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Original Investigations

Finding the Possible Mechanisms for a Given Type of Overall Reaction

The Case of the $(A+B \Rightarrow C+D)$ Overall Reaction Types

Oktay Sinanoğlu*, ** and Lih-Syng Lee***

Departments of Chemistry and of Molecular Biochemistry and Biophysics, Yale University, New Haven, Connecticut 06520, U.S.A.*

and

İstanbul Üniversitesi, Kimya Fakültesi, İstanbul, Türkiye

A systematic way to derive all the *a priori* possible mechanisms classified according to the numbers, ρ, of elementary or molecular reaction steps was presented recently. The method is now applied to overall reactions of the type $A+B \Rightarrow C+D$. The "laminar" (elementary steps' stoichiometric coefficients unity) mechanisms that turn out possible are derived and listed for the important $\rho=2$ case. The $\rho=3$ three step mechanisms were reported in another paper. Many examples from actual chemical, biochemical mechanisms, such as S_E1, S_N1, S_E2, S_N2, activated complex theory of abstraction reactions, free radical chain propagation and biochemical electron transport chains are given. By far most mechanisms usually encountered are of the laminar type, although the method also gives the "turbulent" ones, i.e. with some stoichiometric coefficients in elementary steps larger than one or some species occurring in many of the steps.

Key words: Reaction kinetics

1. Introduction

Recently [1], it was shown that a finite and quite small number of mechanisms are possible *a priori* and obtainable for any kind of chemical reaction in terms only of the number of ρ of *elementary reaction steps*, or of the number σ of *chemical species*

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* Principal address for correspondence related to this article.

** Alexander von Humboldt Senior Scientist Awardee, West Germany.

*** Predoctoral Research Assistant, Yale University 1973–74. Then at the Roswell Park Memorial Institute, Department of Experimental Therapeutics, Buffalo, New York 14203. Now (present address for L.-S. Lee): Institute for Cancer Research, College of Physicians and Surgeons, Columbia University, New York City, N.Y. 10032.

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in the reactant, product, intermediate and catalyst pool. Strong relations between ρ and σ were obtained. For details we refer to Ref. [1] which will be called Paper I below[1].

The mechanisms[2] can be obtained also for only a particular type of *overall reaction* (OVR-type) [1, 2]. In Ref. [2] (hereafter "Paper II")[3], we derived the mechanisms for the OVR-types $A \Rightarrow B$, and $A+B \Rightarrow C$ (or its reverse) with $\rho=2$. For further definitions and methodology, please see papers I and II.

Now we apply the method in its briefest form to get all the basic (laminar) [1, 2] mechanisms possible for OVR's of the type

$$\text{OVR:} \quad A+B \Rightarrow C+D \tag{1}$$

One gets six two-step laminar mechanisms. With $\rho=3$ there are also just a few laminar mechanisms which were given elsewhere [3]. For brevity we shall obtain here only the $\rho=2$ cases and discuss examples from some well-known reactions. The extension to more step mechanisms ($\rho=3$ is in Ref. [3]), as well as to turbulent [1] (e.g. some stoichiometric coefficients >1) will be left outside the scope of the present article.

2. Some Reactions of the OVR: $(A+B \Rightarrow C+D)$ Type

This type of overall reaction is perhaps the most common and important in chemistry. Group transfer reactions, abstraction reactions [4], e.g. with free radicals,

$$Cl\cdot + C_2H_6 \Rightarrow HCl + C_2H_5\cdot; \tag{2}$$

four-center reactions like

$$H_2 + Br_2 \Rightarrow 2HBr \tag{3}$$

or rather its isotopic versions $(HD+BrBr')$; esterifications

$$C_2H_5OH + CH_3COOH \Rightarrow CH_3COOC_2H_5 + H_2O \tag{4}$$

or saponifications, halogenations,

$$C_6H_6 + Br_2 \Rightarrow C_6H_5Br + HBr \tag{5}$$

alkylations, acylations, hydrolyses, . . . are all of this type.

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[1] Paper I: Sinanoğlu, O.: Theory of Chemical Reaction Networks. All Possible Mechanisms or Synthetic Pathways with Given Number of Reaction Steps or Species. J. Am. Chem. Soc. **97**, 2309 (1975).

[2] *Mechanism* is an operational concept dependent on the physical limit set by the current instrumentation and detectability of intermediates of a certain small lifetime. In another but related view, *mechanism* is a focusing on only a number of major pathways among a number of "significant structures" upon the isomeric super-potential energy surface for the collection of atoms making up the pool of possible species in an atom-conserving system.

[3] Paper II: Sinanoğlu, O., Lee, L.-S.: Finding All Possible *a priori* Mechanisms for a Given Type of Overall Reaction. The Cases of 1) Molecular Rearrangements ($A \Rightarrow B$); and 2) Molecular Associations ($A+B \Rightarrow C$) Reaction Types. Theoret. Chim. Acta (Berl.) **48**, 287 (1978)

Other examples include:
Coupling of organometallic compounds with aryl ethers

$$\mathrm{AROP} + \mathrm{R'MgX} \Rightarrow \mathrm{ARR'} + \mathrm{ROMgX} \tag{6}$$

Electron transfer reactions

$$\mathrm{Fe}^{+3} + \mathrm{Cr}^{+2} \Rightarrow \mathrm{Fe}^{+2} + \mathrm{Cr}^{+3}; \tag{7}$$

Biochemical phosphorylations,

$$\mathrm{ATP} + \text{D-glyceraldehyde} \Rightarrow \mathrm{ADP} + \text{D-glyceraldehyde-3-phosphate} \tag{8}$$

and many others.

3. Possible Numbers of Species in All Two-Step Mechanisms for $(A+B \Rightarrow C+D)$

From Paper I [1], with $\rho = 2$, the skeletons possible are still [2],

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

(9)

With the numbers of species obtained from the Fig. 2 of Paper I, the $\sigma(\rho)$-plot, and with $\sigma_{\mathrm{ext}} = 4$ of our present OVR, yielding the laminar σ_{int} possibilities ($\sigma = \sigma_{\mathrm{ext}} + \sigma_{\mathrm{int}}$), we get,

$$\text{(S1)}: \quad 1 \leqslant \sigma_{\mathrm{int}} \leqslant 3 \tag{10a}$$

$$\text{(S2, S3)}: \quad 1 \leqslant \sigma_{\mathrm{int}} \leqslant 2 \tag{10b}$$

$$\text{(4)}: \quad \text{(none possible)} \tag{10c}$$

For the (S4) case, the general inequality in I [1] gives $\sigma_{\mathrm{int}} = 1$, but a two-ring, two-step skeleton, i.e. the (S4), cannot be made with only one internal species. The inequalities are of a nature, stating which σ-values cannot occur. The few integers that they indicate as possible, do not have to occur for sure. Thus the inequalities are *necessary but not sufficient* conditions for a σ to actually occur. This means, the actual number of possible mechanisms obtained at the end will be even smaller than what might have been thought on the basis of σ_{int}-values allowed by the $\sigma(\rho)$ plot[4] alone. We have seen this also in the OVR-cases ($\sigma_{\mathrm{ext}} = 2$; $\sigma_{\mathrm{ext}} = 3$) treated in Paper II [2].

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[4] This may be expected also from the fact that with $\sigma_{\mathrm{ext}} > 3$, several OVR-types are possible (e.g. as listed in Paper I), depending on how the σ_{ext}-species are divided into reactants and products.

4. Possible Two-Step Weighted Skeletons and Networks for the (A+B ⇒ C+D) OVR-Type

As in II [2], one next assigns the possible weights ω_k to each *k-star* (Paper I [1]) *dot-point* [1, 2] of a skeleton. Although skeletons are general, covering the laminar and turbulent networks both, at the weights stage it is convenient to deal with the two types separately. Confining ourselves to the more important case, the laminar ones, ω_k of each dot-point can be $k-1$, k or $k+1$ (not necessarily all will exist) as discussed in I [1]. So again, one expands each dot-point into possible network pieces which then have to match each other in the full network. Not giving the full mathematical details here (cf. Papers I [1], II [2], and the more detailed mathematical papers intended), we list the resulting ω_k's for each of our $\rho=2$ skeletons, Eq. (9), consistent with the OVR: A+B ⇒ C+D, in Table 1.

Table 1. Skeletal weight possible for laminar networks with $\rho=2$ and the OVR type: A+B ⇒ C+D

Skeletons	k-value of the star of dot-point		ω_k^{int}	ω_k^{ext}	ω_k	σ
(S1)	$k=1$ $k'=1$ $k''=2$	$\overset{=}{①}$	0 0 1	1 2 1	1 2 2	5
		$\overset{=}{②}$	0 0 1	1 1 2	1 1 3	5
		$\overset{=}{③}$	0 0 1	2 2 0	2 2 1	5
		$\overset{=}{④}$	0 0 2	2 0 2	2 2 2	6
(S2)	$k=3$ $k'=1$	$\overset{=}{①}$	2 0	2 2	4 2	6
(S3)	$k=2$ $k'=2$	$\overset{=}{①}$	1 1	2 2	3 3	6
(S4)	None possible					

With these weights in Table 1, one can draw the possible laminar networks matching the given numbers of species-mole lines and consistent with the uni- or bi-molecular nature of elementary steps. One gets only the networks given in Fig. 1.

The (S1)$_{\overset{=}{①}}$ weights in Table 1 gives also an *inconsistent network* (SI)$_{\overset{=}{①}/2}$ (cf. Paper II [2] also)

(S1)$_{\overset{=}{①}/2}$; (inconsistent network for laminarity). (11)

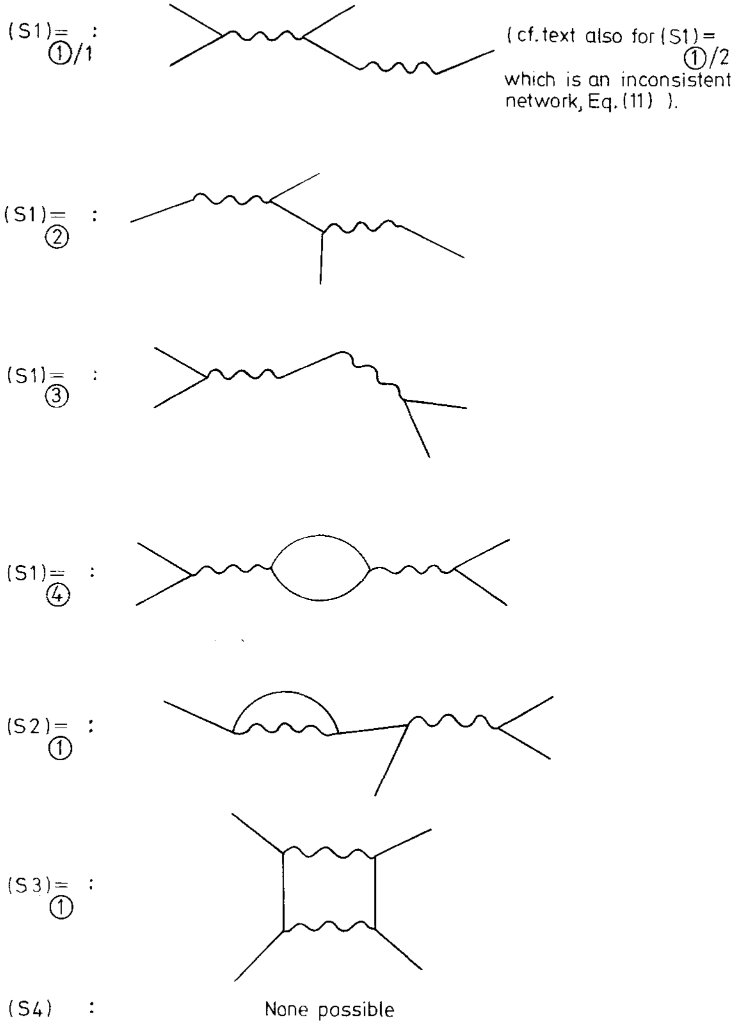
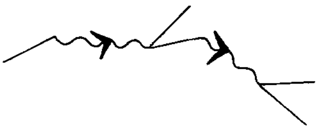


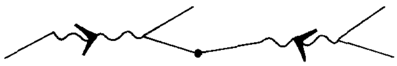
Fig. 1. All possible laminar networks for $\rho=2$ and OVR-type: $(A+B \Rightarrow C+D)$ (compare Table 1)

It will be seen, recalling the discussion of the reaction arrows in Papers I [1] and II [2], that one cannot have a laminar network like this. The procedure for generating the consistent laminar networks (II [2]) was, after getting all the ones given by the weights, to subject them to the "tentative arrows" laminarity-consistency test. We put all possible combinations of arrow directions on the network to see if one or more of them can give the OVR, rather than changing the OVR, or producing the *turbulent kinks* [1, 2]. Thus in Eq. (11), the arrow assignment



(S1)=① (11′)

would be laminar all right, but give[5] the OVR: $A \Rightarrow B+C+D$. On the other hand with two opposing arrows



$(S1)_{\overset{\equiv}{\textcircled{1}}}$ (11″)

a kink develops in the internal species-mole line (intermediates piling up and ending up in the OVR instead of cancelling out) and the OVR comes out all wrong anyway.

Having sorted out and discarded the OVR-and laminarity-inconsistent networks as the last step of the procedure, we end up with only the networks shown in Fig. 1.

5. All Possible Two-Step Laminar Mechanisms for Overall Reactions of the Type: ($A+B \Rightarrow C+D$)

The next step in the derivation of the mechanisms involves assigning the A, B, C, D to the external species-mole lines of the networks of Fig. 1 in all possible distinct ways that give two reactants and two products. Late letters like U, V, X, Y, Z, are used to denote internal species. The mechanisms thus obtained are listed in Table 2 in the conventional chemical kinetics format.

Table 2. All laminar two-step mechanisms possible for overall reactions of the type ($A+B \Rightarrow C+D$) with or without catalysis

$(SI)_{\overset{\equiv}{\textcircled{1}}/1}$:	$\left\{\begin{array}{c} A+B \rightarrow C+X \\ X \rightarrow D \end{array}\right\}$
$(SI)_{\overset{\equiv}{\textcircled{1}}/2}$:	Not possible; Eq. (11) in text
$(S1)_{\overset{\equiv}{\textcircled{2}}}$:	$\left\{\begin{array}{l} \quad\; A \rightarrow C+X \\ X+B \rightarrow D \end{array}\right\}$
$(S1)_{\overset{\equiv}{\textcircled{3}}}$:	$\{A+B \rightarrow X \rightarrow C+D\}$
$(S1)_{\overset{\equiv}{\textcircled{4}}}$:	$\{A+B \rightarrow U+V \rightarrow C+D\}$
$(S2)_{\overset{\equiv}{\textcircled{1}}}$:	$\left\{\begin{array}{l} A+X \rightarrow X+Y \\ Y+B \rightarrow C+D \end{array}\right\}$
$(S3)_{\overset{\equiv}{\textcircled{1}}}$:	$\left\{\begin{array}{l} A+X \rightarrow C+Y \\ B+Y \rightarrow D+X \end{array}\right\}$
(S4):	None possible

Each mechanism type implies also its full reverse with both arrows reversed.

The order in which steps are written is immaterial. In assigning actual chemical species to one of these mechanisms one considers all possible permutations of the known external and internal actual molecular species assigned to the external and internal lines.

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[5] Note that this is not a defect of the mathematics, but of the networks being more general than the dictates of chemical conservation laws. The network would be an admissible one for example if we were doing high-energy physics reactions admitting anti-particles, instead of chemical reactions.

6. Some Chemical Mechanisms as Examples

6.1. The S_E1 and the S_N1 Mechanisms

The uni-molecular electrophilic substitution mechanism, S_E1, with B the electrophilic reagent is an example of $(S1)_{\underset{\textcircled{1}}{=}}$ of Table 2. If B is nucleophilic, then this is the S_N1-mechanism, as in the displacements of tertiary alkyl halides via formation of carbonium ions

$$\left\{\begin{matrix} RX \to R^+ + :X^- \\ R^+ + :N^- \to RN \end{matrix}\right\} \tag{12}$$

($\sigma_{int} = 1$, the carbonium ion). Solvolysis of e.g. a diarylmethylhalide is also S_N1. An example of S_E1 is cleavage of alkoxide.

6.2. The S_E2 and the S_N2 Mechanisms

The bi-molecular electrophilic (S_E2) or nucleophilic (S_N2) substitutions are examples of the mechanism type $(S1)_{\underset{\textcircled{3}}{=}}$ in Table 2, e.g. an S_E2 mechanism for the reaction of di-s-butyl mercury with $HgBr_2$ to give s-butyl mercuric bromide.

$$R^*HgR + HgBr_2 \to \begin{bmatrix} R^*HgR \\ BrHgBr \end{bmatrix} \to R^*HgBr + RHgBr \tag{13}$$

with R^* the optically active s-butyl group. An example of S_N2 is the reaction of allyl chloride with hydroxide ion

$$RX + OH^- \to [HO \cdots R \cdots X]^- \to HOR + X^- \tag{14}$$

6.3. The Activated Complex Theory for Abstraction Reactions

If the observed OVR: $(A + B \Rightarrow C + D)$ happens to be an actual bi-molecular reaction, i.e. basically an elementary step giving rise to a second-order rate law, it is very common to invoke the "transition state" or the "activated complex", $X^{\neq}$

$$A + B \rightleftarrows X^{\neq} \to C + D \tag{15}$$

This, considered as a "submechanism", in the sense that the $X^{\neq}$ is not a true or detectable intermediate, is of the type $(S1)_{\underset{\textcircled{3}}{=}}$. This case emphasizes the point that a mechanism is an idealization singling out certain peaks and valleys on the isomeric potential energy (P.E.) surface. Much experimental (molecular beams) and theoretical (molecular dynamics on the P.E. surface) effort have gone into seeing if there is any validity to the concept of an activated complex. The conclusion appears to be the negative, the $X^{\neq}$ theory amounting to a convenient parametrization of the rate from the P.E. surface dynamics. These considerations have been critically surveyed in a brief article [5]. Our network theory is of course not concerned with the questions of reality or otherwise of any intermediates assumed, it just gives the possible pathways amongst a number of internal and external species that are taken for granted.

For the abstraction reactions [4], e.g.

$$\mathrm{Cl}\cdot + \mathrm{C_2H_6} \rightarrow [\mathrm{CL}\cdots\mathrm{CH_3}\cdots\mathrm{CH_3}]^{\neq} \rightarrow \mathrm{CH_3Cl} + \mathrm{CH_3}\cdot \tag{16}$$

Free radical chain initiation steps are sometimes of this type, e.g., in the peroxide catalyzed free-radical hydrohalogenation

$$\mathrm{ArCOO}\cdot + \mathrm{HX} \rightarrow \mathrm{ArCOOH} + \mathrm{X}\cdot \tag{17}$$

6.4. *Chain Propagation with Free Radicals*

Two-step chain propagations like

$$\left\{\begin{matrix} \mathrm{Br} + \mathrm{H_2} \rightarrow \mathrm{HBr} + \mathrm{H} \\ \mathrm{H} + \mathrm{BrBr'} \rightarrow (\mathrm{HBr})' + \mathrm{Br} \end{matrix}\right\} \tag{18}$$

are examples of the mechanism-type $(\mathrm{S3})_{\underset{\textcircled{1}}{=}}$ in Table 2 and Fig. 1.

6.5. *Biochemical Electron Transport Chain*

In the succession of steps (cf. Eq. (N15) of Paper I [1]) that eventually lead to the oxidation of metabolites, the OVR's of steps taken two-at-a-time as well as the final OVR,

$$\text{Metabolite} + \mathrm{O} \Rightarrow \text{Oxidized Metabolite} + \mathrm{H_2O} \tag{19}$$

are of the OVR: $(\mathrm{A} + \mathrm{B} \Rightarrow \mathrm{C} + \mathrm{D})$ type. For example a two-step segment like

$$\left\{\begin{matrix} \mathrm{FPH_2} + \text{cyt.-c Fe}^{+3} \rightarrow \mathrm{FP} + \text{cyt.-c Fe}^{+2} \\ \text{cyt.-c Fe}^{+2} + \mathrm{O} \rightarrow \text{cyt.-c Fe}^{+3} + \mathrm{H_2O} \end{matrix}\right\} \tag{20}$$

is a *pathway* of the type again of $(\mathrm{S3})_{\underset{\textcircled{1}}{=}}$.

Many other examples from physical organic chemistry, from biochemistry can be found for each of the types of the mechanisms or pathways [1] in Table 2 and Fig. 1. The $(\mathrm{S1})_{\underset{\textcircled{1}}{=}}$ would occur when the bi-molecular step results in an excited species, or an isomer which then relaxes to a more stable form. The $(\mathrm{S2})_{\underset{\textcircled{1}}{=}}$ would require one of the reactants to be transformed catalytically or enzymatically before reacting with B. It is most interesting that all the *a priori* possible mechanisms are few in number. Their numbers are not large even when one goes to three-step ($\rho = 3$) mechanisms [3] and to turbulent ones.

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