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Original Investigations

A Possible Construction of Chemical Reaction Networks

III. The Systematization of the Elementary Processes

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The chemical reaction networks and the sequence networks represent the pathways of a complex chemical process. In order to study the pathways separately the systematization of the elementary processes included in the possible mechanism is inevitable.

This systematization was realized by a special procedure based on linear algebraic methods and enabled us to select the corresponding processes from the possible mechanism. The efficiency of the procedure has been illustrated by its application to the liquid phase oxidation of ethylbenzene and the elementary processes have been selected using a computer program.

Key words: Chemical reaction network – Ethylbenzene oxidation – Classification of elementary processes

1.

In Parts I and II [1, 2] a relatively simple procedure has been suggested for the construction of reaction networks based on the Possible Mechanism (PM) of a given complex chemical reaction. After the introduction of the notion of the kinetic communication the complete network as well as different specific subnetworks and sequence networks (SNW) have been defined.

The PM contains many informations but in a "chaotic" form. One of the main aims of the construction of networks is the systematization of these informations, taking into account primarily the precursor-product relations represented by the sequence network. Any transition ("arrow") in a SNW determines a certain precursor-product relation. In order to visualize these relations we introduce the following concept:

Definition 1. For a complex chemical reaction any transition (that is, a certain set of parallel and/or consecutive elementary processes – eventually one single process) included in its SNW is defined as a pathway of the overall process for given products[1].

The construction of the SNW enables us to determine the pathways. Obviously, if the study of the separate pathways is intended the knowledge of the elementary processes realizing it is of decisive importance.

The present paper deals with a mathematical procedure which enables us to select those elementary processes of the overall reaction – included in the PM – which represent the pathways of the SNW. That is, this procedure means also a certain systematization of the elementary processes of the PM.

The procedure will be illustrated by its application to the carbon-skeleton SNW of the liquid phase oxidation of ethylbenzene between 40–120°C described in detail in Part II.

2.

The subnetworks, as has been shown in Part I, are generated by specific kinetic communications with respect to a chosen atom or atomic group (T_i). Let us consider now the communication matrix of the one-step reaction subnetwork $\boldsymbol{K}(T)$ generated by a certain atom or atomic group. If N is the number of the species which contain the atom or atomic group T, then it is obvious that $\boldsymbol{K}(T)$ is an $N \times N$ quadratic matrix with $N^2 - S$ zero elements and S elements equal 1. Here S means the number of the one-step kinetic communications between the species N. The existence of the one-step kinetic communications between the species A_i and A_j $(i, j = 1, 2 \dots N)$ refers to the fact – according to our previous definition – that the PM contains *at least* one elementary process which represents a transition of the atom or atomic group T from A_i to A_j in one step.

The elementary processes of the PM realizing the one-step kinetic communications $A_i \rightarrow A_j$ can be grouped into reaction subsystems $R(i, j)$ defined in the following way:

Definition 2. The reaction subsystem $R(i, j)$ contains all those elementary processes included in the PM which generate the one-step kinetic communication $A_i \rightarrow A_j$ with respect to the atoms or atomic groups T. (It is obvious, that the number of such subsystems is also S.) The numbers (i, j) are called the coordinates of the reaction subsystem $R(i, j)$. The compilation of the subsystems can be easily carried out using the $\boldsymbol{K}(T)$ communication matrix.

Now, let us define the following operations:

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[1] The term "pathway" is used in the chemical literature in a rather wide interpretation. Here we limit ourselves to the above definition.

Definition 3. The expression:

$$R(i,j)\cdot R(j,k)=R(i,j,k)$$

means the *consecutive coupling* of the elementary processes participating in the reaction subsystems $R(i,j)$ and $R(j,k)$. The new reaction subsystem $R(i,j,k)$ formed in the consecutive coupling contains all those elementary processes which transfer the atom or atomic group T of the species A_i into the species A_k via species A_j.

The consecutive coupling displays the following properties:

1. A consecutive coupling is possible provided that the last coordinate of the first subsystem is identical with the first coordinate of the second subsystem. That is, there exists a species ensuring the consecutive coupling which plays the role of a product in each elementary process of the first subsystem *and* the role of the precursor in each elementary process of the second subsystem.

2. The "unit" of the consecutive coupling is the reaction subsystem $R(i,i)$ and consequently:

a) $R(i,i)\cdot R(i,i)=R(i,i)$
b) $R(i,j)\cdot R(j,k)\ldots R(l,i)=R(i,j,k\ldots l,i)=R(i,i)$
c) $R(i,j)\cdot R(j,j)=R(i,j)$
d) $R(i,i)\cdot R(i,j)=R(i,j)$

3. If there is no kinetic communication between two species it is denoted by zero and:

$$0\cdot R(i,j)=R(i,j)\cdot 0=0$$

4. If the notation $R(i,j)$ is considered as the logical statement "true" (↑), in the case when the reaction subsystem $R(i,j)$ is not "empty", the consecutive coupling $R(i,j)\cdot R(j,k)$ corresponds to the logical "*and*" operation (logical multiplication), that is:

$$R(i,j)\cdot R(j,k)=\uparrow \quad \text{if} \quad R(i,j)=\uparrow \quad \text{and} \quad R(j,k)=\uparrow$$

It should be mentioned that the consecutive coupling is mathematically a multiplication-type operation being non-commutative, associative and the inverse of the subsystem $R(i,j)$ is the subsystem $R(j,i)$.

Definition 4. The *parallel coupling* of the elementary processes included in the subsystems $R(i,j,\ldots k)$ and $R(i,k)$ can be expressed by $R(i,j,\ldots k)+R(i,k)$. The new subsystem $R(i,j,\ldots k)+R(i,k)$ stemming from the parallel coupling contains all those elementary processes of the PM which realize the transfer of the atom T from the species A_i into the species A_k *via the species* A_j *or directly*. The parallel coupling displays the following properties:

1. Elementary processes can be coupled parallel only if *both* subsystems formed from them have identical first and last coordinates. That is, if each elementary process included in the two subsystems contains identical initial compounds and end-products.

2. It follows from *Definition 4* that:

$$R(i,j)+R(i,j)=R(i,j)$$

3. Considering $R(i,j,k)$ and $R(i,k)$ as simple true statements $(\uparrow)$ if the subsystems are not "empty", the parallel coupling $R(i,j,k)+R(i,k)$ can be regarded as "inconclusive or" operation or logical addition, that is $R(i,j,k)+R(i,k)=\downarrow$ (false statement), if and only if $R(i,j,k)=\downarrow$ *and* $R(i,k)=\downarrow$.

It should be noted that the parallel coupling is mathematically an addition.

Now, we can construct the matrix of the subsystems, $\boldsymbol{R}(\mathrm{T})$. The element j of the row i in the one-step kinetic communication matrix $\boldsymbol{K}(\mathrm{T})$ – if it is equal *one* – should be exchanged to $R(i,j)$. On the other hand, if it is zero, no exchange should be carried out.

Similarly to the $\boldsymbol{K}(\mathrm{T})$ the subsystem-matrix $\boldsymbol{R}(\mathrm{T})$ has the following properties:

a) The matrix $\boldsymbol{R}\cdot\boldsymbol{R}$ summarizes all those reaction subsystems coupled consecutively and parallel which transfer the atom or atomic group T from the species i to the species j *via an intermediate species.*

b) The matrix-sum $\tilde{\boldsymbol{R}}=\sum_{k=1}^{L}\boldsymbol{R}^{L}$ represents those reaction systems coupled consecutively or parallel which transfer atom or atomic group T from the species i to species j either directly or *via* 1, 2. . ., L-1 species.

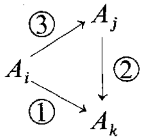
Both a) and b) properties can be easily proved by the use of the Appendix in Part I. L means the characteristic stepnumber introduced in the same paper and can be determined analyzing $\boldsymbol{K}(\mathrm{T})$.

The multiplication of the matrices should be carried out according to the conventional row-column multiplication rules.

Taking into account the properties of the consecutive and parallel couplings, we can consider the elements of the matrix-sum $\tilde{\boldsymbol{R}}$ as logical operations. E.g. let us assume that the element j of the row i in $\tilde{\boldsymbol{R}}$ is

$$R(i,l,k,j)+R(i,p,j)+R(i,j)=\tilde{R}(i,j)$$

and that the sequence network contains the following reaction pathways:



If we intended to study the pathway ③ then the first member of $R(i,j)$ should be disregarded since the species A_k participates in the sequence network. Thus the pathway ③ will be realized either by subsystems $R(i,p)$ and $R(p,j)$ or directly by $R(i,j)$ (eventually by all of them). This can be expressed as:

$$[R(i,p)\wedge R(p,j)]\vee R(i,j)=\uparrow$$

and this expression is the condition for the realization of pathway ③. It is obvious

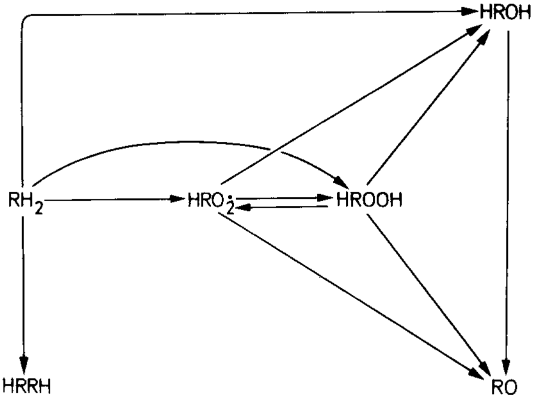


Fig. 1. Theoretical sequence network of the oxidation of ethylbenzene in the liquid phase. (Among the chosen species radical $HR'O_2^{\cdot}$ has been included)

that if we exclude pathway ③ by experimental evidences, the reactions of the subsystem *R*(*i*, *j*) and the reactions of at least one of the subsystems *R*(*i*, *p*) or *R*(*p*, *j*) must be excluded from the PM.

3.

In order to illustrate the entire procedure we analyze now the PM of the liquid phase oxidation of ethylbenzene given in Part II. In the same publication we have referred to the carbon-skeleton sequence network of this process which has been proved experimentally. The corresponding sequence studies [3–6] resulted in a slight modification of the "theoretical" network, namely, the radical $HR'O_2^{\cdot}$ has to be included. This enlarged network is given in Fig. 1.

This SNW contains 11 different pathways and the elementary processes of these pathways will be selected accordingly.

Firstly the one-step communication matrix – given in Part II – will be rewritten in the form *R*(*i*, *j*) where the coordinates (*i*, *j*) are unambiguously determined

Table 1. Matrix of the reaction subsystem

	1 RH_2	2 $HR^{\cdot}$	3 $HRO_2^{\cdot}$	4 HROH	5 $HRO^{\cdot}$	6 $^{\cdot}ROH$	7 HROOH	8 RO	9 HRRH
1 RH_2	0	*R*(1, 2)	0	0	0	0	0	0	0
2 $HR^{\cdot}$	*R*(2, 1)	0	*R*(2, 3)	*R*(2, 4)	0	0	*R*(2, 7)	0	*R*(2, 9)
3 $HRO_2^{\cdot}$	0	0	0	*R*(3, 4)	*R*(3, 5)	0	*R*(3, 7)	*R*(3, 8)	0
4 HROH	0	0	0	0	*R*(4, 5)	*R*(4, 6)	0	0	0
5 $HRO^{\cdot}$	0	0	0	*R*(5, 4)	0	0	0	*R*(5, 8)	0
6 $^{\cdot}ROH$	0	0	0	*R*(6, 4)	0	0	0	*R*(6, 8)	0
7 HROOH	0	0	*R*(7, 3)	0	*R*(7, 5)	0	0	*R*(7, 8)	0
8 RO	0	0	0	0	0	0	0	0	0
9 HRRH	0	0	0	0	0	0	0	0	0

Table 2. Elementary processes of the subsystems in the liquid phase oxidation of ethylbenzene

One-step kinetic communications	Elementary processes realizing the subsystem (based on Table 1, Part II)	Symbol of the reaction subsystem
$RH_2 \rightarrow HR^\bullet$	1, 2, 3, 7, 9, 12, 18, 31	$R(1, 2)$
$HR^\bullet \rightarrow RH_2$	5a, 5b, 6b, 28	$R(2, 1)$
$HR^\bullet \rightarrow HRO_2^\bullet$	4	$R(2, 3)$
$HR^\bullet \rightarrow HROH$	6a, 25, 29	$R(2, 4)$
$HR^\bullet \rightarrow HROOH$	35	$R(2, 7)$
$HR^\bullet \rightarrow HRRH$	22	$R(2, 9)$
$HRO_2^\bullet \rightarrow HROH$	11b, 24b, 27	$R(3, 4)$
$HRO_2^\bullet \rightarrow HRO^\bullet$	10a, 24a, 37a	$R(3, 5)$
$HRO_2^\bullet \rightarrow HROOH$	9, 10b, 11a, 30	$R(3, 7)$
$HRO_2^\bullet \rightarrow RO$	16, 24b, 29, 37b	$R(3, 8)$
$HROH \rightarrow HRO^\bullet$	5a, 10a, 13a, 19, 39a	$R(4, 5)$
$HROH \rightarrow \dot{R}OH$	5b, 10b, 13b, 32, 39b	$R(4, 6)$
$HRO^\bullet \rightarrow HROH$	7, 8a, 8b, 23, 32	$R(5, 4)$
$HRO^\bullet \rightarrow RO$	23, 26, 28, 30, 36	$R(5, 8)$
$\dot{R}OH \rightarrow HROH$	31	$R(6, 4)$
$\dot{R}OH \rightarrow RO$	33	$R(6, 8)$
$HROOH \rightarrow HRO_2^\bullet$	8a, 14c, 20, 38c	$R(7, 3)$
$HROOH \rightarrow HRO^\bullet$	6a, 11b, 14a, 17, 18, 19, 20, 38b	$R(7, 5)$
$HROOH \rightarrow RO$	6b, 8b, 11a, 14b, 38a	$R(7, 8)$

by the simple numeration of the species. Thus we obtain the subsystem-matrix $R(i, j)$ shown in Table 1.

Table 2 summarizes all the communications dealt with, the corresponding elementary processes – according to the PM – and the coordinates of the reaction subsystems.

The matrix-sums $\boldsymbol{R}\cdot\boldsymbol{R}+\boldsymbol{R}$ is given in Table 3, the elements of which are the elementary processes realizing the pathways and coupled parallel or consecutively. The matrix-sum shown in Table 3 contain only two members. Though the characteristic step-number of the carbon-skeleton transfer is $L=3$, the matrix $\boldsymbol{R}^3$ did not yield new information compared with $\boldsymbol{R}^2$.

Table 4 includes the reaction subsystems belonging to the pathways of the oxidation derived from the PM for the carbon-skeleton transfer. The subsystems are coupled with logical "and" ($\wedge$) and with logical "inclusive-or" ($\vee$) operations. It is the task of the experimentation to prove or to disprove the reaction-subsystem(s) when studying a certain reaction pathway. If a subsystem is excluded experimentally, it means that all of its elementary processes must be excluded from the PM. On the contrary, if a subsystem is proved to occur, the detailed investigation of its elementary processes becomes desirable and subsequently the above procedure becomes important in planning the study of the pathways of a complex chemical process.

Table 3. The matrix-sum $\boldsymbol{R} \cdot \boldsymbol{R} + \boldsymbol{R}$

	1	2	3	4	5	6	7	8	9
1	$R(1, 1)$	$R(1, 2)$	$R(1, 2, 3)$	$R(1, 2, 4)$	0	0	$R(1, 2, 7)$	0	$R(1, 2, 9)$
2	$R(2, 1)$	$R(2. 2)$	$R(2, 7, 3)+$ $+R(2, 3)$	$R(2, 3, 4)+$ $+R(2, 4)$	$R(2, 3, 5)+$ $+R(2, 4, 5)+$ $+R(2, 7, 5)$	$R(2, 4, 6)$	$R(2, 3, 7)+$ $+R(2, 7)$	$R(2, 3, 8)+$ $+R(2, 7, 8)$	$R(2, 9)$
3	0	0	$R(3, 3)$	$R(3, 5, 4)+$ $+R(3, 4)$	$R(3, 4, 5)+$ $+R(3, 7, 5)+$ $+R(3, 5)$	$R(3, 4, 6)$	$R(3, 7)$	$R(3, 5, 8)+$ $+R(3, 7, 8)+$ $+R(3, 8)$	0
4	0	0	0	$R(4, 4)$	$R(4, 5)$	$R(4, 6)$	0	$R(4, 5, 8)+$ $+R(4, 6, 8)$	0
5	0	0	0	$R(5, 4)$	$R(5, 5)$	$R(5, 4, 6)$	0	$R(5, 8)$	0
6	0	0	0	$R(6, 4)$	$R(6, 4, 5)$	$R(6, 6)$	0	$R(6, 8)$	0
7	0	0	$R(7, 3)$	$R(7, 3, 4)+$ $+R(7, 5, 4)$	$R(7, 3, 5)+$ $+R(7, 5)$	0	$R(7, 7)$	$R(7, 3, 8)+$ $+R(7, 5, 8)+$ $+R(7, 8)$	0
8	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0

Table 4. Subsystems corresponding to the pathways in the liquid phase oxidation of ethylbenzene

Pathways of the theoretical sequence network	Coupled reaction subsystems realizing the given reaction pathways
$RH_2 \to HROH$	$R(1, 2) \wedge R(2, 4)$
$RH_2 \to HROOH$	$R(1, 2) \wedge R(2, 7)$
$RH_2 \to HR\dot{O}_2$	$R(1, 2) \wedge R(2, 3)$
$RH_2 \to HRRH$	$R(1, 2) \wedge R(2, 9)$
$HR\dot{O}_2 \to HROH$	$R(3, 4) + R(3, 5) \wedge R(5, 4)$
$HR\dot{O}_2 \to HROOH$	$R(3, 7)$
$HR\dot{O}_2 \to RO$	$R(3, 8) + R(3, 5) \wedge R(5, 8)$
$HROOH \to HR\dot{O}_2$	$R(7, 3)$
$HROOH \to HROH$	$R(7, 5) \wedge R(5, 4)$
$HROOH \to RO$	$R(7, 8) + R(7, 5) \wedge R(5, 8)$
$HROH \to RO$	$R(4, 5) \wedge R(5, 8) + R(4, 6) \wedge R(6, 8)$

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