

Application of Graph Theory to Chemical Kinetics. 3. Topological Specificity of Multiroute Reaction Mechanisms

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Received October 10, 1995[®]

A structural analysis and classification of the reaction networks of the multiroute reactions is made using the bipartite graph method. Simple submechanisms of the overall reaction mechanism are defined, so as to correspond to routes with minimal stoichiometric numbers. The possibility for balancing the intermediate species is advocated as the major classificational criterion which discriminates three categories of multiroute mechanisms: balanced, partially balanced, and unbalanced ones. Balanced mechanisms are further classified according to the number and topological type (catalytic and noncatalytic, C- and N-type, respectively) of the simple submechanisms. The common classes of purely catalytic, noncatalytic conjugated, and chain reactions appear with distinct mechanistic topology, as do the subclasses of nonbranched and branched chain reactions.

1. INTRODUCTION

This paper continues the series in which we discuss the application of graph theory to chemical kinetics and mechanistic studies. In part 1, we discussed an approach based on the so-called kinetic graphs, reaction routes, and linear mechanisms.¹ In part 2, we extended our analysis to nonlinear mechanisms.² Nonlinear mechanisms are characterized by the presence of more than one reaction intermediate on any side of the chemical equation of any of the mechanism elementary steps. (A mechanism is said to be nonlinear when at least one of its elementary steps consumes or produces more than one molecule of intermediate species.) Also in part 2, we presented a brief overview of the methods for depicting and graph-theoretical description of nonlinear mechanisms. Among other methods, we focused on **bipartite graphs**.^{2–6} (A bipartite graph is a graph whose vertex set is partitioned into two proper subsets so that no two vertexes from the same subset are adjacent.) It was shown that this formalism provides the classification of the single-route mechanisms into three classes: catalytic, noncatalytic, and mixed, the latter including among others autocatalytic and autoinhibition reactions.

In the past, much efforts have been devoted to classify chemical reactions, the methods of mechanistic classification being of particular importance. Bawden⁷ considered at least four application areas of the reaction classification: (a) information retrieval, (b) information discovery through deductive reasoning, (c) teaching and exposition of the variety and scope of chemical reactions, and (d) systematization of knowledge. Reaction classification is closely related to the computer-assisted elucidation and discovery of mechanistic pathways. Since times when Ingold proposed the first mechanistic classification, this area of research gained much attention of chemists and mathematicians.^{4,7–25} The methods

based on graph theory have been prominently used in the mechanistic classification.^{4,14–24}

In this paper, we employ one of these methods, which is based on reaction networks in the form of bipartite graphs. These graphs are shown to provide a better understanding of the topological specificity of multiroute mechanisms as well as to produce a classification of these mechanisms that correlates to the commonly accepted mechanistic concepts.

2. BASIC PRINCIPLES OF THE STRUCTURAL CLASSIFICATION OF REACTION MECHANISMS

As shown in part 1, a multistep reaction may involve one or more reaction routes. The concept of a **reaction route** was developed by Horiuti²⁶ and Temkin,^{27,28} and further treated time and again by other authors (for a review, see refs 29 and 30). If a reaction occurs via one route, the reaction mechanism is said to be single-routed. If a reaction occurs via several routes (a multiroute reaction) they can be identified by our algorithm and computer program **GERM** (Generic Ensembles of Reaction Mechanisms).³ These reaction routes are not necessarily linearly independent, but they induce a special set of the so-called **simple submechanisms** which are finite in number. A simple submechanism is a set of elementary reactions of a general mechanism with the following features:

- (i) It is irreducible into other simple mechanisms.³
- (ii) The number of steps s in a simple submechanism is one greater than the rank of the stoichiometric matrix of intermediates B_x .
- (iii) A set of stoichiometric numbers can be found for the elementary steps of a simple submechanism, such that all intermediates vanish in the resulting overall equation of this submechanism. Stoichiometric numbers must be nonzero integers; for irreversible steps they must also be positive. The vector of the stoichiometric numbers thus determined is termed a **route**.

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

Therefore, a simple submechanism corresponds to a route with the minimal integer stoichiometric numbers. Unless otherwise stated, as will omit for brevity the word "simple" in our discussion.

The concept of a route expresses the possibility of **balancing** the intermediates in a mechanism. (In this paper we use the term "balancing" differently than in Horn's,³¹ Jackson's,³² and Feinberg's³³ papers.) As shown in part 2, some single-route mechanisms do not allow for balancing the intermediates, autocatalytic reactions being a typical example.² However, an artificial expedient made it possible to transform such submechanisms to the form allowing for balancing. This expedient, called **pseudobalancing**, transfers one of the species from the set of intermediates to that of terminal species (reactants or products). The transferred species is termed **dualistic species**.

In a single-route mechanism, the choice of a dualistic species for pseudobalancing is mathematically arbitrary, and the overall equation of the single-route mechanism depends on this choice. If a chemist proceeds from a known overall equation the dualistic species can be uniquely defined. In the general case, the reaction requiring pseudobalancing in intermediates can be conducted in a number of ways, each resulting in different overall equations.

In part 2, we discussed the procedure for identifying the type of the single-route mechanism based on the consecutive construction of the bipartite network, the subnetwork of intermediates, and the residual subnetwork (*vide infra*).² A **reaction network** is a bipartite graph in which w -vertexes correspond to species and u -vertexes correspond to elementary reactions. If the w_i species is consumed or formed by the reaction u_j , the respective vertexes in the network are joined by an arc a_{ij} or (a_{ij}) , the order of subscripts denoting the arc direction.

The **subnetwork of intermediate (SI)** is obtained from the network by removing the vertexes corresponding to reactants and products. These species are terminal in a sense that either their indegrees or their outdegrees are equal to zero. (In Clarke's papers⁶ these species were termed **external** and were excluded from consideration from the very beginning. So, all Clarke's bipartite graphs are subnetworks of intermediates in our notation.) If some elementary steps are reversible while others are irreversible, the reversible steps should be treated as two reactions with opposite directions. In this case, all species involved in reversible steps formally appear as intermediates which is chemically incorrect. To avoid this disagreement with the chemical sense, we changed by convention the status of the species that are consumed and produced *only* in such pairs of steps from intermediate to terminal species.

The **residual subnetwork of intermediates (RSI)** is obtained from *SI* by the removal of vertexes corresponding to dualistic species (if any). If the subnetwork of intermediates contains no terminal vertexes, the single-route mechanism is either of catalytic or mixed type (types *C* and *M*, respectively); otherwise, the single-route mechanism is of the noncatalytic type (*N*). If both *SI* and *RSI* contain no terminal vertexes, the single-route mechanism is of the *C* type.

If a reaction occurs via several routes, the above mentioned types of simple submechanisms define the class of the overall multiroute mechanism. However, there is no formal method for identifying submechanisms of type *M*. To determine the

submechanisms of this type, one should know in advance the overall equation from experiment. Due to this, the mixed type *M* and the residual subnetwork *RSI* can not be used in a theory-based classification of multiroute mechanisms. All simple submechanisms of types *C* (catalytic) and *N* (non-catalytic) for a specified set of reactions can be exhaustively found by the formal procedure *GERM*.³ Once this is done, the *SI*s of the submechanisms are obtained and then embedded on the *SI* of the overall mechanism.

Three **types of multiroute mechanisms** can exist:

(i) The *SI*s of the simple submechanisms (*SISS*) cover the entire *SI* of the overall mechanism (*SIOM*). Intersections between the *SISS*s are allowed and even necessary in some instances. In this case, the overall mechanism allows for balancing in intermediate species and can be termed a **balanced mechanism**.

(ii) The *SISS*s cover only part of the *SIOM*. One or several steps remain incorporated in no submechanism. Such mechanisms are classified as **partially balanced**.

(iii) Neither *C*-type nor *N*-type submechanisms are found, and the mechanism is formally inseparable into submechanisms. Mechanisms of this kind are said to be **unbalanced**.

Cases (ii) and (iii) imply that the overall mechanism requires pseudobalancing. However, owing to the mathematically arbitrary choice of the dualistic species, the mechanism class would depend on this choice, and similar mechanisms would be categorized in different classes. This suggests that the choice of a dualistic species must be conducted in a mathematically orderly fashion, but such an ordering would be of no chemical sense. We had thus to decide between mathematical generality and adherence to the chemical sense. To overcome these difficulties we treat (ii) and (iii) as topologically distinct cases.

3. BALANCED MECHANISMS

3.1. General Discussion. As explained in the foregoing, these mechanisms result when all *SISS*s can be embedded on the subnetwork of intermediate of the overall mechanism (*SIOM*), so as to entirely cover it. This implies that all elementary reactions are included in submechanisms.

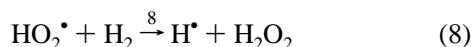
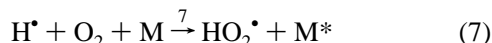
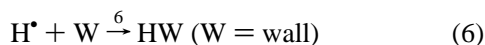
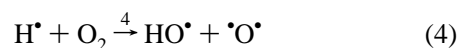
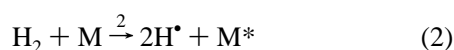
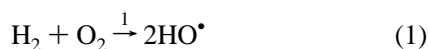
Balanced mechanisms can be classified into **classes of multiroute mechanisms** according to their composition, i.e., according to the type and number of their submechanisms. Thus, for example, the two-route mechanisms can exist in only three classes: *CC*, *NN*, and *CN*. In classifying more complex balanced mechanisms one needs to take into account not only their submechanistic composition but also the manner in which submechanisms interact with each other, i.e., one needs to make use of the topological structure of the overall mechanism. The simplest example demonstrating this necessity is provided by the three-route balanced mechanisms in which three submechanisms can be connected by forming either a three-membered ring or a chain.

An exhaustive classification and enumeration of multiroute balanced mechanisms is possible proceeding from the **submechanism graphs (SGs)** which we proposed recently.¹⁸ A vertex in such a graph stands for a submechanism, and two vertexes are joined by an edge when the corresponding submechanisms have common step(s) or/and common intermediate(s). These are connected bicolor graphs without loops, which allow for multiple edges in some cases of complex topologies of submechanism interaction (overlap-

ping of the submechanisms *SI* in two or more nonadjacent subgraphs). Two colors corresponding to *C* and *N* are assigned to the vertexes of these graphs.

Methods for the enumeration of connected graphs are well-known.^{34–37} Computer-assisted methods for assigning colors to generated connected graphs were also reported.³⁸ Since our primary goal is to present the general method for the classification of multistep reaction mechanisms (networks) proceeding from their topological structure, we do not dwell here on the details of enumeration of the relevant graphs. These problems are addressed in a forthcoming paper.³⁹

In this study, examples of mechanisms and reaction sets are chosen so as to provide a convenient illustration of our classification ideas. In some instances, these mechanisms might be simplified or incomplete, or their adequacy might be controversial. The discussion of the purely chemical aspects of these examples is out of the scope of this paper. To illustrate the procedure of finding the *SG* graph, characterizing the topological structure of the overall mechanism, consider the following set of elementary reactions.⁴⁰ (Hereinafter, we use serial numbers given above arrows in equations to number vertexes of graphs depicted in figures, while numbers placed after equations in parentheses are used to number equations sequentially throughout the text.)



The reaction network is given in Figure 1. According to the definitions given in section 2, one can determine that HO^\bullet , H^\bullet , $\cdot\text{O}^\bullet$, and HO_2^\bullet are intermediates, and the other species are terminal species because they have either zero indegree or zero outdegree. Four submechanisms can be identified for this set of reactions. They are denoted by their type (*C* or *N*) as well as by the number of elementary steps they incorporate: $N\langle 2, 6 \rangle$, $C\langle 7, 8 \rangle$, $N\langle 1, 3, 6 \rangle$, and $N\langle 3, 4, 5, 6 \rangle$. The subnetworks of intermediates of these submechanisms are shown in Figure 2.

The *SG* that defines the topological structure of the above mechanism is shown in Figure 3. Each vertex in Figure 3 stands for a submechanism, while the edge between two vertexes implies that the respective submechanisms have common intermediates or/and steps. As can be seen, the system of elementary reactions (1–8) presents a rather complex combination of submechanisms of *C* and *N* types.

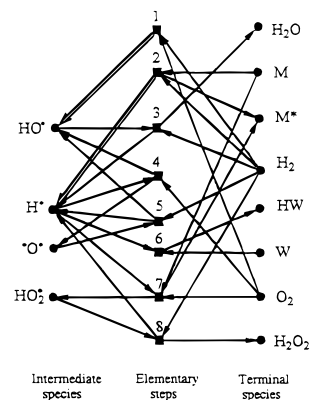


Figure 1. The reaction network describing the set of eqs 1–8. Quadrangles denote species and circles (or dots) denote elementary reactions. Intermediates are shown separately from reactants and products. The arc directions show whether the species is consumed or formed upon the elementary reaction. The arc multiplicity denotes a stoichiometric coefficient.

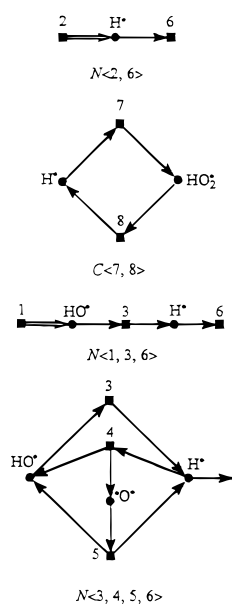


Figure 2. The subnetworks of intermediates of the four submechanisms (*SISSs*) identified for the set of reactions 1–8. The notation used describes the type of submechanism (*C* or *N*) and the steps involved.

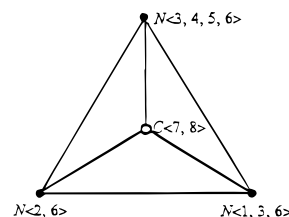


Figure 3. The submechanism graph for the set of reactions 1–8. Solid and open circles denote *N*- and *C*-submechanisms, respectively.

Balanced mechanisms describe a rich variety of reactions. Our topological criterion provided the identification of different classes of balanced mechanisms, the most important being purely catalytic reactions, chain reactions, and non-catalytic conjugated reactions. **Purely catalytic reactions** involve only submechanisms of type *C*. **Chain reactions** include both *C*- and *N*-submechanisms. **Noncatalytic conjugated reactions** incorporate only *N*-submechanisms.

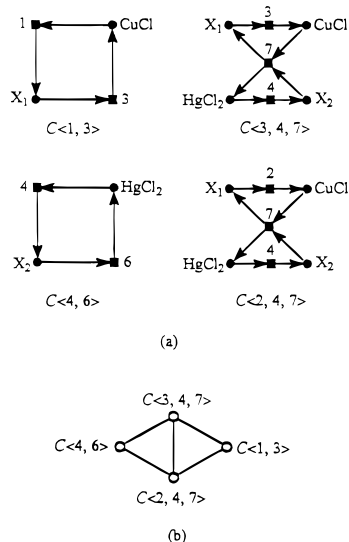
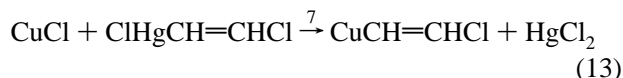
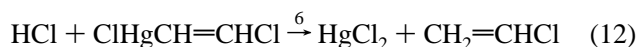
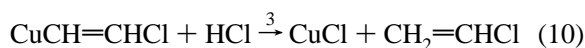
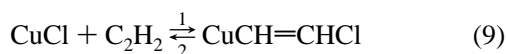


Figure 4. (a) The subnetworks of intermediates of the four submechanisms of the reaction set 9–13: $X_1 = \text{CuCH}=\text{CHCl}$, $X_2 = \text{ClHgCH}=\text{CHCl}$, and (b) the submechanism graph of the same reaction set.

3.2. Purely Catalytic Reactions. Purely catalytic reactions contain submechanisms of type *C* which are conjugated to each other by common intermediates or steps. As an example, consider the acetylene hydrochlorination in the polyfunctional catalytic Cu(I)–Hg(II) system⁴¹



In this system of elementary reactions, CuCl, HgCl₂, CuCH=CHCl, and ClHgCH=CHCl are intermediates, and the other substances are terminal species. Four submechanisms are identified (by definition, the reversible reactions <1,2> and <4,5> cannot be regarded as submechanisms) and shown in Figure 4 with their *SISSs* and *SG*.

Note that the submechanism <2,4,7> is of a special sort: In the overall equation of this submechanism not only intermediates but also all terminal species vanish. Happel and Sellers termed submechanisms of this sort *cycles*.^{42,43} In Temkin's notation, the submechanisms of this sort induce a route which is called *empty*,⁴⁴ because, after assigning the minimal integer stoichiometric numbers to the elementary reactions of submechanism <2,4,7>, the resulting overall equation is $0 = 0$.

3.3. Noncatalytic Conjugated Reactions. This class of reactions describes mechanisms involving at least two submechanisms of type *N* only. The submechanisms must have a common subgraph so as to make the *SG* graph connected. Each submechanism produces an overall reaction. If two *SISS* within the overall mechanism have a common subgraph, the respective overall reactions cannot

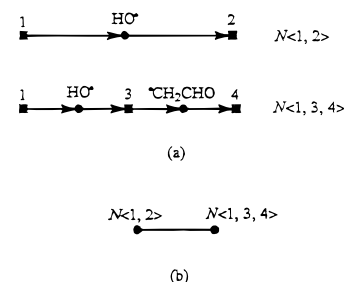
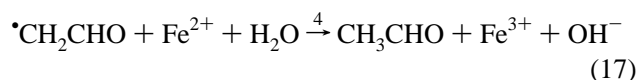
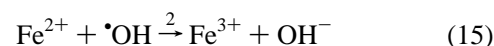
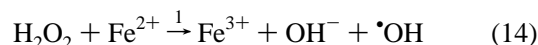
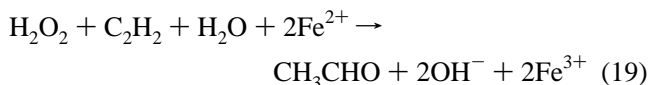


Figure 5. (a) The subnetworks of intermediates of the two submechanisms of the reaction set 14–17 and (b) the submechanism graph of the same reaction set.

occur in the absence of one another. An example is the process occurring in the H₂O₂/Fe²⁺ (the Fenton reagent) system to which acetylene is added. The mechanism involves two submechanisms⁴⁵



The two overall equations are



The *SISSs* of the reaction set (14–17) and its *SG* characterizing its topology are shown in Figure 5.

3.4. Chain Reactions. Chain reactions are a subject of much interest and speculation, but there is little agreement between different authors in defining the chain process. The typical diversity of opinion regarding chain reactions is related to the role of free radicals as chain carriers, the step repetition, and the inclusion of the active species in reaction products. In our opinion, the graph-theoretical standpoint lends a clearer understanding of the terms *chain reactions* and *chain mechanisms*.

The concept of mechanistic classification, based on the topological structure of the overall mechanism as composed of submechanisms, allows one to characterize a reaction as a chain process without being affected by the nature of intermediates and their reactivities. The traditional approach implies that in a chain mechanism elementary steps are divided into initiation, propagation, branching (if any), and termination steps. A branching step is characteristic for branched chain reactions. Within a branching step, the number of active species produced is greater than those consumed. The buildup of active species is compensated in the chain termination step. When one deals with a nonbranched chain mechanism, the reaction sequence called chain propagation presents a catalytic cycle. From the graph-theoretical viewpoint, chain reactions can be treated as mechanisms containing *C*- and *N*- submechanisms.

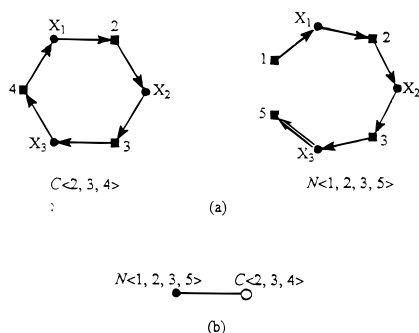
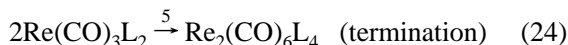
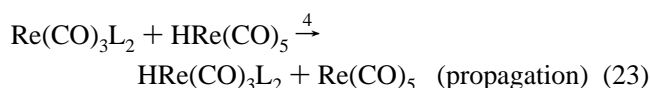
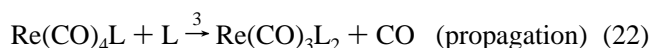
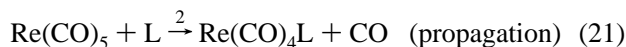
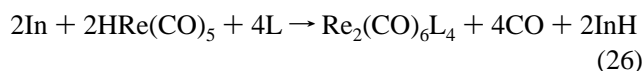
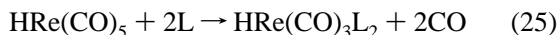


Figure 6. (a) The subnetworks of intermediates of the two submechanisms of the reaction set 20–26. Intermediates X_1 , X_2 , and X_3 are $\text{Re}(\text{CO})_5$, $\text{Re}(\text{CO})_4\text{L}$, and $\text{Re}(\text{CO})_3\text{L}_2$ complexes, respectively; the ligand L is PBu_3 and (b) the submechanism graph of the reaction set.

3.4.1. Nonbranched chain reaction involves at least one C -submechanism and at least one N -submechanism. The former is induced by the chain propagation steps, the latter being induced by the chain initiation and chain termination steps. An example of a nonbranched chain mechanism is provided by the ligand exchange in rhenium complexes occurring in liquid phase, the ligand being PBu_3 ⁴⁶



This mechanism was observed for a number of phosphine ligands. The two overall equations are



Two submechanisms are identified for this set of reactions: $C\langle 2,3,4 \rangle$ and $N\langle 1,2,3,5 \rangle$. Their subnetworks of intermediates are given in Figure 6 along with the SG of the entire mechanism.

This example reveals the lack of necessity of free radicals for the chain process. It should be noted that during the last 20 years numerous reactions appeared displaying all features of chain reactions except for the chain carriers. The reactive intermediates in these processes were not free radicals but paramagnetic or diamagnetic species and coordinatively unsaturated metal complexes. All features of chain processes are observed in reactions of alkene metathesis,⁴⁷ nucleophilic substitution in aromatic rings,⁴⁸ ligand exchange,^{46,48,49} and other reactions.⁵⁰ The structural similarity of chain mechanisms thus contributes to the interplay between organic, inorganic, and organometallic chemistry.

3.4.2. Branched chain reactions must involve one basic N -submechanism, which must contain chain termination and

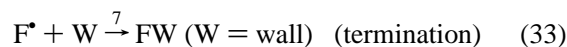
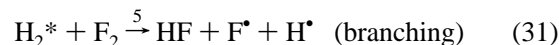
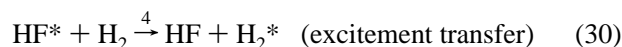
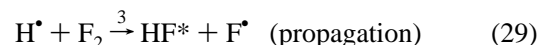
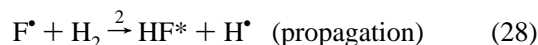
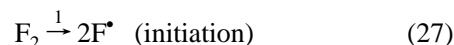
chain initiation steps and one or more other N -submechanisms. C -submechanisms are also possible but are not obligatory. The additional N -submechanisms must have the distinctive feature to involve a chain termination step which to compensate for chain branching. Without a chain termination step these N -submechanisms cannot be balanced in intermediates. Each of the $SISS$ s of these specific submechanisms must thus contain at least one terminal u -vertex.

Graph-theoretically, there are two subtypes of N -submechanisms. To identify the subtype, one should conduct the following procedure: Delete consecutively all terminal u - and v -vertexes from $SISS$ and all incident arcs. Then, if some terminal vertexes remain, repeat the deletion. Continue iterations until the reduced $SISS$ will not contain terminal vertexes. Then,

(i) if the entire $SISS$ thus appear deleted, then the submechanism does not contain branched propagation sequence of steps. Submechanisms of this sort are contained in conjugated noncatalytic reactions.

(ii) if part of $SISS$ remains undeleted, the submechanism can be categorized as another subtype, which involves chain branching. The presence of submechanisms of this subtype distinguishes branched chain reactions from conjugated noncatalytic reactions.

For brevity, we will refer to submechanisms that contain and that do not contain chain branching as N_1 - and N_2 -submechanisms, respectively. The presence of N_2 -submechanisms also differentiate branched chain mechanisms from nonbranched chain ones. A branched chain mechanism was illustrated in the foregoing by the mechanism of hydrogen oxidation (eqs 1–8), which involves two N_1 -submechanisms ($\langle 2,6 \rangle$ and $\langle 1,3,6 \rangle$), an N_2 -submechanism ($\langle 3,4,5,6 \rangle$), and C -submechanism ($\langle 7,8 \rangle$). An example of a branched chain mechanism containing only N -submechanisms is provided by the simplified sequence of elementary steps in the $\text{H}_2 + \text{F}_2$ system⁵¹



In eqs 27–33, HF^\bullet and H_2^* are the molecules of HF and H_2 excited at the expense of the exothermic reactions.

This mechanism contains one N_1 -submechanism: $\langle 1,7 \rangle$ and two N_2 -submechanisms: $\langle 2,4,5,6 \rangle$ and $\langle 3,4,5,7 \rangle$. They are shown in Figure 7 with the respective $SISS$ s and correspond

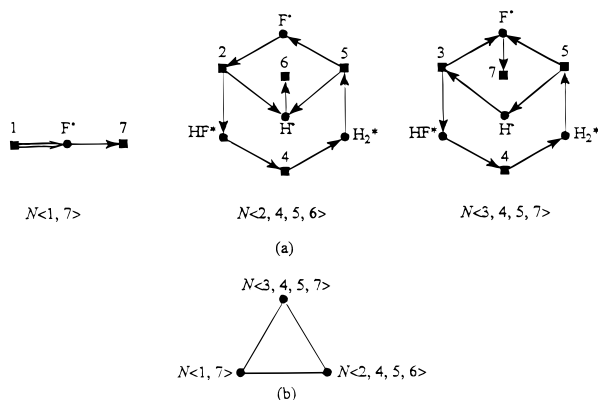
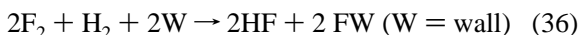
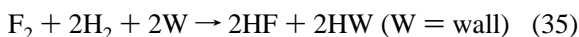
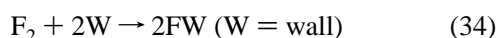


Figure 7. (a) The subnetworks of intermediates of the two submechanisms of the reaction set 27–36. HF* and H₂* are the exothermically excited molecules of HF and H₂. (b) The submechanism graph of the reaction set.

to the overall eqs 34–36:

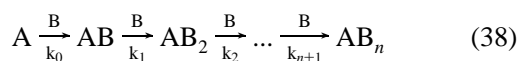


As seen in Figure 7, the consecutive deletion of terminal vertexes from *SISS* of $N_1<1,7>$ results in complete deletion of this *SISS*. The same procedure applied to $N_2<2,4,5,6>$ results in deletion of only two vertexes: u_6 and w -vertex for H*. The rest of *SISS* remains undeleted. Similar results can be obtained for $N_2<3,4,5,7>$: u_7 and w -vertex for F* will be deleted, and the rest of *SISS* will remain unchanged.

Interestingly, some reactions are often misinterpreted as chain processes. A typical example is the ionic (“living”) polymerization having the overall equation



where A is the reaction “initiator” and B is a monomer. The typical mechanistic scheme



provides no evidence for a chain mechanism. Apparently, one cannot find here the chain mechanism features except for step repetition. In fact, this is a noncatalytic one-route reaction. Although rate constants are close to each other ($k_1 \approx k_2 \approx \dots = k_{n+1}$), no structural similarity to chain reaction can be stated. In this case, the word “chain” refers to polymer chain rather than to mechanistic chain.

4. PARTIALLY BALANCED MECHANISMS

Upon conducting the formal procedure of finding submechanisms, one can retrieve only the balanced components of the overall mechanism. A step (or several steps) could remain outside this balanced part of the mechanism (see ref 52 for more details concerning partial balancing). These steps, which fall outside the balanced components, often manifest “unusual” kinetic behavior. Sometimes, they are simply not reflected in the kinetic laws. Several examples of these partially balanced reactions are listed below.

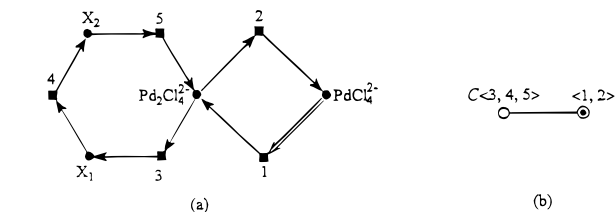
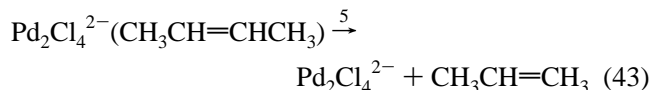
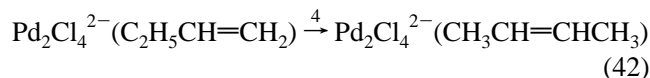
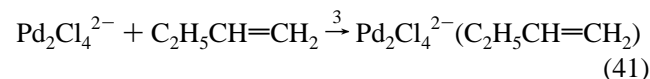
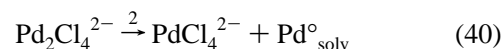
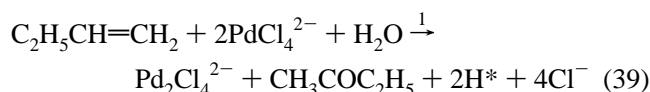


Figure 8. (a) The subnetwork of intermediates of the overall mechanism described by eqs 39–43. Intermediates X₁ and X₂ are Pd₂Cl₄²⁻ (1-C₂H₅CH=CH₂) and Pd₂Cl₄²⁻(CH₃CH=CHCH₃), respectively. (b) The submechanism graph. The unbalanced component is depicted by a solid circle inside an open circle.

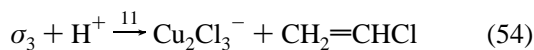
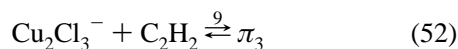
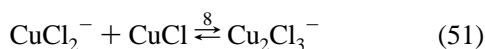
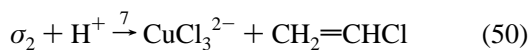
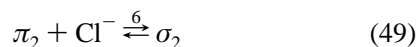
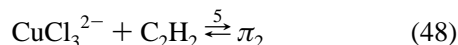
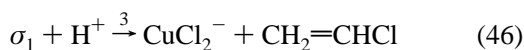
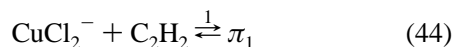
The butene isomerization reaction occurs in solutions of palladium complexes.⁵³ The reactive intermediate responsible for the catalysis of the isomerization reaction was found to be PdCl₄²⁻, while Pd(II) is a catalyst precursor:



The only submechanism, $\langle 3,4,5 \rangle$, is of C-type. Steps 1 and 2 fall outside the balanced component. The subnetwork of intermediates of the overall mechanism is shown in Figure 8a. Elementary steps 1 and 2 represent a connected unbalanced component sharing a common vertex with the C-submechanism $\langle 3,4,5 \rangle$. In the submechanism graph (Figure 8b), characterizing the mechanism topology, the unbalanced component of the mechanism is presented by a vertex $\langle 1,2 \rangle$ connected to that of the balanced component.

The kinetic findings and the entire amount of experimental data obtained made it possible to suggest that this reaction occurs via the chain mechanism. We adopted this opinion and adhered to it until the graph-theoretical approach was applied to this mechanism and the formal procedure for finding submechanisms was conducted. Indeed, steps 1 and 2 of this mechanism resemble the “chain initiation–chain termination” submechanism (N_1 -submechanism), which is typical for chain reactions; however, structurally this is a dissimilar mechanism.

Another case of a partially balanced mechanism is the set of reactions containing the so-called *bridging steps*.⁵⁴ An example is provided by the acetylene hydrochlorination reaction on different Cu(I) centers within the same reaction system.⁴¹ In solutions of CuCl three active centers were found to be carriers of catalytic cycles: CuCl₂⁻, CuCl₃²⁻, and Cu₂Cl₃⁻. Each of them is capable of producing π -complex with acetylene that transforms into σ -complex under the influence of Cl⁻ anion. Each σ -complex yields chlorovinyl and the respective metal center by acycolysis:



Because this mechanism is linear, we can depict it as ordinary kinetic graph (Figure 9a),¹ which is generally simpler than the bipartite subnetwork of intermediates. The set of reactions 44–54 has three *C*-submechanisms and an unbalanced component containing two bridging steps. The edges of the kinetic graph that correspond to these steps are bridges of the graph.⁵⁵ The *SG* characterizing the mechanism topology is shown in Figure 9b. In this graph, the removal of the vertex that corresponds to the unbalanced component makes the vertexes of the balanced submechanisms disconnected.

Partially balanced mechanisms may contain in their balanced components *C*- and *N*-submechanisms, and, hence, they may resemble purely catalytic, noncatalytic, and chain reactions. Development of further classification principles is a subject of future publications.

5. UNBALANCED MECHANISMS

As indicated above, elementary steps of a mechanism can be either reversible or irreversible. In a reaction route, the stoichiometric number of a reversible step can be either a positive or a negative integer. The stoichiometric number of an irreversible step can be only a positive integer. We also mentioned that each submechanism corresponds to a route which is a vector of integers. When conducting the formal procedure for finding all submechanisms, we discard those of them which necessarily contain negative stoichiometric numbers for irreversible steps and treat them as unbalanced component of the overall mechanism. If **all** potential submechanisms are thus discarded, the overall mechanism is categorized as a completely unbalanced one. To avoid the loss of generality, such a mechanism should be viewed as a set of reactions, inseparable into submechanisms. An example is presented by the following set of reactions⁵⁶

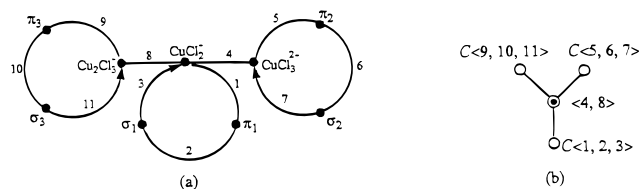


Figure 9. (a) The kinetic graph representing the linear mechanism of the acetylene hydrochlorination reaction 44–54 and (b) The submechanism graph of the overall mechanism.

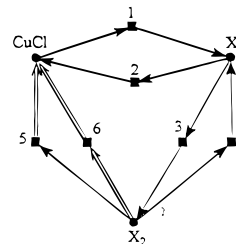
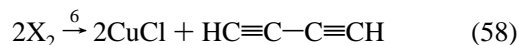
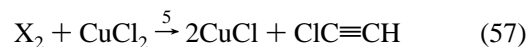
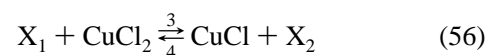
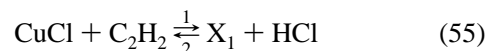
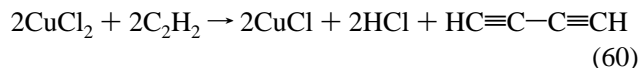
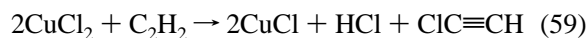


Figure 10. The subnetwork of intermediates of the mechanism described by eqs 55–58. X_1 and X_2 are intermediates. Note the lack of terminal vertexes which is typical for unbalanced mechanisms.



where CuCl , X_1 , and X_2 are intermediates. This is an autocatalytic mechanism in which $\text{ClC}\equiv\text{CH}$ and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ are produced by the following overall reactions



This choice of the overall reactions stems from real facts and observations. However, from a mathematical viewpoint this choice of the overall reactions is arbitrary. The formal number of linearly independent routes (according to the Horiuti rule: $M = S - \text{rank}(\mathbf{B}_x)$) is one, but all variants of routes imply negative stoichiometric numbers for either step 3 or 4. Therefore, all overall reactions necessarily involve some intermediates, which are more or less stable.

It should also be mentioned that *SIs* of unbalanced mechanisms contain neither terminal *u*-vertexes nor terminal *v*-vertexes (Figure 10).

6. CONCLUSIONS

We proposed a new classification of complex reactions based on the structure of the mechanism. According to this classification, there are three reaction categories: (i) balanced mechanisms, (ii) partially unbalanced mechanisms, and (iii) unbalanced mechanisms. (Definitions were given at the end of section 2.) Balanced mechanisms were further classified according to the types of mechanisms and the manner of their linkage. All commonly used terms like catalytic,

noncatalytic conjugated, and chain reactions were interpreted in terms of their specific topological features. More specifically, in order to categorize a balanced multiroute reaction mechanism, one should find all submechanisms and characterize them graph-theoretically as N_1 , N_2 , or C-type. Then, the mechanistic category can be identified by making use of the table given below.

Table 1. Graph-Theoretical Characterization of the Categories of Reaction Mechanisms^a

no.	mechanistic category	C	N_1	N_2
1	noncatalytic conjugated reaction	—	+	—
2	purely catalytic reaction	+	—	—
3	nonbranched chain reaction	+	+	—
4	branched chain reaction	±	+	+

^a Notation: “+” must be present; “—” must not be present; “±” can be present but it is not obligatory.

A detailed graph-theoretical classification and enumeration of the multiroute reactions, according to their categories, types, classes, and subclasses, will be reported in a forthcoming paper.³⁹ The structural characterization of reaction mechanisms provides a unified general view on reaction mechanisms and a rigorous systematization of the available experimental facts. Moreover, proceeding “from first principles”, this approach enables the predicting of new classes of reaction mechanisms. The results of this study are of direct applicability to databases of chemical reactions and to the computer handling of mechanistic information. They also provide correct and self-consistent method for naming reaction mechanisms.

ACKNOWLEDGMENT

This work was supported in part by the Russian Foundation for Fundamental Research (Grant No. 93-03-18050) as well as by Robert A. Welch Foundation, Houston, Texas. D.B. is indebted to Dr. W. A. Seitz (Galveston) and the Department of Chemistry at Rice University, Houston, for their hospitality.

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CI950268N