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Finding All Possible *a priori* Mechanisms for a Given Type of Overall Reaction

The Cases of 1) Molecular Rearrangements (A ⇒ B); and 2) Molecular Associations (A + B ⇒ C) Reaction Types

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The method, presented for finding all the *a priori* possible mechanisms of a certain number of steps for a given type of overall reaction, is applied to finding the possible two-step mechanisms for: overall reactions of the type of molecular rearrangements, and of the type of molecular associations. Many examples from organic, physical or biochemistry are given such as mutarotation of glucose, Henry–Michaelis–Menten enzyme mechanism, rearrangements of halogenoamines, hydration of epoxides, etc. The approach provides a systematics for otherwise diverse mechanisms.

Key words: Overall reactions – Reaction networks – Molecular rearrangements and associations

1. Introduction. Chemical, Biochemical Reactions and Their Mechanisms

In chemical or biochemical kinetics one has an *overall reaction* (OVR) and its presumably measured overall rate law. Then one tries to find a mechanism whose steps will add up to the OVR and will also reproduce the rate law. In general this involves guessing a mechanism consistent with what is known as to intermediates, enzymes, catalysts in the system. It is hard to guess mechanisms, to know if there were any others possible, how many, etc. In fact, there had not been any systematic *a priori* way to find mechanisms. Further, even with OVR's of the same abstract type, e.g. A + B ⇒ C + D, etc., each case with specified chemicals for A, B, C, D, ... has looked like a special problem in mechanisms. Could it be that all

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possible mechanisms could be found abstractly once and for all for a given OVR type, not stating what A, B, C, D, ... are at first, then assigning actual chemical species, thus getting some systematics into seemingly diverse mechanisms proposed or perhaps some missed, for distinct chemical reactions? Could this be possible though there would be a seemingly endless variety of catalysts, intermediates, etc., that could be invoked?

It was shown recently [1][1] that there are strong restrictions between the number of elementary steps, ρ, constituting a mechanism, and the number of chemical species, σ, that can occur in any and all mechanisms of ρ-steps. A $\rho(\sigma)$ plot was given. Possible OVR types, possible numbers of external species (reactants and products, all in the OVR), σ_{ext}, and internal species (intermediates, catalysts, etc. cancelling out in the OVR), σ_{int}, with $\sigma = \sigma_{int} + \sigma_{ext}$, were predicted once ρ is given or assumed as a start. All possible mechanisms[2] $\{\mathscr{M}\}$, and their convenient pictorial representations as chemical networks $\{\mathscr{N}\}$ could be found and classified given the ρ (or conversely σ). The topological features of $\{\mathscr{N}\}$'s, how many catalytic or chain-type loops they contain, etc., become more clearly and simply apparent from the *skeletons* $\{\mathscr{S}\}$ that the networks condense into[3].

That Paper [1] examined the classes of mechanisms obtained starting just with the number of steps, ρ, increased each time by one, $\rho = 1, 2, 3, 4, \ldots$ noting the general features of chain reactions, enzyme mechanisms, etc., noting the basic difference that emerges between biochemical pathways of nature on the one hand and the synthetic organic chemists' laboratory pathways on the other.

We remind the reader (cf. Ref. [1] for more detailed definitions, equations, etc.) that "mechanism" is a set of elementary, i.e. molecular, chemical reaction step equations which add up to the OVR while the "network" is a pictorial representation in which a solid line (—) is drawn for each mole of each chemical species in the mechanism, and a wiggly line (⁓) for each elementary reaction arrow. On a network several assignments of chemical species labels may be possible each one giving a chemical specific mechanism. Further, a network is compressed into a "skeleton" graph by replacing each block of directly connected species-mole lines with a solid dot (cf. e.g. Eq. (1) which are the skeletons of the networks given in Figs. 1 and 2).

In the present paper we deal with the problem of: given a specific overall reaction

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[1] Ref. [1] will be referred to hereafter as Paper I.

[2] A mechanism has two aspects: 1) a statement of the elementary steps that connect a number of "significant structure" species singled out as having special significance out of a whole set of continuous points on a super potential energy surface, that is a *pathway* or *network* aspect, and 2) assumptions as to the relative magnitudes and significance of rate constants on each step. The two are analogous to 1) a highway map, 2) a sort of topographic map showing also the ups and downs, the grades and quality of the individual roads. We are concerned in these papers with the network aspects not neglecting any of the passages, any of the rate constants. Thus for each network $\mathscr{N}$ one can write an exact rate expression, in usual kinetics usually further approximated afterwards assuming "fast"–"slow" steps, "equilibrium steps", etc. Thus many reactions all of the same OVR-type like A ⇒ B, will have one of the networks/exact mechanisms found abstractly regardless of the actual atoms and energetics.

[3] For further detailed definitions, etc. the reader is referred to Ref. [1], hereafter called "Paper I".

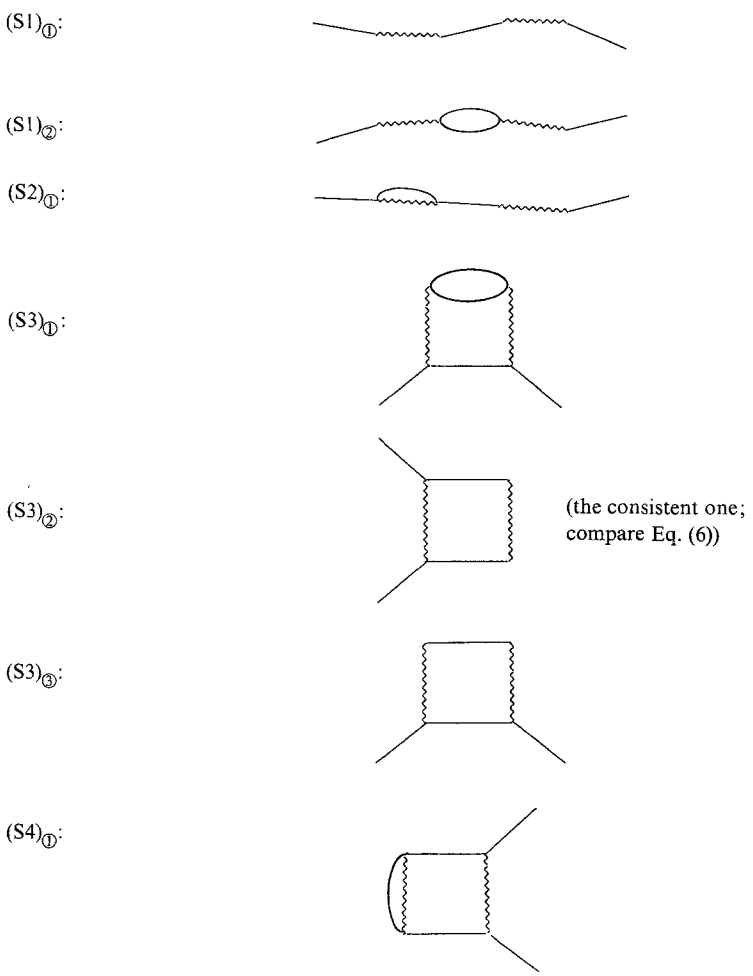

Fig. 1. Networks for $\rho = 2$ and overall reaction type A ⇒ B (compare Table 1)

type, denoted abstractly[4] as A + B + ... ⇒ C + D + ... etc., how to find all of its possible kinetic mechanisms[5]. In particular we will do the cases of

$$A \Longrightarrow B \tag{I}$$

and

$$A + B \Longrightarrow C \text{ (or its reverse)} \tag{II}$$

here.

Case (I) are isomerizations, molecular rearrangements, enzyme catalyzed transformations of a substrate into a product, S ⇒ P. Case (II) are molecular associations, or break-ups.

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[4] We shall use A, B, C, D,... for external species; X, Y, Z,... for internal ones.

[5] As distinct from non-kinetic organic synthetic pathways (cf. Ref. [1]).

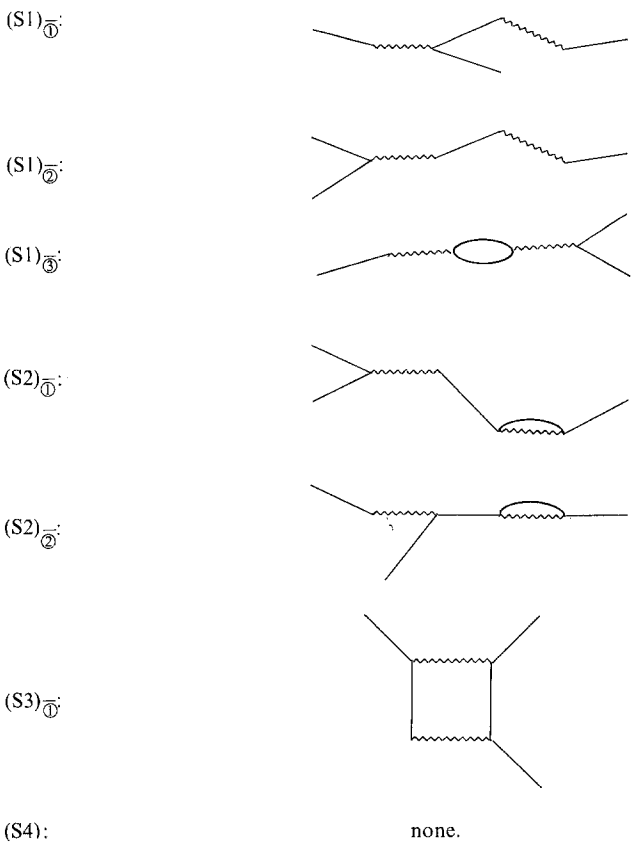


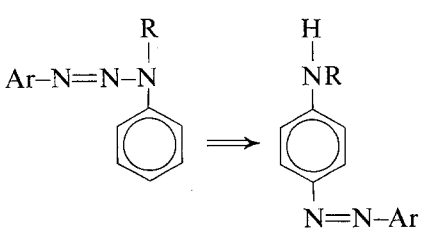
Fig. 2. Networks for $\rho = 2$ and overall reaction type A + B ⇒ C (or reverse) (compare Table 3)

All the mechanisms (networks) possible for any A or B or C result, and then we examine known mechanisms in chemistry and biochemistry invented and tested to analyze a specific OVR corresponding to such OVR-types. This will demonstrate the methodology of the theory as well as providing a list and classification of possible mechanisms for Cases (I) and (II).

2. Examples of Overall Reaction Types

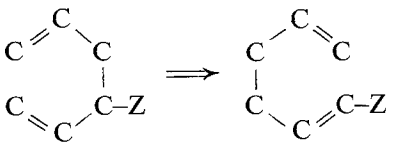
Examples of OVR-type A ⇒ B are:

Migration of an arylazo group,



(11)

The Cope rearrangement,



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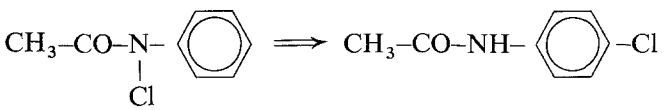
The Orton rearrangement,



(13)

Migration of double bonds,

$$CH_3–CH_2–CH=CH_2 \Longrightarrow CH_3–CH=CH–CH_3 \tag{14}$$

An enzyme catalyzed substrate-to-product transformation, $S \overset{E}{\Rightarrow} P$, e.g.

$$\text{D-ribulose-5-phosphate} \overset{\text{epimerases}}{\Longrightarrow} \text{D-xylutose-5-phosphate} \tag{15}$$

or e.g.

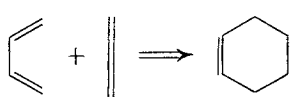
$$\text{methylmalonyl-CoA} \overset{\text{mutases or intramolec. transferases}}{\Longrightarrow} \text{succinyl-CoA}$$

etc.

Some examples of OVR-type $A + B \Leftrightarrow C$ are:

Organic:

Diels-Alder reaction,



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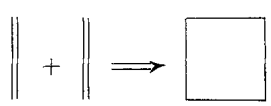
Dimerization of olefins



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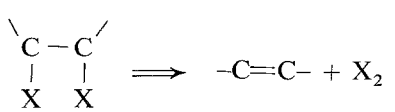
Dehalogenation of vicinal halides,



(113)

Dehydration

$$RCONH_2 \Longrightarrow RC{\equiv}N + H_2O \tag{114}$$

Inorganic:

Acid-base reaction,

$$A^+ + B^- \Longrightarrow AB; \text{ another type of reaction:} \tag{115}$$

$$2NO_2 \Longrightarrow N_2O_4 \tag{116}$$

Enzymic:

$$\text{Adenylosuccinate} \xRightarrow{E} \text{fumarate} + \text{AMP}$$
$$(E = \text{adenylosuccinate AMP-lyase}) \tag{117}$$

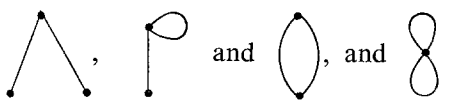
$$L_s\text{-Isocitrate} \xRightarrow{E} \text{succinate} + \text{glyoxylate}$$
$$(E = L_s\text{-isocitrate glyoxylate-lyase}) \tag{118}$$

etc.

3. All Two-Step Molecular Rearrangements

3.1. Skeletons

Let us find all the $\rho = 2$, i.e. two-step mechanisms for OVR-types A $\Rightarrow$ B. The skeletons possible with $\rho = 2$ were already given [1]. They are



(S1) (S2) (S3) (S4) (1)

with the numbers of rings $r = 0$, 1, and 2 respectively.

3.2. Possible Numbers of Internal Species

Next from the results of Paper I, let us find the possible numbers of species $\sigma_{\text{int}} + \sigma_{\text{ext}} = \sigma$ for each of the skeletons. For the present OVR: A $\Rightarrow$ B case

$$\sigma_{\text{ext}}(A \Longrightarrow B) = 2 \tag{2}$$

Eq. (25) of Paper I gives[6]

$$\begin{cases} \text{Skeleton:} & \text{S1} & \text{S2} & \text{S3} & \text{S4} \\ \sigma_{\text{ext}}^{\max, L}: & 6 & 4 & 4 & 2 \end{cases} \tag{3}$$

[6] This $\sigma_{\text{ext}}^{\max}$ is for laminar networks [1], i.e. all stoichiometric coefficients, ν_i in the mechanism equaling unity, none greater. For turbulent cases ($\nu_i > 1$ possible), we have Eq. (28b) of paper I which also allow all the skeletons of Eq. (1). Paper I's results were general, given for both laminar and turbulent networks [1]. With very simple types of OVR, like A $\Rightarrow$ B, most mechanisms will be of the laminar type. But in any case one can treat the simpler laminar cases first, then get a few more mechanisms by extending to turbulent.

Thus all of the skeletons are consistent with this OVR.

We have from Eq. (28c) of Paper I, i.e. allowing turbulence too,

$$\begin{cases} \text{(S1):} & 3 \leqslant \sigma_{\text{int}} + \sigma_{\text{ext}} \leqslant 7 \\ \text{(S2, S3):} & 2 \leqslant \sigma_{\text{int}} + \sigma_{\text{ext}} \leqslant 6 \\ \text{(S4):} & 1 \leqslant \sigma_{\text{int}} + \sigma_{\text{ext}} \leqslant 5 \end{cases} \tag{5}$$

And with $\sigma_{\text{ext}} = 2$, again allowing turbulence,

$$\begin{cases} \text{(S1):} & 1 \leqslant \sigma_{\text{int}} \leqslant 5 \\ \text{(S2, S3):} & 0 \leqslant \sigma_{\text{int}} \leqslant 4 \\ \text{(S4):} & 0 \leqslant \sigma_{\text{int}} \leqslant 3 \end{cases} \tag{5a}$$

The ranges of σ_{int}'s possible are narrowed down some more for laminar-only cases. These can be read off from the $\rho(\sigma)$ plot of Paper I (Fig. 2 of Paper I). [(S1): $1 \leqslant \sigma_{\text{int}}^{L} \leqslant 5$; (S2, S3): $2 \leqslant \sigma_{\text{int}}^{L} \leqslant 4$; (S4): $\sigma_{\text{int}}^{L} = 3$].

We have seen that contrary to what one might have thought at first, only a few internal species are possible with their possible numbers found *a priori*. The only restrictions that enabled these results in Paper I were that elementary steps can only be uni- or bi-molecular, a restriction invoked very commonly in chemical kinetics by the improbability of three-body collisions.

3.3. Weighted Skeletons Possible

Each dot-point of a skeleton is a lineblock of directly connected species-mole lines of a network, the weight assigned to a dot-point with a k-star, $\bar{\omega}_k$, giving the number of species-mole lines there (cf. Ref. [1] of Paper I). Thus we had $\Sigma \omega_k = \sigma$ for laminar cases as each mole-line there, is a different species. Having found the skeletons of $\rho = 2$ and σ_{int} numbers compatible with A $\Rightarrow$ B, we now need to find the possible weights $\bar{\omega}_k$ for each dot-point consistent however with A $\Rightarrow$ B as the OVR.

Table 1 gives the possible weights for all laminar networks from the theorem given in Ref. [1] of Paper I that $\bar{\omega}_k = k - 1, k, k + 1$, but in addition, consistent also with A $\Rightarrow$ B. Not all σ-values possible (σ_{int}^{L} ranges) occur in Table 1 because while those ranges are consistent with $\sigma_{\text{ext}} = 2$, not all of these would give the required overall reaction and consistent networks.

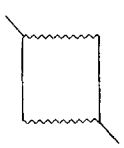
3.4. Possible Networks

From the weighted skeletons $\{S^{\bar{\omega}}\}$, one can now draw the possible laminar networks by drawing the wiggly lines (~~~) for the reaction steps (which are the solid lines of the skeletons) and connecting the possible species–mole lines (—) of each dot-point to satisfy Table 1. An alternative way would be to draw the network piece at each dot-point-star, then joining these pieces in all consistent ways, then assigning reaction arrows to the network wiggly lines to be sure they can lead to the

Table 1. Skeletal weights possible for laminar networks with $\rho = 2$ and OVR: A $\Rightarrow$ B only

Skeleton	k-Value of the star of a dot-point		$\bar{\omega}_k^{\text{int}}$	$\bar{\omega}_k^{\text{ext}}$	$\bar{\omega}_k$	σ
(S1)	$k = 1$	①	0	1	1	
	$k' = 1$		0	1	1	3
	$k'' = 2$		1	0	1	
		②	0	1	1	
			0	1	1	4
			2	0	2	
(S2)	$k = 3$	①	2	1	3	4
	$k' = 1$		0	1	1	
(S3)	$k = 2$	①	2	0	2	5
	$k' = 2$		1	2	3	
		②	1	1	2	4
			1	1	2	
		③	1	0	1	4
			1	2	3	
(S4)	$k = 4$	①	3	2	5	5

correct OVR, i.e. A $\Rightarrow$ B, and if not consistent, then discarding those networks[7]. For example, one of the two networks resulting from (S3) with the second $\bar{\omega}_k$-assignments, i.e.



(6)

is an inconsistent network to be discarded. A cyclic assignment of arrows leads to an OVR: A + B $\Rightarrow$ 0, a parallel assignment of arrows leading to a turbulent network (with two kinks) [1], resulting in the OVR: A + 2X $\Rightarrow$ 2Y + B. This is the only inconsistent network that results for the $\rho = 2$, A $\Rightarrow$ B problem. The other networks are shown in Fig. 1.

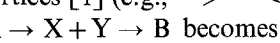
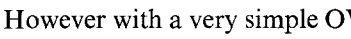
The abstract mechanisms these networks correspond to are written out in Table 2 in the chemical equations forms. Note that, as in the (S2)① and the (S4)① cases, several mechanisms can result from the same network depending on assignment of the external species labels still consistent with the same OVR.

[7] Details of these procedures in a more mathematical and systematic way will be given in other papers. In the present paper, the OVR's treated A $\Rightarrow$ B, A + B $\Rightarrow$ C, etc. are simple enough that they are easily obtained. Our concern here is more on a chemical presentation seeing how diverse mechanisms for such actual OVR's will fit into a system. Therefore presently we do not encumber the reader with the lengthy details of our more general treatment.

Thus all two-step molecular rearrangements, catalyzed or not, can have nine possible types of mechanisms given in Table 2. A few more turbulent [1] mechanisms could be found with some stoichiometric coefficients in elementary steps

Table 2. All mechanisms possible for two-step rearrangements with or without catalysis (laminar ones); $\rho = 2$; OVR: A $\Rightarrow$ B

$(S1)_{①}$:	$A \rightarrow X \rightarrow B$
$(S1)_{②}$:	$A \rightarrow X + Y \rightarrow B$
$(S2)_{①/1}$:	$\begin{cases} A \rightarrow X \\ X + Y \rightarrow Y + B \end{cases}$
$(S2)_{①/2}$:	$\begin{cases} A + Y \rightarrow Y + Z \\ Z \rightarrow B \end{cases}$
$(S3)_{①}$:	$A + X \rightarrow U + V \rightarrow X + B$
$(S3)_{②}$:	$\begin{cases} A + Y \rightarrow B + X \\ X \rightarrow Y \end{cases}$
$(S3)_{③}$:	$A + X \rightarrow Y \rightarrow X + B$
$(S4)_{①/1}$:	$\begin{cases} A + X \rightarrow Y + B \\ Y + Z \rightarrow Z + X \end{cases}$
$(S4)_{①/2}$:	$\begin{cases} A + Z \rightarrow Z + X \\ X + Y \rightarrow Y + B \end{cases}$

greater than unity. Some of these are derived from the same networks of Fig. 1 by introducing some "kinks", i.e. species-vertices [1] (e.g.,  can become  so that $A \rightarrow X+Y \rightarrow B$ becomes $A \rightarrow 2X \rightarrow B$). However with a very simple OVR like A $\Rightarrow$ B, there are few such that are possible or of interest, by far most mechanisms being laminar. For more complicated OVR's and for completeness, turbulent mechanisms will be treated in a separate paper. (Cases like $C+A \rightarrow A+X$; $X \rightarrow A+B$, i.e. with auto-catalysis which look like laminar ($\nu_i = 1$ in steps, and in OVR) cases, but are turbulent as they lead to species-vertices, e.g. for A here, are also not contained in the present "laminar" mechanisms derivation.)

4. Some Chemical Examples of Two-Step Rearrangement Mechanisms

It is interesting to now look at various two-step mechanisms that have been proposed in the past for A $\Rightarrow$ B type reactions to see how many of the nine possible mechanisms of Table 1 have been invoked at one time or another, and whether some additional, new possibilities could also have been considered.

4.1. The Henry–Michaelis–Menten Mechanism of Enzyme Catalysis

This well known case, $E+S \rightarrow (ES) \rightarrow E+P$, we see now is of type $(S3)_{③}$ in Table 2 and Fig. 1. Note that its skeleton has one ring ($r=1$) (cf. Ref. [1] for remarks on enzymatic networks).

4.2. Mutarotation of Glucose

The mechanism found [2],

$$\left.\begin{matrix} G_\alpha + HA \rightarrow X^+ + A^- \\ X^+ + A^- \rightarrow G_\beta + HA \end{matrix}\right\} \tag{7}$$

falls in the case (S3)① having a different network than the example (A) above, but the same skeleton.

4.3. Keto–Enol Tautomerization

This would follow (S3)③or (S3)①depending on whether it is acid or base catalyzed.

4.4. Rearrangement of Halogenoamines

Consider for example

$$C_6H_5NClAc \xrightarrow{HCl} Cl \cdot C_6H_4 \cdot NHAc \tag{8}$$

Up to 1909 this was considered an intramolecular rearrangement following the mechanisms (S1)① or (S3)③ depending on whether solvent or other catalysts play any role in the mechanism or not. In 1909, Orton and Jones [3] proposed that a more reasonable mechanism should be

$$\begin{matrix} C_6H_5 \cdot NClAc + HCl \underset{k^2}{\overset{k^1}{\rightleftharpoons}} \underbrace{C_6H_5 \cdot NHAc + Cl_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow k^3 \\ (o\text{-}, p\text{-})\ Cl \cdot C_6H_4 \cdot NHAc + HCl \end{matrix} \tag{9}$$

This one corresponds to the mechanism (S3)①, which means that (S1)② is also a possibility. The last two mechanisms (S3)① and (S1)② would be distinguished from each other by checking the rate determining steps. It was found that k_1 and k_2 in Eq. (9) happened to be the rate determining steps. Thus Orton rearrangement is now usually considered to be an intermolecular rearrangement favoring (S3)①. This does not rule out the other mechanisms occurring at least to some extent of course. In principle an OVR may be considered the result of a superposition of several of the possible mechanisms, such as the nine found in Table 1. The phenomonological rate curve may fit better one or several of these under different conditions with differing weighting factors.

Alternatively, the list of allowed networks and abstract mechanisms can act as a checklist for the kineticist to see if he has considered other possible mechanisms and intermediates.

5. All Two-Step Mechanisms for the Overall Reaction Type A + B ⇒ C (or Its Reverse)

We now turn to Case (II), to find all the networks/mechanisms possible for the OVR-type A + B ⇒ C following the procedure similar to that summarized for A ⇒ B.

With $\rho = 2$, the skeletons are still the same, i.e. Eq. (1). There are now narrower σ_{int} ranges, as $\sigma_{ext}=3$ for A+B ⇒ C (cf. Eqs. (5)). Thus fewer networks will be possible than in case (I) above.

Table 3 gives the skeletal weights for the laminar cases consistent with the OVR: A+B ⇒ C.

Table 3. Skeletal weights for laminar networks with $\rho = 2$ and for OVR: A + B ⇒ C only

Skeleton	k-Value of dot-point star in S		$\bar{\omega}_k^{int}$	$\bar{\omega}_k^{ext}$	$\bar{\omega}_k$	σ
(S1)	$k = 1$ $k' = 1$ $k'' = 2$	①	0 0 1	1 1 1	1 1 2	4
		②	0 0 1	2 1 0	2 1 1	4
		③	0 0 2	1 2 0	1 2 2	5
(S2)	$k = 3$ $k' = 1$	①	2 0	1 2	3 2	5
		②	2 0	2 1	4 1	5
(S3)	$k = 2$ $k' = 2$	①	1 1	1 2	2 3	5
(S4)	$k = 4$			none		

Again, from these, by expanding the dot-points of each $S^{\bar{\omega}}$ into lineblocks and matching them in consistent ways, one gets the laminar networks, shown in Fig. 2.

In the conventional chemical equations form these yield six mechanisms after the possible assignments of A, B, and C to the external species-mole lines, listed in Table 4.

An interesting corollary is for example, that A+B ⇒ C type overall reactions cannot have two step mechanisms (laminar) containing two enzymes such that each step has one enzyme. This is seen right away from Table 3 already, since no mechanisms are possible for (S4), Eq. (1). The (S4) has two loops ($\rho = r = 2$) and this means a fully "enzymated" mechanism (cf. Ref. [1] of Paper I).

6. Some Examples of Mechanisms for Overall Reactions of the Type A+B ⇒ C (or Its Reverse)

We found above that there are only six possible two-step mechanisms for OVR's of type A+B ⇒ C, not counting any turbulent variations and extensions which are

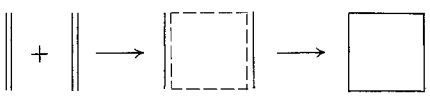
(S1)①:	$\left\{\begin{matrix} C \rightarrow B + X \\ X \rightarrow A \end{matrix}\right\}$
(S1)②:	$\{C \rightarrow X \rightarrow B + A\}$
(S1)③:	$\{C \rightarrow U + V \rightarrow A + B\}$
(S2)①:	$\left\{\begin{matrix} C + Z \rightarrow Z + X \\ X \rightarrow A + B \end{matrix}\right\}$
(S2)②:	$\left\{\begin{matrix} C \rightarrow B + Y \\ Y + X \rightarrow X + A \end{matrix}\right\}$
(S3)①:	$\left\{\begin{matrix} C + X \rightarrow A + Y \\ Y \rightarrow X + B \end{matrix}\right\}$
(S4):	none

Table 4. All mechanisms possible for two-step two-molecule associations or dissociations with or without catalysis ($\rho = 2$; OVR: A + B ⇒ C) (laminar mechanisms). The A, B, C denote external species, X, Y, Z, U, V, . . . internal ones, i.e. intermediates, catalysts, etc.

less likely to be of significance with $\rho=2$ only, and for as simple an OVR as A+B ⇒ C. It is interesting to identify these types among some mechanisms that have been invoked in the past.

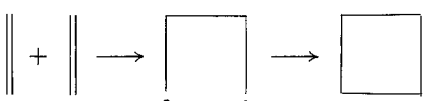
Example 1)

For the dimerization of olefins we could consider either a concerted reaction with an in-between-σ-π delocalized intermediate



(10)

which is of mechanism type (S1)②(its reverse), or a two-step reaction with diradical intermediates



(10a)

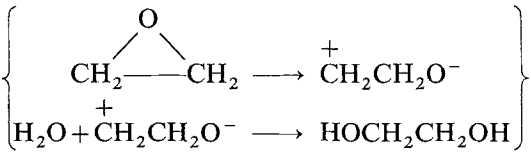
which is also of type (S1)②.We would take the concerted reaction as a two-step one, Eq. (10), if we were interested in the quantum mechanics of the process, but from a detectable intermediates point of view, we could also choose to consider it as a one step reaction.

Mechanism (S2)①(its reverse) would correspond to the relaxation of an energized intermediate X formed first, by the action of a catalyst Z, or a collisional deactivator.

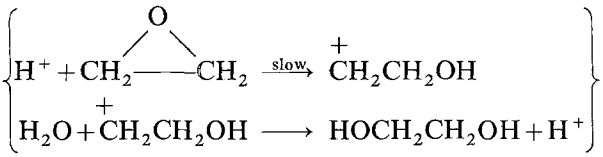
Example 2)

Hydration of epoxides in aqueous solutions:

$$\left\{\begin{matrix} \mathrm{CH_2{-}CH_2} + \mathrm{OH^-} \xrightarrow{\text{slow}} \mathrm{HOCH_2CH_2O^-} \\ \mathrm{HOCH_2CH_2O^- + H_2O} \xrightarrow{\text{fast}} \mathrm{HOCH_2CH_2OH + OH^-} \end{matrix}\right\} \qquad (11a)$$



(11b)



(11c)

Eqs. (11a) and (11c) are of type $(S3)_{\overline{\textcircled{1}}}$ (in reverse) in Table 4, Eq. (11b) is of type $(S1)_{\overline{\textcircled{1}}}$ (in reverse).

The $(S2)_{\overline{\textcircled{1}}}$ (in reverse) is similar to $(S1)_{\overline{\textcircled{1}}}$ (in reverse). It is just that its first step involves a catalyst which would seem to be needed in the first step of (11b).

Many more examples can be found. It would be instructive to classify many of the mechanisms in the literature this way. One can also write down the rate law for each case of Table 4. Similar tables are quite easily constructed for three-step mechanisms [4] ($\rho = 3$). One can look at the turbulent extension also adding a few more mechanisms and their rates. In the present paper, we have not included these extensions. Our purpose was to demonstrate the method and provide the tables of possible mechanisms for some of the most likely cases (i.e. $\rho = 2$ and laminar ones) to occur. In another paper [5] we shall treat the important OVR type $A+B \Rightarrow C+D$ finding its *a priori* possible mechanisms and giving various applications from physical organic chemistry. We note also two new papers by Gál *et al.* [6] on very complex mechanisms treated from a different viewpoint with some different aims in mind.

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