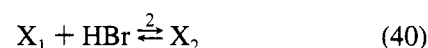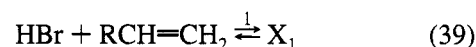**Figure 17.** The *SI* of the reaction network shown in Figure 16.

41)

$$HBr + RCH{=}CH_2 \overset{1}{\rightleftarrows} X_1 \quad (39)$$

$$X_1 + HBr \overset{2}{\rightleftarrows} X_2 \quad (40)$$

$$X_2 \overset{3}{\rightarrow} RCH(Br)CH_3 + HBr \quad (41)$$

where X_1 and X_2 are intermediates.[33] The reaction network, *SI*, and *RSI* for this mechanism are shown in Figures 16, 17, and 15, respectively. For the sake of simplicity, steps 1 and 2 are depicted as irreversible. In Figure 17, steps 1 and 3 are of type *X*, and step 2 of type *Z* is not compensated for by a step of type *Y*.

By analogy with the autocatalytic reactions, this reaction may be referred to as *autoinhibition* since a mol of HBr is consumed as a reactant, while another mol of HBr recycles in the course of the reaction, i.e., behaves as a catalyst. A certain similarity between these examples of autocatalytic and autoinhibition reactions is obvious: in both cases rank- $(\mathbf{B_X}^T) = S$ and $\Gamma = 0$ is the unique solution to eq 22.

From the standpoint of the formal logic this special class of mechanisms, which, by analogy with the Christiansen's nomenclature, can be referred to as *partially closed*, forms a structurally distinct type. However, in actual practice, a computer using algorithms for retrieving simple submechanisms[20] or direct routes[24] in a sequence of steps is unable to distinguish between this mixed type and the pure types. To overcome this difficulty, we have to declare dualistic intermediates as terminal species; then, the computer will find all simple submechanisms among which some may appear to be catalytic and others noncatalytic. Among the latter, we may find those that are "partially closed" by reconstructing the vertexes corresponding to dualistic species in subgraphs associated with these simple submechanisms.

To determine the type of the single-route mechanism one should follow a simple procedure:

1. Write a reaction mechanism (reaction scheme).
2. Construct the reaction network.
3. Delete terminal *w*-vertexes, thus arriving at the *SI*.
4. Check whether the *SI* contains w-vertexes corresponding to the dualistic species by way of verifying whether the condition rank$(\mathbf{B_X}^T) = S$ is met, in order to state which intermediates are dualistic and to construct the *RSI*.
5. Determine, by the use of Table 2 herein, whether the mechanism is a catalytic, noncatalytic, or mixed.

Table 2. Graphic Features of the Bipartite Subnetworks of Intermediates (*SI*) and Residual Subnetwork of Intermediates (*RSI*) for the Different Types of Single-Route Mechanisms[a]

mechanistic type	SI	RSN
catalytic (type C)	−	−
noncatalytic (type N)	+	+
mixed (type M)	−	+

[a] "+" and "−" denote the presence and absence of terminal vertexes, respectively.

The simple submechanisms of the multiroute mechanisms treated separately can be viewed as single-route mechanisms. Each of these mechanisms can be either catalytic or noncatalytic. This allows us to discuss the multiroute mechanisms in terms of the single-route ones. In a future paper[34] we will show which types of single-route mechanisms constitute the multiroute ones and what specificity is introduced by the "multirouteness". Meanwhile, we list here only some examples of the two-route reactions: the non-branched chain reactions (catalytic−noncatalytic), the non-catalytic conjugated reactions (noncatalytic−noncatalytic), and the catalytic reactions (catalytic−catalytic).

CONCLUSIONS

There are several methods for depicting complex reaction mechanisms. Among them, the method of bipartite graphs is likely most convenient and allows the mechanistic classification of the single-route mechanisms according to their topology. To reveal the structure of a single-route mechanisms, a mathematically rigorous and easy-to-use procedure for obtaining the reaction network, the subnetwork of intermediates, and the residual subnetwork *RSI* was developed. Distinctive features of the resulting graphs identify three classes of the single-route mechanisms: catalytic, noncatalytic, and mixed. This approach is directly applicable to the classification of the complex reactions according to their mechanisms and to the formulation of mechanistic nomenclature. The mechanisms of all multiroute reactions can be described and classified in terms of the single-route mechanisms they incorporate. We will dwell on this problem in the next paper in this series.[34]

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