COMPLEXITY INDEX FOR THE LINEAR MECHANISMS OF CHEMICAL REACTIONS

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Abstract

A complexity measure is proposed for the kinetic models of chemical reactions with linear mechanisms. The index is related to the structure of fractional-rational kinetic laws for chemical reactions, as well as to the structure of cyclic graphs used to describe them. The complexity index is shown to be closely related to the detailed hierarchical classification and to the code of linear reaction mechanisms, recently introduced. A number of index properties are proved for two- and three-reaction routes. They reflect the influence of the various classification criteria, such as the number of reaction routes and intermediates, the type, class and subclasses of the mechanism, and the number of intermediates in each reaction route. Hierarchical levels of mechanisms with the same complexity (isocomplex mechanisms) are specified. Standard tables are presented with complexity indices for all topologically distinct linear reaction mechanisms having one to three reaction routes, two to six intermediates, and reversible elementary steps.

1. Introduction

During the last fifteen to twenty years, the mechanisms of catalytic and non-catalytic reactions have been studied, bringing about significant progress in the theory of reaction mechanism. Most of the catalytic reactions in the homogeneous, metal-complex, and enzymatic catalyses were found not to be inferior in mechanistic complexity as compared with radical-chain processes. Moreover, they appear to be much more complicated. Many examples of complicated mechanisms can be found in the literature [1–7]. At present, multiroute mechanisms (with two to four reaction routes) involving up to eight intermediates and up to twelve elementary steps, are

widely known to exist even in metal and non-metal assisted heterogeneous catalysis [8–10], where the simplest two-step schemes have enjoyed popularity for a long time. The existence of many routes and elementary steps is the most important general feature of the catalytic and numerous non-catalytic reaction mechanisms.

Contemporary chemical kinetics and the theory of reaction mechanisms exhibit typically not only increasing mechanistic complexity (hypotheses of mechanisms), but also have a considerable number of hypotheses (possible mechanisms describing each reaction). The greater mechanistic complexity and the large number of hypotheses raise the problem of formalizing and automating the hypothesis-generating procedure. The importance of the problem may be grasped from the example of conjugated catalytic reactions in which acrylic, propionic, succinic and maleic acid esters are prepared from CO and C_2H_2 in alcoholic solutions of Pd(I) complexes [11,12]. The total number of hypotheses, generated on the simplest possible assumption that the final product is formed in a single sequence of intermediates, is 1344!

The first general theory for generating the maximal number of hypotheses was proposed by Sellers [13,14]. It was based on an elegant group-theoretical formalism. Other approaches to the same problem are also known [8,11,15]. To develop an automated procedure for generating all possible hypotheses, and to create a bank of mechanisms, however, a convenient coding of mechanisms is needed.

The mechanism of each complicated reaction contains two kinds of information: chemical (or physicochemical) and topological (or formal-kinetic). The chemical information is governed by the type, composition, and properties of intermediates. The formal-kinetic information is determined by the number of reaction routes and intermediates, as well as by the different ways in which the routes are connected. The information that can be extracted from kinetic data is very useful in the preliminary selection and discrimination of hypotheses.

The best way of expressing the formal-kinetic information is by means of cyclic graphs, as proposed by Temkin [16]. (In the following, these graphs will be called "kinetic graphs".) In the case of mechanisms whose elementary steps incorporate one intermediate on the left-hand side and one on the right-hand side of the reaction equation (by Temkin called "linear mechanisms"), each edge in the cyclic graph denotes an elementary step of the reaction mechanism, i.e. for a pair of mutually reversible elementary reactions. Each vertex of the kinetic graph corresponds to a certain intermediate, while the linearly independent reaction routes are presented by graph cycles.

If the rate of a reverse elementary reaction is zero, then such an edge becomes irreversible and uniquely oriented, and is denoted by an arrow in the graph. By using such depictions, one arrives at a directed graph (digraph). All products from the interactions of intermediates with reagents not participating in the elementary steps are depicted by pendant vertices (vertices of degree 1). Nonlinear elementary steps

can also be depicted by cyclic graphs where additional "secondary" edges are used [17]. The nonlinear mechanisms can also be represented by so-called Volpert graphs [18].

Cyclic graphs proved to be very useful in the deduction of kinetic laws and in the analysis of kinetic data for linear mechanisms. In order to elucidate the connection between the graph's structure and the formal-kinetic laws, we have developed general principles for the classification and coding of linear mechanisms on the topological basis of cyclic graphs [19,20]. Our classification is free from the pitfalls of some previous attempts and it develops extensively ideas published elsewhere [21–24]. This graph-theoretical approach unites classification and coding with a procedure for deriving kinetic laws, and allows us to specify a hierarchy of mechanisms which seems to parallel their complexity [25]. The problem of mechanistic complexity and its relation to the classification and coding of mechanisms necessitates, however, further studies. The successful solution of the problem would be very important in the creation of automated systems for chemical kinetics studies. In this paper, we discuss a promising approach to the complexity of reaction mechanisms.

2. The classification and coding of chemical reactions with linear mechanisms

The principles of classification and coding recently developed [20] will be briefly stated here as a basis for now treating the complexity of reaction mechansims. The problem of the classification of linear mechanisms when taking into account solely the structural information, is reduced to the classification of kinetic graphs. With this purpose in mind, a hierarchical system of criteria is used to construct an appropriate linear code. Consider the system of criteria, as well as the code for the undirected kinetic graphs (KG) without the so-called pendant vertices (vertices of degree 1). Further examples will be given in table 1 and fig. 1.

(1) Number of reaction routes (KG cycles), $M = 1, 2, 3, \ldots$.
(2) Number of intermediates (KG vertices), $N = 2, 3, 4, \ldots$.
(3) Type of mechanism (the supergraph structure), $S = 0, 1, 2, \ldots$. Here, S is the serial number of the so-called supergraph. Each supergraph vertex represents a cycle in the initial KG while a pair of the supergraph vertices is connected with an edge when the respective KG cycles are joined by means of common edge(s), vertex(ices), or a bridge, but not through another cycle.
(4) Class of mechanism defined by the way of connecting two cycles in KG: bridging (class A), common vertex (class B), and common edge (class C). The classes of KG having more than two cycles are combinations of these three elements.
(5) Number of elements that are common for two cycles. These are the length of the bridge connecting two cyclces (the reaction routes), the number of

common vertices or edges of the two cycles (the number of common intermediates or elementary steps) which determine the subclasses I, V, and L, respectively.

(6) Mutual location of two cycles linked to a third one (subclasses K).

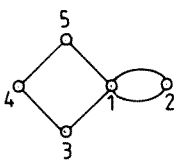
(7) The number of vertices in each cycle (the number of intermediates in each reaction route), N_i.

The notation needed in expressing the classification criteria form a unique linear code:

$$M-N-S-A^{X}_{I,K}\,B^{Y}_{V,K}\,C^{Z}_{L,K}-N_1,N_2,\ldots,N_M\,.$$

The detailed code actually includes a more detailed class notation which lists the connections between the pair of cycles in an increasing alphabetic order. The codes of all undirected kinetic graphs having one to four cycles and two to six vertices are given in table 1 (vide infra).

As an example, consider the mechanism of the conversion of water-vapor methane on nickel. It incorporates two independent reaction routes, five intermediates, and six elementary steps, as seen from the respective undirected kinetic graph:



code 2-5-B-2,4

The mechanism itself is given by the following scheme:

1. $CH_4 + Z \rightleftarrows ZCH_2 + H_2$
2. $ZCH_2 + H_2O \rightleftarrows ZCHOH + H_2$
3. $ZCHOH \rightleftarrows ZCO + H_2$
4. $ZCO \rightleftarrows Z + CO$
5. $Z + H_2O \rightleftarrows ZO + H_2$
6. $ZO + CO \rightleftarrows Z + CO_2$

$$CH_4 + H_2O = CO + 3H_2$$
$$CO + H_2O = CO_2 + H_2\,.$$

The following intermediates are included: Z is the reaction site on the surface of nickel, assumed to be bivalent; CH_2, CHOH, CO and O are chemosorped radicals. In the order presented, these intermediates correspond to vertices 1, 3, 4, 5 and 2 in the kinetic graph, respectively.

3. Complexity of linear mechanisms. Quantitative estimations

In formulating hypotheses for the mechanism of a certain complicated reaction, as well as in using different procedures for the selection of one out of many hypotheses (discrimination of hypotheses), the question arises as to the hierarchy of hypotheses. The intuitive principle of simplicity cannot play the role of a device for the selection of hypotheses in the case of multiroute reactions because the number of vertices and cycles, as well as the ways of linking cycles in the kinetic graph, are already variable. Proceeding from linear mechanisms, we examine here a possible approach to the construction of a quantitative scale for mechanistic complexity or to the selection of a "complexity index".

3.1. COMPLEXITY OF KINETIC GRAPHS

The first complexity level of a linear mechanism is obviously related to the kinetic graph complexity. The complexity of graphs is a subject of interest to both mathematicians [26–28] and theoretical chemists [29–32], who proposed a number of numerical quantities called topological indices. Some pitfalls of these complexity measures were soon recognized. Thus, all simple indices are degenerate, i.e. some non-isomorphic graphs are characterized by the same numerical value of the topological index.

In chemical graph theory, ways to avoid the degeneracy are usually sought by constructing more sophisticated topological indices such as the Bertz index and, particularly, the Balaban index [34]. A combined topological index which reflects the topological structure of the graph as fully as possible has also been proposed [35]. The ultimate unique and relatively simple solution of the problem of how to estimate graph complexity is, however, still lacking. For this reason, the complexity of kinetic graphs is not explored here as a possible approach to the complexity of chemical reactions.

3.2. COMPLEXITY OF THE KINETIC MODEL

The second complexity level of chemical reaction mechanisms is the level of the kinetic model reflecting a certain mechanism (or KG). Proceeding from the fact that ultimately the mechanistic complexity manifests itself in kinetics, it seems reasonable to look for a complexity index that reflects the complexity of the kinetic model. Two kinds of kinetic models may be used for this purpose: (a) fractional-rational equations for the rate of a route in stationary or quasi-stationary processes with linear mechanisms; (b) systems of differential equations describing any kind of mechanism.

We have proposed the complexity index K based on the fractional-rational form of the rate laws for reaction routes [25]. This index is defined as the total number of weights (rate constants) for the elementary steps included in the kinetic

laws' numerator and denominator for all routes of multiroute reactions. Our choice is based on the simple and intuitively evident assumption that the reaction mechanism (as well as its kinetic model) will be more complex when it includes more reaction routes (independent stoichiometric equations), with more elementary steps and reaction intermediates in each route. This change runs also parallel with the increase in complexity of the respective kinetic graphs with the increasing number of its cycles, edges, and vertices. Moreover, as shown in the next sections, the index proposed satisfactorily reflects the enhanced mechanistic complexity (KG) caused by the stronger interdependence between reaction routes (KG cycles). Thus, for example, the complexity decreases in the following order: routes with common elementary step(s), routes with a common intermediate, and routes having no common elements at all. Finer aspects of this kind are taken into account by our complexity index.

By reflecting both the formal-kinetic and topological aspects of the reaction mechanisms, the complexity index K proposed here certainly cannot take into account all complexity features of chemical reactions. Thus, complexity of the reacting species (the nature of the KG vertices), as well as the different types of elementary reaction steps, such as syntheses, exchange reactions, etc. (the nature of the KG edges), are not taken into consideration. However, being related to the kinetic graph, these features could be regarded as components of a more sophisticated complexity measure in addition to the K index.

In calculating the quantity K, it is convenient to use the Vol'kenstein–Gol'dstein algorithm [36,37] to derive the rate laws for the routes of all catalytic and non-catalytic reactions with linear mechanisms.

The rate of route p in a reaction with M routes is:

$$r_p = [X_i] \sum_{k=0}^{k \leqslant M-1} (\vec{C}_{pk} - \overleftarrow{C}_{pk}) D_{pk}/D_i \,, \tag{1}$$

where D_i is the vertex determinant (the sum of the weights of all trees containing this vertex), C_{pk} is the length of the cycle corresponding to route p ($k = 0$) or the length of the cycles encompassing the $k = 0$ cycle. The cycle is the product of the elementary step's weights constituting the kth cycle; D_{pk} is the base determinant of the subgraph formed after contracting the pk cycle to a vertex (it is also called the algebraic complement of cycle pk). $[X_i]$ is the reagent concentration in vertex i (if the substance is a catalyst, active site or zero reagent, then $[X_0] = 1$).

This algorithm is very convenient, particularly for catalytic reactions, since if written as eq. (2) it accounts for the material balance with respect to the catalyst:

$$r_p = [K]_\Sigma \frac{\sum_{k=0}^{k \leq M-1} (\vec{C}_{pk} - \overleftarrow{C}_{pk}) D_{pk}}{\sum_{i=1}^{N} D_i} \tag{2}$$

Here, $[K]_\Sigma$ is the total concentration of all catalyst species. In the case of surface reactions, $[K]_\Sigma = 1$.

The complexity index K is defined by the equation:

$$K = M(N-1)\, T_p^d + N \sum_{p=1}^{M} T_p^n , \tag{3}$$

where T_p^n and T_p^d are the total numbers of the rate constants in the numerator and denominator, respectively, of the kinetic laws for r_p.

3.3. CALCULATION OF THE SPANNING TREES IN KG

The calculation of K is evidently reduced to the calculation of the KG spanning trees and some specific KG subgraphs. General methods are known in graph theory for constructing and enumerating spanning trees [38]. Alternatively, in order to evaluate the complexity of bicyclic and tricyclic non-directed graphs, we shall use the explicit formulae for the number of KG spanning trees derived earlier [25];

$$T_2 = N_1 N_2 - E_{12}^2 \tag{4}$$

$$T_3 = N_1 N_2 N_3 - E_{12}^2 N_3 - E_{13}^2 N_2 - E_{23}^2 N_1 - 2E_{12} E_{13} E_{23}. \tag{5}$$

Here, N_p and E_{pk} denote the number of vertices of cycle p and the number of edges common to cycles p and k, respectively. In deriving eqs. (4) and (5), it is assumed that no edge is common to more than two cycles.

Equation (4) is used in its complete form for class C of the bicyclic KG only where cycles 1 and 2 have a common edge $E_{12} \neq 0$. $E_{12} = 0$, however, for classes A and B of the bicyclic KG, in which the two cycles are connected by a bridge or a common vertex, respectively.

In the case of tricyclic KG, any connection of type A or B between cycles i and j results in $E_{ij} = 0$, which greatly simplifies eq. (5). The latter is used in its complete form only for the C^3 class out of the fourteen classes of three-route reaction mechanisms. The other thirteen classes [20] are treated by the following simplified equations:

$$T_3 = N_1 N_2 N_3 - E_{12}^2 N_3 - E_{13}^2 N_2 \qquad (5')$$

for classes C^2, BC^2, and B_2C^2,

$$T_3 = N_1 N_2 N_3 - E_{12}^2 N_3 \qquad (5'')$$

for classes AC, BC, A^2C, and B^2C,

$$T_3 = N_1 N_2 N_3 \qquad (5''')$$

for classes A^2, B^2, AB, A^3, B^3, and A^2B.

When dealing with non-directed KGs, it should be borne in mind that the number of spanning trees in vertex i, T_i, calculated by eqs. (5) to (5'''), is the same for every N graph vertex. Hence, the first term in eq. (3) will transform into

$$K_1 = M(N-1)T_p^d = MN(N-1)T_i \,. \qquad (6)$$

3.4. DETERMINATION OF THE ALGEBRAIC COMPLEMENTS D_{pk} IN KG

The second term in the basic eq. (3) for the complexity index can also be transformed into:

$$K_2 = N \sum_{p=1}^{M} T_p^n = 2N \sum_{p=1}^{M} \sum_{k=0}^{k_{max}} D_{pk} \,, \qquad (7)$$

where the factor 2 accounts for the two different directions $\vec{C}_{pk}$ and $\overleftarrow{C}_{pk}$ in eq. (2).

It will be shown that the double sum in (7) can be expressed as the number of spanning trees in some specific subgraphs. We will consider in detail bicyclic and tricyclic KGs, but the result can be readily generalized for any cyclic graph.

3.4.1. Bicyclic kinetic graphs

The double sum in (7) can be expanded into

$$\sum_{p=1}^{M=2} \sum_{k=0}^{1} D_{pk} = D_p + D_{p \cup k} + D_k + D_{k \cup p} \,.$$

For bicyclic graphs, however,

$$D_p = N_k - E_{pk}, \quad D_k = N_p - E_{pk}, \quad \text{and} \quad D_{p \cup k} = D_{k \cup p} = E_{pk} .$$

Hence, one obtains:

$$\sum_{p=1}^{M=2} \sum_{k=0}^{1} D_{pk} = N_p + N_k . \tag{8}$$

3.4.2. Tricyclic kinetic graphs;

Similarly, the double sum in (7) is expanded into

$$\sum_{p=1}^{M=3} \sum_{k=0}^{3} D_{pk} = D_p + D_k + D_\ell + 2D_{p \cup k} + 2D_{p \cup \ell} + 2D_{k \cup \ell} + 3D_{p \cup k \cup \ell}$$

$$= (N_p N_k - E_{pk}^2) + (N_p N_\ell - E_{p\ell}^2) + (N_k N_\ell - E_{k\ell}^2). \tag{9}$$

Comparing eqs. (9) and (4), one concludes that in tricyclic graphs the algebraic complement of an arbitrary cycle ℓ and its encompassing cycles equals the number of spanning trees in the bicyclic subgraph containing the remaining two cycles p and k:

$$\sum_{k=0}^{3} D_{\ell k} = T_{p \cup k} . \tag{10}$$

For bicyclic graphs, eq. (8) can be interpreted in a similar way:

$$\sum_{k=0}^{1} D_{pk} = T_p . \tag{11}$$

These results can easily be generalized for multiroute reaction mechanisms. Equations (4) and (5) will also be used to calculate the second term of the complexity index K_2 for tri- and four-route reaction mechanisms, respectively.

It should be noted that the number of spanning trees, as defined by eqs. (4) and (5), and hence the KG complexity index, can be calculated from their code. The latter provides all the information needed, such as the size of all cycles N_i, the type of their linking (A, B or C), the number of cycles M, and vertices N. Thus, the KG code described in sect. 2 is not only a convenient hierarchical description of these

graphs, but is associated directly with their complexity, which is essential in the computer handling of linear reaction mechanisms.

4. Standard tables of all topologically different linear reaction mechansims with 1, 2 and 3 reaction routes and 2 to 6 intermediates

The influence of the different kinetic code constituents on the complexity index K of linear reaction mechanisms will be considered in detail in sects. 5 and 6. Here, we present in fig. 1 and table 2 the codes and complexity indices for all 135 linear reaction mechanisms having up to six intermediates and 1, 2, and 3 reaction routes (5, 24, and 106, respectively). The kinetic graphs presented there are non-directed and devoid of pendant vertices (vertices of degree 1), i.e. these linear mechanisms contain reversible elementary steps only and do not contain intermediates that are involved only in an equilibrium elementary step. Clearly, each of the presented 135 mechanisms corresponds to a certain number of mechanisms with irreversible steps, as well as to a certain number of mechanisms described by means of a kinetic graph with pendant vertices.

The standard tables will be extended so as to comprise the linear reaction mechanisms with four reaction routes in a subsequent publication [40]. The algorithms used to generate KGs will also be described elsewhere [41].

5. Some general relations for the complexity index of linear reaction mechanisms. Two-route mechanisms

The complexity indices of two arbitrary graphs K^r and K^t will be compared in this section in order to derive some basic relations concerning the complexity of linear reaction mechanisms.

Proceeding from eqs. (3), (6) and (7), the difference in the complexity indices of two such mechanisms can be represented as a sum of two terms:

$$\Delta K = K^t - K^r = M^t N^t (N^t - 1) T^t - M^r N^r (N^r - 1) T^r$$

$$+ 2N^t \sum_{p=1}^{M^t} \sum_{k=0}^{K_{\max}} D_{pk}^t - 2N^r \sum_{p=1}^{M^r} \sum_{k=0}^{K_{\max}} D_{pk}^r = \Delta K_1 + \Delta K_2 . \qquad (12)$$

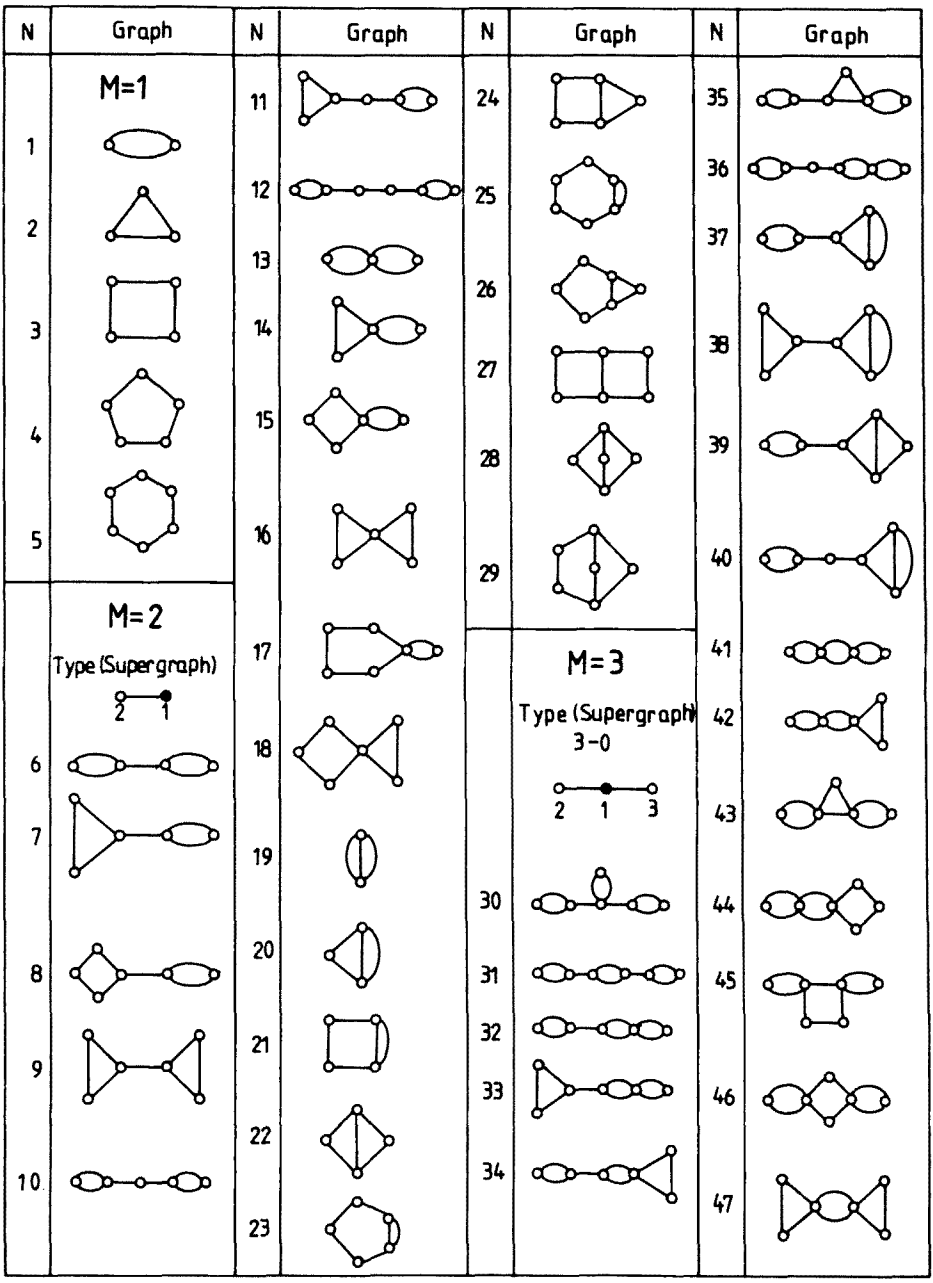


Fig. 1.

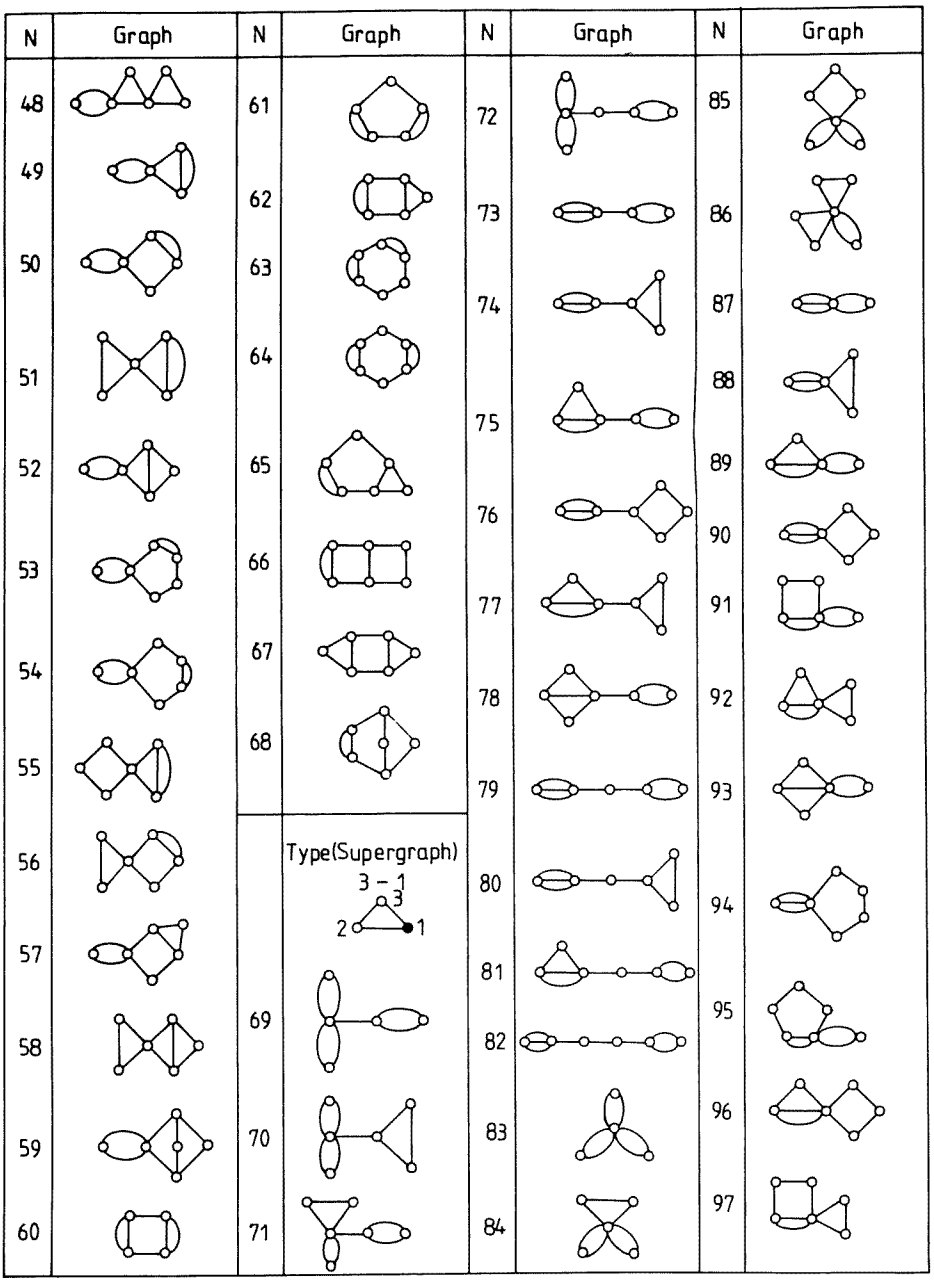

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Fig. 1.

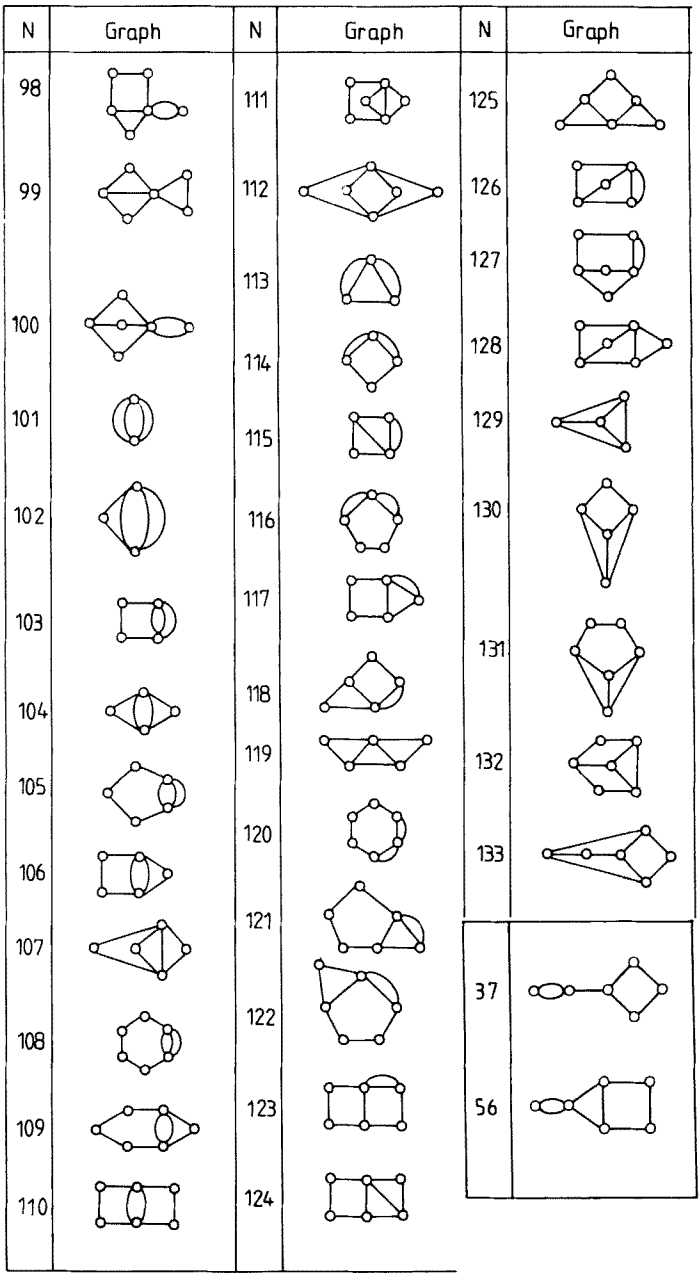

Fig. 1. All the simple connected cyclic graphs (kinetic graphs) with 1, 2, and 3 cycles and 2 to 6 vertices expressing all topologically distinct linear reaction mechanisms with 1 to 3 routes and 2 to 6 intermediates.

Table 1

Classification, code and complexity index of the chemical reactions' linear mechanisms

I. One-route mechanisms

N	Code	Index
1.	1-2	8
2.	1-3	24
3.	1-4	56
4.	1-5	110
5.	1-6	192

II. Two-route mechanisms

N	Code	Index	*N*	Code	Index	*N*	Code	Index
	Class A			*Class B*			*Class C*	
6.	2-4-*A*-2,2	128	13.	2-3-*B*-2,2	72	19.	2-2-*C*-2,2	28
7.	2-5-*A*-2,3	290	14.	2-4-*B*-2,3	184	20.	2-3-*C*-2,3	90
8.	2-6-*A*-2,4	552	15.	2-5-*B*-2,4	380	21.	2-4-*C*-2,4	216
9.	2-6-*A*-3,3	612	16.	2-5-*B*-3,3	420	22.	2-4-*C*-3,3	240
10.	2-5-A_2-2,2	200	17.	2-6-*B*-2,5	684	23.	2-5-*C*-2,5	430
11.	2-6-A_2-2,3	420	18.	2-6-*B*-3,4	804	24.	2-5-*C*-3,4	510
12.	2-6-A_3-2,2	288				25.	2-6-*C*-2,6	756
						26.	2-6-*C*-3,5	936
						27.	2-6-*C*-4,4	996
						28.	2-5-C_2-4,4	560
						29.	2-6-C_2-4,5	1068

III. Three-route mechanisms

N	Code	Index	*N*	Code	Index
		TYPE 3-0			
	Class A^2			*Class AC*	
30.	3-6-0-$A^2_{1,0}$-2,2,2	864	37.	3-5-0-*AC*-3,2,2	750
31.	3-6-0-$A^{2'}_{1,1}$-2,2,2	864	37′	3-6-0-*AC*-4,2,2	1488
			38.	3-6-0-*AC*-3,3,2	1590
	Class AB		39.	3-6-0-*AC*-3,2,3	1680
32.	3-5-0-*AB*-2,2,2	600	40.	3-6-0-A_2C-3,2,2	1080
33.	3-6-0-*AB*-2,3,2	1272			
34.	3-6-0-*AB*-2,2,3	1272			
35.	3-6-0-*AB*-3,2,2	1272			
36.	3-6-0-A_2B-2,2,2	864			

Table 1 (continued)

N	Code	Index	N	Code	Index
		TYPE 3-0			
	Class B^2			*Class C^2*	
41.	3-4-0-B^2-2, 2, 2	384	60.	3-4-0-C^2-4, 2, 2	576
42.	3-5-0-B^2-2, 2, 3	880	61.	3-5-0-C^2-5, 2, 2	1180
43.	3-5-0-B^2-3, 2, 2	880	62.	3-5-0-C^2-4, 2, 3	1380
44.	3-6-0-B^2-2, 2, 4	1680	63.	3-6-0-$CC_{1,1}$-6, 2, 2	2112
45.	3-6-0-$BB_{1,1}$-4, 2, 2	1680	64.	3-6-0-$CC_{1,2}$-6, 2, 2	2112
46.	3-6-0-$BB_{1,2}$-4, 2, 2	1680	65.	3-6-0-C^2-5, 2, 3	2598
47.	3-6-0-B^2-2, 3, 3	1872	66.	3-6-0-C^2-4, 2, 4	2700
48.	3-6-0-B^2-3, 2, 3	1872	67.	3-6-0-C^2-4, 3, 3	3072
			68.	3-6-0-CC_2-5, 2, 4	2916
	Class BC				
49.	3-4-0-BC-3, 2, 2	480			
50.	3-5-0-BC-4, 2, 2	1030			
51.	3-5-0-BC-3, 3, 2	1100			
52.	3-5-0-BC-3, 2, 3	1160			
53.	3-6-0-$B_{1,1}C$-5, 2, 2	1896			
54.	3-6-0-$B_{1,2}C$-5, 2, 2	1896			
55.	3-6-0-BC-3, 4, 2	2100			
56.	3-6-0-BC-4, 3, 2	2190			
56′	3-6-0-BC-3, 2, 4	2220			
57.	3-6-0-BC-4, 2, 3	2280			
58.	3-6-0-BC-3, 3, 3	2472			
59.	3-6-0-BC_2-4, 2, 4	2496			
		TYPE 3-1			
	Class A^2B			*Class B^3*	
69.	3-5-1-A^2B-2, 2, 2	600	83.	3-4-1-B^3-2, 2, 2	384
70.	3-6-1-A^2B-3, 2, 2	1272	84.	3-5-1-B^3-2, 2, 3	880
71.	3-6-1-A^2B-2, 2, 3	1272	85.	3-6-1-B^3-2, 2, 4	1680
72.	3-6-1-A_2^2B-2, 2, 2	864	86.	3-6-1-B^3-2, 3, 3	1872
	Class A^2C			*Class B^2C*	
73.	3-4-1-A^2C-2, 2, 2	304	87.	3-3-1-B^2C-2, 2, 2	174
74.	3-5-1-A^2C-3, 2, 2	690	88.	3-4-1-B^2C-3, 2, 2	444
75.	3-5-1-A^2C-2, 2, 3	750	89.	3-4-1-B^2C-2, 2, 3	480
76.	3-6-1-A^2C-4, 2, 2	1308	90.	3-5-1-B^2C-4, 2, 2	910
77.	3-6-1-A^2C-3, 2, 3	1590			
78.	3-6-1-A^2C-2, 3, 3	1680			
79.	3-5-1-A_2^2C-2, 2, 2	470			
80.	3-6-1-A_2^2C-3, 2, 2	990			
81.	3-6-1-A_2^2C-2, 2, 3	1080			
82.	3-6-1-A_3^2C-2, 2, 2	672			

Table 1 (continued)

N	Code	Index	N	Code	Index
			TYPE 3-1		
	Class B^2C			*Class BC^2*	
91.	3-5-1-B^2C-2, 2, 4	1030	113.	3-3-1-BC^2-2, 2, 3	228
92.	3-5-1-B^2C-3, 2, 3	1100	114.	3-4-1-BC^2-2, 2, 4	576
93.	3-5-1-B^2C-2, 3, 3	1160	115.	3-4-1-BC^2-2, 3, 3	620
94.	3-6-1-B^2C-5, 2, 2	1626	116.	3-5-1-BC^2-2, 2, 5	1180
95.	3-6-1-B^2C-2, 2, 5	1896	117.	3-5-1-BC^2-2, 4, 3	1320
96.	3-6-1-B^2C-4, 2, 3	2100	118.	3-5-1-BC^2-2, 3, 4	1380
97.	3-6-1-B^2C-3, 2, 4	2190	119.	3-5-1-BC^2-3, 3, 3	1510
98.	3-6-1-B^2C-2, 3, 4	2280	120.	3-6-1-BC^2-2, 2, 6	2112
99.	3-6-1-B^2C-3, 3, 3	2472	121.	3-6-1-BC^2-2, 5, 3	2418
100.	3-6-1-B^2C_2-2, 4, 4	2496	122.	3-6-1-BC^2-2, 3, 5	2598
			123.	3-6-1-BC^2-2, 4, 4	2700
	Class B_2C^2		124.	3-6-1-BC^2-3, 4, 3	2982
101.	3-2-1-B_2C^2-2, 2, 2	64	125.	3-6-1-BC^2-3, 3, 4	3072
102.	3-3-1-B_2C^2-2, 3, 2	210	126.	3-5-1-BCC_2-2, 4, 4	1470
103.	3-4-1-B_2C^2-2, 4, 2	504	127.	3-6-1-BCC_2-2, 4, 5	2916
104.	3-4-1-B_2C^2-3, 3, 2	584	128.	3-6-1-BCC_2-3, 4, 4	3300
105.	3-5-1-B_2C^2-2, 5, 2	1000			
106.	3-5-1-B_2C^2-3, 4, 2	1260		*Class C^3*	
107.	3-5-1-B_2CC_2-3, 4, 3	1480	129.	3-4-1-C^3-3, 3, 3	768
108.	3-6-1-B_2C^2-2, 6, 2	1752	130.	3-5-1-C^3-3, 3, 4	1740
109.	3-6-1-B_2C^2-3, 5, 2	2328	131.	3-6-1-C^3-3, 3, 5	3312
110.	3-6-1-B_2C^2-4, 4, 2	2520	132.	3-6-1-C^3-3, 4, 4	3594
111.	3-6-1-B_2CC_2-3, 5, 3	2490	133.	3-6-1-C^2C_2-4, 4, 4	3744
112.	3-6-1-$B_2C_2^2$-4, 4, 4	3360			

Fig. 2. A bicyclic kinetic graph in a general position. p, k stand for the two cycles, while E_{pk} is the number of common edges of the two cycles.

Consider now the complexity of two-route reaction mechanisms. Let the two cycles in the respective kinetic graph be denoted by p and k, respectively. Let also the number of edges common for p and k be denoted by E_{pk}. The influence of three classification criteria will be considered. These are the total number of intermediates N, the type of cycle linkage (the class and subclass of the mechanism), and the number of intermediates in each cycle N_p and N_k. Each of these complexity factors will be studied as a single variable, i.e. keeping all other factors constant.

5.1. COMPLEXITY INDEX DEPENDENCE ON THE TOTAL NUMBER OF REACTION INTERMEDIATES N

For the same class and subclass of the kinetic graph, consider the simpler case with intermediates whose number increases only in one of the two reaction routes:

$$N^t = N^r + s, \quad N_p^t = N_p^r, \quad N_k^t = N_k^r + s.$$

Inserting these conditions in eqs. (12), (4), and (8), one arrives at the expression

$$\Delta K = 2sN^r(N^r - 1)N_p^r + T^t(2N^r + s - 1) + (N^r + N_p^r + N_k^r + s) > 0, \quad (13)$$

which is always positive. Therefore, the complexity index of the two-route reaction mechansims always increases with increasing total number of reaction intermediates:

$$\Delta K = K(N^r + s, N_p, N_k^r + s) - K(N^r, N_p, N_k^r) > 0. \quad (13')$$

5.2. RELATIVE COMPLEXITY OF CLASSES AND SUBCLASSES

The initial conditions are now $N^t = N^r = N$, $N_p^t = N_p^r$, and $N_k^t = N_k^r + s$, i.e. the complexity of two classes or subclasses of KGs is compared for a constant total number of graph vertices, as well as for a constant number of vertices in one of the two graph cycles.

Similarly to eq. (13), we derived the expression

$$\Delta K = 2N(N-1)[N_p^r . S - (E_{pk}^t)^2 + (E_{pk}^r)^2] + 2Ns > 0, \tag{14}$$

which in its full form manifests the increase in graph complexity of the subclasses C_L of class C ($E_{pk}^t > 0$, $E_{pk}^r > 0$). The case $E_{pk}^r = 0$, $E_{pk}^t > 0$ refers to the transition from class B to class C, while the annulment of both E_{pk}^t and E_{pk}^r occurs upon the transitions between the subclasses A_I of class A, as well as upon the $A \rightarrow B$ transition. Therefore, eq. (14) proves the existence of a definite hierarchy between the classes and subclasses for the two-route reaction mechanisms:

$$\ldots < K_{A_3} < K_{A_2} < K_A < K_B < K_C < K_{C_2} < K_{C_3} . \tag{15}$$

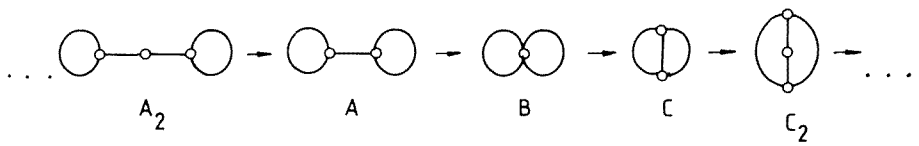

Fig. 3. A sequence of classes and subclasses of bicyclic kinetic graphs (two-route reaction mechanisms) ordered according to their increasing complexity.

The analysis of eq. (14) also shows that inequality (15) does not extend further than the C_3 subclasses, since for $S = 1$ the $C_3 \rightarrow C_4$ transition diminishes the complexity index. The two-route reaction mechanisms with four common elementary steps are, however, of no practical importance. One can conclude that the complexity index K reflects correctly the increase in complexity of the two-route mechanisms occurring when the two reaction routes become more interdependent.

The inspection of table 1 confirms inequalities (15) with only one exception (numbers 18 and 25, $\Delta K = 756 - 804 = -48 < 0$), which occurs when the initial condition $N_p^t = N_p^r$ is violated and the distribution of intermediates between the two routes changes essentially. The latter, however, is regarded as the third factor influencing the mechanism complexity and it is examined separately.

5.3. COMPLEXITY INDEX DEPENDENCE ON THE INTERMEDIATES DISTRIBUTION BETWEEN THE TWO-REACTION ROUTES

Proceeding from the conditions $N^t = N^r$, class, subclass = const, $N_p^t = N_p^r - s$, $N_k^t = N_k^r + s$, eq. (12) transforms into

$$\Delta K = 2N(N-1)(N_p^r - N_k^r - s)s. \tag{16}$$

It follows from eq. (16) that for constant other factors, the more even the vertex distribution between the two cycles, the more complex is the respective reaction

mechanism (e.g. numbers 25 to 27 from table 1 having vertex distribution 2, 6; 3, 5; and 4, 4, respectively). Proceeding from the most even distribution $N_p^r = N_k^r$, one finds the remaining mechanisms to be always less complex:

$$\Delta K = K(N_p, N_k) - K(N_p + s, N_k - s) > 0. \tag{16'}$$

6. Some general relations for the complexity index of linear reaction mechanisms. Three-route mechanisms

Denote the three graph cycles in the kinetic graph by p, k, and ℓ, respectively. Denote also the number of edges that are common for the pairs of cycles by E_{pk}, $E_{p\ell}$, and $E_{k\ell}$, respectively (fig. 4).

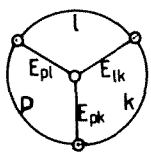

Fig. 4. A tricyclic kinetic graph in a general position. The three cycles are denoted by p, k, and ℓ, while the number of edges common for each pair of cycles is denoted by E_{pk}, $E_{p\ell}$, resp.

The latter have non-zero values in the case of the most complex class C^3 (fig. 4), while for the remaining thirteen classes, some of these quantities, or all of them, equal zero.

In studying the complexity of the three-route mechanisms, all factors used as classification criteria (or as kinetic code constituents) will be examined.

6.1. COMPLEXITY INDEX DEPENDENCE ON THE NUMBER OF REACTION ROUTES (GRAPH CYCLES) M

6.1.1. Consider first the case where the number of cycles increases by unity for a constant number of vertices (intermediates)

Conditions: $M^t = 3$, $M^r = 2$, $N^t = N^r$, $N_p^t = N_p^r$, $N_k^t = N_k^r$, $N_\ell^r = 0$, $N_\ell^t \geqslant 2$. From (12) one obtains:

$$\Delta K = \Delta K_1 + \Delta K_2 = N(N-1)(3T^t - 2T^r)$$

$$+ 2N[(N_\ell^t - 1)(N_p + N_k) - E_{p\ell}^2 - E_{k\ell}^2 + N_p N_k - E_{pk}^2], \tag{17}$$

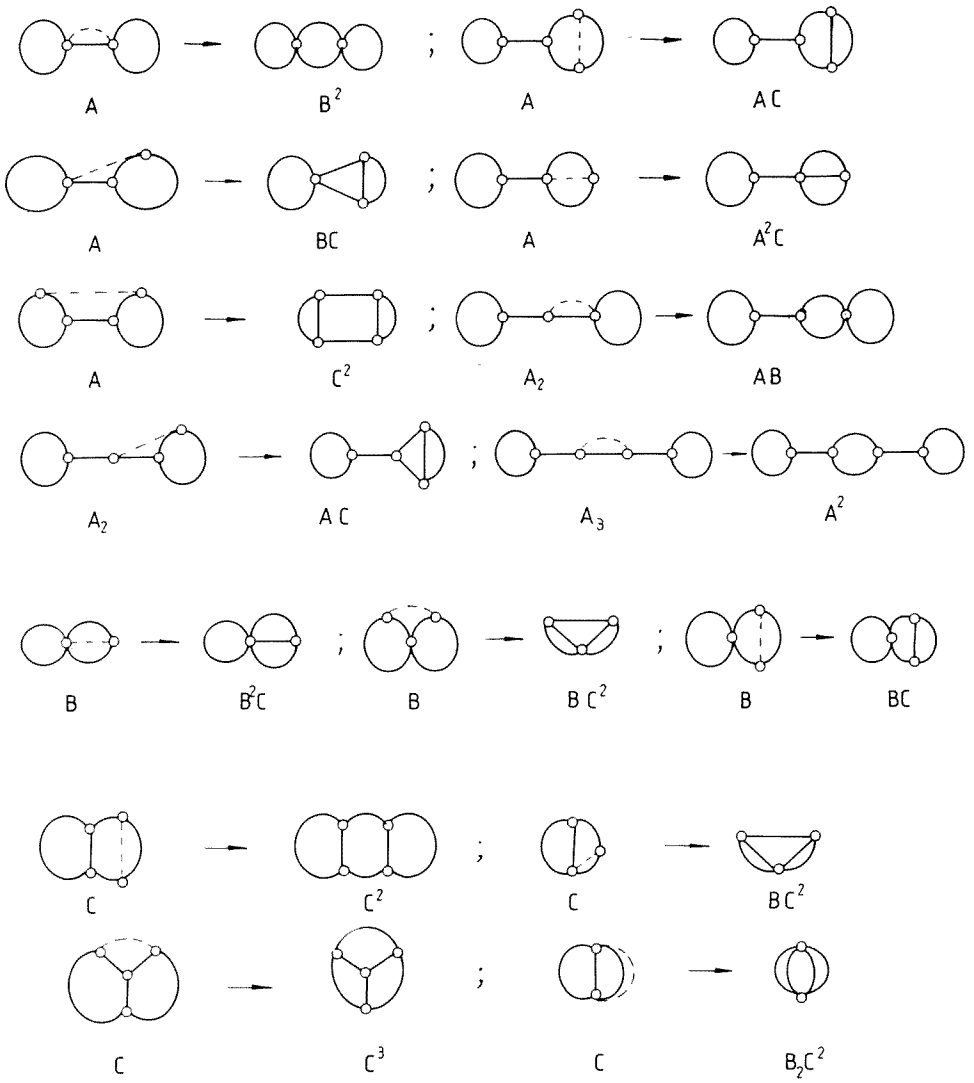

Fig. 5. Generation of the respective classes of two-route mechanisms to the classes of three-route reaction mechanisms. The mechanism complexity increases in all cases, as follows from eq. (17).

but

$$T^t > T^r \; (T^{M=3} > T^{M=2}); \; N_p \geqslant E_{pk} + E_{p\varrho}, \; N_k \geqslant E_{pk} + E_{k\varrho}, \; N_\varrho \geqslant N_{p\varrho} + N_{k\varrho}.$$

Hence, $\Delta K_1 > 0$ and $\Delta K_2 > 0$, i.e. $\Delta K > 0$.

The complexity index always increases for a constant number of intermediates in each of the routes of a two-route mechanism when a third route is formed by adding a new elemenatry reaction step:

$$\Delta K = K(M, N) - K(M-1, N) > 0. \tag{17'}$$

This general conclusion is illustrated by all possible transitions between the respective classes of two- and tricyclic mechanisms in fig. 5. For more detailed examples, see table 1 and fig. 1. The A^3, A^2B and B^3 classes of three-route mechanisms cannot be generated under the same conditions, but they can be done by adding two or more elementary reaction steps (i.e. by also adding one intermediate).

6.1.2. The number of reaction routes as a factor more strongly affecting the mechanism complexity than the number of intermediates

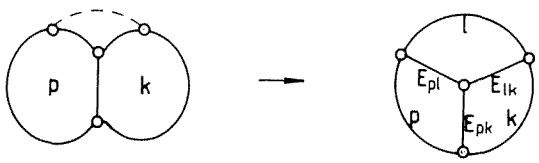

Fig. 6. Comparison of two kinetic graphs, the second of which has one cycle more but one vertex less than the first one (or, otherwise, one reaction route more but one intermediate less).

Assumptions: $M^r = 2, M^t = 3; N^t = N^r - 1; N_p^t = N_p^r, N_k^t = N_k^r - 1, E_{pk}^t = E_{pk}^r$. We thus compare the complexity of two mechanisms having two and three routes, respectively, but with the three-route mechanism being one intermediate less than the two-route mechanism.

$$\Delta K = K^{M^r+1, N^r-1} - K^{M^r, N^r} = \Delta K_1 + \Delta K_2.$$

From eqs. (12), (4), (5), (8) and (9), one obtains under the assumptions made above:

$$\Delta K_2 = 2N^t \left\{[N_p(N_k^t - 1) - E_{pk}^2] + [N_k^t(N_\varrho^t - 1) - (E_{k\varrho}^t)^2] \right.$$

$$\left. + [N_p N_\varrho^t - (E_{p\varrho}^t)^2] - 1 \right\} - 2(N_p^r + N_k^r). \tag{18}$$

However, $N_i^{\min} = N_j^{\min} = 2$, and the respective $E_{ij} = 1$. Hence, $N_i(N_j - 1) - E_{ij}^2 \geqslant 1$, $N_i N_j - E_{ij}^2 \geqslant 3$. Thus, the first term in (18) is $K_2' = 2N^t$, $\Delta \geqslant 2N^t.4$. On the other hand, for $M = 2$, $N_p^r + N_k^r = N^r$ (class A), $N_p^r + N_k^r = N^r + 1$ (class B), and $N_p^r + N_k^r = N^r + 2$ (class C). Hence, the second term in (18) is $\Delta K_2'' = 2(N_p^r + N_k^r) \leqslant 2(N^r + 2) = 2(N^t + 3)$. From the comparison of $\Delta K_2'$ and $\Delta K_2''$, it follows that $\Delta K_2 < 0$.

$$\Delta K_1 = N^t[3(N^t - 1)T^t - 2(N^t + 1)T^r]$$

$$= N^t(RT^t - ST^r) \tag{19}$$

$$\Delta T = T^t - T^r = N_p[N_k^t(N_\varrho - 1) - 1]$$

$$- (E_{pk}^2 \cdot N_\varrho + E_{p\varrho}^2 \cdot N_k^t + E_{k\varrho}^2 \cdot N_p - E_{pk}^2 + 2E_{pk}E_{p\varrho}E_{k\varrho}). \tag{20}$$

The fifteen pairs of genetically related two- and three-route mechanisms from fig. 5 will be analyzed in detail.

6.1.2.1. $E_{pk} = 0, E_{p\varrho} = 0, E_{k\varrho} = 0$ (Cases $A \to B^2$, $A_2 \to AB$, $A_3 \to A^2$, with $N_p, N_k^t, N_\varrho \geqslant 2$, see fig. 2). $\Delta T > 0$ follows immediately.

6.1.2.2. $E_{pk} = 0, E_{p\varrho} = 0, E_{k\varrho} \neq 0$ (Cases $A \to AC$, $A \to BC$, $B \to BC$, and $A_2 \to AC$, with $N_p \geqslant 2$, $N_k^t \geqslant 3$, $N_\varrho \geqslant 2$, as well as cases $A \to A^2C$ and $B \to B^2C$, with $N_p, N_k^t, N_\varrho \geqslant 2$),

$$\Delta T = N_p[N_k^t(N_\varrho - 1) - (E_{k\varrho}^2 + 1)] \geqslant 0, \tag{20'}$$

where $\Delta T = 0$ holds for $N_k^t = 2, N_\varrho = 2, E_{k\varrho} = 1$ only. (Examples: nos. $7 \to 73, 9 \to 74$ ($A \to A^2C$); nos. $14-87, 16 \to 88, 18 \to 90$ ($B \to B^2C$)).

6.1.2.3. $E_{pk} = 0, E_{p\varrho} \neq 0, E_{k\varrho} \neq 0$ (The $A \to C^2$ case, with $N_p, N_k^t \geqslant 2, N_\varrho \geqslant 4$, as well as the $B \to BC^2$ case, with $N_p, N_k^t \geqslant 2, N_\varrho \geqslant 3$)

$$\Delta T = N_p[N_k^t(N_\varrho - 1) - 1] - (E_{p\varrho}^2 N_k^t + E_{k\varrho}^2 \cdot N_p). \tag{20''}$$

Inserting the minimal N_p, N_k^t, and N_ϱ values in (20'''), together with the respective E_{ij} values $E_{pk} = E_{k\varrho} = 1$, one arrives at $\Delta T > 0$. The inequality

becomes stronger when $E_{ij} > 1$, due to the respective increase in the N_p, N_k^t, and N_ϱ size.

6.1.2.4. $E_{pk} \neq 0$, $E_{p\varrho} = 0$, $E_{k\varrho} \neq 0$ (The $C \rightarrow B_2C^2$ case, with $N_p \geqslant 3$, N_k^t, $N_\varrho \geqslant 2$)

$$\Delta T = N_p[N_k^t(N_\varrho - 1) - (E_{k\varrho}^2 + 1)] - E_{pk}^2(N_\varrho - 1). \qquad (20^{iv})$$

Here, $\Delta T < 0$ for $N_k = N_\varrho = 2$, $E_{pk} = E_{k\varrho} = 1$ (the $C \rightarrow B_2C^2$ cases, example nos. $20 \rightarrow 101$, $22 \rightarrow 102$, $24 \rightarrow 103$, $26 \rightarrow 105$); $\Delta T > 0$ otherwise.

6.1.2.5. $E_{pk} \neq 0$, $E_{p\varrho} \neq 0$, $E_{k\varrho} = 0$ (The $C \rightarrow C^2$ and $C \rightarrow BC^2$ cases, with N_p, $N_\varrho \geqslant 2$, and $N_k^t \geqslant 4$ and 3, respectively. The $C \rightarrow B_2C^2$ case with $N_p = N_\varrho = 2$, $N_k^t \geqslant 2$ also belongs here.)

$$\Delta T = N_p[N_k^t(N_\varrho - 1) - 1] - (E_{pk}^2 N_\varrho + E_{p\varrho}^2 N_k^t - E_{pk}^2) \ldots \qquad (20^{v})$$

Here, $\Delta T = 0$ for $N_p = 3$, $N_k^t = N_\varrho = 2$, $E_{pk} = E_{p\varrho} = 1$. (Examples: nos. $22 \rightarrow 113$ (the $C \rightarrow BC^2$ case), $21 \rightarrow 102$ (the $C \rightarrow B_2C^2$ case)); $\Delta T > 0$ otherwise.

6.1.2.6. $E_{pk} \neq 0$, $E_{p\varrho} \neq 0$, $E_{k\varrho} \neq 0$ (The $C \rightarrow C^3$ case, with N_p, N_k^t, $N_\varrho \geqslant 3$); $\Delta T > 0$ always holds.

Having obtained the ΔT estimates in all cases under study, the R and S magnitudes from eq. (19) will now be determined. It is easily seen that $R > S$ at $N^t > 5$, $R = S$ at $N^t = 5$, and $R < S$ at $N^t < 5$. It can be shown that for $R < S$, $\Delta K_1 < 0$ in the limited number of cases where $\Delta T \leqslant +1$. Examples with $\Delta T = 1 > 0$, $R < S$, and $\Delta K_1 < 0$ are numbers $21 \rightarrow 113$, $24 \rightarrow 114$ ($C \rightarrow BC^2$), $24 \rightarrow 104$ ($C \rightarrow B_2C^2$), $24 \rightarrow 60$ ($C \rightarrow C^2$), etc. Examples with $\Delta T = 0$ and $\Delta T < 0$ were given above.

Taking into account that ΔK_2 is always positive, one finds that ΔK_2 overcomes the negative ΔK_1 in all cases with $\Delta T = +1$. Thus, $\Delta K = \Delta K_1 + \Delta K_2 < 0$ results only in six cases with $R < S$, three of them with $\Delta T < 0$ (numbers $20 \rightarrow 101$, $22 \rightarrow 102$, and $24 \rightarrow 103$ ($C \rightarrow B_2C^2$) and the other three with $\Delta T = 0$ (numbers $21 \rightarrow 102$ ($C \rightarrow B_2C^2$), $22 \rightarrow 113$ ($C \rightarrow BC^2$), and $14 \rightarrow 87$ ($B \rightarrow B^2C$)). We thus arrive at the conclusion that for a small total number of intermediates ($N^t = 2$ or 3), this factor is superior to the number of reaction routes. Vice versa, the number of routes is the superior factor for reactions involving more than three intermediates.

6.2. COMPLEXITY INDEX DEPENDENCE ON THE TOTAL NUMBER OF INTERMEDIATES N

We consider the simplest case where the total number of intermediates increases by unity for a constant number of reaction routes ($M = 3$) and number of intermediates in two of the three cycles, as well as for a constant type, class, and subclass of the reaction mechanism:

$$M^t = M^r = 3, \quad N^t = N^r + 1; \qquad S^t = S^r, \quad A^x_{I,K} B^y_{L,K} C^z_{L,K} = \text{const},$$

$$N^t_p = N^r_p, \quad N^t_k = N^r_k, \quad N^t_\varrho = N^r_\varrho + 1; \quad E^t_{pk} = E^r_{pk}, \quad E^t_{p\varrho} = E^r_{p\varrho}, \quad E^t_{k\varrho} = E^r_{k\varrho}.$$

(i) General expressions for $\Delta K = \Delta K_1 + \Delta K_2$

$$\Delta K_1 = 3N^r [N^r (T^t - T^r) + (T^t + T^r)] \tag{21}$$

$$T^t + T^r = N_p N_k (2N^r_\varrho + 1) - E^2_{pk}(2N^r_\varrho + 1) - 2E^2_{p\varrho} N_k - 2E^2_{k\varrho} N_p - 4E_{pk} E_{p\varrho} E_{k\varrho} > 0 \tag{22}$$

$$\Delta T = T^t - T^r = N_p N_k - E^2_{pk} > 0. \tag{23}$$

Hence, $\Delta K_1 > 0$ always holds.

$$\Delta K_2 = 2N^r (N_p + N_k) + 2[N_p N_k + N_p N^t_k + N_k N^t_\varrho - E^2_{pk} - E^2_{p\varrho} - E^2_{k\varrho}] \tag{24}$$

$$\Delta K_2 > 0.$$

Hence, $\Delta K > 0$ always holds.

The complexity of the three-route reaction mechanisms increases with increasing total number of intermediates for constant other factors:

$$\Delta K = K(N^r + 1) - K(N^r) \geqslant 0.$$

6.3. COMPLEXITY INDEX DEPENDENCE ON THE TYPE OF MECHANISM

Here, we consider the change in the complexity index of kinetic graphs occurring upon the increase in their serial number from $S = 0$ to $S = 1$, the latter determining the two types of three-route reaction mechanisms.

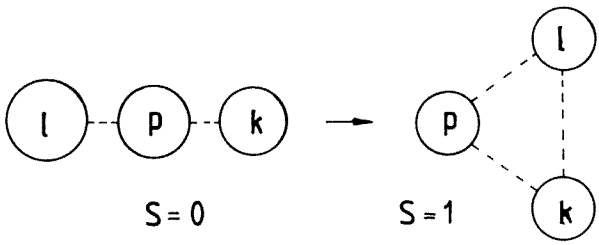

Fig. 7. Schematic description of the kinetic graphs transformation during the change in the mechanism type. The dashed lines connecting cycles p, k, and ℓ denote the bridge between the two cycles (class A) or a common vertex (class B) or a common edge(s), (class C).

As seen from fig. 7, only two pairs of cycles are joined in the $S = 0$ case, while all three of them do so in the $S = 1$ case, i.e. the change in the mechanistic type implies that an interrelation is involved between the third pair of reaction routes ($k - \ell$). The scheme resulting for the transformation of the six classes of type $S = 0$ mechanism into the eight classes of type $S = 1$ mechanism is shown in fig. 8.

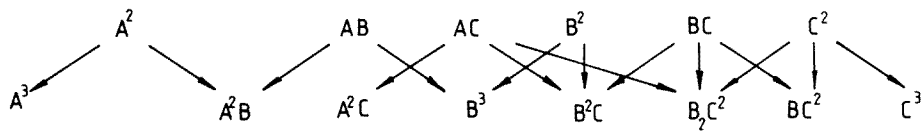

Fig. 8. A scheme showing the transformation of the six classes of mechanisms of $S = 0$ type into the eight classes of $S = 1$ type.

All these sixteen transformations are performed for a constant number of reaction routes and intermediates, as well as for a constant number of intermediates in two or all three reaction routes:

$$M^t = M^r = 3,\ N^t = N^r,\ N_p^t = N_p^r,\ N_k^t = N_k^r;\ E_{pk}^t = E_{pk}^r \geqslant 0,$$

$$E_{p\ell}^t = E_{p\ell}^r \geqslant 0,\ E_{p\ell}^r = 0,\ E_{k\ell}^t \geqslant 0,\ N_\ell^t = N_\ell^r + n, \qquad n = 0, 1, 2, \ldots$$

$$\Delta K_1 = 3N(N-1)\left[n(N_p N_k - E_{pk}^2) - N_p E_{k\ell}^t - 2E_{pk} E_{p\ell} E_{k\ell}^t\right] \tag{24}$$

$$\Delta K_2 = 2N\left[n(N_p + N_k) - (E_{k\ell}^t)^2\right]. \tag{25}$$

6.3.1. The change in the mechanistic type does not change the mechanism complexity (isocomplex mechanisms)

Assumptions: $E^t_{k\ell} = 0$, $n = 0$. Cases $A_2A \rightarrow A^3$, $A^2 \rightarrow A_2^2B$, $AB \rightarrow A^2B$, $B^2 \rightarrow B^3$, $AC \rightarrow A^2C$, $BC \rightarrow B^2C$, $C^2 \rightarrow BC^2$ (fig. 9).

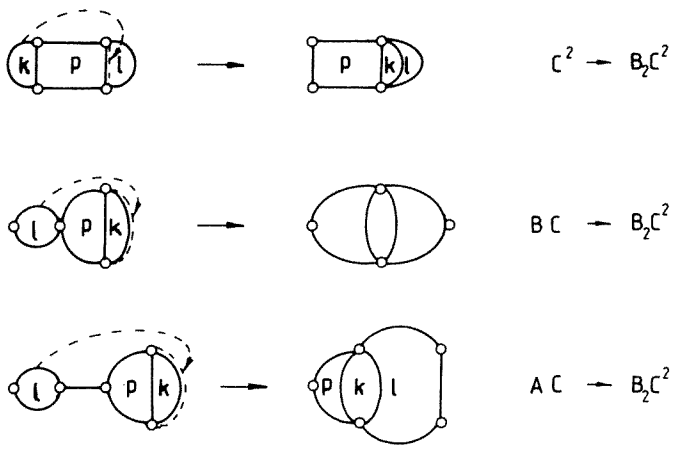

Fig. 9. Illustration of the cases where the change in the mechanism type from $S = 0$ to $S = 1$ does not change the mechanism complexity (isocomplex mechanisms).

All graph transformations shown in fig. 9 do not change the complexity index, as follows from eqs. (24) and (25). Mechanisms which have the same complexity index will be called *isocomplex mechanisms*. In the seven cases examined, isocomplexity results from the weak connection (i.e. by a bridge or by a common vertex) that is formed between the third pair of cycles during the transformation that increases the serial number (or changes the type) of the kinetic graph from $S = 0$ to $S = 1$. Other cases of isocomplex mechanisms will be handled in the next subsections. It should be noted that a change in the subclass ($A \rightarrow A_2$) of the reaction mechanism takes place in the first two examples in fig. 9 in order to meet the condition for a constant total number of intermediates.

6.3.2. The change in the mechanistic type increases the mechanism complexity

(i) $n = 1$. Cases $A^2 \rightarrow A^2B$, $AB \rightarrow B^3$, $AC \rightarrow B^2C$, $B^2 \rightarrow B^2C$, $BC \rightarrow BC^2$, $C^2 \rightarrow C^3$ (see fig. 10).

(ii) $n = 2$. Case $A^2 \rightarrow A^2C$.

In proving the inequality $\Delta K > 0$ in the cases in fig. 10, one should take into account that ΔK_2 in eq. (25) is always positive. $\Delta K_1 > 0$, which follows immediately

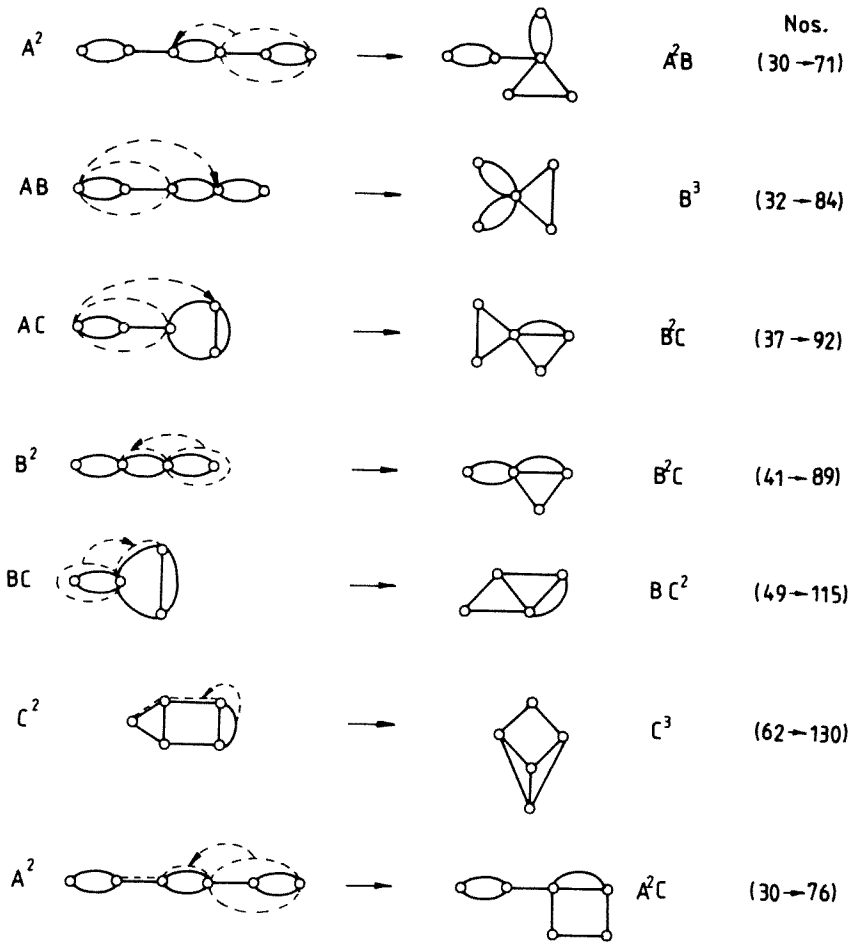

Fig. 10. Illustration of the cases where the change in the mechanism type from $S = 0$ to $S = 1$ increases the mechanism complexity.

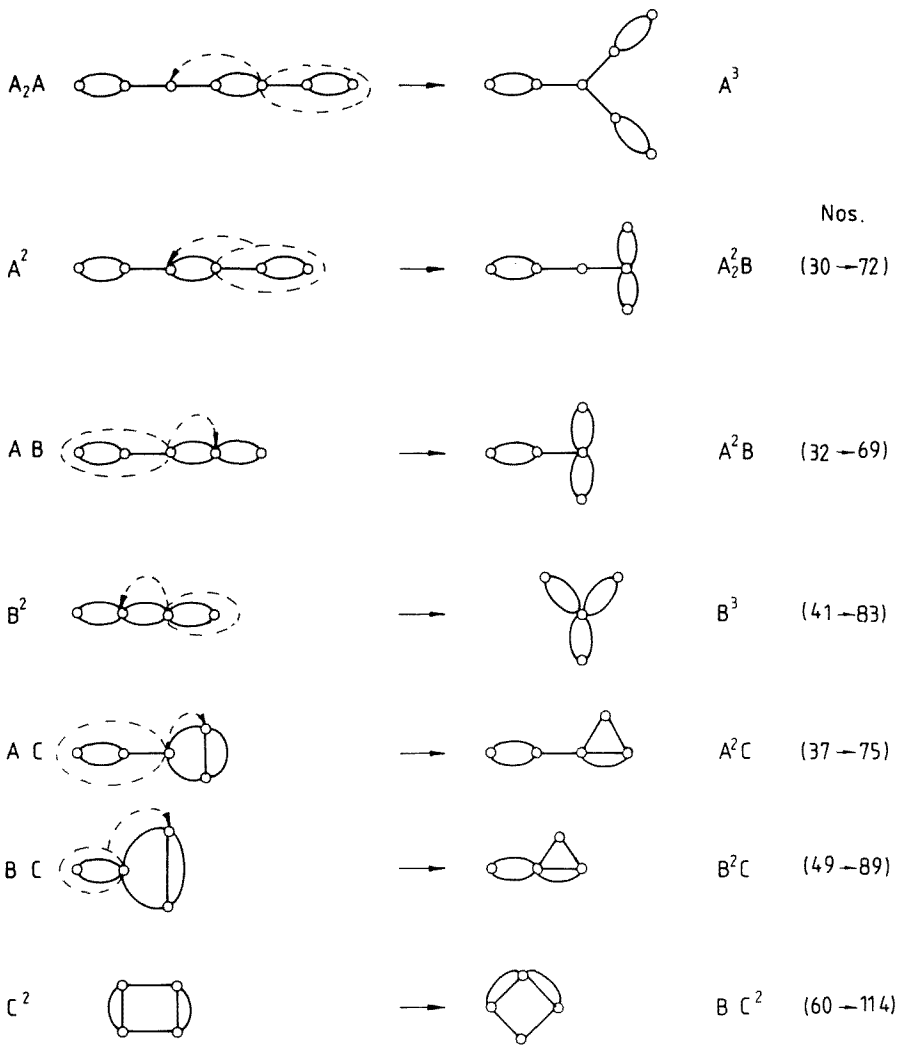

Fig. 11. Illustration of the cases with a change in the mechanism type related to the B_2C^2 class of reaction mechanisms.

for five out of the seven cases examined provided $E^t_{k\ell} = 0$. In the case of $B^2 \rightarrow B^2C$ transformation, the least ΔK_1 estimate is obtained from the conditions $N_p \geqslant 2$, $N_k \geqslant 2$, $N^t_\ell \geqslant 3$, $E_{k\ell} \geqslant 1$, $E_{pk} = E_{p\ell} = 0$. The latter is $\Delta K_1 = 2 > 0$. Similarly, for $C^2 \rightarrow C^3$ transition, where $N_p \geqslant 4$, $N_k \geqslant 3$, $N^t_\ell \geqslant 3$; $E_{p\ell}$, E_{pk}, $E_{k\ell} \geqslant 1$, $\Delta K_1 \geqslant 5$ is found.

6.3.3. Some specific cases

The three transitions to the B_2C^2 class (see fig. 11) require more specific conditions:

$$M^t = M^r = 3, \quad N^t = N^r, \quad N^t_p = N^r_p, \quad N^t_k = N^r_k, \quad N^t_\ell = N^r_\ell + n, \quad n = 0, 1, 2,$$

$$E^r_{k\ell} = 0, \quad E^t_{k\ell} > 0, \quad E^t_{pk} = E^r_{pk}, \quad E^t_{p\ell} = 0, \quad E^r_{p\ell} \geqslant 0,$$

from which one obtains:

$$\Delta K_1 = 3N(N-1)\{n[N_p N_k - (E^t_{pk})^2] + N_k(E^r_{p\ell})^2 - N_p(E^t_{k\ell})^2\} \tag{26}$$

$$\Delta K_2 = 2N[n(N_p + N_k) + (E^r_{p\ell})^2 - (E^t_{k\ell})^2]. \tag{27}$$

Here, $\Delta K_2 \geqslant 0$, where the equality holds for $n = 0$, $E^r_{p\ell} = E^t_{k\ell}$ only ($C^2 \rightarrow B_2C^2$ transition). $\Delta K_1 < 0$ for $n = 0$, $N_k(E^r_{p\ell})^2 < N_p(E^t_{k\ell})^2$. Examples: numbers 60 → 103, 62 → 106, 66 → 110 from table 1. $\Delta K_1 < 0$ also in some peculiar cases with $n > 0$ and $E^t_{k\ell} \geqslant E^r_{p\ell}$ (examples: $BC \rightarrow B_2C^2$ and $C^2 \rightarrow B_2C^2$ transitions, with $N_p = N_k = 4$, $E^t_{pk} = 1$, $E^t_{k\ell} = 3$, $E^r_{p\ell} = 0$ or 1, respectively). A conclusion may be drawn that the change in the type of reaction mechanism from $S = 0$ to $S = 1$ almost always increases the mechanism complexity in the case of $BC \rightarrow B_2C^2$ and $AC \rightarrow B_2C^2$ transitions, while in the case of $C^2 \rightarrow B_2C^2$ transitions, the complexity most frequently decreases.

6.4. COMPLEXITY INDEX DEPENDENCE ON THE MECHANISM CLASS

The dependence is examined by keeping constant the number of reaction routes and intermediates, the type and subclass of mechanism, as well as the number of intermediates in two out of the three routes. The single exception to the latter condition, related to the B_2C^2 class, will be specifically dealt with later. In dealing with the $G^r \rightarrow G^t$ graph transformation under the above conditions, one can order the fourteen classes of tricyclic kinetic graphs into two sequences referring to the two types of mechanisms: those with serial numbers $S = 0$ and $S = 1$, respectively. These sequences can be regarded as genetic lines of the classes generating them from the preceding class in the sequence by replacing some of the class symbols A or B

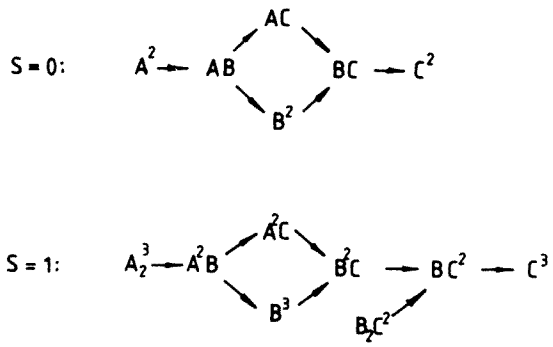

Fig. 12. Sequences of increasing complexity of the mechanism classes for the same mechanism type ($S = 0$ or $S = 1$).

by another class symbol of higher complexity (B or C, respectively). The ordered sequences of expected increasing class complexities were thus constructed (see fig. 12).

The second sequence includes the A^3 class in its A_2^3 subclass because $A_1^3 \equiv A^3$ is non-existent (a fourth cycle is formed when bridges of zero length connect the three cycles p, k, and ℓ).

In proving the complexity relationships between different classes of reaction mechanisms, we proceed from the following conditions: $N^r = N^t$, $S = \text{const}$ (0 or 1), the sublass index $L = \text{const}$; $N_p^r = N_p^t$, $N_k^r = N_k^t$, $N_\ell^t = N_\ell^r + s$, where $s = 2$ for the $A_2^3 \rightarrow A_2B$ case and $s = 1$ otherwise; (a) $E_{pk}^r = E_{pk}^t$, $E_{p\ell}^r = E_{p\ell}^t$, $E_{k\ell}^t = E_{k\ell}^r + n$, where $n = 0$ in the case of $A^2 \rightarrow AB$, $AB \rightarrow B^2$, $A_2^3 \rightarrow A^2B$, $A^2B \rightarrow B^3$, $AC \rightarrow BC$, and $A^2C \rightarrow B^2C$ transformations, while $n = 1$ for $AB \rightarrow AC$, $B^2 \rightarrow BC$, $A^2B \rightarrow A^2C$, $B^3 \rightarrow B^2C$, $BC \rightarrow C^2$, $B^2C \rightarrow BC^2$, and $BC^2 \rightarrow C^3$ cases (see fig. 13). When the cycle increasing its number of vertices does not form a new edge with another cycle (all cases with $n = 1$ but with different cycle notations), the last part of the above conditions must be modified as follows: (b) $E_{p\ell}^r = E_{p\ell}^t$, $E_{k\ell}^r = E_{k\ell}^t$; $E_{pk}^r = 0$, $E_{pk}^t = 1$ (see fig. 14). Each of the classes is represented in figs. 13 and 14 by the least possible number of intermediates.

Under these conditions, the following equations result:

6.4.1.

$$\Delta K_1 = 3N(N-1)\{(N_p N_k - E_{pk}^2)s + (E_{k\ell}^r - E_{k\ell}^t)[(E_{k\ell}^r + E_{k\ell}^t)N_p + 2E_{pk}E_{p\ell}]\} \quad (28)$$

$$\Delta K_2 = 2N[(N_p + N_k)s + (E_{k\ell}^r)^2 - (E_{k\ell}^t)^2]. \quad (29)$$

6.4.1.1. $n = 0$, $E_{k\ell}^r = E_{k\ell}^t$ $(A^{X_1}B^{Y_1}C_L^Z \rightarrow A^{X_2}B^{Y_2}C_L^Z)$ cases, with $X_2 < X_1$, $Y_2 > Y_1$: $A^2 \rightarrow AB$, $AB \rightarrow B^2$, $AC_L \rightarrow BC_L$. $A_2^3 \rightarrow A^2B$, $A^2B \rightarrow B^3$, $A^2C_L \rightarrow B^2C_L$ (fig. 13), where $L = 1, 2, 3, \ldots$

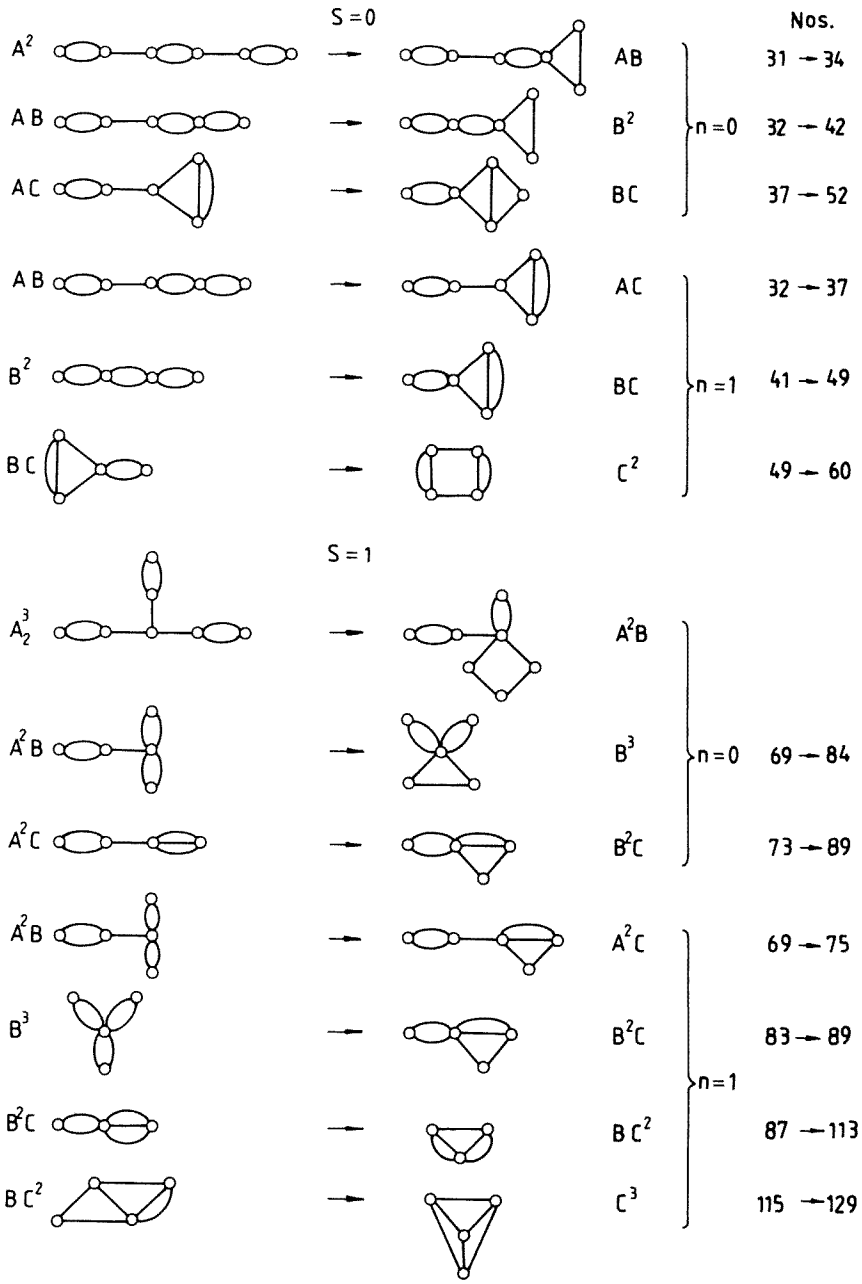

Fig. 13. Illustration of the cases where the change in the mechanism class increases its complexity. In all the cases with $n = 1$, the cycle increasing its number of vertices forms a new edge with another cycle.

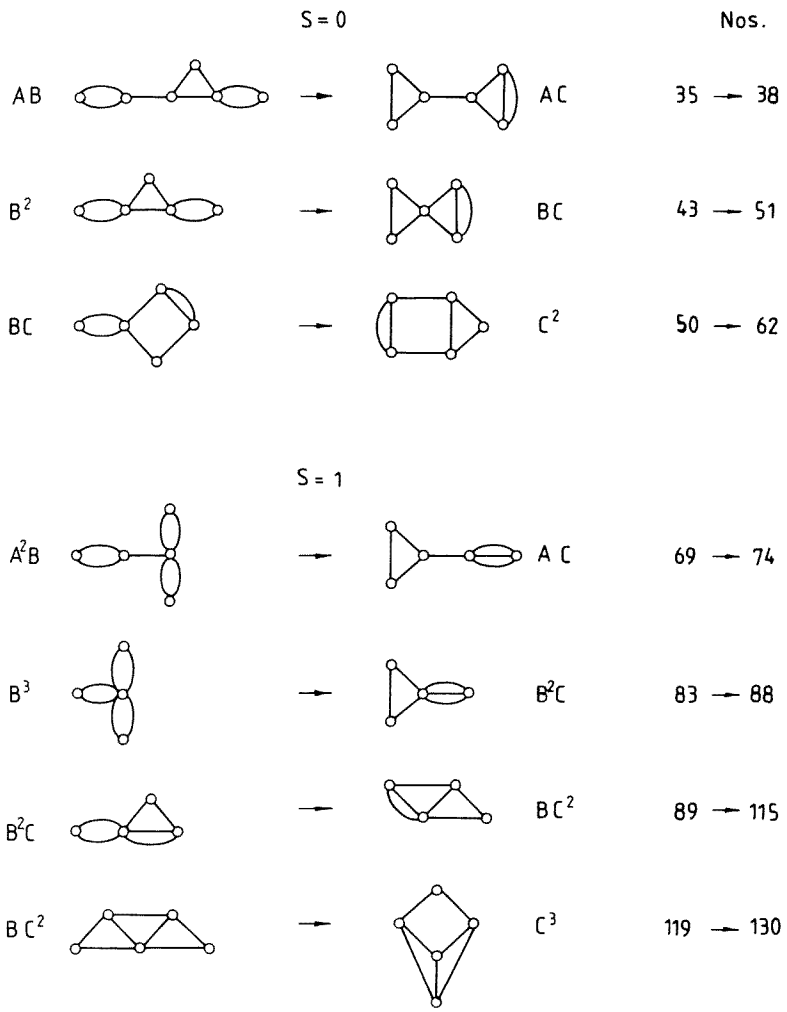

Fig. 14. The second group of cases in which the change in the mechanism class increases its complexity. The cycle increasing its number of vertices does not form a new edge with another cycle.

$$\Delta K = 3N(N-1)(N_p N_k - E_{pk}^2)s + 2N(N_p + N_k)s > 0. \tag{30}$$

6.4.1.2. $n = 1$, $E_{k\varrho}^t = E_{k\varrho}^r + 1$ ($A^X B^{Y_1} C_L^{Z_1} \rightarrow A^X B^{Y_2} C_L^{Z_2}$ cases, with $Y_2 < Y_1$, $Z_2 > Z_1$: $AB \rightarrow AC$, $B^2 \rightarrow BC$, $BC_L \rightarrow C_L^2$, $A^2B \rightarrow A^2C$, $B^3 \rightarrow B^2C$, $B^2C_L \rightarrow BC_L^2$, $BC_L^2 \rightarrow C_L^3$, where $L = 1, 2, 3, \ldots$). Inspection of fig. 13 shows that in all seven cases with $n = 1$, $E_{k\varrho}^r = 0$, $E_{k\varrho}^t = 1$. Hence

$$\Delta K_2 = 2N(N_p + N_k - 1) > 0 \tag{31}$$

$$\Delta K_1 = 3N(N-1)\,[N_p(N_k - 1) - E_{pk}(E_{pk} + 2E_{p\varrho})]\,. \tag{32}$$

In the case of $E_{pk} = 0$ ($AB \rightarrow AC$, $B^2 \rightarrow BC$, $A^2B \rightarrow A^2C$, $B^3 \rightarrow B^2C$, as well as $BC \rightarrow C^2$ with $E_{p\varrho} > 0$), the second term in (32): $\Delta = E_{pk}(E_{pk} + 2E_{p\varrho}) = 0$. Hence,

$$\Delta K_1 = 3N(N-1).N_p(N_k - 1) > 0. \tag{33}$$

In the case of $BC \rightarrow C^2$, with $E_{pk} > 0$, $E_{p\varrho} = 0$,

$$\Delta K_1 = 3N(N-1)(N_p + N_\varrho - 1 - E_{pk}^2) > 0. \tag{33'}$$

For $BC_L^2 \rightarrow C_L^3$, the full eq. (32) should be used. The least ΔK_1 value is obtained for $E_{pk} = E_{p\varrho} = L$, where $L = 1, 2, 3, \ldots$:

$$\Delta K_1 \geqslant 3N(N-1)\,[N_p(N_k - 1) - 3L^2]\,.$$

Taking into account that in this case $N_p \geqslant 2L + 1$, $N_k \geqslant 2L$ for $L = 2, 3, \ldots$ and $N_k = 2L + 1 = 3$ for $L = 1$, one gets $\Delta K_1 \geqslant 3N(N-1)(L^2 - 1) > 0$ for $L = 2$, and $\Delta K_1 = 9N(N-1) > 0$ for $L = 1$. Therefore, $\Delta K > 0$ always holds for the cases examined in fig. 13.

6.4.2. Equation (31) holds also for ΔK_2

$$\Delta K_1 = 3N(N-1)(N_p N_k - N_\varrho^t - 2E_{p\varrho}E_{k\varrho}). \tag{34}$$

Clearly, $\Delta K_1 > 0$ for $N_p N_k > N_\varrho^t - 2E_{p\varrho}E_{k\varrho}$ and $\Delta K_1 < 0$ when the opposite inequality holds. In the latter case, the positive ΔK_2 cannot compensate the negative ΔK_1 and $\Delta K < 0$. One can thus find that the first negative ΔK appears for $A^2B \rightarrow A^2C$ and $B^3 \rightarrow B^2C$ at $N_p = N_k = 2$, $N_\varrho^t = 5$; for $AB \rightarrow AC$, $B^2 \rightarrow BC$, and $B^2C \rightarrow BC^2$ at $N_p = 2$, $N_k = 3$, $N_\varrho^t = 7$; for $BC^2 \rightarrow C^3$ at $N_p = N_k = 3$, $N_\varrho = 8$, and for $BC \rightarrow C^2$ at $N_p = 2$, $N_k = 4$, $N_\varrho = 9$. Evidently, in all these cases of negative ΔK

the uneveness in the cycle size prevails over the higher hierarchy of the KG class. When the cycle sizes do not differ so drastically, $\Delta K > 0$ always holds.

One more relation between the mechanism classes is to be examined, which requires more specific conditions.

6.4.3. The $B_2C^2 \rightarrow BC^2$ transition

$N^r = N^t$, S = const, L = const, $N_p^r = N_p^t$, $N_k^t = N_k^r - 1$, $N_\varrho^t = N_\varrho^r + 1$, $E_{pk}^r = E_{pk}^t = 0$, $E_{p\varrho}^r = E_{p\varrho}^t > 0$, $E_{k\varrho}^t = E_{k\varrho}^r$. The latter three equalities imply that the ϱ cycle is always positioned between p and k.

Equation (35) thus produces

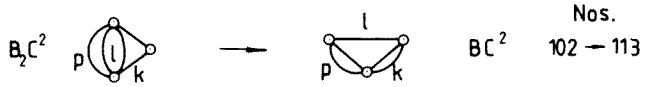

Fig. 15. Illustration of the transition between two classes of kinetic graphs, $B_2C^2 \rightarrow BC^2$, requiring a specific location of the three graph cycles p, k, and ϱ.

$$\Delta K = 3N(N-1)\,[N_p(N_k^r - N_\varrho^r - 1) + E_{p\varrho}^2] + 2N(N_k^r - N_\varrho^r - 1). \qquad (35)$$

As seen in fig. 11, $N_k^r \geqslant N_\varrho^r - 1$ (otherwise k and ϱ interchange and the same relation holds). Hence, $\Delta K \geqslant 3N(N-1)E_{p\varrho}^2 > 0$. We have thus proved the last inequality for the hierarchical ordering of the fourteen classes of linear reaction mechanisms shown in fig. 12.

The general conclusion can be made that, with all other factors remaining constant, the complexity of three-route reaction mechanisms increases on replacing the equilibrium elementary step connecting two reaction routes by a common intermediate, as well as when the latter is replaced by a common elementary step. In terms of our kinetic graph classification, the complexity of a three-route reaction mechanism will increase when A or B_2 symbols in the class notation are replaced by B, as well as when B is replaced by C:

$$K(A^{X_2}B^{Y_2}C^{Z_2}) > K(A^{X_1}B^{Y_1}B^{Z_1}),$$

for $X_2 < X_1$, $Y_2 > Y_1$, $Z_2 = Z_1$ or $Y_2 < Y_1$, $Z_2 > Z_1$, $X_2 = X_1$; and

$$K(B_2C^2) < K(BC^2).$$

6.5. COMPLEXITY INDEX DEPENDENCE ON THE MECHANISMS' FIRST SUBCLASS

6.5.1. *The first subclass I of class* A^X

As mentioned in sect. 2, the notation A_I means that two cycles in the kinetic graph are connected by a bridge having I edges or, otherwise, that two reaction routes are related through I equilibrium elementary steps. We shall prove that the decrease in the first subclass index I increases the complexity index when all other factors are kept constant.

$$\Delta K(G^t \rightarrow G^r) = K(A^X_{I_2} B^Y C^Z_L) - K(A^X_{I_1} B^Y C^Z_L) > 0$$

for $I_2 < I_1$ at $N^t = N^r$, $S^t = S^r$; $X, Y, Z, L = \text{const}$, $N^t_p = N^r_p$, $N^t_k = N^r_k$, $N^t_\varrho = N^r_\varrho + s$, $s = 1, 2, 3, \ldots$, $E^t_{pk} = E^r_{pk}$, $E^t_{p\varrho} = E^r_{p\varrho}$, $E^t_{k\varrho} = E^r_{k\varrho}$. The six classes of the three-route mechanisms referring to 6.5.1 are shown in fig. 16. Under these conditions, one obtains eq. (30), i.e. $\Delta K > 0$ always holds.

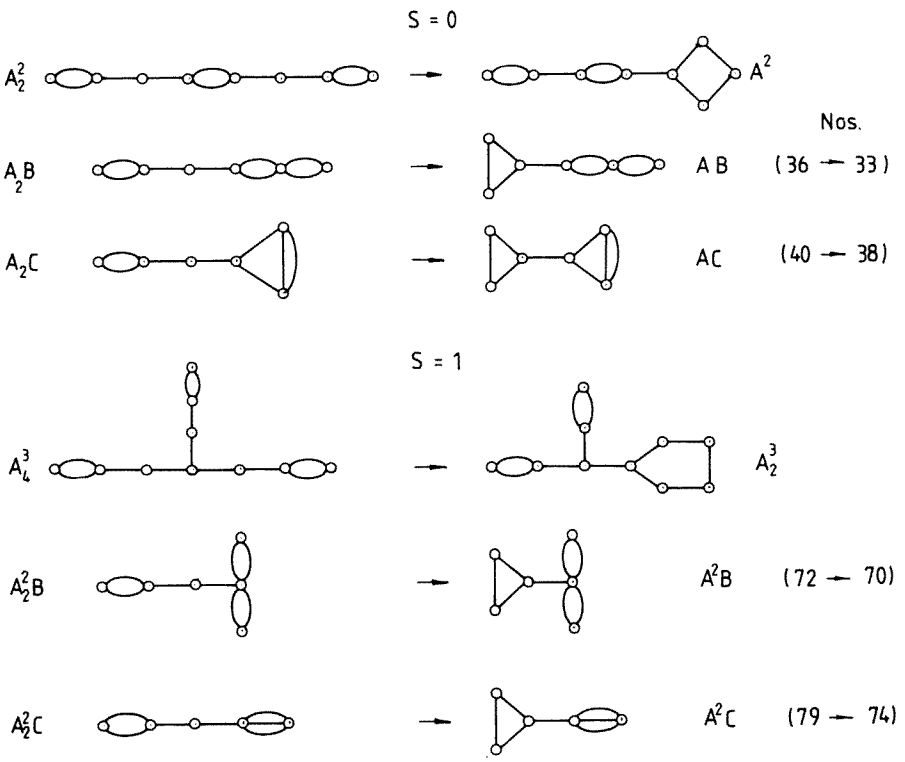

Fig. 16. Illustration of the six classes of three-route mechanisms in which the decrease in the length of the bridge connecting two cycles (or the decrease in the first subclass index I) increases the mechanism complexity.

6.5.2. *The first subclass L of class* C^Z

The subclass notation C_L means that two cycles in the kinetic graph have L edges in common or, otherwise, that two reaction routes have L common elementary steps. We shall prove that the increase in the first subclass index L increases the complexity index with other constant factors influencing the mechanism complexity:

$$\Delta K(G^t \rightarrow G^r) = K(A_I^X B^Y C_{L_2}^Z) - K(A_I^X B^Y C_{L_1}^Z) > 0$$

for $L_2 > L_1$ at $N^t = N^r$, $S^t = S^r$; X, Y, Z, I = const; $N_p^t = N_p^r$, $N_k^t = N_k^r$, $N_\ell^t = N_\ell^r + 1$; $E_{pk}^t = E_{pk}^r$, $E_{p\ell}^t = E_{p\ell}^r$, $E_{k\ell}^t = E_{k\ell}^r + 1$.

The seven classes of the three-route mechanisms referring to 6.5.2 are shown in fig. 17. Under these conditions, one obtains:

$$\Delta K_1 = 3N(N-1)\,[(N_p(N_k - 2L - 1) - E_{pk}(E_{pk} + 2E_{p\ell})]\,. \tag{36}$$

$$\Delta K_2 = 2N(N_p + N_k - 2L - 1), \tag{37}$$

where L denotes L_1 for the sake of simplicity. Equations (32) and (31) are then specific cases of eqs. (36) and (37), respectively, for $L = 0$.

In analyzing eqs. (36) and (37), one should take into account that $E_{pk} = 0$, $E_{p\ell} = 0$ for AC_L, BC_L, A^2C_L, and B^2C_L, while for C_L^2 and BC_L^2 classes, two cases are possible: $E_{pk} = 0$, $E_{p\ell} > 0$ and, vice versa, $E_{pk} > 0$, $E_{p\ell} = 0$, which correspond to different locations of cycle k with respect to p and ℓ: external and internal locations, respectively (figs. 17 and 18).

Inspection of the seven C_L^Z classes in fig. 17 also leads to the conclusion about the minimal size of k where preserves the L-subclass: $N_k \geqslant 2(L + 1)$ for A^2C_L, B^2C_L, as well as for AC_L, BC_L, BCC_L, and CC_L with external location of cycle k, while $N_k \geqslant L + 3$ and $N_k \geqslant L + 4$ holds for the external location of k in the first three and in the fourth class, respectively. Finally, it is also found in the C^2C_L case that $N_k \geqslant L + 3$ and $N_p \geqslant L + 3$.

Hence, one obtains for A^2C and B^2C, as well as for AC, BC, C^2, and BC^2 with external k, $\Delta K_1 \geqslant 3N(N-1)N_p > 0$, and $\Delta K_2 \geqslant 2N(N_p + 1) > 0$. When AC, BC, C^2, and BC^2 classes are regarded with internal k, $\Delta K_2 \geqslant 2N(N_p + J - L)$ and $\Delta K_1 = 3N(N-1).\,[N_p(J-L) - E_{pk}^2]$ result (E_{pk}^2 being zero for AC and BC), where $J = 2$ for the first three classes and $J = 3$ for the fourth one. We thus reach the conclusion that $\Delta K > 0$ for $AC \rightarrow AC_2$, $BC \rightarrow BC_2$, $AC_2 \rightarrow AC_3$, $BC_2 \rightarrow BC_3$, $C^2 \rightarrow C_2^2$, and $BC^2 \rightarrow BC_2^2$, while $\Delta K < 0$ for $AC_3 \rightarrow AC_4$, $BC_3 \rightarrow BC_4$, $C_3^2 \rightarrow C_4^2$, and $BC_2^3 \rightarrow BC_3^3$. In the case of the C_L^3 class (the C^2C_n), $\Delta K_1 \geqslant 3N(N-1)\,[(L+3)(2-L) - E_{pk}.(E_{pk} + 2E_{p\ell})]$, $\Delta K_2 \geqslant 10N$. Taking into account that $|\Delta K_1| > |\Delta K_2|$, one arrives at $\Delta K > 0$ for $C^3 \rightarrow C^2C_2$ transition, while for $C^2C_2 \rightarrow C^2C_3$, $\Delta K < 0$.

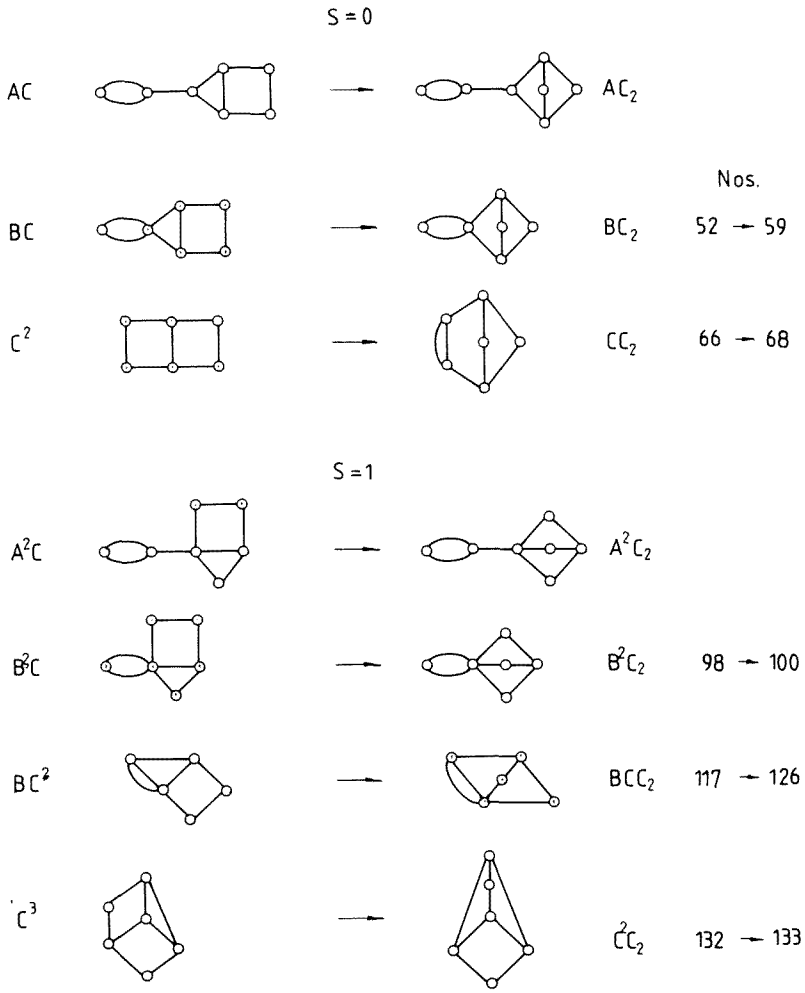

Fig. 17. Illustration of the classes of three-route mechanisms in which the increased number of common elementary steps between the reaction routes (the increased number of common edges between the kinetic graph cycles) increases the mechanism complexity.

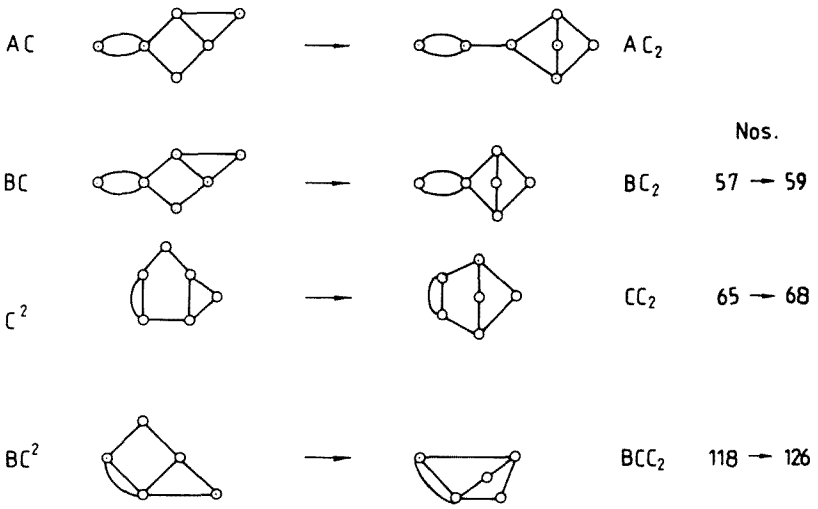

Fig. 18. Cases similar to those in fig. 17, but requiring a specific location of cycle k with respect to cycles p and q: internal but not external one.

Once again, the negative ΔK values are related to a larger difference in the cycle sizes, which is another factor influencing the graph complexity. When the cycle sizes are kept close in size, the increase in the subclass index L increases the graph complexity. In other words, the linear reaction mechanism complexity increases with an increasing number of reaction intermediates that are common for two reaction routes, when all other factors affecting the complexity are constant.

Bringing together all hierarchical relations proved in 6.4 and 6.5, fig. 12 can be generalized as shown in fig. (19).

6.6. COMPLEXITY INDEX DEPENDENCE ON THE MECHANISM'S SECOND SUBCLASS K (THE INTERLOCATION OF TWO REACTION ROUTES (GRAPH CYCLES) BOTH CONNECTED WITH A THIRD ONE)

Inspection of table 1 and fig. 1 shows four pairs of mechanisms differing by this subclass index only: numbers 30, 31, class A^2, subclasses $A^2_{1,0}$ and $A^2_{1,1}$, respectively; numbers 45, 46, class B^2, subclasses $BB_{1,1}$ and $BB_{1,2}$, respectively; numbers 53, 54, class BC, subclasses $B_{1,1}C$ and $B_{1,2}C$, respectively; numbers 63, 64, class C^2, subclasses $CC_{1,1}$ and $CC_{1,2}$, respectively. The change in the mutual positions of graph cycles that are linked with a third one (by a bridge, common vertex or common edge) does not change any parameter in eq. (8) because this structural modification changes neither the number of vertices in the individual cycles, N_i, nor the number of edges common for a pair of cycles. Therefore, a conclusion can be drawn that the change in the location of two graph cycles, both linked with a third one, does not affect the KG complexity. Two reaction mechanisms, differing

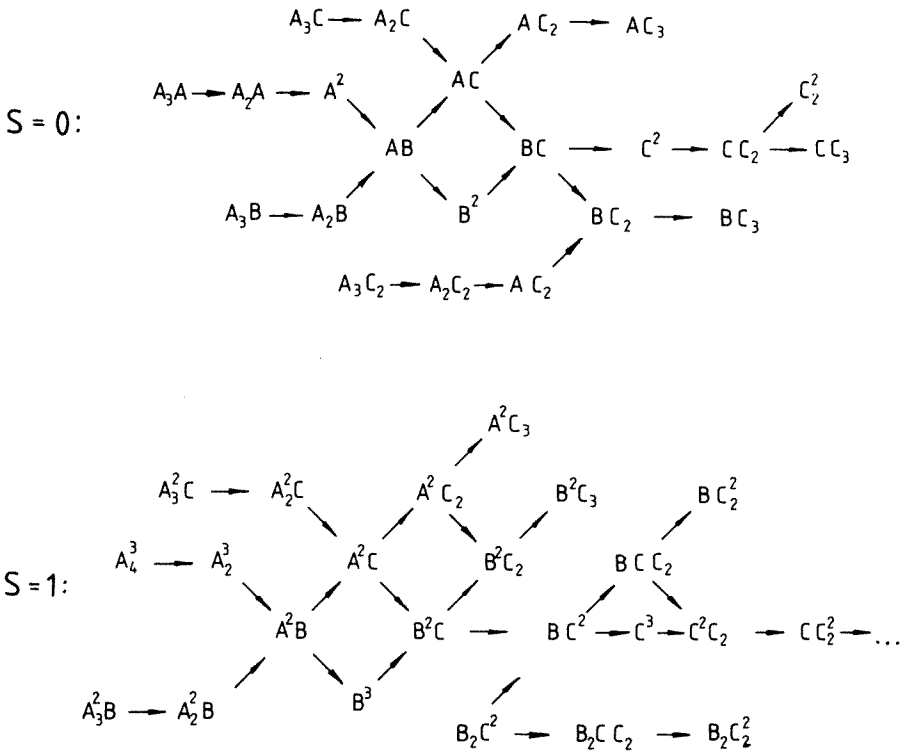

Fig. 19. Generalized sequences of increasing complexity within classes and subclasses of reaction mechanisms belonging to the same type $S = 0$ or $S = 1$.

only in the way two of their reaction routes are connected with a third one, are isocomplex:

$$K(A^{X}_{I,K_1} B^{Y}_{V,K_1} C^{Z}_{L,K_1}) = K(A^{X}_{I,K_2} B^{Y}_{V,K_2} C^{Z}_{L,K_2}).$$

6.7. COMPLEXITY INDEX DEPENDENCE ON THE REACTION INTERMEDIATE DISTRIBUTION OVER THE DIFFERENT REACTION ROUTES

The influence of this factor is studied for a constant: number of reaction routes ($M^t = M^r = 3$), total number of intermediates ($N^t = N^r$), type of mechanism ($S^t = S^r$), class and subclasses ($A^{X_1}_{I_1,K_1} B^{Y_1}_{V_1,K_1} C^{Z_1}_{L_1,K_1} = A^{X_2}_{I_2,K_2} B^{Y_2}_{V_2,K_2} C^{Z_2}_{V_2,K_2}$) of the mechanisms. In order to find which kind of intermediate distribution is related to a greater mechanistic complexity, the more even or the less even one, we have compared the complexity of two model mechanisms. The first one has the same number of intermediates in each of the three routes (an even distribution), while the second mechanism has a less even intermediate distribution:

$$N_p^t = N_k^t = N_\varrho^t = N_p^r, \quad N_k^r = N_k^t + s, \quad N_\varrho^r = N_\varrho^t - s, \quad \text{and } s = 1, 2, 3, \ldots .$$

With this, the following relations hold: $E_{pk}^t = E_{pk}^r \geqslant 0$, $E_{p\varrho}^t = E_{p\varrho}^r \geqslant 0$, $E_{k\varrho}^t = E_{k\varrho}^r \geqslant 0$. Under this conditions, one obtains:

$$\Delta K = [MN(N-1)(N_p . s + E_{p\varrho}^2 - E_{pk}^2) + 2Ns] s. \tag{38}$$

$\Delta K > 0$ in all cases except $\Delta = N_p . s + E_{p\varrho}^2 - E_{pk}^2 < 0$, where $\Delta K < 0$. The latter case requires $E_{pk} \geqslant E_{p\varrho}$, e.g. at $s = 1$, $\Delta K < 0$ for $E_{pk} \geqslant E_{p\varrho} + 2$ (classes C_L^2 and BC_L^2) and $E_{pk} \geqslant E_{p\varrho} + 3$ (classes BC_L and B^2C_L, where $E_{p\varrho} = 0$). Disregarding the case where $\Delta K < 0$, which refers to some higher subclasses L, one arrives at the following conclusion: the more even the intermediate distribution over the different reaction routes, the more complex is the reaction mechanism, with all other factors influencing the mechanism complexity being held constant.

$$\Delta K = K(N_p, N_p, N_p) - K(N_p, N_p + s, N_p - s) > 0.$$

6.8. COMPLEXITY INDEX DEPENDENCE ON THE NUMBER OF INTERMEDIATES IN TWO REACTION ROUTES HAVING A COMMON ELEMENTARY STEP

Inspecting table 1, one can also extract some mechanism with a constant type, class, subclasses, as well as with a constant total number of intermediates and a constant number of intermediates in each of the reaction routes N_i. The codes of the pairs or triplets of such mechanisms differ by the permutation of the N_i values, for example, numbers 38, 39 having codes 3-6-0-AC-3, 3, 2 and 3-6-0-AC-3, 2, 3, respectively. In these cases, the distribution of the N_i values is equally even (or uneven), but it is essential which one out of the three kinetic graph cycles is connected with another one by means of a common elementary step.

To interpret the complexity of such reaction mechanisms, we proceed from the following conditions: $N^t = N^r$, $S^t = S^r$, $A_{I_1,K_1}^{X_1} B_{V_1,K_1}^{Y_1} C_{L_1,K_1}^{Z_1} = A_{I_2,K_2}^{X_2} B_{V_2,K_2}^{Y_2} C_{L_2,K_2}^{Z_2}$; $N_p^t = N_p^r$, $N_\varrho^t = N_k^r$, $N_k^t = N_\varrho^r$; $E_{pk}^t = E_{pk}^r \geqslant 0$; $E_{p\varrho}^t = E_{p\varrho}^r = 0$, $E_{k\varrho}^t = E_{k\varrho}^r \geqslant 0$.

Under these conditions, one obtains $\Delta K_2 = 0$ and

$$\Delta K = \Delta K_1 = 3N(N-1)(N_\varrho^r - N_k^r)E_{pk}^2 . \tag{39}$$

When $E_{pk} = 0$ (classes A^2, AB, B^2, A^3, A^2B, and B^3), $\Delta K = 0$ and we arrive at another level of isocomplex mechanisms (e.g. numbers 33–35, 42–43, 44–46, 47–48, 70–71). When $E_{pk} > 0$ (classes AC, BC, A^2C, B^2C, and BC^2), if the pair of cycles compared are chosen in such a way that $N_\varrho^r > N_k^r$, then $\Delta K > 0$, for example, numbers 38–39, 51–52, 55–57, 74–75, 77–78, 80–81, 88–89,

117–118, etc. Three classes of kinetic graphs (C^2, B_2C^2, and C^3) do not possess such pairs or triplets of graphs with permuting N_i values, due to the graph symmetries. The following conclusion can be drawn for constant factors: the difference in the complexity of two reaction mechanisms with an interchangeable number of intermediates in those two of their reaction routes which have a common edge(s) depends on the difference between these two intermediate numbers, as well as on the number of common edges that the two routes have:

$$\Delta K = K(N_p, N_k, N_\varrho) - K(N_p, N_k, N_\varrho) \geqslant 0.$$

7. Some generalizations concerning isocomplex reaction mechanisms

Several levels of the reaction mechanisms' isocomplexity have been encountered in sect. 6. These can be mechanisms of different types (case 6.3.1), of the same type and class but of different subclass (case 6.6), as well as of the same class and subclass but with a pair of cycles interchanging their locations (case 6.8). A single case of isocomplex mechanisms of different classes and first subclasses was found by inspection from table 1: numbers 30, 31-3-6-0-$A^2_{1,0}$ ($A^2_{1,1}$)-2, 2, 2, and number 36-3-6-0-A_2B-2, 2, 2. Most of these cases are connected with graph transformations in which a cycle that is weakly connected with the other cycles (by a bridge or by a common vertex) changes its location only. In some other cases, such a transformation occurs with a strongly connected cycle (having a common edge with another cycle). The latter transformation is, however, restricted to another edge of the same cycle. All these cases can be uniformly treated by the following.

THEOREM

Two kinetic graphs G^t and G^r are isocomplex when they have the same number of cycles and vertices, the same number of vertices in the respective pairs of cycles, and the same number of common edges between the respective pairs of cycles, but differ as to the mutual location of their cycles only:

$$K(M^r, N^r, N^r_1, N^r_2, \ldots, N^r_k, E^r_{12}, E^r_{13}, \ldots, E^r_{k-1,k})$$

$$= K(M^t, N^t, N^t_1, N^t_2, \ldots, N^t_k, E^t_{12}, E^t_{13}, \ldots, E^t_{k-1,k})$$

for

$$M^r = M^t, N^r = N^t, N^r_1 = N^t_1, N^r_2 = N^t_2, \ldots, N^r_k = N^t_k,$$

$$E^r_{12} = E^t_{12}, E^r_{13} = E^t_{13}, \ldots, E^r_{k-1,k} = E^t_{k-1,k}.$$

Another formulation of the theorem is the following:

Two linear reaction mechanisms are isocomplex when they have the same number of reaction routes and intermediates, the same number of intermediates in the respective pairs of routes, and the same number of elementary steps common for the respective pairs of cycles, but differ in the interconnection of the reaction routes.

The proof of the theorem for two- and three-route mechanisms follows directly from eqs. (8,5,6,14 and 16), since the only variables they incorporate are those specified above as equal for the two kinetic graphs compared. The generalization of eqs. (6) and (14) to reaction mechanisms with larger numbers of routes does not alter this conclusion. Some specific cases of isocomplex mechanisms were proved in the preceding sections (see eq. (25), case 6.3.1, case 6.6; eq. (39), case 6.8).

8. Concluding remarks

Today, automated systems for kinetic studies of chemical reactions are being developed intensively. The theoretical foundation of such systems is the strategy based on the following scheme [42,8,11]: constructing hypotheses about the mechanism → planning and testing of hypotheses for chemical and kinetic experiments → discrimination of hypotheses → mechanisms.

The classification and coding of mechanisms, as well as the estimate of the mechanistic complexity, developed in our work is of importance in each of the kinetic-study stages shown in the above scheme. The automation of the procedure for generating hypotheses by means of different approaches [8,10,13,14,40,41] requires the coding of mechanisms, as well as the organization of a mechanism bank with a convenient system for information retrieval. The coding method we proposed earlier allows the automated (with limited intervention by the researcher) hypothesis generation to be carried out in parallel with the automated coding. The hypothesis-generating procedure is based on the simplicity principle. Because of this, it is justified to use the mechanistic hierarchy and to evaluate quantitatively the mechanistic complexity, as done in the present paper, by means of an appropriate complexity index. It is instructive to examine only the "skeletal" schemes which have solely intermediates, minimum number of elementary reversible steps, and no pendant vertices; the examination is done proceding on the assumption of "one sequence elementary steps – one product". The hypotheses thus generated can then be gradually made more complicated.

The generated hypotheses can be discriminated through chemical (or physicochemical), kinetic, and mathematical methods. In the discriminating experiments, it is important to plan them so as to shed light on the mechanism's topological structure. It is necessary to estimate qualitatively the connectivity of the mechanism graph, the route location in the graph, the route interconnections, as well as the presence of nonlinear elementary steps. A promising approach here is the so-called conjugated node

analysis [10]. The relations found in the present paper between the mechanism complexities of the different types, classes, subclasses, etc., could also be very instructive. Further work to develop an entire network of reaction mechanisms is in progress, along with the extension of the present results to all linear mechanisms having four reaction routes and up to six intermediates, as well as having irreversible elementary steps and pendant vertices [40].

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